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Investigative Study of Crystal Violet Photo-Degradation in The Presence of Lead Chromate

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Abstract

This study addresses the environmental challenges posed by wastewater from dye factories, focusing on Crystal Violet, a dye with severe genotoxic effects. It highlights the photocatalytic efficiency of lead chromate, synthesized via direct co-precipitation, for degrading organic pollutants under visible light. FT-IR and UV-Visible spectroscopy confirmed its structural and optical properties. Key parameters like pH, dye concentration, semiconductor dosage, and light intensity were optimized, and a potential photodegradation mechanism for Crystal Violet was proposed. Figure 1 shows UV Lights Irridiation

Keywords: *Crystal Violet; Degradation; FT-IR; $PbCrO_4$; UV-Visible*

Graphical Abstract

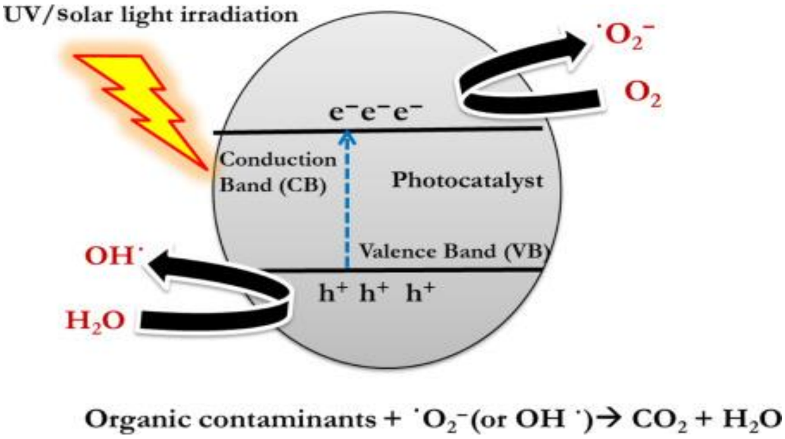

Figure 1 **UV Lights Irridiation**

1. Introduction

Crystal violet is a dye from the tri-phenyl methane class, commonly used as a protein stain to make bloody fingerprints more visible. Contaminated water containing crystal violet poses health risks, including cancer and severe eye irritation. Additionally, it plays a role in the Brown-Hopps method for staining gram-positive and gram-negative bacteria. Crystal violet dye, known for its carcinogenic and mutagenic risks, is still widely used in textiles, biological staining, and dermatology. Excessive exposure can cause skin irritation, digestive issues, and eye discomfort. [1] Photo-catalysis is an eco-friendly technique for degrading pollutants, but industrial use is limited by low light efficiency and charge recombination. Co-catalysts improve performance and hybrid systems with membrane filtration show promise in wastewater treatment. [2] Lead chromate ($PbCrO_4$) acts as an efficient photocatalyst under visible light, degrading organic pollutants like Crystal Violet and Methylene Blue, crucial for preventing water pollution and protecting aquatic life. [3] Methylene blue degradation using lead chromate as a catalyst, analyzing pH, dye concentration, catalyst amount, and proposing a hydroperoxyl radical oxidation mechanism. [4] Crystal structures, lattice vibrations, and electronic band structures of $PbCrO_4$, $PbSeO_4$, $SrCrO_4$, and $SrSeO_4$, revealing that Pb-based chromates have smaller band gaps than Sr-based selenates. [5] Acridine Yellow G (AYG) degradation was examined in aqueous solutions using $BaCrO_4$ as a heterogeneous photocatalyst under environmentally friendly LED irradiation. [6]

The straightforward one-pot solid-state fabrication of a novel binary nanocomposite composed of commercial ZnO and $PbCrO_4$, demonstrating improved photocatalytic degradation of Rhodamine B dye.[7] Sonophotocatalytic treatment of rhodamine B using a visible-light-driven CeO_2/Ag_2CrO_4 composite in batch mode, utilizing ribbon-like CeO_2 nanofibers fabricated via electrospinning. [8] Facile preparation of $PbCrO_4$ and $PbCrO_4$/Ag nanostructure as an effective photocatalyst for degradation of organic contaminants [9].Authors investigated $PbCrO_4/TiO_2$ composite for Rhodamine B dye removal under visible light, showing effective degradation influenced by pH, and characterized by DRS, XRD, and SEM. [10] Authors developed a $PbCrO_4$ photocatalyst for visible-light-driven degradation of microcystin-LR (MC-LR) in water, achieving 100% removal in 27 minutes. The catalyst's high performance is attributed to efficient carrier separation and radical production. [11] Bismuth hydroxide chromate ($Bi(OH)CrO_4$) is a semiconductor material with a narrow bandgap, making it valuable for a range of applications. A straightforward one-pot synthesis method has been devised to produce $Bi(OH)CrO_4$ nanoparticles at room temperature.[12] $PbCrO_4$/ZnO nanocomposite synthesized via a simple, room-temperature method, exhibiting enhanced optical properties, reduced bandgap energy, and improved photocatalytic activity for Rhodamine B degradation under visible light. [13] Authors and co-workers synthesized lead chromate's photocatalytic activity for degrading New Fuchsine dye under visible light, analyzing factors like pH, contact time, and dosage for optimal performance. [14] There needs to be more research on $PbCrO_4$ as a photocatalyst. Therefore, this study aims to fill this research gap by investigating $PbCrO_4$ as a photocatalyst for degrading Crystal Violet. Figure1 gives the structure of crystal violet dye, and the following table provides the chemical properties of crystal violet. Table 1 shows Chemical Properties of Crystal Violet

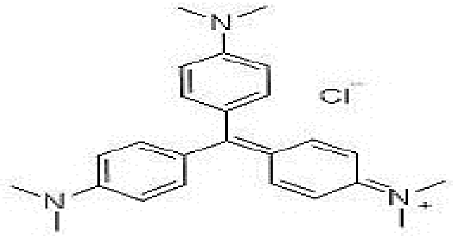

Figure 1 Structure of Crystal Violet Dye

Table 1 Chemical Properties of Crystal Violet

IUPAC Name	N- [4- [bis [4-dimethyl-amino) -phenyl] - methylene] −2,5 cyclohexadien-1-ylidine] -N-methyl-methanaminium chloride.
Chemical Formula	$C25H30ClN3$
Molar Mass	407.99gmol^{-1}
Melting Point	215 °C
Solubility	4g/L(water),30 g/L(ethanol) 30g/L (2-methoxy ethanol)
λmax	590 nm

2. Experimental Analysis

2.1 Materials and Reagents

Through a wet chemical process, lead chromate was synthesized by co-precipitating potassium chromate with water-soluble lead nitrate. As illustrated in Figure 2, two separate beakers containing 27.60g of lead nitrate and 16.182g of potassium chromate were dissolved in distilled water. When the two solutions were combined, a precipitate formed, producing lead chromate with a vibrant lemon-yellow color. The precipitate was then filtered, thoroughly washed with water to remove impurities, and finally dried by baking at 100°C.

$$\begin{gathered} K_2CrO_4\,(aq) + Pb\,(NO_3)_2(aq) \\ \Downarrow \\ PbCrO_4(s) + 2KNO_3 \end{gathered}$$

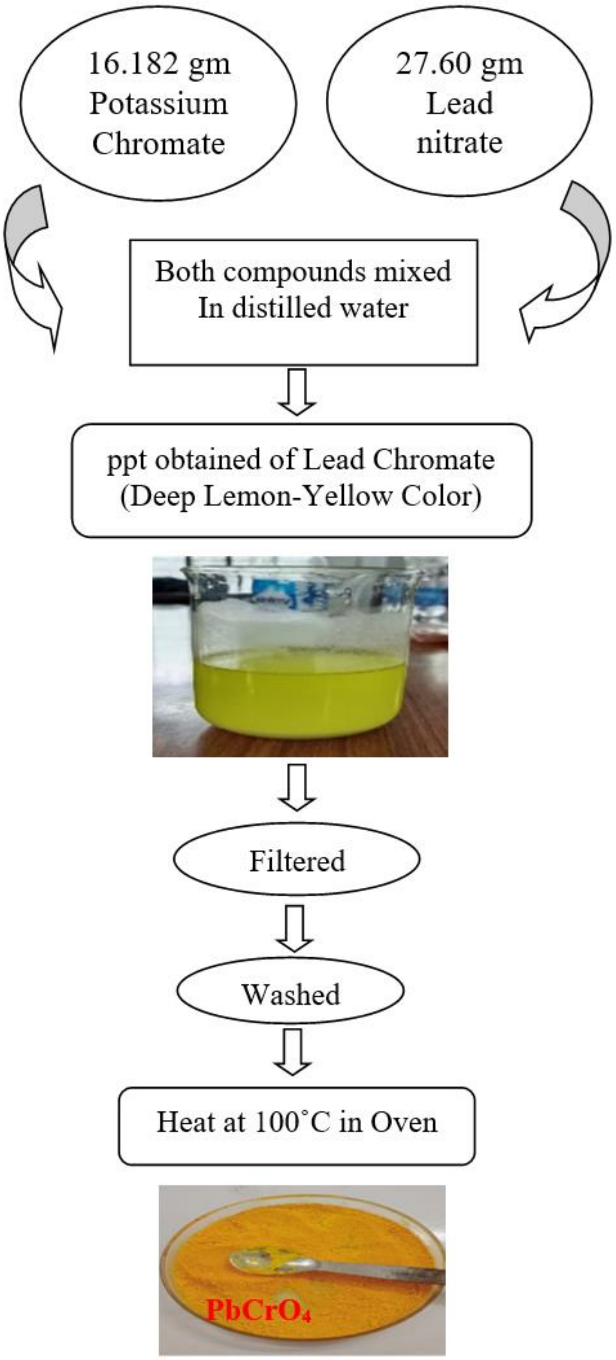

Figure 2 Flow Chart for The Synthesis of Lead Chromate

2.2 Photocatalytic process

The photocatalytic activity of the catalyst was assessed by measuring the degradation rate of Crystal Violet dye. A stock solution (1.0 x 10^{-3} M) was prepared by dissolving 0.101g of dye in 250 mL of doubly distilled water, and the pH was adjusted as needed. The solution was divided into four beakers:

- Dye solution kept in the dark.
- Dye solution exposed to light.
- Dye solution with 0.10 g of lead chromate in the dark.
- Dye solution with 0.10 g of lead chromate exposed to light.

After six hours, no absorbance change was seen in the first and third beakers, while the second showed a slight decrease and the fourth showed a significant decrease, indicating that photocatalytic degradation requires both the semiconductor and light. A reaction mixture with 0.10g photocatalyst was illuminated with a 200W tungsten lamp, and absorbance was measured every 10 minutes using UV spectroscopy (λmax = 590 nm). The absorbance decreased over time, confirming the degradation of Crystal Violet dye by the photocatalyst.

3. Characterization Techniques

Characterization and optimization are crucial for evaluating the suitability of prepared films for their specific applications. This section discusses the different techniques employed.

3.1 FT-IR Analysis

The FT-IR spectrum of the synthesized $PbCrO_4$ nanocomposite shows characteristic peaks for the chromate group (CrO_4^{-2}) between 400 and 900 cm^{-1}. Notable peaks at 491, 480, and 859 cm^{-1} correspond to CrO_4^{-2} absorption bands, while the band at 1384 cm^{-1} represents the Cr–O bond. Peaks at 1628 cm^{-1} and 3427 cm^{-1} are attributed to OH^- bending vibrations and adsorbed water, respectively. [15] (Figure3)

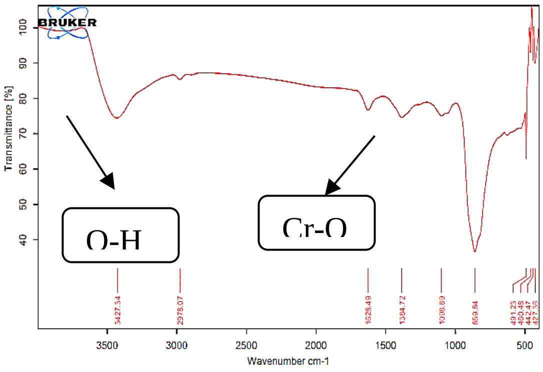

Figure 3 FT-IR Spectra of $PbCrO_4$

3.2 UV–VIS. Spectroscopy Analysis

To determine the band gap of the synthesized $PbCrO_4$, diffuse reflectance spectroscopy was performed across a broad absorption spectrum of 200 nm to 800 nm. Absorbance peaks at 226 nm, 272 nm, 379 nm, and 566 nm are observed in Figure 4. This broad absorption range enables the semiconductor to absorb radiation from the UV to the visible region, making it an efficient photocatalyst under visible light irradiation. The band gap of the semiconductor is determined using the Tauc plot shown in Figure 5, where $(\alpha h\nu)^2$ is plotted against photon energy ($h\nu$).[16] The composite's estimated band gap (Eg) is approximately 3.20 eV.

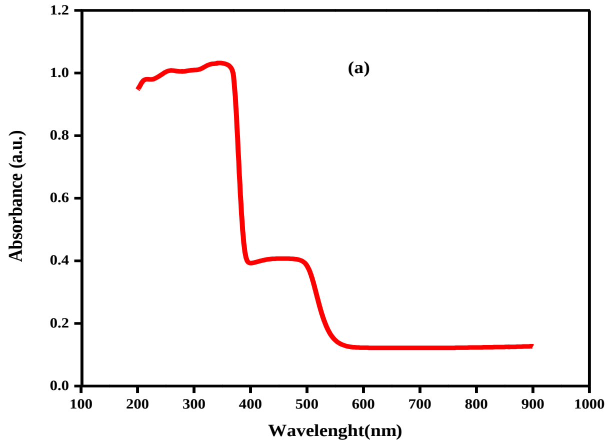

Figure 4 UV-Vis Absorption Spectrum of Lead Chromate

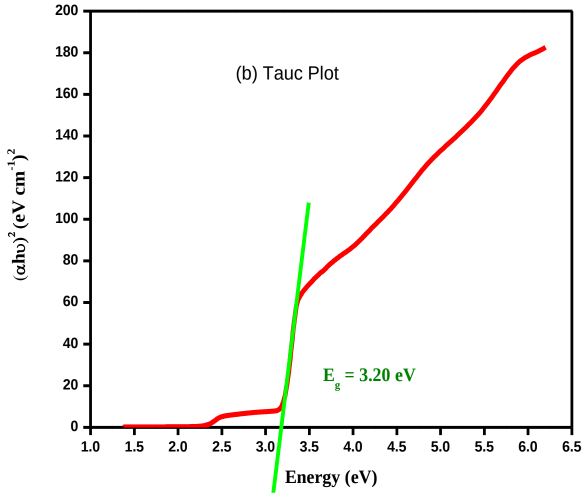

Figure 5 Plot of $(\alpha h\nu)^2$ versus Photon Energy ($h\nu$) for the Lead Chromate

4. Results and Discussion

A plot of 1 + log A against time yielded a linear line, confirming that the degradation of Crystal Violet dye adheres to pseudo-first-order kinetics. The rate constant under optimal conditions was calculated as k = 2.303 x slope.

Dye Degradation (%) = Initial OD−Final OD/ Initial OD ×100.

5. Typical Run

The standard experiment is illustrated in Figure 5, with a rate constant of 1.51 x 10^{-4} sec^{-1}. The pH is 9.5, the concentration of Crystal Violet is 4.2 x 10^{-5} M, the amount of semiconductor used is 0.10 g, and the light intensity is 60.0 mW cm^{-2}.

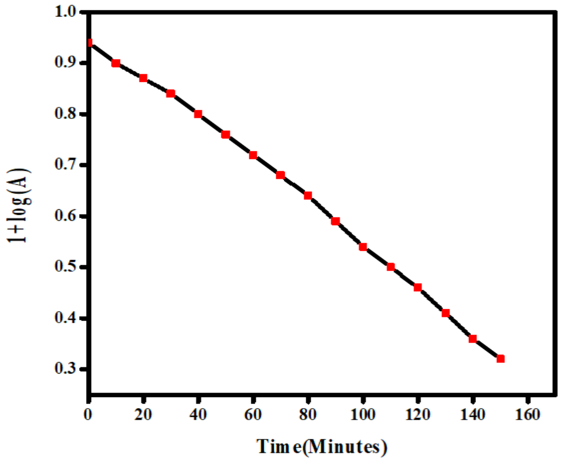

Figure 5 Typical Run

6. Effect of Parameters

6.1 pH Variation

The photocatalytic degradation rate of Crystal Violet increases with rising pH, reaching a maximum at pH 9.5, after which it declines. This increase is linked to the greater formation of superoxide anion radicals ($O_2^{\bullet -}$) as pH increases, which arise when O_2 reacts with electrons in the semiconductor's conduction band. At the optimal pH, these radicals react with protons to produce hydroxyl radicals ($HO^{\bullet}$), enhancing dye degradation through photo-catalysis. However, beyond pH 9.5, the degradation rate decreases, likely due to the conversion of Crystal Violet from its cationic to neutral form, reducing its attraction to the negatively charged semiconductor surface influenced by adsorbed ^{-}OH ions as shown in Figure 6. The concentration of Crystal Violet is 4.2 x 10^{-5} M, the amount of semiconductor used is 0.10 g, and the light intensity is 30.0 mW cm^{-2}. Figure 6 shows PH Variation.

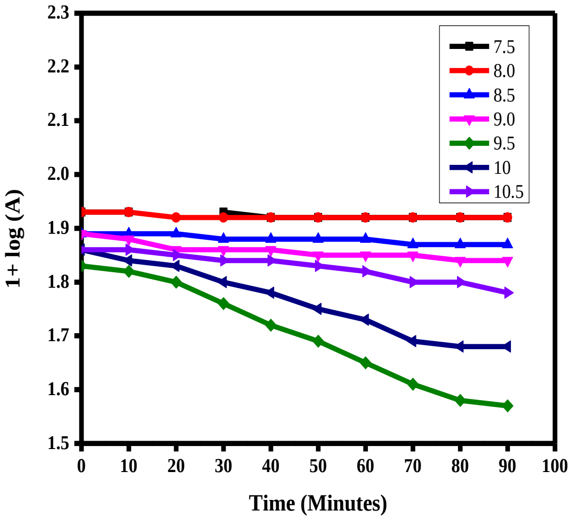

Figure 6 **P^H Variation**

6.2 Varied concentrations of Crystal Violet

The results presented in Figure 7 illustrate how dye concentration affects the photocatalytic degradation of Crystal Violet, which was effective within the range of 4.0 x 10^{-5} to 5.2 x 10^{-5} M. However, at approximately 4.2 x 10^{-5} M, identified as the optimal condition, the effectiveness of photocatalytic degradation began to decline. Although dye degradation increased with higher concentrations, at elevated levels, the dye began to function as an internal filter, obstructing the desired process.

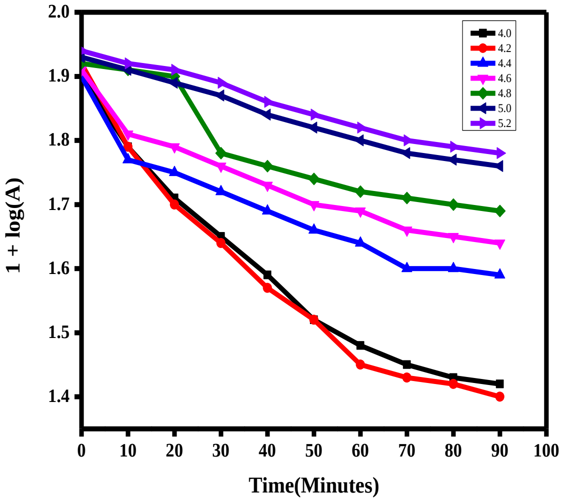

Figure 7 **Varied Concentrations of Crystal Violet**

6.3 Different Quantities of Lead Chromate

The study examined the impact of different catalyst quantities on dye degradation rates within the range of 0.02 to 0.16 g. Figure 8 illustrates that the rate constant varies with the amount of semiconductor employed. The photocatalytic activity rises with increased photocatalyst, reaching its highest efficiency at a dosage of 0.10 g, which produces the most rapid degradation rate. However, beyond this amount, the rate constant begins to decline slightly due to the increased thickness of the photocatalyst rather than the available surface area, as evidenced by experiments with reaction vessels of varying sizes. This reduction is likely due to the excess photocatalyst obstructing and limiting light penetration at higher concentrations. pH = 9.5, concentration of Crystal Violet = 4.2 x 10^{-5} M, and light intensity = 30 mW cm^{-2}.

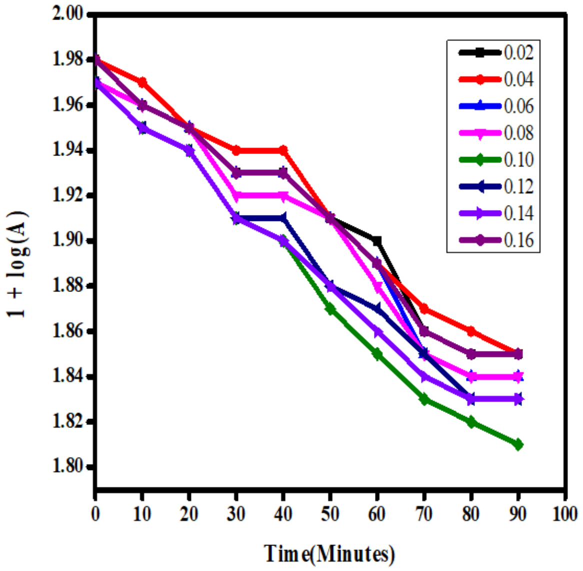

Figure 8 **Variation of Amount of $PbCrO_4$**

6.4 Variation of Light Intensity

Various experiments were conducted to assess the impact of light intensity on the photocatalytic degradation of Crystal Violet. Adjusting the distance between the light source and the reaction mixture created different conditions, as illustrated in Figure 9. The findings indicate that increased light exposure enhances the degradation process; more photons hitting the semiconductor surface lead to a higher degradation rate. However, little change in the degradation rate was observed once light intensity surpassed the optimal value of 60 mWcm^{-2}, indicating that there is a specific range of light intensity for effective photocatalytic degradation, beyond which further increases do not significantly improve the rate.

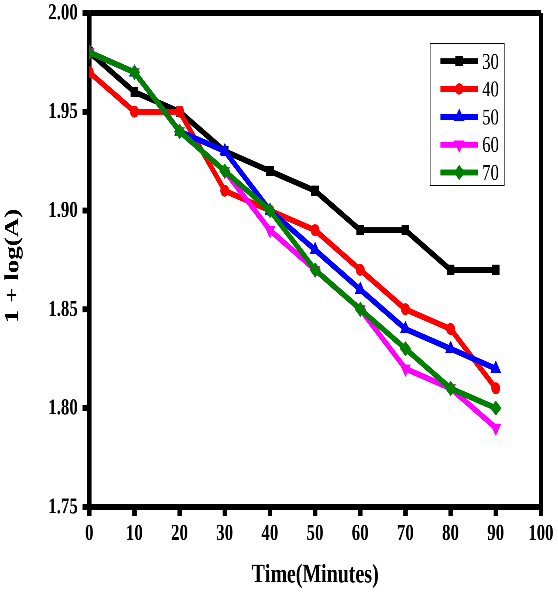

Figure 9 **Increasing Light Intensity Enhanced the Photocatalytic Degradation of Crystal Violet.**

6.5 Mechanism

Based on the observations mentioned, a method for the photocatalytic degradation of Crystal Violet using lead chromate has been proposed. An experimental mechanism for the Crystal Violet molecule suggests that it absorbs radiation at its peak wavelength of λmax = 590 nm. The process involves intersystem crossing, which converts the initial singlet state of the Crystal Violet molecules to the first triplet state. The Lead Chromate photocatalyst absorbs photons, creating a hole-electron pair due to electron transition from the valence band to the conduction band. These electrons then react with oxygen, producing superoxide anion radicals. The interaction between the superoxide anion radical and the triplet state of crystal violet dye forms the leuco phase of the crystal violet dye molecule. This leuco phase ultimately degrades into less harmful by-products. Figure 10 shows Mechanism.

$$^{1}CV_0 \xrightarrow{h\nu} {}^{1}CV_1$$
$$^{1}CV_1 \xrightarrow{ISC} {}^{3}CV_1$$
$$SC \longrightarrow e^-(CB) + h^+(VB)$$
$$e^- + O_2 \longrightarrow O_2^{\cdot -}$$
$$^{-}OH + H^+ \longrightarrow HO^-$$
$$HO^- + {}^{3}CV_1 \longrightarrow \text{Leuco CV}$$
$$\text{Products} \longrightarrow \text{Leuco CV}$$

Figure 10 **Mechanism**

6.6 Stability and Reusability

The stability and reusability of lead chromate were evaluated through successive tests of crystal violet dye degradation using the same batch of lead chromate photocatalyst. Each batch of lead chromate showed less degradation than the previous one. The research results showed that the first batch of lead chromate achieved a degradation rate of 76.34%, while the second batch reached 75.22%. The third and fourth batches demonstrated degradation rates of 72.39% and 71.14%, respectively, with the final batch achieving 70.02%. This slight decline in efficiency indicates that the synthesized $PbCrO_4$ remains a viable catalyst for practical use. Furthermore, the stability of the lead chromate photocatalyst was evaluated by conducting repeated photocatalytic degradation cycles using the same batch, as shown in Figure 10. The findings revealed that the lead chromate maintained consistent degradation performance over multiple cycles, underscoring its potential for reuse in practical applications.

6.7 Radical Trapping Experiments

Radical trapping experiments were performed to identify the radicals responsible for the degradation of Crystal Violet dye. Isopropyl alcohol was used to trap hydroxyl radicals ($OH^{\bullet}$), while p-benzoquinone was employed to capture superoxide anion radicals ($O_2^{-\bullet}$). The results indicated that both quenchers reduced the dye's degradation rate, with isopropyl alcohol leading to a more significant reduction compared to the control. Specifically, p-benzoquinone decreased the degradation by 6.33%, and isopropyl alcohol by 1.14%, suggesting that superoxide anion radicals, along with hydroxyl radicals, play a key role in the photocatalytic degradation process, as shown in Figure 11.

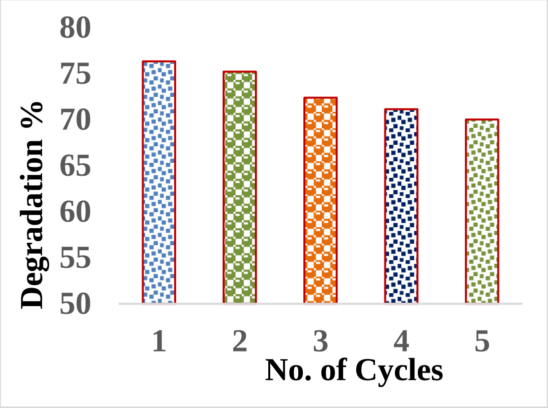

Figure 10 The stability and reusability of Lead Chromate were assessed through repeated tests of crystal violet dye degradation using the same photocatalyst batch.

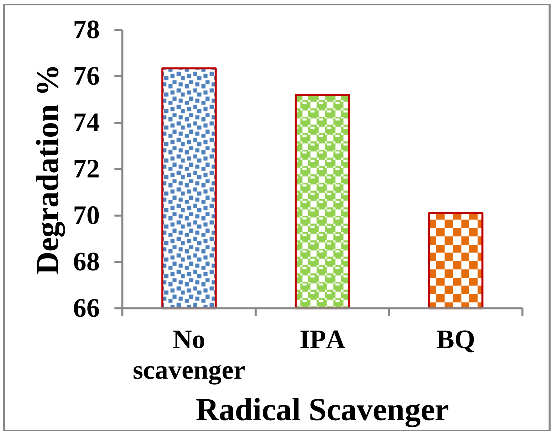

Figure 11 Radical trapping experiments were conducted using various quenchers to study the degradation of crystal violet dye.

Conclusion

In conclusion, the study found that lead chromate synthesized through a hydrothermal method exhibited high photocatalytic activity in degrading Crystal Violet dye under UV irradiation. The photocatalyst demonstrated stability and reusability across multiple degradation cycles, highlighting its potential for practical applications. Additionally, the study revealed that both hydroxyl radicals and superoxide anion radicals play a role in the degradation process when lead chromate is used as a photocatalyst. Overall, the results indicate that lead chromate is an effective photocatalyst for degrading Crystal Violet dye, with promising applications in wastewater treatment.

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Conflict of Interest

The authors say they have no conflicting interests.

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