



Sonophotocatalytic Treatment Of Hexamethyl Pararosaniline Chloride Degradation By Cobalt-Doped Titanium Dioxide-Zinc Oxide Photocatalyst

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Abstract

The objective of this work is to produce Cobalt-doped Titanium dioxide and Zinc oxide nanoparticles (Co-TiO₂-ZnO) by a sol-gel technique and evaluate their efficiency in photocatalytically breaking down hexamethyl pararosaniline chloride dye under sunlight. The composition of the synthesised photocatalysts has been analysed using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction analysis (XRD) & UV-Vis diffuse reflectance spectroscopy. The catalysts were assessed for their sonophotocatalytic and photocatalytic capabilities by conducting the degradation of hexamethyl pararosaniline chloride in an aqueous solution. The findings demonstrate that the presence of ultrasonication significantly enhances the photocatalytic efficiency of photocatalysts. Furthermore, it was stated that the degradation efficiencies of hexamethyl pararosaniline chloride using photocatalysis and sonophotocatalysis were 72% and 93% respectively.

Keywords: Titanium dioxide, hexamethyl pararosaniline chloride, sonophotocatalysis, ultrasonication and cobalt.

I. Introduction

The rapid advancement of industry has brought several chemical compounds into common use, including dye, phenolic compound and pharmaceuticals. In the present day, the field of medicine provides an abundance of pharmaceuticals to address a wide range of illnesses, a significant portion of which may be obtained without a prescription and administered without seeking guidance from a healthcare practitioner (M.Y. Frei et al, 2010, P. Tfelt-Hansen and T.J. Steiner 2007 and J. Dułęba et al, 2021). Dyes are difficult to decolorize due to its visible colour. Water pollution caused by organic contaminants is a significant environmental issue. The contamination levels in several nations are rising as a result of significant industrial growth and the ongoing expansion of the human population (Akhundi et al, 2015 and Reemtsma et al, 2006). Various techniques are used to remediate polluted water, including adsorption, coagulation, purification, and so on. Photocatalytic breakdown of organic pollutants is a treatment approach that continues to get interest due to its cost-effectiveness and potential as an ecological technology (Zaki, A.H., et al, 2017 and 2018).

Photocatalysis is a very promising method for addressing several contemporary environmental challenges (Ravelli D et al 2009 and Hoffmann RM et al (1995). The possibility of removing organic contaminants exists with semiconductor adsorbents (Hu J-S et al, 2005). Titanium dioxide (TiO_2) and zinc oxide (ZnO) are extensively researched transition oxide semiconductors for photochemical and photoelectrochemical purposes (Fujishima A 1972 and Linsebigler AL et al, 1995). Consequently, they serve as a widely used standard for study. It is a ubiquitous and enduring substance, exhibiting a higher degree of defence against photo corrosion compared to other often examined oxides. In the field of photocatalysis, ZnO has been proposed as a viable substitute for TiO_2 . This is because ZnO has a band-gap energy that is comparable to TiO_2 , which is the most commonly used and representative photocatalytic material. Therefore, it is hypothesised that ZnO possesses similar photocatalytic capabilities as TiO_2 . Additionally, ZnO demonstrates superior performance in breaking down organic pollutant molecules in both acidic and basic environments (Hariharan C 2006).

II. Materials & Methods

Reagents used in the production of Co-doped TiO_2 - ZnO included Tetra-n-butyl-Ortho titanate (97%), Zinc Acetate (99.9%) and Cobalt (II) Chloride (97%). Demineralized water was used throughout the experiments. Hexamethyl parosaniline chloride was purchased from Sigma Aldrich.

Co- TiO_2 - ZnO was prepared using the sol-gel method, which involves combining 50 mL of Tetra-n-butyl-ortho titanate with 100 mL of ethanol and stirring for 30 minutes. A 2% solution of cobalt (II) chloride and 80 mL of zinc acetate in distilled water were also prepared. A solution of 4.4 M HCl was added to the zinc acetate mixture, sonicated for 15 minutes, and then added to the titanium mixture. The solution forms gels and is dried for 5 days at 100 °C. The gel is dehydrated to generate crystals, which are then calcined for 2 hours at 600 °C.

III. Result & Discussion

3.1 SEM & EDAX

The surface morphology of the Co-doped TiO_2 - ZnO photocatalyst was examined. The electron from the surface of the particles is analysed, revealing a rod-shaped structure for the Co-doped TiO_2 - ZnO photocatalyst. The particles exhibit aggregation with an asymmetrical distribution of morphologies. Figure 1 (a) illustrates the pixel resolution of Co- TiO_2 - ZnO at a nanoscale level of X3,500. The elemental compositions were analysed by the use of an EDAX research. The Co doped TiO_2 - ZnO photocatalyst exhibits a complete elemental composition of 100%. Figure 1 (b) shows the presence of titanium (Ti), zinc (Zn), cobalt (Co), oxygen (O), and chlorine (Cl) in the Co-doped TiO_2 - ZnO sample. The energy levels of Titanium (Ti) are 0.4, 4.5, and 4.9 KeV. Zinc (Zn) is detected at energy levels between 1 and 8.6 kiloelectron volts (KeV). The element cobalt (Co) has maximum energy levels at 1.8, 6.9, and 7.7 kiloelectron volts (KeV). Oxygen and chlorine may be detected at energy levels of 2.7, 2.9, and 0.5 kiloelectron volts (KeV), respectively. Therefore, the existence of elemental composition provides evidence for the production of co-doped TiO_2 - ZnO .

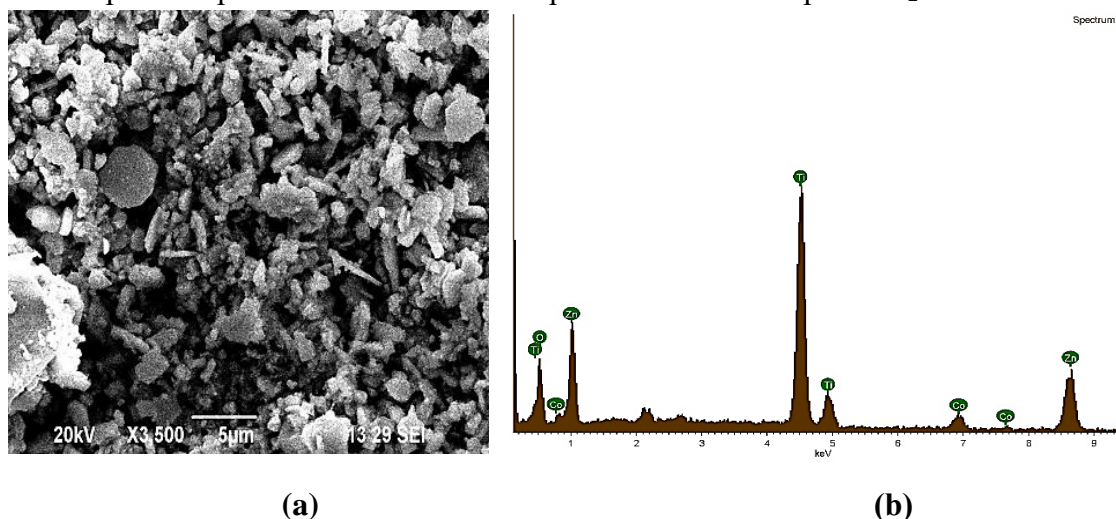


Fig. 1 (a) SEM image of Co-doped TiO_2 - ZnO & (b) EDAX of Co-doped TiO_2 - ZnO

3.2 XRD

The Co-TiO₂-ZnO sample was subjected to analysis in order to investigate its crystal structure. Figure 1 illustrates the link between the 2 θ value of Co-doped TiO₂-ZnO and the peaks seen at 33°, 35°, 49°, 53°, 57°, 62°, and 63°. The peaks correspond to the crystallographic planes (100), (002), (200), (105), (110), (213), and (103). The discovered planes align with the crystal structures of hexagonal ZnO and Co, as well as tetragonal TiO₂. The detected peaks were assessed in relation to the standard values documented on the JCPDS card (JCPDS no. 21-1272 & JCPDS no. 36-1451).

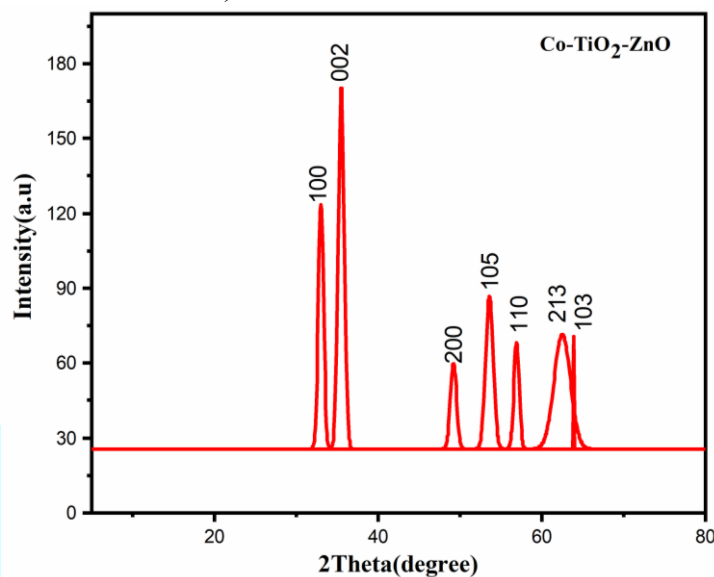


Fig. 2 XRD analysis of Co-doped TiO₂-ZnO

3.3 UV-VIS analysis

The band gap energy of undoped and co-doped TiO₂-ZnO was determined by analysing UV-Vis absorption data. The optical band gap was derived from the UV data using a Tauc relation plot, where $(\alpha h\nu)^2 = A(h\nu - E_g)$. The graph depicts photon energy (x-axis) versus the square root of the absorption coefficient and absorption coefficient (y-axis). Co-TiO₂-ZnO has a band gap of 3.12 eV, which represents the space between the conduction and valance bands. This indicates that a reduction in band gap would result in enhanced photocatalytic degradation.

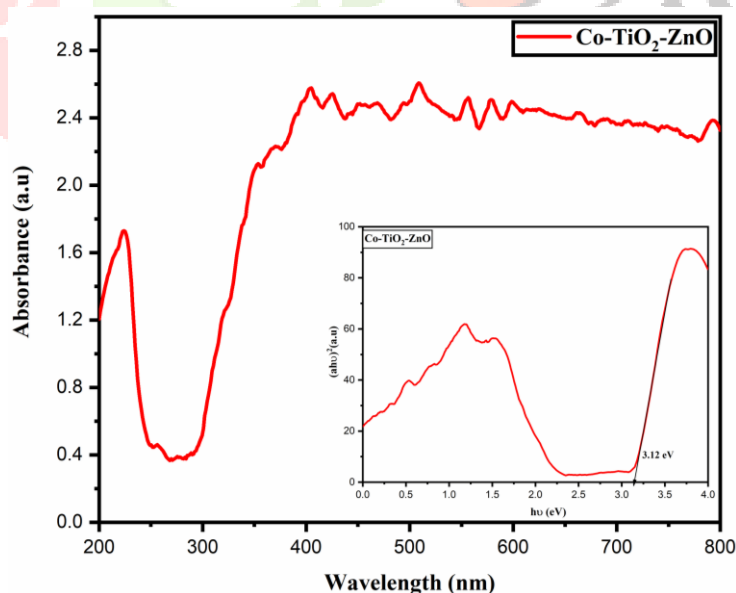


Fig. 3 UV-vis analysis and tauc plot of Co-doped TiO₂-ZnO

IV. Photocatalytic degradation

The Co-TiO₂-ZnO catalyst was evaluated for its photocatalytic efficiency in the degradation of hexamethyl pararosaniline chloride dye. 0.02 g of the catalyst were evenly distributed in a 50 mL solution of hexamethyl pararosaniline chloride, with a dye concentration of 5 mg per litre. The adsorption-desorption equilibrium was established under dark settings with slight changes observed, and the mixture was subsequently exposed to sunlight for 3 hours with continual stirring. The sample solution was removed and centrifuged every 30 minutes to quantify the residual hexamethyl pararosaniline chloride dye concentration using a UV-vis spectrophotometer having an absorption band at 590 nm. The degradation percentage was determined using the following formula $C_0 - C_t / C_0 \times 100$. Where C_t stands for a variable concentration and C_0 for the starting concentration.

4.1 Sonophotocatalytic degradation

Experiments were conducted to assess the catalytic activity of a produced catalyst by subjecting hexamethyl pararosaniline chloride to degradation in the presence of cobalt-doped TiO₂-ZnO nanoparticles. In a standard process, an ultrasonic bath with an output power of 300 W and a frequency of 50–60 Hz was used to irradiate 50 mL of hexamethyl pararosaniline chloride solution with a known dye concentration of 5 mg and an appropriate amount of 0.02g of catalyst. Samples are taken from the reactor at regular intervals of 30 minutes, with each sample consisting of 3 mL. The catalyst particles in suspension were gathered by centrifugation of the samples, and the remaining pollutant in the sample was quantified using a SYSTRONICS 2203 double beam spectrophotometer at a maximum wavelength of 590 nm.

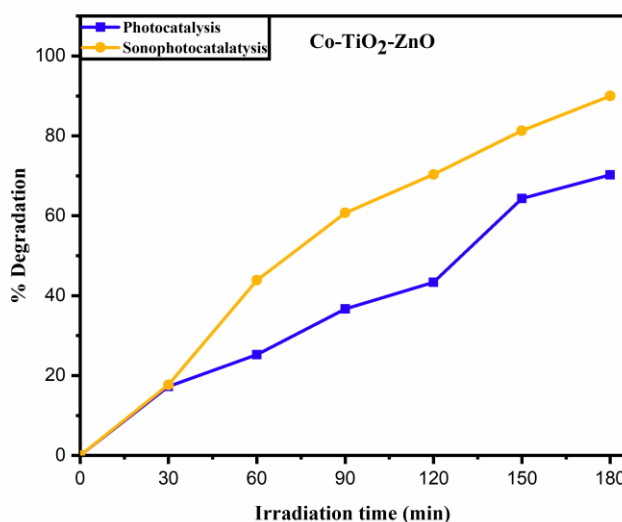


Fig. 4 Photocatalytic & Sonophotocatalytic degradation in presence of sunlight with Co-doped TiO₂-ZnO photocatalyst

4.2 Ideal condition for degradation

The degradation of hexamethyl pararosaniline chloride was achieved using Co-TiO₂-ZnO as a catalyst. A 50-mL solution of hexamethyl pararosaniline chloride at a concentration of 5 ppm was supplemented with 0.02 g of catalyst. The pH of the solution was adjusted to a range of 12. The reaction solution was agitated in a darkly illuminated chamber for a duration of 30 minutes in order to achieve adsorption equilibrium. Since hexamethyl pararosaniline chloride shows very slight decolourisation in the absence of light, it implies that light is essential for the breakdown of hexamethyl pararosaniline chloride. Subsequently, the solution was subjected to sonication in the presence of sunlight. The hexamethyl pararosaniline chloride photodegradation process was examined by periodically removing samples from the resultant combination at 30-minute intervals. The evaluation of the pollutant molecule present in the supernatant solution was conducted by measuring the absorbance at 590 nm for HRC dye after centrifugation. A 90% decline was seen after 180 minutes. Therefore, the optimal arrangement significantly influences the decolourisation of hexamethyl pararosaniline chloride.

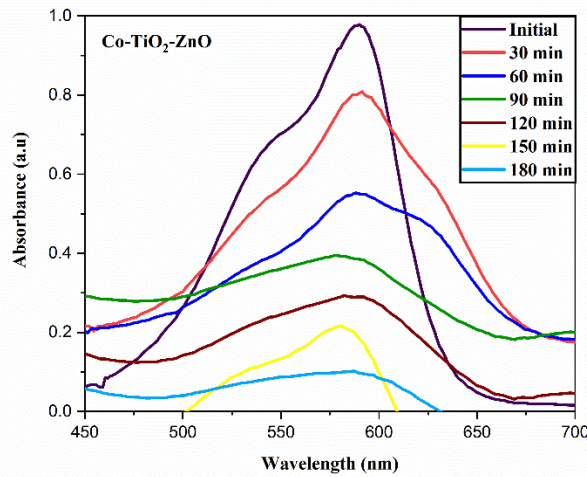
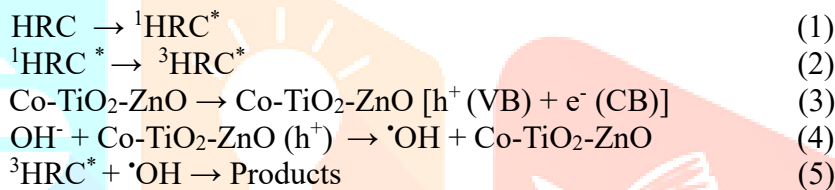


Fig. 5 Photocatalytic degradation under optimum condition

4.3 Mechanism proposed for the degradation of hexamethyl pararosaniline chloride

Experimental evidence suggests the following as a potential mechanism for the photocatalytic decomposition of hexamethyl pararosaniline chloride (HRC):



When exposed to sunlight in the presence of the catalyst Co-TiO₂-ZnO, the HRC molecules were excited to the first excited singlet state (¹HRC^{*}). Intersystem crossover (ISC) then transfers these excited molecules to the triplet state (³HRC^{*}). The semiconductor Co-TiO₂-ZnO, on the other hand, absorbs photons and produces an electron-hole pair as a consequence Co-TiO₂-ZnO [h⁺ (VB) + e⁻ (CB)]. The OH⁻ will react with the semiconductor's hole to produce [•]OH radicals, which will then transform the triplet state ³HRC^{*} dye molecules into products (Rameshwar Ameta et al, 2014).

V. Recycling of Photocatalyst

The stability of the Co-TiO₂-ZnO photocatalyst was evaluated by subjecting it to four photodegradation trials with the same concentration of hexamethyl pararosaniline chloride. The percentage degradation was measured to estimate the efficacy of the catalyst in degrading hexamethyl pararosaniline chloride. Following each degrading stage, the catalyst was thoroughly rinsed with deionized water and ethanol to remove any HRC dye that may have been adsorbed on its surface. Subsequently, it was dried in an oven. Figure 19 demonstrates that the photocatalyst maintained notable stability across four cycles, achieving maximum degradation rates of 93%, 85%, 79%, and 64% accordingly for HRC. The decline in degradation efficiency may be attributed to the depletion of the photocatalyst caused by washing between cycles.

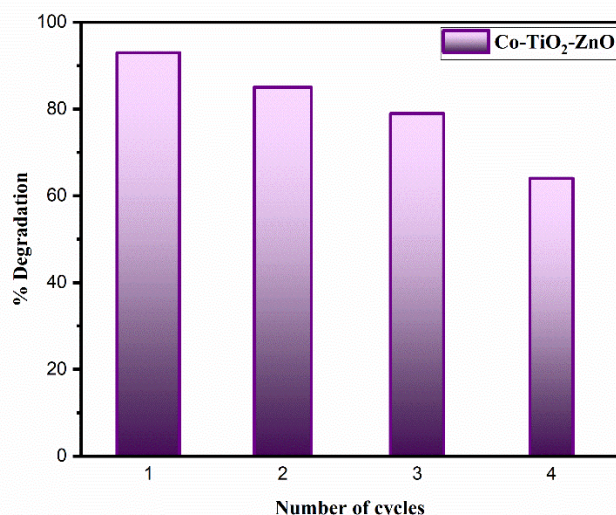


Fig. 6 Recycling of Co-doped TiO₂-ZnO photocatalyst

VI. Conclusion

Co-doped TiO₂-ZnO nanoparticles were effectively synthesised utilising a straightforward Sol-gel process. The SEM investigation findings indicated that the morphology is rod-shaped. The efficacy of the synthesised catalyst in sonophotocatalytic degradation of hexamethyl pararosaniline chloride (HRC) was investigated. The results demonstrate that Co-TiO₂-ZnO is a very efficient photocatalyst for the decomposition of HRC dye. An optimal dye concentration of 5 parts per million (ppm), a catalyst concentration of 0.02 (g/50 mL), and a solution pH of 12 have been shown to enhance degradation rates. The Co-doped TiO₂-ZnO nanoparticles exhibited maximum catalytic activity, achieving a degradation efficiency of 90% after a reaction time of 180 minutes.

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Conflict of interest

The authors certify that they do not have any known financial or personal affiliations that would appear to conflict with the work described in this publication.

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