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Photoreduction of cr^{6+} by Cu loaded hierarchical n-doped TiO_2 nano structures

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ABSTRACT

Background:

Hexavalent chromium (Cr^{6+}) is a toxic and persistent contaminant in aquatic environments. Photocatalysis offers a sustainable pathway for Cr^{6+} reduction under solar irradiation. This study develops hierarchical N-doped TiO_2 nanostructures attached with Cu nanoparticles to enhance visible-light absorption and photocatalytic activity.

Objective:

The work aims to synthesize Cu-loaded N-doped TiO_2 with hierarchical porosity, characterize their structural features, and evaluate their efficiency for sunlight-driven Cr^{6+} reduction. The influence of Cu loading, catalyst dosage, pH, and irradiation time on reduction efficiency is evaluated.

Methods:

N-doped TiO_2 was prepared using titanium isopropoxide and ammonia, followed by integration of Cu nanoparticles (1–5 wt%) through wet impregnation and calcination. XRD, SEM, and EDX analyses confirmed the structural and compositional characteristics. Photocatalytic reduction experiments used 20 ppm Cr^{6+} solutions under sunlight, and chromium concentrations were observed using the diphenyl carbazide method.

Results:

The Cu–N–TiO_2 catalysts showed mixed anatase–rutile phases and uniform Cu nanoparticle dispersion. Among all samples, the 1 wt% Cu-loaded catalyst achieved the highest Cr^{6+} reduction of 77.73% after 2 hours of sunlight exposure. Maximum performance was observed at pH 4 along with a catalyst dosage of 0.04–0.05 g. Reduction efficiency increased with irradiation time, reaching a maximum at 120 minutes.

Conclusion:

The hierarchical Cu-loaded N-doped TiO_2 catalyst improves Cr^{6+} reduction through enhanced visible-light absorption, efficient charge separation, and hierarchical porosity. The 1 wt% Cu–N–TiO_2 catalyst shows strong potential for sunlight-assisted remediation of chromium-contaminated water.

KEY WORDS

Photoreduction; Titanium isopropoxide; Photocatalysis; Cu nanoparticles; Chromium

ARTICLE HISTORY

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Introduction

Cr^{6+} is one of the most persistent and hazardous heavy-metal pollutants in aquatic environments. Its high solubility and strong oxidizing character allows it to dissolve easily through soil and water systems, where it poses long-term risks to ecological and human health [1]. Exposure to Cr^{6+} leads to respiratory disorders, liver and kidney damage, mutagenicity, and carcinogenic effects. Industrial effluents from electroplating, leather tanning, dye manufacturing, and stainless-steel processing are major contributors to Cr^{6+} contamination, making its removal from water streams a critical challenge in environmental chemistry [2].

Traditional treatments, such as chemical reduction, coagulation, adsorption, and membrane-based separation, often suffer from practical limitations. These include high operating costs, secondary waste production, and reduced efficiency when applied to dilute or fluctuating pollutant concentrations. As a result, there is a continuous search for sustainable, cost-effective alternatives capable of treating Cr^{6+} under environment friendly conditions [3]. Photocatalysis, has gained considerable push as an alternative method for reducing Cr^{6+} to its less toxic trivalent form (Cr^{3+}) [Figure 1]. This process relies on semiconductor materials that generate electron–hole pairs upon illumination, enabling redox transformations at their surface without the need for external chemical inputs [4].

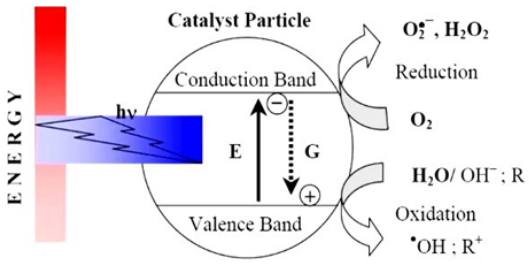

Figure 1. Mechanism of photocatalysis.

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Titanium dioxide (TiO_2) remains a widely studied photocatalysts due to its stability, non-toxicity, and strong oxidative properties. However, pristine TiO_2 possesses a wide band gap, limiting its activity mainly to the ultraviolet region, which accounts for only a small portion of natural sunlight. Also, the rapid recombination of photogenerated charge carriers reduces their photocatalytic efficiency [5]. Addressing these limitations require strategies that shift absorption into the visible range and improve electron–hole separation. Nitrogen doping is known to introduce electronic states near the valence band, effectively narrowing the band gap and enhancing visible-light activity. Also, the addition of metal nanoparticles such as copper promotes charge separation and contributes to enhanced light absorption through plasmonic effects [6].

Hierarchical nanostructures have emerged as promising design strategy, as they provide higher surface area, improved diffusion pathways, and more effective light harvesting. Such architectures facilitate rapid charge transport and increase the number of active sites available for photocatalytic reactions. Although various doped TiO_2 systems have been explored, there remains limited understanding of how nitrogen doping, copper loading, and hierarchical porosity collectively influence the visible-light-driven reduction of Cr^{6+} under real sunlight. Many published articles depend on noble metals, UV-dominant catalysts, or non-scalable synthesis routes, leaving a gap in the development of cost-effective and practical photocatalysts suitable for large-scale environmental applications [7].

The present study addresses this gap by synthesizing hierarchical N-doped TiO_2 nanostructures loaded with copper nanoparticles across a range of weight percentages. The objective is to understand how the combined contributions of nitrogen-induced band-gap narrowing, copper-assisted charge separation, and hierarchical porosity influence the photocatalytic reduction of Cr^{6+} under natural sunlight. The catalysts were synthesized through a simple wet-chemical process, allowing uniform incorporation of nitrogen and controlled dispersion of copper. Structural and morphological features were evaluated using XRD, SEM, and EDX analyses to establish the relationship between material design and photocatalytic behavior.

While the results highlight the potential of Cu-loaded N-doped TiO_2, the study also acknowledges its limitations. The experiments rely on natural sunlight, which introduces variations in irradiation intensity and makes it difficult to achieve full reproducibility. Additionally, the long-term stability, reusability, and potential copper leaching were not examined.

The hierarchical Cu–N–TiO_2 system demonstrates that tailored doping and controlled metal loading, when combined with porous architectures, can yield significant improvements in Cr^{6+} reduction performance. Based on these outcomes, future research may focus on evaluating catalyst durability across multiple cycles, examining the mechanistic pathways of electron transfer using advanced spectroscopic techniques, and testing the catalyst in more complex water matrices. Integrating the material into immobilized or floating photocatalytic platforms may further enhance its practical applicability by simplifying recovery and reducing catalyst loss [8].

Materials and Methods

Preparation of N-TIO_2

12 mL of TTIP was added drop wise to 120 mL of 10% NH3 at room temperature without stirring, and a white ppt was formed. After 30mins, it was filtered, washed several times with distilled water and dried at 60 °C for the remaining day or overnight under ambient temperature. Later, TiO_2 is grinded into a fine powder using a mortar and pestle. Some of the remaining ammonia breaks down, allowing N to enter the TiO_2 matrix and create N- doped TiO_2 [9].

Preparation of different weight % CuNPs

10 mmol of CuCl solution of 1wt%, 2wt%, 3wt%, 4wt%, and 5wt% was made by adding 0.0155g, 0.031g, 0.0465g, 0.062g, and 0.0775g of CuCl and dissolving it in 16mL, 32mL, 48mL, 63mL, and 79mL of deionized water, respectively. These solutions were then heated with magnetic stirring to an internal temperature of 80 °C [10].

With the use of a burette, 1M of L-Ascorbic acid of 8mL, 16mL, 24mL, 32mL, and 40mL were added to the different wt.% CuCl solutions respectively. After brown-red colored solutions were obtained, the resultant dispersion was centrifuged at 6000 rpm for 10 minutes. These were then cleaned with ethanol before being rinsed with distilled water [11].

Preparation of different weight% Cu-N-TiO_2

Each of the synthesized CuNPs was dissolved in 5mL of ethanol then mixed for an hour at 30 °C. Then, these solutions were calcined for two hours at 500 °C after being dried in an oven at 60 degrees centigrade. After the addition of CuCl, the required amount of reducing agent is added and stirred at a certain temperature. After drying, the material is compressed into powder by calcining it for two hours at 400°C in a muffle furnace [12].

Preparation of working solution of $K_2Cr_2O_7$

28.2mg of $K_2Cr_2O_7$ was dissolved in 100mL of distilled water and 20ppm of working solution was prepared by taking 4mL of 100ppm solution and with 16mL of distilled water to make 20ml of 20ppm solution. In the spectrophotometer, the observed concentration of 20ppm solution was 20.21ppm [13].

Preparation of Diphenyl Carbazide (DPC): 100ml of acetone and 1 drop of HCL-acidified 1gm DPC are appropriately combined. A pink color solution is formed when the DPC, a coloring agent, combines with Cr in an acidic medium [14].

Preparation of diluted HCL: In a beaker, 50ml of concentrated HCL was added gently after adding 50ml of diluted HCL and 50ml of distilled water. The Cr solution is made acidic using this dilute HCL for the DPC to react accordingly [15].

Photodegradation of Chromium using different weight% Cu-N-TiO_2

Each sample weighed 0.05g and was added to 20mL of 20ppm solution. Then it was kept dark for 30mins with constant stirring to get an equilibrium. Then these solutions were exposed to sunlight, and the upper sections of the beakers were wrapped with aluminum foils and were stirred

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for 2hrs. Then these solutions were filtered and the absorbances were recorded by adding 1 drop of 50% HCl, and 1 drop of DPC solution. Pink coloured solutions appeared indicating the chromium concentration. Then the concentration was measured to calculate the removal efficiency [16].

Time variation of 1wt%Cu-N-TiO

For the time variation, -30mins, 30mins, 60mins, 90mins, 120mins were taken. For each time, 0.05g of sample was weighed and was added to 20mL of 20ppm solution. Then it was kept dark for 30mins with constant stirring to get an equilibrium. After this, only -30mins solution was filtered and the rest were exposed to sunlight and the upper section of those beakers were wrapped with aluminum foil and were stirred for 30mis, 60mins, 90mins, 120mins respectively. These solutions were filtered and the absorbances were taken by adding 1drop of 50% HCl, and 1drop of DPC solution. Pink coloured solutions appeared indicating the chromium concentration. Then the concentration of those solutions was measured to calculate the removal efficiency [17].

Effect of pH for 1wt%Cu-N-TiO

For the effect of pH, pH 2, pH 4, and pH 9 of 20mL of 20ppm solutions were maintained. Then it was kept dark for 30mins with constant stirring and later these solutions were exposed to sunlight, and the upper section of those beakers were wrapped with aluminum foil and were stirred for 2hrs. Then these solutions were filtered and the absorbances were taken by adding 1drop of 50% HCl, and 1drop of DPC solution. Pink coloured solutions appeared indicating the chromium concentration. Then the concentration was measured to calculate the removal efficiency [18].

Results and Discussions

Characterization

Powder analysis of XRD

X-Ray Diffraction spectrum analysis for the nano material containing Cu dopped N-TiO_2. The composite consist of two types of crystalline phase TiO_2, anatase and rutile phase whose peaks appears at 2θ of value of 25^0, 28^0, 48^0, 54^0, 55^0, 63^0 at planes of (101), (200), (004), (105), and (211). The nano composite displays Cu in cubic and monoclinic crystalline structure whose peaks seem to appear in the planes such as (111), (200), (311), (220) representing 2θ value at 37^0 ,38^0, 42^0, 62^0, 74^0 [Figure 2].

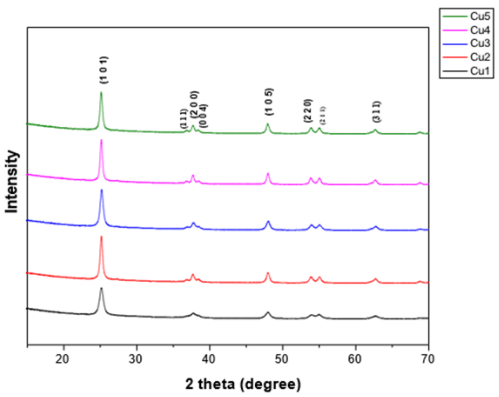

Figure 2. XRD analysisfor Cu-N-TiO_2.

SEM Analysis

SEM images were taken to observe the size and morphology of the prepared 1wt% Cu-N-TiO2 nanocomposite [Figure 3]. All the particles prepared were spherical in nature and appeared to be a homogeneous repetition of nanosphere with average diameter of approximately 65 ± 15 nm. Thecorresponding EDX analysisgives 60.4% of TiO_2 and 1.7% of Cu [Figure 4].

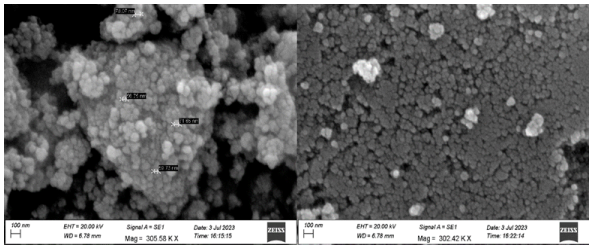

Figure 3. SEM image of 1wt% Cu-N-TiO2, (b)SEM image of 1wt% Cu-N-TiO2 at 100nm magnification with different size of nanospheres.

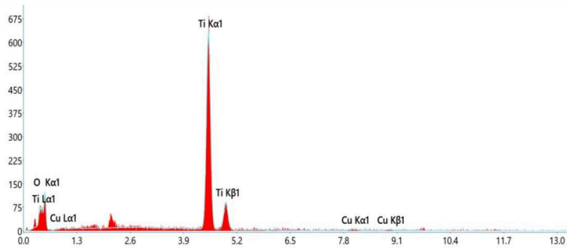

Figure 4. EDX analysis graphof 1wt% Cu-N-TiO_2.

Different weight% of Cu-N-TiO2

Graph plotted between the different weight% Cu vs degradation % where 1%-Cu shows maximum degradation and eventually decreases with increases in wt.% of Cu. But it is observed that at 5%wt of Cu, the graph shows a rise with 72.24% degradation [Table 1 and Figure 5].

Table 1. Photoreduction of Cr+6 using different wt.% of Cu-N-TIO_2.

Catalyst	Concentration	Absorbance	% degradation
Cu-wt. 1%	4.5	0.891	77.73
Cu-wt. 2%	11.88	2.352	55.51
Cu-wt. 3%	8.99	1.778	48.04
Cu- wt4%	10.5	2.078	41.21
Cu-wt. 5%	5.61	1.11	72.24

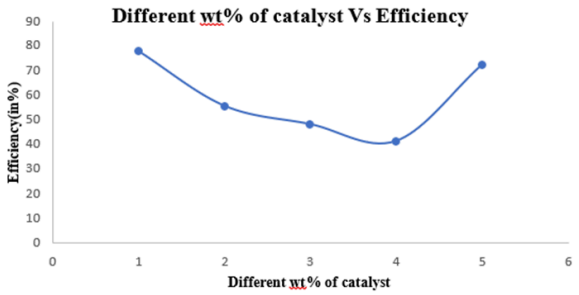

Figure 5. Different weight%of Cu-N-TiO_2.

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Effect of catalyst

Cr reduction at using different weight of photocatalyst. It is observed that around 40mg to 50 mg of photocatalyst shows around 75 to 77 % degradation. While for 50mg it shows a decline in the % of degradation due to various weight of photocatalyst [Table 2 and Figure 6].

Table 2. Effect of catalyst in photocatalysis.

Catalyst	Concentration	Absorbance	% degradation
0.03 g	9.42	1.864	53.38
0.04 g	4.74	0.938	76.54
0.05 g	4.5	0.891	77.73
0.06 g	9.65	1.909	52.25

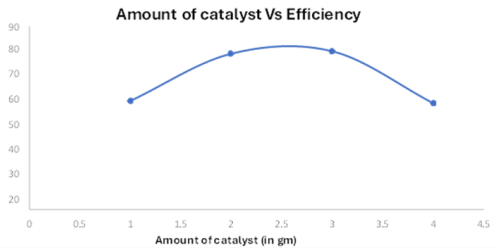

Figure 6. Percentage of degradation usingvarious concentration of catalyst.

Time variation

At different time interval Cr^{+6} shows highest degradation Cr^{+3} at 120min (77.73%) at where the efficiency of degradation increases with increases in time interval [Figure 7].

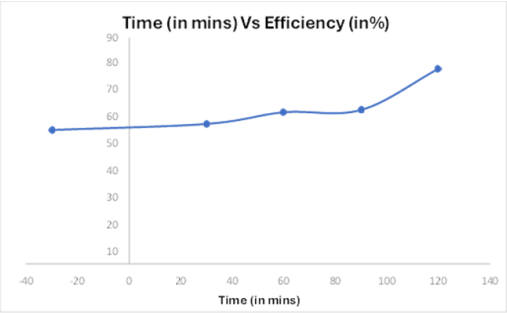

Figure 7. Effect of time variation in photocatalysis.

Effect of pH variation

At different pH variation shows highest degradation at pH 4 (73.87%) where the efficiency of degradation increases with increases in time interval [Figure 8].

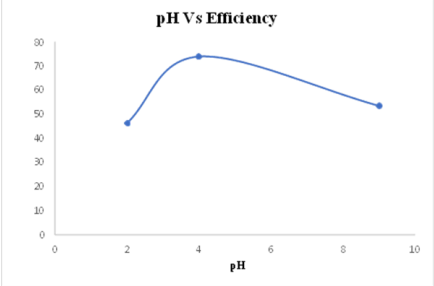

Figure 8. Effect of pH variation in photocatalysis.

Conclusion

Sunlight is green energy and infinite energy resource. Using sunlight by the photocatalyst Cu- loaded hierarchical N-doped TiO_2 the heavy metal Chromium was removed. The photocatalyst was prepared by self-formation and wetness impregnation method. By doping Cu and N, the band gap of TiO_2 is decreased so, its absorption efficiency shift from UV to UV-Visible. Hence its photocatalytic activity increased. The metal is characterized by X-ray Diffraction (XRD). Different wt.% of the catalyst is used for the treatment of Chromium. It is shown that 1 wt.% of the catalyst shows maximum reduction. Different parameters such as catalyst amount, pH of the solution, time of light irradiation, affect the rate of the reaction. At effect of catalyst (0.04 g) under 2 hour of sunlight irradiation the maximum reduction occurs that is 77.73%.

Disclosure Statement

The author does not have conflict of interest in this research.

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