

Enhanced Visible-Light-Induced Photocatalytic Activity for Cr(VI) Reduction over Magnetic Fe₃O₄-CdS Nanocomposites

(Aktiviti Fotopemangkinan Teraruh Cahaya Nampak yang Dipertingkatkan untuk Pengurangan Cr(VI) berbanding Nanokomposit Fe₃O₄-CdS Magnetik)

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ABSTRACT

Photocatalytic reduction of toxic hexavalent chromium (Cr(VI)) to less harmful Cr(III) using semiconductor nanomaterials under ambient conditions is a promising solar-driven remediation approach. However, conventional photocatalysts (such as CdS) often suffer from low efficiency and poor recyclability. A multifunctional visible-light photocatalyst, Fe₃O₄-CdS nanocomposite, with magnetic separation capability and improved Cr(VI) reduction activity, was successfully fabricated via a hydrothermal method in this study. Structural characterization confirmed the formation of spherical nanoparticles (the average particle size was approximately 66.5 nm) with good magnetic responsiveness. Although nanoscale Fe₃O₄ (nFe₃O₄) itself showed no photocatalytic activity under visible light, its composite with CdS significantly improved the transfer of photogenerated electrons in CdS. This enhanced charge extraction, thereby suppressing electron-hole recombination and ultimately leading to improved Cr(VI) reduction efficiency. The incorporation of Fe₃O₄ effectively enhances the visible-light response capability of the Fe₃O₄-CdS nanocomposite. The optimal nFe₃O₄ content was 20 wt%, with the composite exhibiting a reaction rate three times higher than that of pure CdS. Photocatalytic performance was positively influenced by lower Cr(VI) concentration, higher catalyst dosage, and acidic pH. Notably, the catalyst remained effective over a broad pH range (3.2 - 9.6). After six reuse cycles, the Cr(VI) removal efficiency decreased slightly from 99.3% to 90.5%, indicating excellent stability and reusability. These findings suggest that Fe₃O₄-CdS nanocomposites are promising photocatalyst for efficient and sustainable Cr(VI) remediation under visible light.

Keywords: Cr(VI); enhanced photocatalysis; Fe₃O₄-CdS nanocomposites; magnetic recovery; reduction

ABSTRAK

Penurunan fotokatalitik kromium heksavalen toksik (Cr(VI)) kepada Cr(III) yang kurang berbahaya menggunakan bahan nano semikonduktor di bawah keadaan ambien merupakan pendekatan pemulihan berasaskan tenaga suria yang berpotensi. Namun begitu, fotokatalis konvensional (seperti CdS) sering menghadapi masalah kecekapan rendah dan kebolegunaan semula yang lemah. Dalam kajian ini, satu fotopemangkin cahaya tampak pelbagai fungsi, iaitu nanokomposit Fe₃O₄-CdS dengan keupayaan pemisahan magnet dan aktiviti penurunan Cr(VI) yang dipertingkatkan, telah berjaya dihasilkan melalui kaedah hidroterma. Pencirian struktur mengesahkan pembentukan nanozarah berbentuk sfera (saiz purata zarah kira-kira 66.5 nm) dengan tindak balas magnet yang baik. Walaupun nanosfera Fe₃O₄ (nFe₃O₄) sendiri tidak menunjukkan sebarang aktiviti fotokatalitik di bawah cahaya tampak, gabungannya dengan CdS secara signifikan meningkatkan pemindahan elektron terjana cahaya dalam CdS. Ini mempertingkatkan pengekstrakan cas, seterusnya menekan rekombinasi elektron-lubang dan akhirnya meningkatkan kecekapan penurunan Cr(VI). Penggabungan Fe₃O₄ dengan berkesan meningkatkan keupayaan respons cahaya tampak bagi nanokomposit Fe₃O₄-CdS. Kandungan optimum nFe₃O₄ ialah 20 wt% dengan komposit menunjukkan kadar tindak balas tiga kali ganda lebih tinggi berbanding CdS tulen. Prestasi fotokatalitik turut dipengaruhi secara positif oleh kepekatan Cr(VI) yang lebih rendah, dos pemangkin yang lebih tinggi, dan pH berasid. Menariknya, pemangkin kekal berkesan dalam julat pH yang luas (3.2-9.6). Selepas enam kitaran penggunaan semula, kecekapan penyingkiran Cr(VI) hanya menurun sedikit daripada 99.3% kepada 90.5%, menunjukkan kestabilan dan kebolegunaan semula yang sangat baik. Keputusan ini menunjukkan bahawa nanokomposit Fe₃O₄-CdS merupakan fotokatalis yang berpotensi tinggi untuk pemulihan Cr(VI) yang cekap dan lestari di bawah cahaya tampak.

Kata kunci: Cr(VI); fotokatalisis dipertingkat; nanokomposit Fe₃O₄-CdS; pemulihan magnet; penurunan

INTRODUCTION

Hexavalent chromium (Cr(VI)) is a common industrial pollutant frequently found in aquatic environments, originating primarily from leather tanning, pigment manufacturing, electroplating, and chromium salt industries (Cui et al. 2025; Zhao et al. 2025). Due to its high mobility, strong corrosiveness, and extreme toxicity—approximately 100 times more toxic than trivalent chromium (Cr(III))—Cr(VI) has been designated as a priority pollutant by China and many other countries (Acharya, Sillanpää & Al-Farraj 2025; Aslam, Yousafzai & Javed 2022; Shi et al. 2021; Wang et al. 2025). In contrast, Cr(III) is an essential trace element for humans and can be effectively removed from water via precipitation as Cr(OH)_3 under neutral or alkaline conditions. Therefore, the reduction of Cr(VI) to Cr(III), followed by precipitation, is a widely adopted strategy for the treatment of chromium-contaminated wastewater (Liu et al. 2025; Niu et al. 2025).

Conventional chemical reduction methods typically rely on large doses of chemical reductants, such as ferrous sulfate or sodium bisulfite, leading to high treatment costs and secondary pollution, which limit their large-scale application (Zhang et al. 2018; Zou et al. 2025). Semiconductor-based photocatalytic reduction technology offers a promising alternative, as it can utilize solar energy to generate photoinduced electrons for the direct reduction of Cr(VI) to Cr(III) under ambient conditions, without the need for additional chemical reagents (Cao et al. 2020; Ghosh, Khan & Saha 2025; Liu et al. 2024).

Among various photocatalysts, metal sulfide semiconductors have been extensively investigated due to their strong visible-light absorption capabilities. Cadmium sulfide (CdS), with a band gap of 2.42 eV, is a typical visible-light-responsive semiconductor (Kalita et al. 2023; Wang et al. 2023). However, its practical application is hindered by limited catalytic efficiency and poor recyclability (Bian et al. 2013; Cheng et al. 2022; McDaniel & Shim 2009). Nanoscale Fe_3O_4 (nFe_3O_4), known for its excellent magnetic properties and biocompatibility, is often employed in constructing composite nanomaterials to facilitate catalyst recovery (Xu et al. 2016). Furthermore, the relatively low electrical resistivity of nFe_3O_4 facilitates charge carrier transfer (Xu et al. 2013b), thereby potentially enhancing the photocatalytic performance. Beyond enabling magnetic separation, the coupling of Fe_3O_4 with CdS offers a promising strategy to boost photocatalytic activity (Mansour, Ibrahim & Azab 2022), leading to multifunctional catalysts. Nevertheless, few studies have focused on the Fe_3O_4 -CdS system for Cr(VI) photoreduction, and the optimal Fe_3O_4 loading for Cr(VI) removal remains unexplored.

In this study, magnetically separable Fe_3O_4 -CdS nanocomposites were synthesized via a hydrothermal method. The nFe_3O_4 content in the composite was optimized, and the structural and physicochemical

properties of the material were systematically characterized. The photocatalytic performance of the composite for Cr(VI) reduction under visible light was evaluated under various experimental conditions, along with its stability and reusability. The results aim to provide theoretical insights for the design of efficient, recyclable photocatalysts and offer practical guidance for the treatment of Cr(VI)-contaminated wastewater.

MATERIALS AND METHODS

MATERIALS

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), cadmium chloride (CdCl_2), hexahydrate ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonia monohydrate ($\text{NH}_3 \cdot \text{H}_2\text{O}$), hydrochloric acid (HCl), sodium hydroxide (NaOH), anhydrous ethanol, thioacetamide were purchased from the Aladdin Reagent Co. Ltd., China. All chemicals were of analytical grade. The ultrapure water (UPW) used in all experiments was obtained from a Direct-Q system (Millipore, Billerica, MA) with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$.

SYNTHESIS OF Fe_3O_4 -CdS NANOCOMPOSITES

Synthesis of nFe_3O_4 : following the method described in Chang et al. (2011), 2.3318 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.1983 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (molar ratio 2:1) were dissolved in 200 mL of deionized water under a nitrogen atmosphere and ultrasonicated for 10 min in a three-neck flask. Under continuous stirring, ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$) was added dropwise based on the stoichiometric requirement. Upon completion of the addition, a black precipitate of nFe_3O_4 (1 g) formed. The product was washed three times with deionized water after nitrogen purging for 1 hour and stored for further use.

Synthesis of CdS (Sahoo et al. 2014): 5 mL of 0.1 M thioacetamide solution was added to 10 mL of 0.05 M CdCl_2 solution in a 100 mL beaker and stirred for 15 min. The mixture was then transferred to a Teflon-lined stainless-steel autoclave and heated at 100°C for 3 h. After naturally cooling to room temperature, the resulting precipitate was collected by vacuum filtration, washed with deionized water and absolute ethanol, dried under nitrogen, and ground into fine powder to obtain CdS.

Synthesis of Fe_3O_4 -CdS nanocomposites: 10 mL of 0.05 M CdCl_2 solution was added to a predetermined amount of prepared nFe_3O_4 and stirred for 5 min, followed by the addition of 5 mL of 0.1 M thioacetamide solution with further stirring for 15 min. The mixture was then transferred to a Teflon-lined autoclave and heated at 100°C for 3 h. After cooling to room temperature, the product was collected by vacuum filtration, washed thoroughly with deionized water and ethanol, dried under nitrogen, and ground to obtain the Fe_3O_4 -CdS nanocomposite. By varying the amount of

$n\text{Fe}_3\text{O}_4$, composites with $n\text{Fe}_3\text{O}_4$ mass fractions of 5%, 10%, 20%, and 25% were prepared and denoted as 5% Fe_3O_4 -CdS, 10% Fe_3O_4 -CdS, 20% Fe_3O_4 -CdS, and 25% Fe_3O_4 -CdS, respectively.

CHARACTERIZATION

The morphology of the synthesized materials was examined using a Hitachi S-450 scanning electron microscope (SEM), and surface elemental composition was analyzed using an energy-dispersive X-ray spectrometer (EDS) attached to the SEM. The phase composition and crystal structure were determined by X-ray diffraction (XRD) using a DX-2600 diffractometer. The Brunauer–Emmett–Teller (BET) surface area was measured using a Micromeritics TriStar II 3030 analyzer (USA). Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) was measured through a UV-vis spectrophotometer (UV-2550, Shimadzu).

PHOTOCATALYTIC REDUCTION OF Cr(VI) UNDER VISIBLE LIGHT

The photocatalytic performance of the synthesized materials was evaluated via the reduction of Cr(VI) in aqueous solution (using $\text{K}_2\text{Cr}_2\text{O}_7$ as the Cr(VI) source) under visible-light irradiation. A 250 W xenon lamp equipped with a cutoff filter ($\lambda > 420$ nm) served as the visible-light source (Zhang et al. 2011). The reaction was conducted at room temperature in a quartz reactor containing 100 mL of Cr(VI) solution and a specified amount of photocatalyst. A circulating water system was used to control the reaction temperature. Prior to illumination, the suspension was stirred in the dark for 30 min to establish adsorption-desorption equilibrium (Zhang et al. 2011).

During irradiation, 4.0 mL aliquots were withdrawn every 20 min, centrifuged at $14,972 \times g$ for 3 min, and the supernatant was analyzed for Cr(VI) concentration using the diphenylcarbazide spectrophotometric method (Xv et al. 2025). The Cr(VI) removal efficiency was calculated using the following equation (Zhang, Li & Xu 2012).

$$\text{Cr(VI) removal efficiency (\%)} = (A_0 - A_t) / A_0 \times 100\% \quad (1)$$

where A_0 and A_t represent the absorbance of the Cr(VI) solution at initial time and visible-light irradiation time t , respectively.

Experimental Conditions

Photocatalytic performance comparison of different materials: catalyst dosage, 0.1 g; initial Cr(VI) concentration, $10 \text{ mg} \cdot \text{L}^{-1}$; initial pH, 5.2. Effect of initial Cr(VI) concentration: using 0.1 g of 20% Fe_3O_4 -CdS as the catalyst, Cr(VI) concentrations of 10, 15, 20, 30, and $40 \text{ mg} \cdot \text{L}^{-1}$ were tested at pH 5.2. Effect of catalyst

dosage: with initial Cr(VI) concentration at $30 \text{ mg} \cdot \text{L}^{-1}$ and pH 5.2, 20% Fe_3O_4 -CdS catalyst dosages of 0.05, 0.1, 0.3, and 0.5 g were examined. Effect of initial pH: using 0.1 g of 20% Fe_3O_4 -CdS and $30 \text{ mg} \cdot \text{L}^{-1}$ Cr(VI), initial pH values of 3.2, 5.2 (unaltered), 6.3, 7.0, and 9.6 were tested. The pH was adjusted using 0.1 M NaOH or HCl solutions. Stability and reusability tests: under conditions of $30 \text{ mg} \cdot \text{L}^{-1}$ Cr(VI), 0.1 g of 20% Fe_3O_4 -CdS, and pH 5.2, the photocatalyst was recovered after each 120-min irradiation cycle via magnetic separation. The used catalyst was washed with 1.0 mM HNO_3 and deionized water, dried in a vacuum oven at 100°C for 4 h, and reused. To ensure sufficient material for subsequent cycles, parallel experiments were conducted in some cycles (e.g., the 4th and 5th runs) to accumulate recovered catalyst.

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE Fe_3O_4 -CdS NANOCOMPOSITES

To confirm the phase composition of all prepared composites, XRD patterns of Fe_3O_4 -CdS with different $n\text{Fe}_3\text{O}_4$ mass fractions (5%, 10%, 20%, and 25%) were recorded and are presented in Figure 1(A). All samples exhibit distinct diffraction peaks corresponding to CdS (greenockite) and Fe_3O_4 (magnetite). In all patterns, peaks at $2\theta = 30.2^\circ, 35.6^\circ, 43.3^\circ, 53.7^\circ, 57.3^\circ$, and 62.8° are assigned to Fe_3O_4 , while those at $24.9^\circ, 26.6^\circ, 28.3^\circ, 36.7^\circ, 43.7^\circ, 47.9^\circ, 52.9^\circ, 66.9^\circ, 70.9^\circ$, and 75.6° correspond to CdS, this is the hexagonal crystal structure of CdS (Tuz Johra & Jung 2014). As the $n\text{Fe}_3\text{O}_4$ content increases from 5% to 25%, the characteristic peaks of Fe_3O_4 at $2\theta = 30.2^\circ, 35.6^\circ$, and 62.8° gradually intensify, while the CdS peaks remain clearly observable. This indicates that the Fe_3O_4 -CdS nanocomposites have been successfully synthesized across the entire composition range without the formation of any detectable impurity phases.

The theoretical Cd: Fe molar ratio for the 20% Fe_3O_4 -CdS composite is 2.14, and EDS analysis (Figure 1(C)) yields a value of 2.03, in good agreement with the calculation. As seen in Figure 1(B), the 20% Fe_3O_4 -CdS composite consists of nearly spherical particles, the average particle size was approximately 66.5 nm, which show agglomeration due to interparticle interactions. Moreover, the composite can be readily separated from solution under an external magnetic field (Figure 1(D)).

EFFECT OF $n\text{Fe}_3\text{O}_4$ CONTENT ON THE PHOTOCATALYTIC REDUCTION OF Cr(VI) BY Fe_3O_4 -CdS

The adsorption and visible-light-driven photocatalytic reduction of Cr(VI) were investigated using various catalysts (0.1 g dosage) in an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ with an initial Cr(VI) concentration of $10 \text{ mg} \cdot \text{L}^{-1}$. As shown in Figure 2(a), after 30 min of dark adsorption,

the Cr(VI) removal efficiencies for $n\text{Fe}_3\text{O}_4$, CdS, 5% Fe_3O_4 -CdS, 10% Fe_3O_4 -CdS, 20% Fe_3O_4 -CdS, and 25% Fe_3O_4 -CdS were 18.1%, 17.5%, 14.2%, 17.3%, 21.8%, and 18.7%, respectively. The specific surface areas of these materials were 32.2, 30.3, 24.2, 27.4, 40.6, and 38.5 $\text{m}^2\cdot\text{g}^{-1}$, respectively. Generally, a larger specific surface area correlates with a stronger adsorption capacity for pollutants (Wang et al. 2021).

In the absence of any photocatalyst, Cr(VI) was barely reduced under 120 min of visible light irradiation. Upon the addition of $n\text{Fe}_3\text{O}_4$, the Cr(VI) removal remained at approximately 18%, consistent with the dark adsorption result. This indicates that $n\text{Fe}_3\text{O}_4$ synthesized in this study lacks visible-light photocatalytic activity for Cr(VI) reduction, and its removal effect is primarily attributed to adsorption. In contrast, both CdS and Fe_3O_4 -CdS nanocomposites exhibited significant photocatalytic reduction activity. After 20 min of visible light irradiation, the Cr(VI) removal efficiencies for CdS, 5% Fe_3O_4 -CdS, 10% Fe_3O_4 -CdS, 20% Fe_3O_4 -CdS, and 25% Fe_3O_4 -CdS reached 67.8%, 85.4%, 90.1%, 95.4%, and 80.3%, respectively -substantially exceeding the removal due to dark adsorption. This suggests that photocatalytic reduction is the dominant mechanism

for Cr(VI) removal, and that the composite materials outperform pure CdS in photocatalytic efficiency.

Further analysis showed that the introduction of an appropriate amount of $n\text{Fe}_3\text{O}_4$ enhanced the photocatalytic reduction efficiency of CdS. When the $n\text{Fe}_3\text{O}_4$ content was below 20%, photocatalytic activity increased with the loading amount, with the 20% $n\text{Fe}_3\text{O}_4$ -CdS composite exhibiting the highest catalytic efficiency. However, excessive loading (25%) led to a decline in photocatalytic performance.

The photocatalytic reduction of Cr(VI) under different conditions was fitted using a pseudo-first-order kinetic model (Xuan, Li & Hao 2024):

$$\ln(C_0/C_t) = kt \quad (2)$$

where C_0 is the Cr(VI) concentration after adsorption equilibrium; C_t is the concentration at irradiation time t ; and k is the rate constant. As shown in Figure 2(B), all fitted linear correlations had coefficients (R^2) greater than 0.93, indicating good agreement with the model. The rate constants k for CdS, 5% Fe_3O_4 -CdS, 10% Fe_3O_4 -CdS, 20% Fe_3O_4 -CdS, and 25% Fe_3O_4 -CdS were 0.0278, 0.0575, 0.0604, 0.0851, and 0.0663 min^{-1} ,

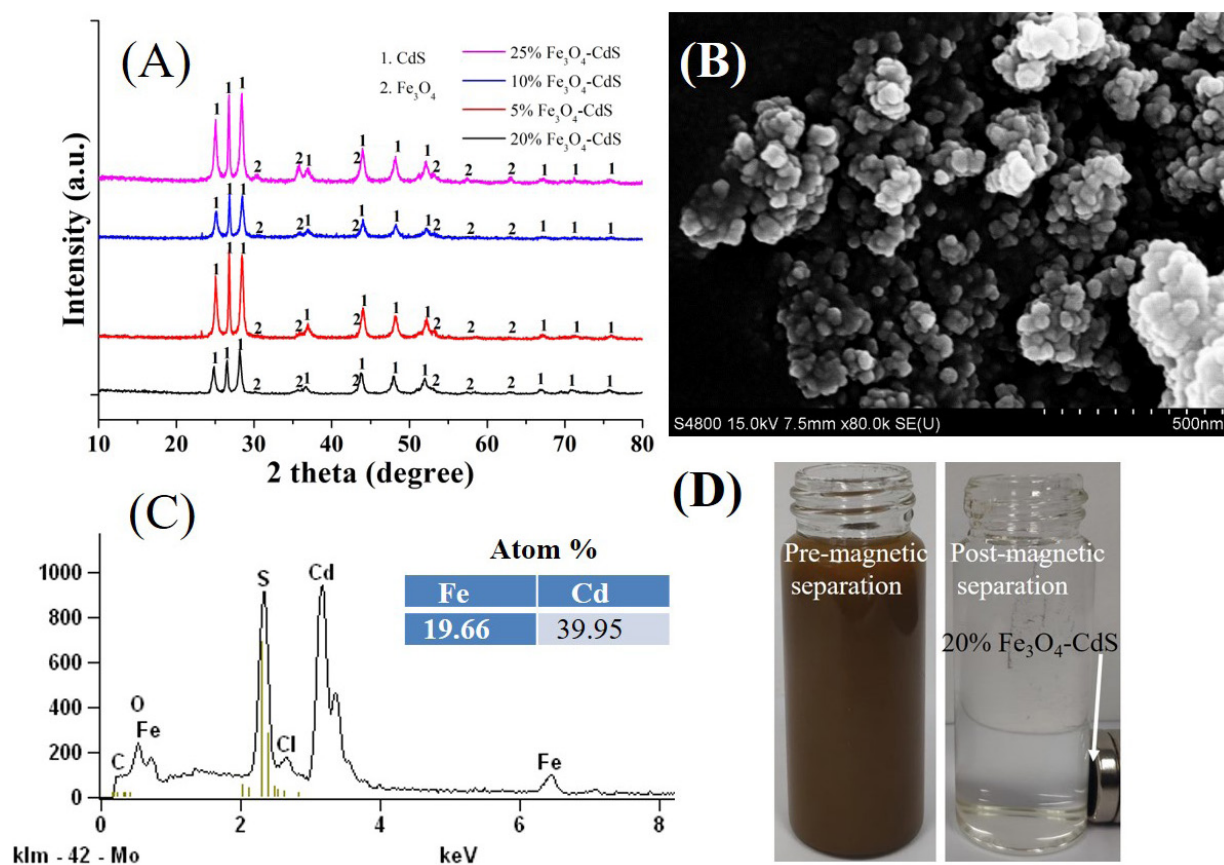


FIGURE 1. Characterization of Fe_3O_4 -CdS nanocomposite: (A) XRD pattern; (B) SEM image (20% Fe_3O_4 -CdS); (C) EDS spectrum (20% Fe_3O_4 -CdS); and (D) magnetic separation behavior (20% Fe_3O_4 -CdS)

respectively, with the 20% Fe₃O₄-CdS composite showing the highest value, approximately three times that of pure CdS.

The performance enhancement can be attributed to two main factors: (1) nFe₃O₄, as a low-resistance semiconductor (resistivity 10⁻³ Ω·cm), exhibits excellent electron transport properties (Xu et al. 2013), facilitating the transfer of photogenerated electrons from CdS to Cr(VI), thereby improving the reduction efficiency. This is the primary reason for the observed enhancement. (2) The 20% Fe₃O₄-CdS composite possessed the largest specific surface area, improving pollutant adsorption on the catalyst surface and providing more active contact sites for the photocatalytic reaction. However, excessive loading of nFe₃O₄ may lead to coverage of the active sites on the CdS surface, hindering light absorption and interaction with reactants, ultimately suppressing the photocatalytic activity. In summary, the optimal loading of nFe₃O₄ in the Fe₃O₄-CdS composite for Cr(VI) photocatalytic reduction was determined to be 20%.

EFFECT OF INITIAL Cr(VI) CONCENTRATION ON THE PHOTOCATALYTIC PERFORMANCE OF Fe₃O₄-CdS

As shown in Figure 3, the photocatalytic reduction performance of the 20% Fe₃O₄-CdS composite (0.1 g dosage) was investigated under visible light irradiation at various initial concentrations of Cr(VI). The results indicate that, under the same irradiation time, the reduction efficiency of Cr(VI) increased with decreasing initial concentration. Specifically, at initial Cr(VI) concentrations of 10, 15, and 20 mg·L⁻¹, the removal efficiencies reached 99.3%, 98.7%, and 98.7%, respectively, after 40 min of light exposure, indicating that Cr(VI) was almost completely reduced in all three cases.

In addition, the composite also demonstrated excellent photocatalytic reduction capability at higher initial concentrations of Cr(VI). When the initial Cr(VI) concentrations were increased to 30 and 40 mg·L⁻¹, the removal efficiencies still reached 99.3% and 88.2%, respectively, after 120 min of visible light irradiation. These results confirm that the 20% Fe₃O₄-CdS composite exhibits high photocatalytic reduction efficiency across a wide range of Cr(VI) concentrations, highlighting its potential for practical applications in the treatment of Cr(VI)-contaminated wastewater.

EFFECT OF CATALYST DOSAGE ON PHOTOCATALYTIC PERFORMANCE

As shown in Figure 4, the photocatalytic reduction performance of Cr(VI) (initial concentration, 30 mg·L⁻¹) was investigated using varying dosages of 20% Fe₃O₄-CdS nanocomposites. The results demonstrate that the Cr(VI) reduction efficiency significantly increased with increasing catalyst dosage under identical irradiation

times. When the catalyst dosages were 0.3 g and 0.5 g, nearly complete reduction of Cr(VI) was achieved within 20 min of visible light irradiation. In contrast, when the dosage was reduced to 0.05 g, the Cr(VI) removal efficiency was only 62.4% even after 120 min of irradiation. At a dosage of 0.1 g, a removal efficiency of 99.3% was achieved within 120 min. Considering both removal efficiency and economic feasibility, a dosage of 0.1 g was identified as the optimal amount for 20% Fe₃O₄-CdS.

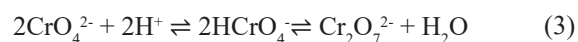
Furthermore, as also observed in Figure 4, the adsorption capacity of the catalyst for Cr(VI) increased markedly with higher dosages of 20% Fe₃O₄-CdS, accompanied by enhanced photocatalytic reduction efficiency. This phenomenon can be attributed to the increased number of surface active sites on the catalyst. At lower dosages, the limited number of active sites restricts the reduction reaction between photogenerated electrons and Cr(VI). Increasing the catalyst dosage provides more active sites for the reaction, thereby promoting charge separation and transfer, and ultimately enhancing the overall photocatalytic performance. Furthermore, the increased catalyst dosage results in a larger total surface area, improving pollutant adsorption and consequently the efficiency of photocatalytic reduction (Ullah et al. 2021).

EFFECT OF INITIAL pH OF Cr(VI) AQUEOUS SOLUTION ON THE PHOTOCATALYTIC PERFORMANCE OF Fe₃O₄-CdS

Figure 5 presents the visible - light photocatalytic reduction performance of 0.1 g 20% Fe₃O₄-CdS toward 30 mg·L⁻¹ Cr(VI) under different initial pH conditions. The results show that as the pH decreases, the removal rate of Cr(VI) increases; under alkaline conditions (pH 9.6), the removal efficiency is minimal. This trend may be attributed to the following factors (Qi et al. 2023; Zhang et al. 2020):

Speciation of Cr(VI) and redox potential differences

The speciation of Cr(VI) in solution depends strongly on pH. At pH = 1.2, almost all Cr(VI) exists as Cr₂O₇²⁻, whereas at pH = 11, it predominantly forms CrO₄²⁻. Within the pH range of 3 to 9.6 investigated here, the following equilibrium holds:



The corresponding standard electrode potentials are: CrO₄²⁻/Cr³⁺ (-0.13 V), HCrO₄⁻/Cr³⁺ (1.35 V), Cr₂O₇²⁻/Cr³⁺ (1.232 V).

These relate to the following half-reactions:



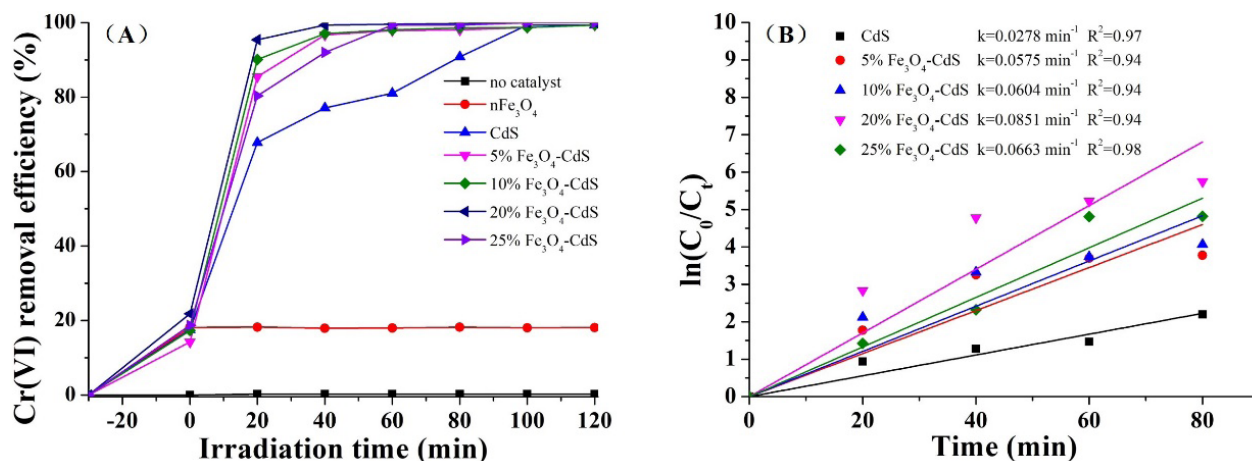


FIGURE 2. (A) Comparison of photocatalytic activity of different catalysts for Cr(VI) reduction under visible light irradiation; and (B) photocatalytic reaction kinetics of Cr(VI) with reaction time

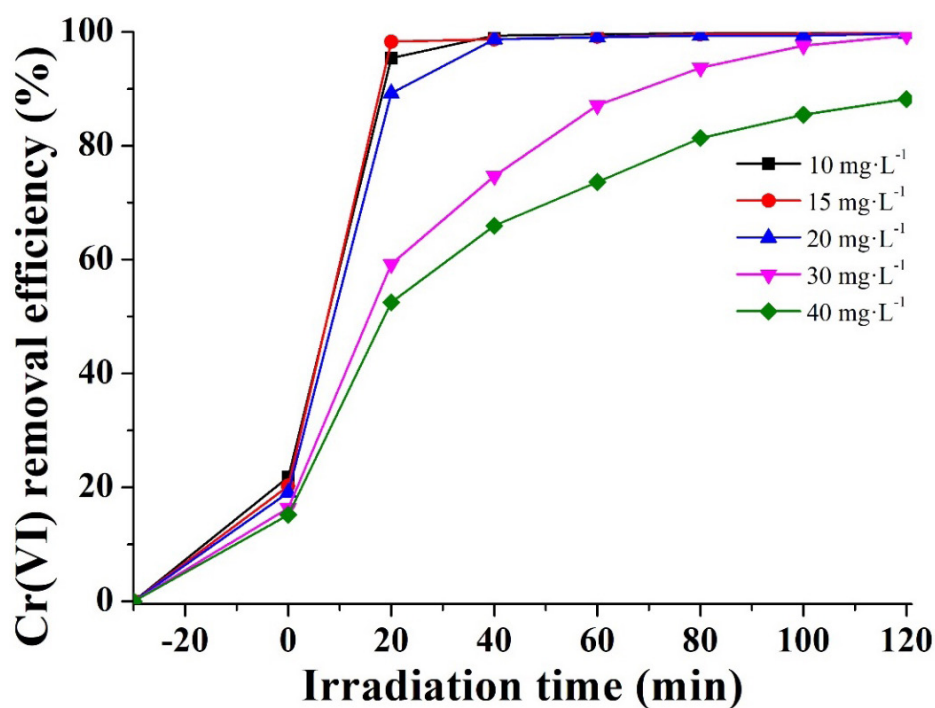
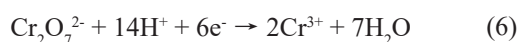
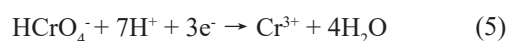


FIGURE 3. Effect of initial Cr(VI) concentration on the photocatalytic performance of 20% Fe_3O_4 -CdS



Applying the Nernst equation:

$$\varphi = \varphi^\theta + (0.059/6) \lg ([\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}^+]^{14} / [\text{Cr}^{3+}]^2). \quad (7)$$

As the H^+ concentration increases (i.e., pH decreases), the electrode potential increases, enhancing the oxidizing

ability of Cr(VI) and making reduction by photogenerated electrons more favorable. Conversely, under alkaline conditions, the $\text{CrO}_4^{2-}/\text{Cr}^{3+}$ couple has a lower electrode potential and thus weaker electron acceptance capability, which is unfavorable for photocatalytic reduction. Meanwhile, because the 20% Fe_3O_4 -CdS reduction process consumes H^+ , the presence of higher H^+ concentration further drives the reduction reaction forward.

Effect of by-product precipitation under alkaline conditions

Under alkaline conditions, Cr^{3+} may react with OH^- to form $\text{Cr}(\text{OH})_3$ precipitate. This precipitate can deposit on the surface of the catalyst, blocking active sites and impeding further reaction, thus reducing photocatalytic activity.

Influence of initial pH on adsorption

At different pH values, the adsorption capacity of 20% $\text{Fe}_3\text{O}_4\text{-CdS}$ toward Cr(VI) varies. When the initial pH values were 3.2, 5.2, 6.3, 7.0, and 9.6, the corresponding Cr(VI) adsorption ratios were 31.0%, 16.4%, 15.2%, 14.7%, and 10.3%, respectively. Higher adsorption facilitates greater local concentration of Cr(VI) at the catalyst surface, enhancing the probability of electron transfer and thus improving photocatalytic reduction. Therefore, the stronger adsorption capacity under acidic conditions is another important reason why 20% $\text{Fe}_3\text{O}_4\text{-CdS}$ demonstrates superior photocatalytic performance in acidity.

As shown in Figure 5, the photocatalytic reduction efficiency of 20% $\text{Fe}_3\text{O}_4\text{-CdS}$ toward $30 \text{ mg}\cdot\text{L}^{-1}$ Cr(VI) increases significantly as the initial pH decreases, and its lowest removal rate is observed at pH 9.6. This behavior primarily arises from the higher redox driving force of Cr(VI) under acidic conditions and the further promotion of reduction by the consumption of H^+ during the catalyst reaction. Under alkaline conditions, the deposited $\text{Cr}(\text{OH})_3$ can block active sites, and the

relatively low adsorption at pH 9.6 (only 10.3%) further weakens the reduction efficiency. Consequently, the material exhibits superior photocatalytic performance in acidic environments.

Under 120 min of visible light irradiation, with initial pH values of 3.2, 5.2 (unadjusted), 6.3, 7.0, and 9.6, the respective Cr(VI) removal rates were 99.8%, 99.3%, 96.7%, 94.8%, and 88.0%. Although the catalyst performs best under acidic conditions, the 20% $\text{Fe}_3\text{O}_4\text{-CdS}$ still maintains good reduction efficiency across the relatively wide pH range of 3.2-9.6, demonstrating strong environmental adaptability.

PHOTOCATALYTIC STABILITY OF $\text{Fe}_3\text{O}_4\text{-CdS}$

Photocatalyst stability is a critical factor in evaluating its practical applicability. To assess the photocatalytic stability of 20% $\text{Fe}_3\text{O}_4\text{-CdS}$, cyclic photocatalytic reduction experiments were conducted using 0.1 g of 20% $\text{Fe}_3\text{O}_4\text{-CdS}$ to treat $30 \text{ mg}\cdot\text{L}^{-1}$ Cr(VI) solutions. As shown in Figure 6, after six consecutive cycles, the Cr(VI) removal efficiency decreased only slightly from 99.3% in the first cycle to 90.5% in the sixth cycle. This result indicates that 20% $\text{Fe}_3\text{O}_4\text{-CdS}$ possesses excellent photocatalytic stability.

PLAUSIBLE REACTION MECHANISM

In this study, it is hypothesized that the introduction of Fe_3O_4 , as compared to pristine CdS, can endow the $\text{Fe}_3\text{O}_4\text{-CdS}$ composite nanomaterials with superior

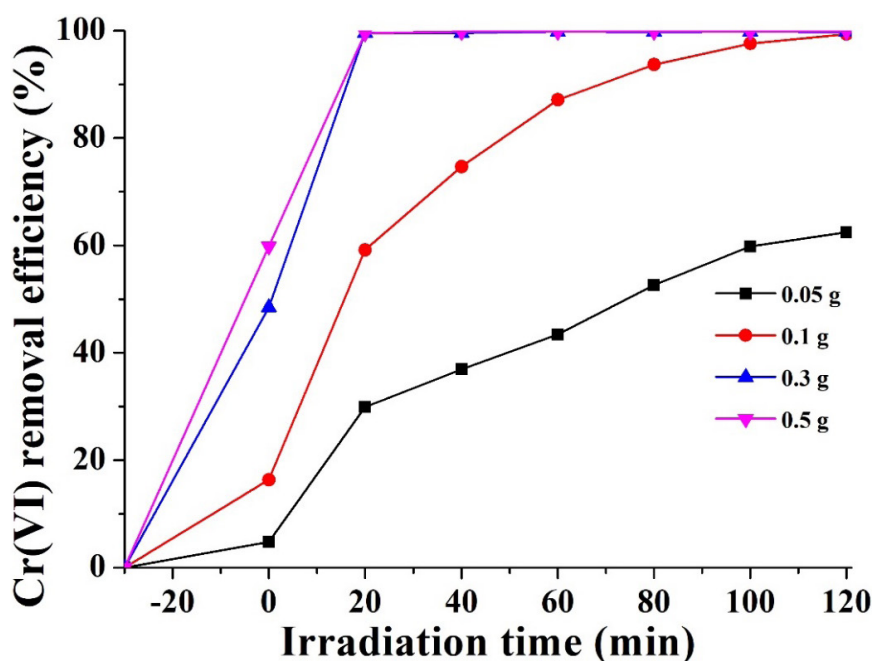


FIGURE 4. Effect of $\text{Fe}_3\text{O}_4\text{-CdS}$ dosage on the photocatalytic reduction efficiency of Cr(VI)

photocatalytic activity through modulating the bandgap structure and promoting charge separation. Meanwhile, the magnetic property of Fe_3O_4 also enables the composites to possess favorable magnetic recoverability.

The optical absorption properties of CdS and Fe_3O_4 -CdS composites with various Fe_3O_4 contents were characterized by UV-Vis DRS spectra. As shown in Figure 7, compared with pristine CdS, the absorption edge of the Fe_3O_4 -CdS composites exhibits an evident red shift, indicating that the incorporation of Fe_3O_4 effectively enhances the visible-light response capability of the material. The bandgap energies (E_g) of the as-prepared samples were estimated according to the Tauc plot equation (Mansour, Ibrahim & Azab 2022): $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where α is the absorption coefficient; $h\nu$ is the incident photon energy; A is a constant; and $n = 0.5$ for CdS as a direct-bandgap semiconductor (Cao et al. 2020). The calculated E_g value of pristine CdS is 2.42 eV, which is in good agreement with the reported value (~ 2.42 eV) (Kalita et al. 2023; Wang et al. 2023). The E_g values of the 5%, 10%, 20%, and 25% Fe_3O_4 -CdS composites were determined to be 2.38, 2.32, 2.21, and 2.26 eV, respectively. When the Fe_3O_4 content does not exceed 20%, the bandgap of the composites gradually narrows with increasing Fe_3O_4 proportion, exhibiting a red-shift trend. However, upon further increasing the Fe_3O_4 content to 25%, the bandgap unexpectedly widens to 2.26 eV. Such variation in bandgap energy may be ascribed to the interaction between CdS nanoparticles and Fe^{3+} ions located in the localized states within the

energy bands (Mansour, Ibrahim & Azab 2022). Overall, the Fe_3O_4 -CdS composites possess narrower bandgaps than pristine CdS, which is favorable for enlarging the energy gap of photogenerated electron-hole pairs under visible-light irradiation (Zhang et al. 2020), thereby promoting photocatalytic activity.

To elucidate the predominant active species involved in the photocatalytic reduction of Cr(VI) over the 20% Fe_3O_4 -CdS composite, radical scavenging experiments were carried out using potassium bromate (KBrO_3) as an electron scavenger. Under identical reaction conditions, the removal efficiency of Cr(VI) over 20% Fe_3O_4 -CdS reached 94.8% in the absence of a scavenger, whereas it dramatically dropped to 36.9% upon the addition of 2 mM KBrO_3 . This result clearly demonstrates that photogenerated electrons play a critical role in the Cr(VI) reduction process. In the Fe_3O_4 -CdS composite, Fe_3O_4 serves as an excellent electron conductor (Xu et al. 2016; Xu et al. 2013a, 2013b), which facilitates the transfer of photogenerated electrons generated from CdS under visible-light excitation, thus accelerating the reduction of Cr(VI). Such efficient electron transfer promotes charge separation and suppresses the recombination of electron-hole pairs (Zhang et al. 2020), ultimately leading to a significant enhancement in the photocatalytic performance of the Fe_3O_4 -CdS nanocomposites. Additionally, some of the excited electrons on the surface of the Fe_3O_4 -CdS composite may react with adsorbed oxygen to generate superoxide radicals ($\cdot\text{O}_2^-$), which can also contribute to the reduction of Cr(VI) to Cr(III) (Ullah et al. 2021).

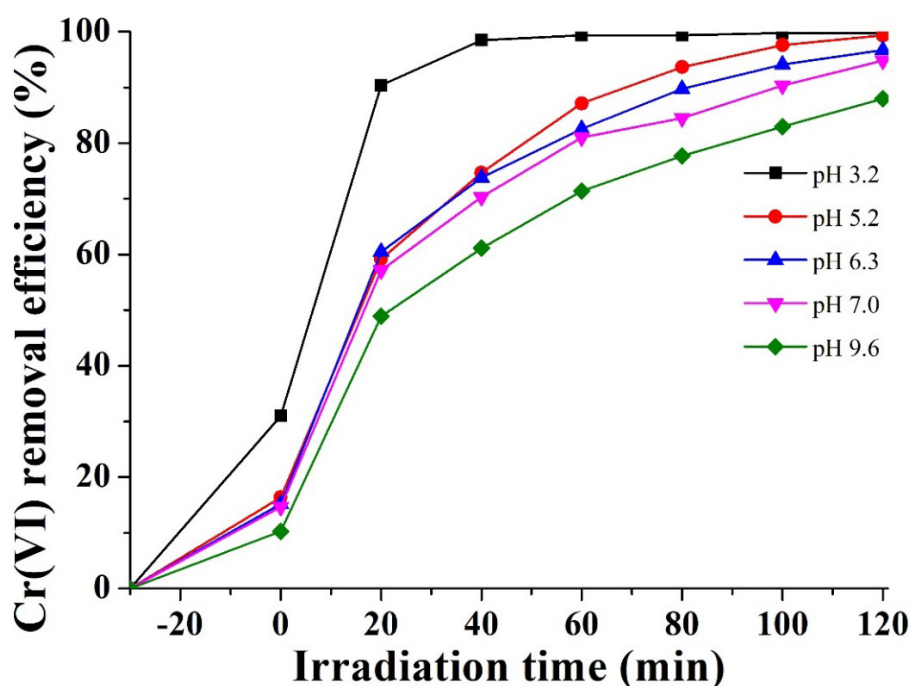


FIGURE 5. Influence of initial pH of Cr(VI) solution on the photocatalytic performance of 20% Fe_3O_4 -CdS

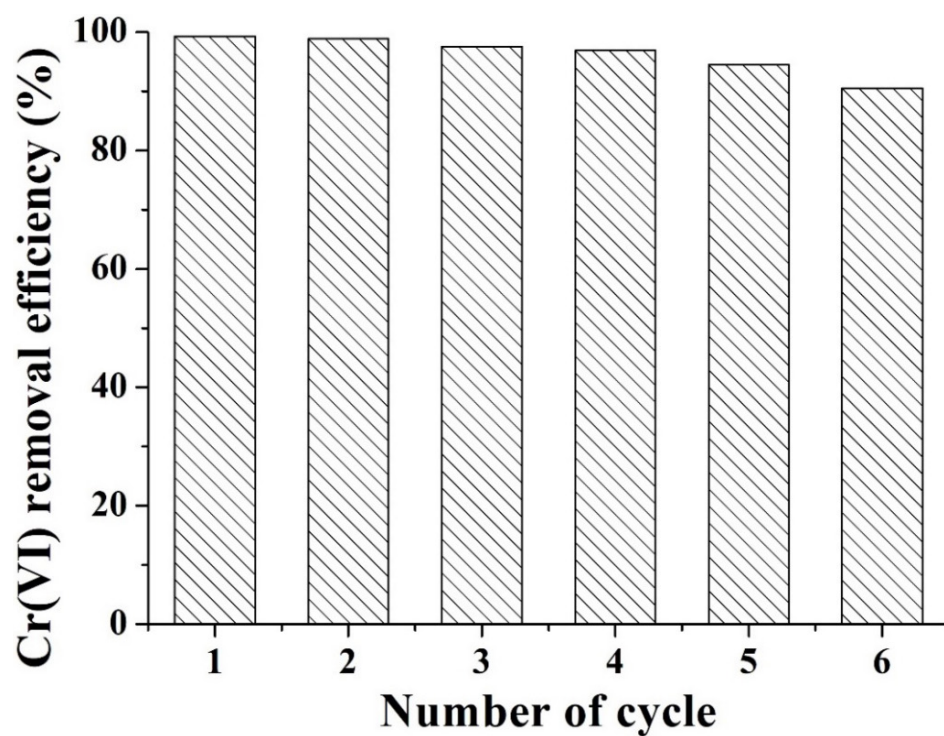


FIGURE 6. Reusability of 20% Fe_3O_4 -CdS in the photocatalytic reduction of Cr(VI)

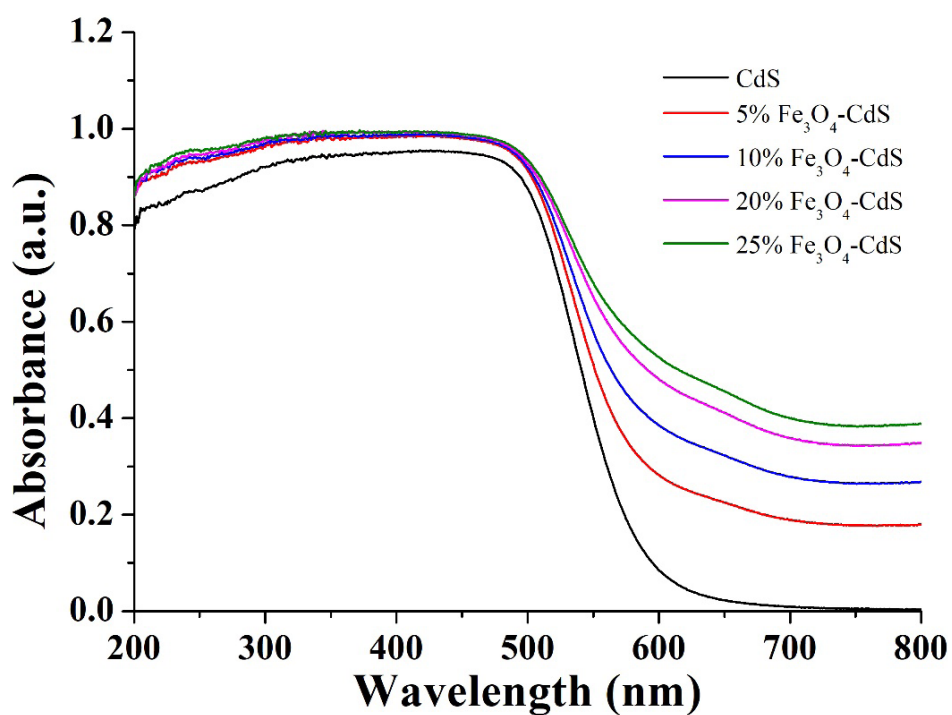


FIGURE 7. UV-Vis absorption spectra of CdS and Fe_3O_4 -CdS samples

CONCLUSIONS

In this study, a multifunctional visible-light photocatalyst, Fe_3O_4 -CdS nanocomposite, with magnetic separation capability and improved Cr(VI) reduction activity, was successfully fabricated via a hydrothermal method. The main findings are as follows: 1) The Fe_3O_4 -CdS composite consists of spherical nanoparticles with an average size of approximately 66.5 nm and exhibits strong magnetic responsiveness, enabling efficient recovery from aqueous solution under an external magnetic field. 2) The optimal nFe_3O_4 loading in the composite for Cr(VI) photoreduction is 20 wt%, at which the reaction rate constant (0.0851 min^{-1}) is approximately three times that of pure CdS (0.0278 min^{-1}). Excessive loading (25 wt%) leads to decreased performance. 3) Photocatalytic reduction efficiency increases with decreasing initial Cr(VI) concentration, increasing catalyst dosage, and acidic pH. The 20% Fe_3O_4 -CdS composite maintains high activity across a broad pH range of 3.2 - 9.6. 4) Under optimal conditions (30 $\text{mg}\cdot\text{L}^{-1}$ Cr(VI), 0.1 g catalyst, pH 5.2), the 20% Fe_3O_4 -CdS composite achieves 99.3% Cr(VI) removal within 120 min. After six reuse cycles, the removal efficiency remains at 90.5%, demonstrating excellent stability and reusability. 5) The incorporation of Fe_3O_4 into CdS not only induces an evident red shift in the absorption edge, enhancing the visible-light response of the composite, but also promotes charge separation by acting as an electron conductor that facilitates electron transfer from CdS to Cr(VI) and suppresses electron - hole recombination. These synergistic effects account for the significantly improved photocatalytic reduction of Cr(VI) over the Fe_3O_4 -CdS nanocomposite. In summary, the 20% Fe_3O_4 -CdS composite catalyst exhibits high photocatalytic activity, excellent reusability, and convenient magnetic recoverability, making it a promising candidate for the visible-light-driven treatment of Cr(VI)-contaminated wastewater.

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REFERENCES

- Acharya, R., Sillanpää, M. & Al-Farraj, S. 2025. A comprehensive review on sequestration of aqueous Cr (VI) over graphene based adsorbents. *Journal of Hazardous Materials Advances* 18: 100670.
- Aslam, S., Yousafzai, A.M. & Javed, A. 2022. Bioaccumulation of hexavalent chromium in commercially edible fish grass carp, *Ctenopharyngodon idella*. *Sains Malaysiana* 51(9): 2757-2762.
- Bian, X.F., Hong, K.Q., Liu, L.Q. & Xu, M.X. 2013. Magnetically separable hybrid $\text{CdS-TiO}_2\text{-Fe}_3\text{O}_4$ nanomaterial: Enhanced photocatalytic activity under UV and visible irradiation. *Applied Surface Science* 280: 349-353.
- Cao, Y., Yin, H.F., Fan, T.L., Liu, X.H. & Chen, S.M. 2020. Morphology-dependent of nanosizes CdS toward efficient photocatalytic Cr (VI) reduction. *Journal of Nanoparticle Research* 22(8): 217.
- Chang, P.R., Zheng, P.W., Liu, B.X., Anderson, D.P., Yu, J.G. & Ma, X.F. 2011. Characterization of magnetic soluble starch-functionalized carbon nanotubes and its application for the adsorption of the dyes. *Journal of Hazardous Materials* 186(2-3): 2144-2150.
- Cheng, T.T., Gao, H.J., Liu, G.R., Pu, Z.S., Wang, S.F., Yi, Z., Wu, X.W. & Yang, H. 2022. Preparation of core-shell heterojunction photocatalysts by coating CdS nanoparticles onto $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ hierarchical microspheres and their photocatalytic removal of organic pollutants and Cr(VI) ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 633: 127918.
- Cui, L.L., Xie, Y.P., Xue, T.M., Lan, M.Y., Li, R.T., He, X.Y., Gao, Y.X., Dai, X.M., Cui, J., Zhai, X.F., Li, Y.X. & Ye, Z.F. 2025. Adsorption performance of TAB/PDDA composite-modified bentonite on Cr(VI) and TNT wastewater. *Journal of Water Process Engineering* 70: 107028.
- Ghosh, T., Khan, I. & Saha, S. 2025. Pyrocatalytic removal of Cr(VI) by MoS_2 nanosheets under controlled thermal fluctuation. *Catalysis Today* 446: 115123.
- Kalita, L., Sonowal, K., Basyach, P., Saha, B. & Saikia, L. 2023. Multifunctional CdS nanoparticle-decorated CeO_2 as efficient visible light photocatalysts and toxic Cr(VI) sensors. *ACS Omega* 8: 11768-11781.
- Liu, L.P., Liu, R., Wang, F., Wu, Y.J., Ge, F., Tian, J., Li, F. & Xue, S. 2025. Cr(VI)-bioremediation mechanism of a novel strain *Bacillus* sp. Cr02 with simultaneous aerobic/anaerobic reduction for Cr(VI) from soil to groundwater. *Journal of Hazardous Materials* 495: 139034.
- Liu, N., Zhang, Y.Q., Huang, J.Y., Liu, S.C., Qing, T.P., Zhang, P. & Feng, B. 2024. Multifunctional CDs as photoinitiators: Detection and reduction for Cr(VI). *Journal of Industrial and Engineering Chemistry* 130: 297-230.
- Mansour, A.M., Ibrahim, R.S. & Azab, A.A. 2022. Structure, morphology, optical and magnetic studies of Fe_3O_4 -doped CdS nanocomposite. *Journal of Materials Science: Materials in Electronics* 33(13): 10251-10258.
- McDaniel, H. & Shim, M. 2009. Size and growth rate dependent structural diversification of $\text{Fe}_3\text{O}_4/\text{CdS}$ anisotropic nanocrystal heterostructures. *ACS Nano* 3(2): 434-440.

- Niu, K.Q., Zhang, X.Z., Zhu, P.F., Liu, J.R., Liu, H., Wang, L.K., Wang, J.G., Zhang, J.Y., Liu, Q., Ma, S.H. & Sillanpää, M. 2025. Facile synthesis of polyethyleneimine-reinforced PHTA resin for efficient Cr (VI) removal. *Separation and Purification Technology* 377: 134343.
- Qi, X.M., Cai, H.X., Zhang, X.F., Ouyang, J., Lu, D.Q., Guo, X. & Jia, S.S. 2023. CdS quantum dots/nano-TiO₂ incorporated wood as a long-term stable and easily separable photocatalytic adsorbent for efficient Cr(VI) removal. *Chemical Engineering Journal* 475: 146320.
- Sahoo, R., Roy, A., Ray, C., Mondal, C., Negishi, Y., Yusuf, S.M., Pal, A. & Pal, T. 2014. Decoration of Fe₃O₄ base material with Pd loaded CdS nanoparticle for superior photocatalytic efficiency. *The Journal of Physical Chemistry C* 118(21): 11485-11494.
- Shi, H.B., Zhang, W.B., Chen, F., Shi, Q.S., Chen, F., Fu, L. & Zhao, S.C. 2021. Preparation of nano-iron loaded cassava fibre composite material for hexavalent chromium removal. *Sains Malaysiana* 50(11): 3373-3382.
- Tuz Johra, F. & Jung, W.G. 2014. Effect of pH on the synthesis and characteristics of RGO-CdS nanocomposites. *Applied Surface Science* 317(1): 1015-1021.
- Ullah, H., Balkan, T., Butler, I.S., Kaya, S. & Rehman, Z.U. 2021. Surfactant-free synthesis of CdS nanorods for efficient reduction of carcinogenic Cr(VI). *Journal of Coordination Chemistry* 74(9-10): 1628-1640.
- Wang, J., Li, X.J., Zhang, B.T. & Bai, L. 2023. Hollow CdS-ZnS-ZIF-8 polyhedron for visible light-induced Cr(VI) reduction. *Inorganic Chemistry* 62: 1047-1053.
- Wang, S.Y., Zhao, X., Muhammad Adeel Sharif, H., Chen, Z.W., Chen, Y.T., Zhou, B., Xiao, K., Yang, B. & Duan, Q.S. 2021. Amine-CdS for exfoliating and distributing bulk MoO₃ for photocatalytic hydrogen evolution and Cr(VI) reduction. *Chemical Engineering Journal* 406: 126849.
- Wang, Y.Z., Mo, T.D., Luo, Y.W., Luo, L., Li, C.X., He, J.Y., Jiang, D.H., Huang, X.J. & Huang, Z.G. 2025. Cr(VI) bioremediation mechanism of a novel *Microbacterium oxydans* S-1 strain. *Journal of Environmental Chemical Engineering* 13: 117200.
- Xu, C.C., Liu, R., Chen, L.J. & Tang, J.L. 2016. Enhanced dechlorination of 2,4-dichlorophenol by recoverable Ni/Fe-Fe₃O₄ nanocomposites. *Journal of Environmental Sciences* 48(10): 92-101.
- Xu, J., Tan, L.S., Baig, S.A., Wu, D.L., Lv, X.S. & Xu, X.H. 2013a. Dechlorination of 2, 4-dichlorophenol by nanoscale magnetic Pd/Fe particles: Effects of pH, temperature, common dissolved ions and humic acid. *Chemical Engineering Journal* 231: 26-35.
- Xu, J., Tang, J., Baig, S.A., Lv, X.S. & Xu, X.H. 2013b. Enhanced dechlorination of 2, 4-dichlorophenol by Pd/Fe-Fe₃O₄ nanocomposites. *Journal of Hazardous Materials* 244: 628-636.
- Xuan, K., Li, T.G. & Hao, Y.M. 2024. Spatially separated noble-metal-free CdS photocatalyst with redox surface exposure for photodegradation of PPCPs and Cr (VI). *Ceramics International* 50(2): 3701-3709.
- Xv, H., Yang, J.X., Zheng, X.R., Wang, R.K., Park, S., Kim, J., Deng, Y.D. & Wang, J.G. 2025. Atomic epitaxial heterojunction of BiOI for efficient Cr(VI) photocatalytic removal. *Separation and Purification Technology* 376: 133918.
- Zhang, G.P., Chen, D.Y., Li, N.J., Xu, Q.F., Li, H., He, J.H. & Lu, J.M. 2018. Preparation of ZnIn₂S₄ nanosheet-coated CdS nanorod heterostructures for efficient photocatalytic reduction of Cr(VI). *Applied Catalysis B: Environmental* 232: 164-174.
- Zhang, L.X., Li, P., Feng, L.P., Chen, X., Jiang, J.T., Zhang, S., Zhang, A.C., Chen, G.F. & Wang, H. 2020a. Controllable fabrication of visible-light-driven CoSx/CdS photocatalysts with direct Z-scheme heterojunctions for photocatalytic Cr(VI) reduction with high efficiency. *Chemical Engineering Journal* 397: 125464.
- Zhang, Y.C., Li, J. & Xu, H.Y. 2012. One-step *in situ* solvothermal synthesis of SnS₂/TiO₂ nanocomposites with high performance in visible light-driven photocatalytic reduction of aqueous Cr(VI). *Applied Catalysis B: Environmental* 123-124: 18-26.
- Zhang, Y.C., Li, J., Zhang, M. & Dionysiou, D.D. 2011. Size-tunable hydrothermal synthesis of SnS₂ nanocrystals with high performance in visible light-driven photocatalytic reduction of aqueous Cr(VI). *Environmental Science & Technology* 45(21): 9324-9331.
- Zhang, Y.H., Zhao, Y.Y., Xu, Z.L., Su, H.M., Bian, X.Y., Zhang, S.S., Dong, X.P., Zeng, L.X., Zeng, T., Feng, M.B., Li, L.X. & Sharma, V.K. 2020b. Carbon quantum dots implanted CdS nanosheets: Efficient visible-light-driven photocatalytic reduction of Cr(VI) under saline conditions. *Applied Catalysis B: Environmental* 262: 118306.
- Zhao, L., Zhang, Y., Yu, J., Liu, Y.H., Cai, Z.H., Li, M.Y. & Liu, M. 2025. Astaxanthin ameliorates Cr (VI) accumulation, antioxidant, digestive, apoptosis and inflammatory response. *Regional Studies in Marine Science* 87: 104240.
- Zou, D., Nie, D.Y., Wang, W.X., Xu, Q.H. & Nie, G.G. 2025. Fabrication of a MoS₂@PAN composite membrane for efficient removal of toxic Cr(VI). *Desalination* 600: 118460.