

Synergistic iron pyrite-modified cobalt aluminate based on a nanocomposite for advanced oxidative degradation of textile dyes, and practical water treatment

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Research Article

Keywords: Photocatalyst, Iron sulfide, Cobalt aluminate, Dye degradation

Posted Date: July 4th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10172322/v1>

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Additional Declarations: No competing interests reported.

Abstract

High levels of pharmaceutical and textile waste and metabolites are commonly found in aquatic systems, where they are causing considerable alarm as to their impact on the environment and human well-being. In the current research, cobalt aluminate nanoparticles (CoAl_2O_4) and iron sulfide/cobalt aluminate nanocomposites ($\text{FeS}_2/\text{CoAl}_2\text{O}_4$) were prepared in two different ways, sol-gel and hydrothermal methods, and their photocatalytic activities were systematically investigated. The structural, morphological and optical properties of the synthesized nanomaterials were analyzed by various characterization techniques. The results confirmed the uniform formation of FeS_2 nanoparticles on the surface of the synthesized CoAl_2O_4 nanoparticles in irregular shape confirming the formation of successful catalysts as expected. The energy band gap of CoAl_2O_4 nanoparticles was calculated to be 2.22eV while that of $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite was calculated to be 1.67eV. The photocatalytic activities were evaluated by the degradation of methylene blue (MB) and crystal violet (CV) dyes under LED irradiation conditions. The degradation efficiencies of MB and CV by $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanoparticle were 92.32% and 98.00%. The $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite achieved over 90% TOC removal within 5 hours for both dyes, confirming its strong mineralization efficiency and potential for real wastewater treatment applications. The $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite maintained over 60% degradation efficiency for MB and CV in real drinking water despite matrix interference, demonstrating promising practical applicability as an adaptable photocatalyst.

1. Introduction

Water resources are among the most vital and essentials for all life. The mercury pollution of aquatic ecosystems has increased tremendously due to rapid industrialization (chemical industry, petrochemical industry, pharmaceutical industry, mines, semiconductors and microelectronics, etc.). At the same time, the growing population in the world has placed a demand for clean water and more people living in urban areas and growing / using pesticides and herbicides have made clean water less available. By 2050 it is estimated that 75% of the world's population will be living in urban areas, introducing new strain on strained water supplies. Increased water demand over the past decade has been six times larger than gravity was and about 60% of the current population is already facing water shortage conditions [1–3].

Traditional wastewater treatment methods such as air stripping, granular activated carbon (GAC) adsorption, chlorination and ozonation have drawbacks. These techniques tend to move contaminants from one phase to another, leading to the removal of molecules instead of contaminants, or leaving behind by-products from chlorination which are dangerous like trihalomethanes. The incineration of organic waste products is common, although the danger of introducing more toxic products into the atmosphere exists. The limitations have been impelled to develop Advanced Oxidation Processes (AOPs) that use the production of highly reactive and destabilized oxygen-containing intermediates, mainly hydroxyl radicals ($\cdot\text{OH}$), to non-selectively mineralize a wide range of organic pollutants to CO_2 , water and non-toxic small molecules [4, 5].

Heterogeneous photocatalysis is the one method which has gained significant importance among AOPs as the process of water purification is a cheap, reusable and environment friendly process. In this operation, the semiconductor photocatalyst absorbs photons whose energy is at or above the band gaps, and creates electron-hole pairs that traverse to the surface of the semiconductor to bring about oxidation-reduction reactions. The valence band holes are used to oxidize adsorbed water or hydroxyl ions to produce $\cdot\text{OH}$ groups; and the conduction band electrons are used to reduce dissolved oxygen to superoxide ($\cdot\text{O}_2^-$), both of which are involved in organic contaminant degradation [6, 7]. One of the most persistent types of water pollutants, which are discharged from textiles and industrial waste is the Organic Dyes. More than 50% of all dyes used in the textile industries are azo dyes and about 1–20% of dyes used in dyeing processes are discharged into the wastewater. In particular, such dyes are hardly currently attainable of most of the biological and physical including aerobic digestion, biological, precipitation, and filtration treatment strategies as they possess a high degree of aromatic substitution in their molecular structure [8]. In contrast, photocatalytic oxidation has the following advantages: complete mineralization, no formation of secondary wastes and mild temperature and pressure conditions.

CoAl_2O_4 shows a photocatalytic activity under visible light illumination due to the high chemical stability, optimal optical and electrical properties, and suitable bandgap, and is regarded as one of the most promising photocatalytic semiconductors [9, 10]. Iron pyrite FeS_2 is a naturally occurring, non-toxic semiconductor material with a narrow band gap (~ 0.95 eV) that has high light absorption over a wide spectrum and has good electron transfer properties. FeS_2 is thus used in combination with CoAl_2O_4 as a co-catalyst for accelerating charge carrier transitions and separation in CoAl_2O_4 , to make the system much more efficient as a photocatalyst [11, 12]. Although both materials have some merits, $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ hybrid nanocomposites have never been fabricated before [13–16]. Kaci et al. [17] studied the photocatalytic and electrochemical characteristics of CuAl_3O_4 nanoparticles, which were prepared using co-precipitation method. The formation of spherical-nanoparticles with the average diameter of ~ 9 nm observed by TEM was confirmed. The CuAl_2O_4 catalyst under sunlight could degrade MV dye by pseudo-first order kinetics with half-life of 82 minutes, and highly degraded after 3 hours with the efficiency of 89%. The catalyst was active for four consecutive cycles, with $\cdot\text{OH}$ being the major oxidizing species identified. Raju et al. [18] showed the applicability of metal oxide–metal sulfide composite system for photocatalytic degradation of dye using a simple hydrothermal method to prepare CuO-FeS_2 heterostructure composite. The composite could decolorize brilliant green (BG) completely in 90 minutes. The photocatalytic activity of their composite system was explained by a heterostructure formation which increases the charge separation, and smaller size of the composite particles (24.2 nm) than individual CuO (8.6 nm) and FeS_2 (28.6 nm) nanoparticles.

Here, the bypass preparation of CoAl_2O_4 nanoparticles and the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite is reported using the sol-gel and the hydrothermal methods, and their photocatalytic activity against the degradation of methylene blue (MB) and crystal violet (CV) in LED irradiation is systematically investigated. Physicochemical properties of the produced materials are analyzed in great detail and effect of certain operating parameters such as pH, dye concentration and catalyst amount is investigated. Radical

scavenging experiments are also used to observe that the dominant reactive species involved in the mechanism of the photodegradation.

2. Materials and Methods

2.1. Chemical Materials

2.1.1. Organic Dyes as Target Pollutants

Crystal violet and methylene blue dyes, used as target pollutants in this study, were purchased from Sigma-Aldrich and used without further purification.

2.1.2. Chemical Compounds

All chemical reagents were purchased from Merck with high purity grades:

- Cobalt nitrate hexahydrate — $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- Aluminum nitrate nonahydrate — $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
- Citric acid — $\text{C}_6\text{H}_8\text{O}_7$
- Ferric chloride — FeCl_3
- Sodium thiosulfate pentahydrate — $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
- Nitric acid — HNO_3
- Benzoquinone (BQ)
- Isopropyl alcohol (IPA)
- Ethylenediaminetetraacetic acid (EDTA)

2.2. Synthesis of Cobalt Aluminate Nanoparticles

CoAl_2O_4 nanoparticles were synthesized via a combined sol-gel and hydrothermal method. Initially, 50 mL of 0.5 M cobalt nitrate solution and 50 mL of 0.5 M aluminum nitrate solution were prepared separately. The two metal solutions were then combined and mixed thoroughly. Subsequently, 50 mL of citric acid solution was added to the mixture and stirred homogeneously for 2 hours. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 200°C for 6 hours. After the reaction, the autoclave was allowed to cool gradually to room temperature. The obtained precipitate was washed several times with a water-ethanol solution, then dried in an oven at 120°C for 8 hours. The final product was calcined in a furnace at 400°C for 3 hours.

2.3. Synthesis of $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ Nanocomposite

Initially, 1 g of CoAl_2O_4 nanoparticles was dispersed in 100 mL of deionized water using an ultrasonic bath. Subsequently, 50 mL of 0.5 M ferric chloride solution was added to the suspension. Then, 50 mL of 0.5 M sodium thiosulfate pentahydrate solution was added to the main solution and stirred

homogeneously at 60°C for 2 hours. The mixture was then transferred into a Teflon-lined autoclave and hydrothermally treated at 180°C for 5 hours. After cooling gradually to room temperature, the precipitate was washed several times with a water-ethanol solution and dried in an oven at 150°C for 6 hours. The final product was calcined in a furnace at 600°C for 5 hours.

2.4. Characterization Techniques

The following instrumentation was employed for comprehensive characterization of the synthesized nanomaterials:

- Thermogravimetric Analysis (TGA): Thermal decomposition behavior was analyzed using a Q600 SDT TGA/DSC analyzer under a nitrogen atmosphere.
- X-ray Diffraction (XRD): Crystalline phase identification was performed using an X-ray diffractometer (Philips, model XLS30) with a copper tube ($\lambda = 0.15418$ nm).
- Fourier Transform Infrared Spectroscopy (FT-IR): Surface functional groups were identified using a Nicolet 750 spectrometer.
- Field Emission Scanning Electron Microscopy (FESEM): Surface morphology and elemental composition were examined using a TESCAN MIRA field emission scanning electron microscope equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector.
- Dynamic Light Scattering (DLS): Particle size distribution of the synthesized nanomaterials was determined using a Nano Zetasizer instrument.
- UV-Vis Spectrophotometry (optical absorption): Optical absorption spectra of the samples were recorded using an Avaspec 2048 TEC UV-Vis spectrophotometer.
- Kubelka-Munk Transformation: The optical bandgap energy of the synthesized nanomaterials was estimated from diffuse reflectance data using the Kubelka-Munk function.
- UV-Vis Spectrophotometry (concentration measurement): Dye concentration during photocatalytic experiments was monitored using a Shimadzu 3600 UV-Vis spectrophotometer in the wavelength range of 300–700 nm.

2.5. Photocatalytic Experiments

Photocatalytic degradation reactions were carried out in an open plexiglass reactor with a volume of 500 mL. Prior to illumination, the suspension was stirred in the dark for 30 minutes to establish adsorption-desorption equilibrium. The outer wall of the reactor was wrapped tightly with an aluminum foil layer to prevent light scattering and heat dissipation. The reactor was positioned at a distance of 5 cm from the light source. Irradiation was provided by a LED lamp emitting at a wavelength of 365 nm, positioned vertically above the reactor to ensure uniform illumination across the entire surface of the reaction solution. The reaction temperature was maintained at $20 \pm 0.5^\circ\text{C}$ throughout the photocatalytic process using a cryostat, with cooling water continuously circulating around the outer wall of the reactor (Fig. 3–3).

The photocatalytic behavior of the prepared nanomaterials was evaluated by monitoring the degradation of methylene blue (MB) and crystal violet (CV) under visible LED irradiation. In a typical experimental procedure, 0.1 g of the synthesized photocatalyst was dispersed in 100 mL of an aqueous dye solution at a concentration of 10 mg/L. The suspension was then exposed to irradiation for 120 minutes. Dye concentration at various time intervals was determined by measuring the absorbance using a UV-Vis spectrophotometer. The maximum absorption wavelengths of methylene blue and crystal violet were identified at 663 nm and 583 nm, respectively.

The reusability of the synthesized nanocomposites was evaluated over four consecutive cycles. After each cycle, the photocatalyst particles were collected from the reaction solution by centrifugation, washed several times with deionized water, and dried prior to reuse in the subsequent cycle.

Radical scavenging experiments were conducted to identify the dominant reactive species involved in the photodegradation process. Isopropyl alcohol (IPA), EDTA, and benzoquinone (BQ) were used as scavengers for hydroxyl radicals ($\cdot\text{OH}$), holes (h^+), and superoxide radicals ($\cdot\text{O}_2^-$), respectively. In each scavenging test, 1 mL of the respective scavenger solution was added to the reaction mixture, and the experiment was conducted under identical reaction conditions. After 30 minutes of irradiation, the dye degradation percentage was measured and compared to the control experiment conducted without any scavenger.

3. Results and Discussion

3.1. Characterization of Synthesized Nanomaterials

3.1.1. Thermogravimetric Analysis (TGA)

Thermal analysis of the synthesized nanomaterials indicated from the TG/DTA scan the occurrence of two weight lost events as depicted in Fig. 1. This first weight loss is roughly 17% at about 200°C and is believed to mainly be attributable to the evaporation of any trace of water and the decomposition of the cobalt nitrate precursors. The second weight loss of around 20% occurred at ca 350°C is believed to be due to the total loss of nitrate species and has been confirmed by the production of brownish NO_x vapor [19]. The temperature performance of the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite was also found to be superior to that of the pure CoAl_2O_4 Nanoparticles, showing that the addition of FeS_2 on to the surface of CoAl_2O_4 significantly boosts the thermal stability of the composite system.

3.1.2. X-ray Diffraction (XRD) Analysis

The XRD patterns of the synthesized $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite and CoAl_2O_4 nanoparticles are plotted in Fig. 2. The XRD patterns of the synthesized CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite are plotted as shown in Fig. 2. The high purity of the synthesized samples is evident from the absence of other diffraction peaks associated with other impurity phases when all observed diffraction peaks were indexing the samples belong to the orthorhombic phase of pyrite FeS_2 (JCPDS

Card No.00-037-0475) [11] and the cubic spinel phase of CoAl_2O_4 (JCPDS Card No.10-458) [20]. For CoAl_2O_4 nanoparticles, diffraction peaks were observed at 2θ values of 32.2° , 37.4° , 44.9° , 48.4° , 56.78° , 59.72° , and 65.82° , corresponding to the (220), (311), (400), (331), (422), (511), and (440) crystal planes, respectively. For the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite, additional peaks appeared at 2θ values of 28.88° , 38.86° , 40.57° , 53.1° , 54.55° , 61.72° , 68.5° , and 69.62° , corresponding to the (110), (120), (200), (220), (130), (131), (122), and (040) planes of the FeS_2 phase, respectively. The Debye-Scherrer equation [11] was used to estimate the average crystallite size for the synthesized samples. The average crystallite sizes of CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite were calculated to be 40.00 nm and 59.12 nm, respectively.

3.1.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR studies were performed to ascertain the presence of metal sulfide and metal oxide species on the catalyst surface and the results are shown in Fig. 3. Both CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite showed O-H stretching vibrations corresponding to the presence of water molecules in its structure at 3416 cm^{-1} and 1642 cm^{-1} . The fourth additional band at 1431 cm^{-1} is attributed to the C = C stretch vibration while the fourth additional band at 1180 cm^{-1} is attributed to the C-O stretch vibration [21]. The sharp bands at 636 cm^{-1} and 521 cm^{-1} are associated with Fe-S stretching vibrations and distinct features at 1087 cm^{-1} is assigned to the metal-hydroxide stretching, respectively [11]. The band at 622 cm^{-1} is attributed to Co-O and Al-O vibration stretches which corresponds with the Spinel CoAl_2O_4 [51] structure.

3.1.4. UV-Vis Diffuse Reflectance Spectroscopy

The important factors affecting the photocatalytic activity would be optical absorption properties of photocatalysts. The absorption spectra in the visible (UV-Vis) and the Kubelka-Munk plot are shown in Fig. 4 for the synthesized samples. The nanocomposite $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ had a remarkably high light absorption, and when FeS_2 was added to CoAl_2O_4 , the absorption edge shifted towards longer wavelengths sharply. A significant amount of absorption was observed for both samples in the visible region [23–25]. Different plot of Kubelka-Munk analysis for synthesized materials was used to determine their optical band gap energy. The bandgap was 2.22 eV in the case of CoAl_2O_4 nanoparticles and when FeS_2 was loaded on the surface of CoAl_2O_4 , the bandgap was reduced to 1.67 eV for the nanocomposite $\text{FeS}_2/\text{CoAl}_2\text{O}_4$. The decreased band gap when FeS_2 was introduced suggested that the FeS_2 has better photon harvesting under visible light illumination, leading to better photocatalytic performance [26].

3.1.5. Members of the workshop were introduced to the morphology and particle size analysis.

The FESEM images of the synthesized CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite are shown in Fig. 5. The FESEM images of synthesized CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite are presented in Fig. 5A,B. The CoAl_2O_4 nanoparticles showed irregular shaped nanoparticles, among the FeS_2 nanoparticles were found to be uniformly and homogeneously distributed

over the surface of CoAl_2O_4 nanoparticles and showing aggregation. Owing to the intimate contact between the CoAl_2O_4 and FeS_2 components there are ample active surface sites and efficient electron transfer pathways within the catalytic system. Dynamic Light Scattering (DLS) analysis of the synthesized nanomaterials' size distribution is given in Fig. 5C. The particle size range of the CoAl_2O_4 nanoparticles and the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite are found as 34–46 nm and 50–62 nm respectively. Energy Dispersive X-ray Spectroscopy (EDS) was used to determine the elemental composition of $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite, as indicated in Fig. 5D. The content of cobalt, aluminum, oxygen, iron, and sulfur elements contained in the EDS spectrum was detected to be 25.5%, 22.3%, 14.3%, 20.1%, and 15.5% respectively, indicating that $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ composite was successfully synthesized.

3.1.6. Textural Properties

The adsorption–desorption data for CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite are shown in Fig. 6A, B. The adsorption isotherms for both were classified as type IV in the IUPAC classification, and both samples possessed type H3 hysteresis loop with opening at $P/P_0 \sim 0.45$, indicating mesoporous structure with aggregated plate-like particles giving rise to slit-shaped pores. The BET specific surface area of the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite ($68.3 \text{ m}^2/\text{g}$) was also found to be much greater than that of pure CoAl_2O_4 nanoparticles ($42.5 \text{ m}^2/\text{g}$) which is about 60.7% higher. Likewise, the total pore volume decreased from $0.118 \text{ cm}^3/\text{g}$ in case of CoAl_2O_4 to $0.195 \text{ cm}^3/\text{g}$ in case of $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite. The results have confirmed that the addition of FeS_2 particles in the surface of CoAl_2O_4 led to the creation of extra porosity and significantly increased the visible surface area of the composite material. The BJH pore size distribution curves for desorption branch of the isotherms are shown on the inset of figure X. Both the samples had a narrow and well-defined pore size distribution that were centered in the mesopore region. Average pore diameters of CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite, were found to be 11.1 nm and 11.8 nm respectively, suggesting both materials to be mesoporous. The slight increase in the average pore diameter with the increase in FeS_2 load onto the CoAl_2O_4 surface indicates that the load of FeS_2 nanoparticles changes the pore structure of CoAl_2O_4 while maintaining the overall mesoporous structure. The improvement of the texture properties of the nanocomposite $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ is directly related to the improvement of the photocatalytic activity. The higher specific surface area of the preparation offers more active surface sites for the adsorption of dye molecules and catalytic reaction to occur and the larger pore volume provides effective mass transfer of reactant molecules to the surface of the photocatalyst. The uniform pore channels of mesoporous structure facilitate the fast diffusion of the dye molecules and the active species formed in the photocatalytic reaction [27].

3.1.7. Electrochemical Impedance Spectroscopy (EIS) Analysis

The charge transfer kinetics and interfacial properties of the synthesized photocatalysts have been studied using electrochemical impedance spectroscopy (EIS) and the Nyquist plots are illustrated in Fig. 6C. The equivalent circuit used for the fitting of the experimental data was based on the classical Randles circuit consisting of a solution resistance (R_s), charge transfer resistance (R_{ct}), double-layer

capacitance (Cdl) and a Warburg diffusion element (W). A clear semi-circular behavior at a wide range of frequencies and linear Warburg behavior at low frequencies, typical of a diffusion-controlled electrochemical process at an electrode/electrolyte interface, was observed for both samples. The diameter of the semicircle in Nyquist plot is proportional to charge transfer resistance (Rct), with the smaller the diameter, the lower the charge transfer resistance, the better to separate photon-generated electron hole pairs.

The value of resistance Rct for the FeS₂/CoAl₂O₄ nanocomposite was considerably smaller than that of the pure CoAl₂O₄ nanoparticles (6.5 Ω and 12.5 Ω, respectively). This is a ~ 48% drop in charge transfer resistance caused by the incorporation of FeS₂, which shows that the formation of heterojunctions between the two semiconductors opens up a highly efficient charge transfer pathway at the interface between these two semiconductors. Direct contact between FeS₂ and CoAl₂O₄ leads to fast transfer of the photogenerated electron from the conduction band of CoAl₂O₄ into FeS₂, minimizing the electron-hole recombination, and finally extending the lifetime of the charge carriers for use in surface redox reactions. The solution resistance (Rs) values were almost equal to both samples (3.8 Ω for CoAl₂O₄ and 3.2 Ω for FeS₂/CoAl₂O₄) providing the same electrolyte conductivity during the measurement. The slightly higher double-layer capacitance (Cdl) of the FeS₂/CoAl₂O₄ nanocomposite (13.0×10^{-5} F) compared to CoAl₂O₄ (8.0×10^{-5} F) is consistent with the larger specific surface area determined by BET analysis (68.3 vs. 42.5 m²/g), further confirming the enhanced interfacial contact area available for electrochemical and photocatalytic processes.

These photocatalytic performance results are found to be very promising and are in good agreement with the EIS results, after adding FeS₂ on the CoAl₂O₄, the degradation efficiencies of MB and CV increased significantly. Overall, the FeS₂/CoAl₂O₄ nanocomposite exhibited the best photocatalytic performance under LED light due to the reduction in the charge transfer resistance, which achieved effective photocatalytic electron governance, combined with the increased charge carrier mobility, which allowed the active species and electrons to efficiently activate the photocatalytic reactions [28].

3.2. Photocatalytic Degradation of Methylene Blue and Crystal Violet under LED Irradiation

The synthesized CoAl₂O₄ nanoparticles and FeS₂/CoAl₂O₄ nanocomposite were tested by using LED lights as an energy source using methylene blue (MB) and crystal violet (CV) as model pollutants. All synthesized samples' degradation efficiencies as a function of irradiation time are given in Fig. 7. Prior to illumination, dark adsorption capacity of CoAl₂O₄ nanoparticles and FeS₂/CoAl₂O₄ nanocomposite particles have been evaluated. The FeS₂/CoAl₂O₄ nanocomposite had the highest percentage of MB and CV adsorbed, which is 10.12% and 12.22% respectively, while the percentage of MB and CV adsorbed by the CoAl₂O₄ nanoparticles was 8.55% and 10.06% respectively due to increase in number of active surface sites of FeS₂/CoAl₂O₄ nanocomposite as compared to that of the CoAl₂O₄ nanoparticles [29, 30]. LED irradiation had the more pronounced effects on the degradation of both dyes, showing the highest decrease in the first 30 minutes of the reaction. The degradation efficiencies obtained in the absence of

any catalyst (photolysis control experiments) were about 6% for MB and 10% for CV which suggests that direct photolysis was of minor importance. The degradation efficiencies of MB and CV under the FeS₂/CoAl₂O₄ nanocomposite was 92.32% and 98.00% respectively, while they were 80.15% and 88.61% respectively under the CoAl₂O₄ nanoparticles alone. According to the authors, the FeS₂/CoAl₂O₄ nanocomposite has a narrower bandgap and higher visible-light absorption than the pure CoAl₂O₄ nanoparticles, so this is why the former is so good at photocatalytic reactions. Good Kinetic Analysis for Calculating the Photodegradation Data was 1st order pseudo kinetic model as [31]:

$$\ln(C_0/C_t) = k_i t$$

In the above expression, C₀ is the initial concentration of the dye, C_t is the concentration of the dye at a given time, and k_i is the apparent rate constant. The degradation rates of MB and CV with the FeS₂/CoAl₂O₄ nanocomposite were found to be 0.0786 min⁻¹ and 0.0860 min⁻¹, respectively, as shown in Fig. 7.

3.2.1. Effect of pH

Surface charge of the photocatalyst and the electrostatic interaction between the photocatalyst and dye molecules are affected by the solution pH of the photocatalytic degradation process. The zeta potential measurement of the FeS₂/CoAl₂O₄ nanocomposite showed that the point of zero charge (pH_{pzc}) was at pH 8.5, which implied that the surface of the catalyst was positively charged at pH < 8.5, while it was negatively charged at pH > 8.5 (Fig. 8A) [32]. The degradation of MB and CV at different pH was studied in the range of pH 3–11 (Fig. 8B). Because the best degradation efficiency was obtained at pH ≈ 11, degradation was studied at this value. The improved performance under the alkaline conditions may be explained by the electrostatic attraction of the positively charged cationic dyes (MB and CV) to the negatively charged catalyst surface leading to dye adsorption on the surface of the catalyst and hence high degradation efficiency.

3.2.2. Effect of Dye Concentration

The effect of initial dye concentration of photocatalytic degradation was investigated at different concentrations of 20, 40, 60mg/L under optimal conditions at pH = 11, Fig. 8C. The dye concentration of 20 mg/L showed the best degradation efficiency. The degradation percentage decreased gradually as the concentration of the dye adopted increases. This—which is known as screening effect of excess dye molecules—occurs because excess dye molecules prevent illumination from reaching the surface of the catalyst, resulting in a decreased production of photoinduced charge carriers, and consequently a reduced effect of photocatalysis [33].

3.2.3. Effect of Catalyst Dosage

The influence of catalyst loading on the rate of the photodegradation was studied, the quantity of FeS₂/CoAl₂O₄ nanocomposite was varied from 5 to 30 mg (with dye concentration of 20mg/L and pH at 11) and the results are shown in Fig. 8D. The degradation rate was the highest when the amount of

catalyzing was 20 mg. Further increasing the amount of catalyst beyond this optimum resulted in lower efficiency of degradation due to the increased use of catalyst particles for more complex associations and a decrease in the amount of active surface that allows penetration of the photon into the reaction solution [34].

3.2.4. Reusability and stability tests

FeS₂/CoAl₂O₄ nanocomposite's photocatalytic stability and reusability were determined with five subsequent photocatalytic cycles (Fig. 8E). After five cycles no significant decrease in the photocatalytic activity was noticed, which was around 3% and 4% only in the case of MB and CV, respectively. The results indicate the excellent structural stability and recyclability of the synthesized nanocomposite, thus envisaging its practical potential for repeated use in wastewater treatment.

3.2.5. Radical Scavenging Experiments

Several radical scavenging experiments were conducted to determine the major species reacting during the degradation of MB and CV using IPA for removal of •OH, EDTA for removal of h⁺ and BQ for removal of •O₂⁻ species [33]. The addition of IPA and BQ resulted in the most pronounced degradation inhibition whereas the addition of EDTA does not result in significant inhibition as shown in Fig. 8F. The results showed that hydroxyl radicals (•OH) and superoxide radicals (•O₂⁻) play the main role for the photocatalytic degradation mechanism in the FeS₂/CoAl₂O₄ photocatalytic system.

3.2.6. TOC Removal and Mineralization Efficiency of MB and CV Dyes

Beyond the mere decoloration, the organic behavior of FeS₂/CoAl₂O₄ nanocomposite was further demonstrated by assessing the total organic carbon (TOC) removal. The mineralization efficiency of the FeS₂/CoAl₂O₄ nanocomposite was also demonstrated by the organic behavior that is the total organic carbon (TOC) removal. The initial TOC value was set to 100% for both MB and CV, and after 5 h of treatment, the degradation efficiency of the MB and CV was 92.32% and 98.00%, respectively, with the corresponding decrease in TOC values (Fig. 8G). These findings show that the nanocomposite is an efficient catalyst in removing the chromophoric structure in the dyes as well as in mineralizing the dyes to innocuous end-products like CO₂ and H₂O. A little more TOC removal was noticed for CV than MB, implying that the degradation might be more thorough for CV, which may be attributed to some differences in the molecular structure, number of rings or reaction to oxidation in the radical environment of the two dye molecules. It is important to note here that it is usually a stricter guideline for degradation to remove both color and TOC; the presence of intermediate byproducts can cause the color to be removed with no reduction in the amount of TOC. The efficient removal of TOC (more than 90%) in a comparatively short treatment time of 5 hours for both dyes was found to reflect strong degradation efficiency of FeS₂/CoAl₂O₄ nanocomposite and thus further support the potential applicability to remediation of real wastewater, which ultimately aims at complete mineralization rather than merely decolorization [35].

3.2.7. Treatment of an actual water sample

To investigate the practical feasibility of the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ under more practical conditions, the degradation of MB and CV was also studied in two different media, distilled water and drinking water, to evaluate the nanocomposite's degradation performance. It can be seen from the biphasic degradation of the dyes in the removal efficiency profiles that both dyes initially degraded very rapidly for the first 5–10 minutes and then gradually approached some plateau over time before finally reaching the end point of complete degradation at 60 minutes. Under the idealized conditions, the removal efficiency became 98.00% while MB was attained at 92.32% in the same time span. The high amount of available active surface sites and the amount of reactive oxidative species (OH and O_2^- radicals) formed by the nanocomposite in the early stage of the reaction when the concentration of the dyes and the competition for the active sites is still favorable, can explain this initial increase (Fig. 8H).

A significantly lower percentage was found using the same degradation process in drinking water, as response in both cases was 68% and 62%, respectively, after 60 minutes. This marked decrease in performance is as a result of the more complex composition of drinking water as compared to distilled water. The inorganic ions in the drinking water, such as Cl^- , HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} and the natural inorganic matter in the water, are well known to interfere with photocatalytic as well as oxidative degradation processes. These species have the potential to effectively sequester the reactive oxygen species away from the dye molecules and hence change their effective capacity to oxidize. Further, the presence of dissolved ions can lead to partial coverage or inhibition of active sites in the surface of the nanocomposite, reducing the complementarity of the surface sites with the dye molecules to the catalytically active surface sites. An important issue to note regarding the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite in practice is that while the material shows great degradation efficiency under controlled conditions in deionized water environment, its efficiency is significantly lowered in more complex water matrices (such as drinking water matrix environment or by extension, complex industrial or municipal wastewater environments) due to matrix induced interference. However, during these recurring setbacks, the nanocomposite still managed to achieve a > 60% for both dyes in just one hour, showing their practical potential in the field as good and adaptable photocatalysts, and reinforcing the importance of further optimization, namely the increase of the dosage of the catalyst, run time, and pre-treatment of the water matrix, to improve their performance in real aqueous environments.

3.2.8. Proposed Photocatalytic Degradation Mechanism of MB and CV over the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ Nanocomposite

The photocatalytic degradation of MB and CV over the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite is controlled by a heterojunction-related charge separation process which results in a boost of visible light utilization over pristine CoAl_2O_4 . Electronic band structure diagram indicates that, without any additional dopants, pure CoAl_2O_4 nanoparticles have a relatively large band gap of 2.22 eV thereby limiting the absorption of light to the UV region and near visible region. After coupling with FeS_2 , a semiconductor material having a narrower band gap, the effective band gap of the prepared $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite is decreased to

1.67 eV. The bandgap narrowing also increases the light absorption range to a wider range in the visible light of the incident LED, which allows the nanocomposite to collect a larger proportion of incident light in the visible light range and produce more electron–hole pairs (Fig. 9).

In the case of a $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ heterojunction, the visible light causes the electrons in the valence band (VB) of both CoAl_2O_4 and FeS_2 to transition to the conduction band (CB). The VB of FeS_2 is spaced at a more favorable (less negative potential) over the CB of CoAl_2O_4 , which means that when electrons are making their way to the CB of CoAl_2O_4 , holes are moving to the VB of FeS_2 . The distinctive characteristic of a type-II heterojunction is that charge transfer across the interface of two semiconductor domains occurs as a vector (shown with curved arrows) which prevents the recombination of electron-hole pairs and extends the lifetime of charge carriers, enhancing the photocatalytic efficiency of the whole system. The separated charges then undergo separate redox reactions leading to the production of the ROS involved in the degradation of the dye. The accumulated electrons on the CB side convert the molecular oxygen (O_2) that is adsorbed on the catalyst surface to produce superoxide radicals ($\cdot\text{O}_2^-$). VB Oxidation of surface-adsorbed water molecules or hydroxyl ions ($\text{H}_2\text{O}/\text{OH}^-$) generates hydroxyl radicals ($\cdot\text{OH}$). Both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ are highly reactive oxygen species that could interact with the conjugated aromatic and the heteroatoms containing structures of MB and CV, and set the stage for its degradation [36].

Both dyes break down in a similar manner; first, by attack with the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals, followed by ring-opening and breakage of the bonds, causing the formation of various intermediates. These intermediates are then further oxidized to end products that are simple inorganic ions, carbon dioxide (CO_2) and water (H_2O). This step-by-step mineralization reveals that the nanocomposite is not only able to decolorize the dyes but also is able to mineralize the dye molecules completely [37].

Further evidence of the relative importance of each reactive species was obtained using radical scavenging experiments wherein isopropanol (IPA) was used as an $\cdot\text{OH}$ scavenger, benzoquinone (BQ) was used as an $\cdot\text{O}_2^-$ scavenger and ethylenediaminetetraacetic acid (EDTA) was used as a hole (h^+) scavenger. The nanocomposite was found to be intrinsically photocatalytic as the system showed high degradation efficiency in the absence of any scavenger. IPA caused strong inhibition of degradation showing that hydroxyl radicals are the predominant roles in the oxidative degradation process. When BQ was included in the mix, there was moderate inhibition which indicates that superoxide radicals also make a significant contribution, but not as much as $\cdot\text{OH}$. The inhibition was much less with the addition of EDTA, meaning that the direct hole-mediated oxidation is a relatively minor part of the process. The results as a whole indicate that both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ are the main reactive species responsible for the photodegradation of MB and CV. The coupled system could, on the whole, enhance the visible light absorption by reducing the bandgap, while simultaneously promoting the spatial charge separation and reducing the recombination loss created by forming an efficient heterojunction interface between FeS_2 and CoAl_2O_4 . The increased light harvesting and efficient charge transfer provides a synergistic effect for the superior photocatalytic activity of the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite over the removal of organic dye pollutants under visible-light irradiation [38].

4. Conclusion

Among the various methods of synthesis, the sol-gel and hydrothermal processes are successfully employed to synthesize CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposites and systematically investigate its photocatalytic behavior towards the degradation of methylene blue (MB) and crystal violet (CV) in the presence of LED irradiation. XRD analysis of the synthesized materials radiated the existence of the pyrite phase FeS_2 and spinel phase CoAl_2O_4 without any netters, confirming the highly pure of the synthesized materials. The Rietveld refinement results showed that the crystallite size of CoAl_2O_4 nanoparticle and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite were found to be 40.00 nm and 59.12 nm respectively. Bandgap energies of CoAl_2O_4 nanoparticles and $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite were 2.22 eV and 1.67 eV, respectively, as revealed by the Kubelka-Munk analysis and confirmed that FeS_2 helps to narrow the bandgap and wider the range of light absorption into the visible region. Irradiation with LED was tested by analyzing photocatalytic degradation of MB and CV; the degradation was highest when irradiated for the first 30 minutes. The $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite has degradation efficiency of 92.32% and 98.00% for MB and CV superior to pure CoAl_2O_4 nanoparticles which could remove 80.15% and 88.61% of MB and CV respectively by adsorption process. The superior photocatalytic activity of the nanocomposite is attributed to its narrower bandgap and having a higher visible light harvesting capability. The excellent structural stability and reusability of the nanocomposite material was demonstrated by five consecutive degradation cycles of MB and CV, which showed degradation efficiencies of only about 3% and 4% for MB and CV, respectively. Radical scavenging experiments showed that the reactive species which primarily account for the photodegradation process were hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$). The $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ nanocomposite prepared in this work seems to be an excellent, cheap, and environmentally friendly photocatalytic material capable of successfully degrading the organic dye pollutants under LED radiation from water.

Declarations

Consent to participate

Not applicable.

Ethical approval

No research involving human participants and/or animals and no informed consent.

Clinical trial

Not applicable.

Consent to publish

Not applicable.

Declaration of Competing Interest

The authors declare no conflicts of interest.

Funding

Not applicable.

Author Contribution

Leila Fatolahi: Data acquisition, analysis, and interpretation, writing original draft; Supervision, Project administration, Funding, and resources acquisition, Review & Editing.

Acknowledgements

The authors wish to express their sincere gratitude to the Payame noor university, Tehran, Iran.

Data availability

Data will be made available on request.

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Figures

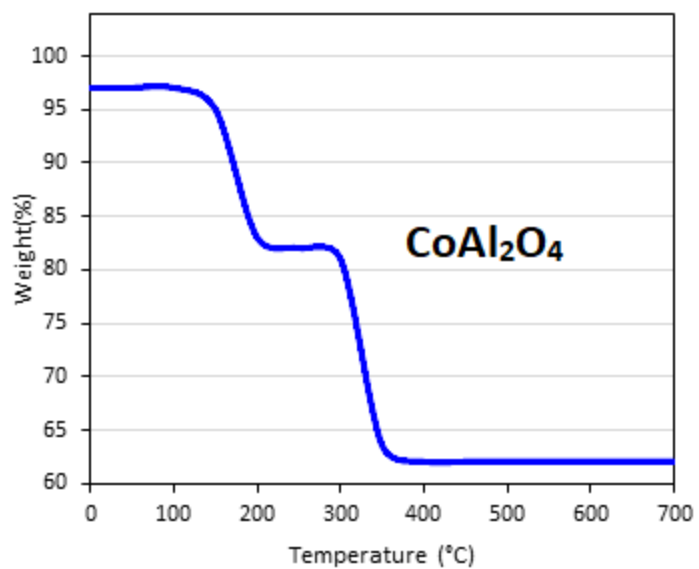
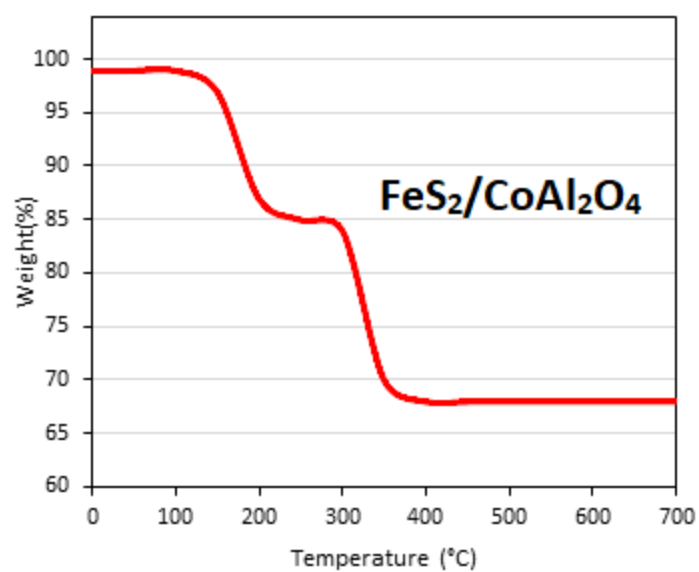


Figure 1

TGA curves of the prepared samples

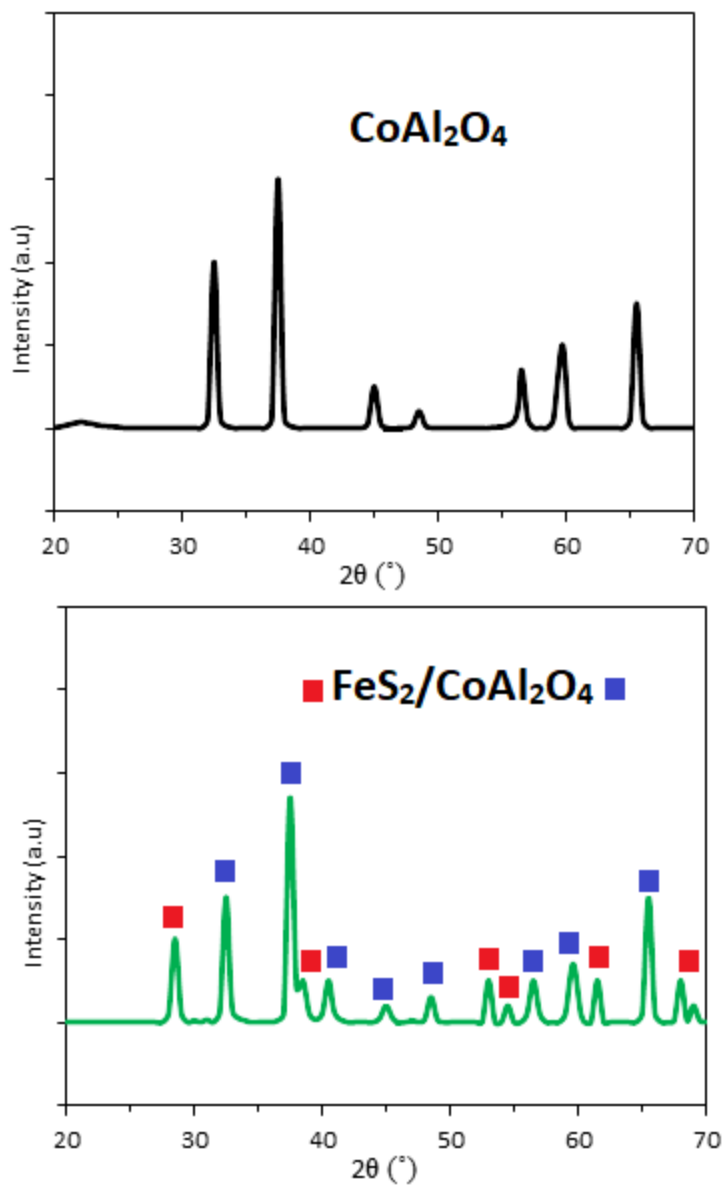


Figure 2

The XRD curves of the prepared samples

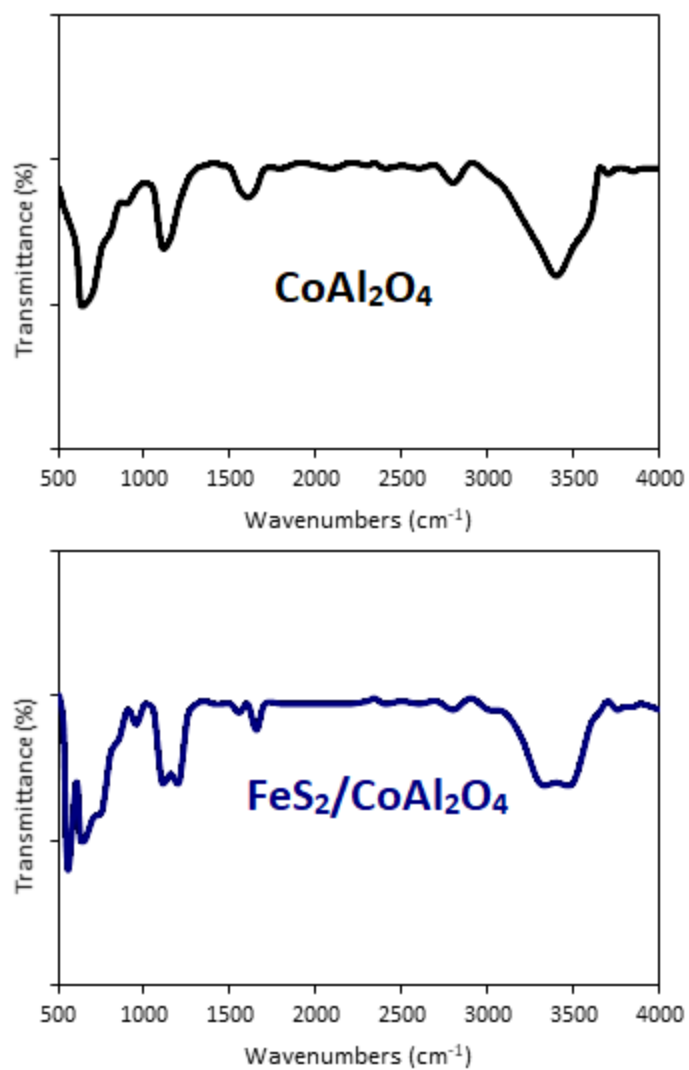


Figure 3

FTIR spectrum of the prepared samples

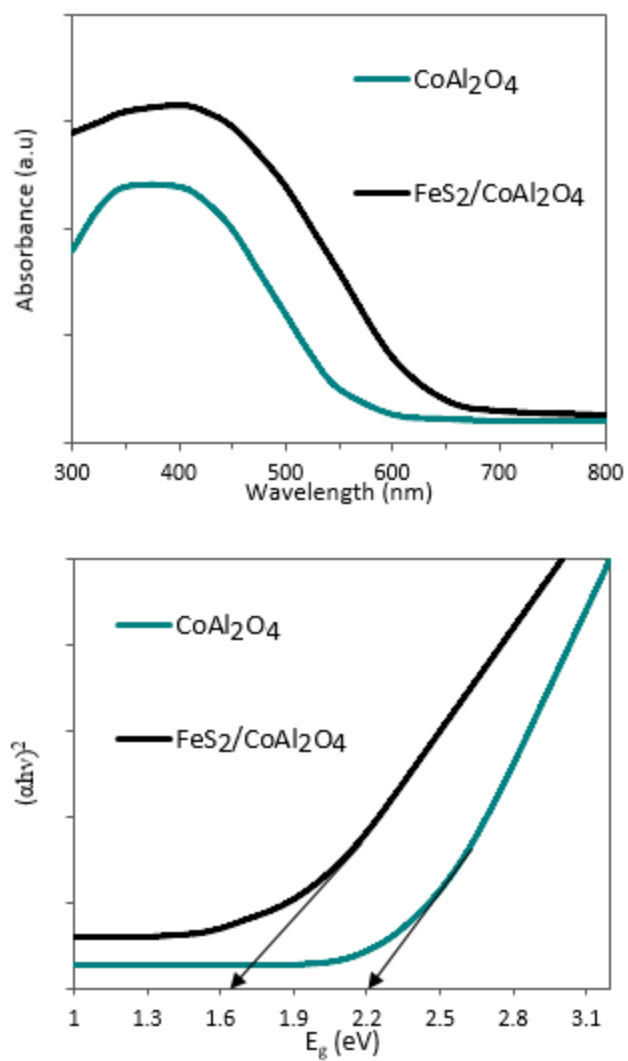


Figure 4

The UV-vis spectra (A), and the Kubelka-Munk plot (B) of the prepared samples

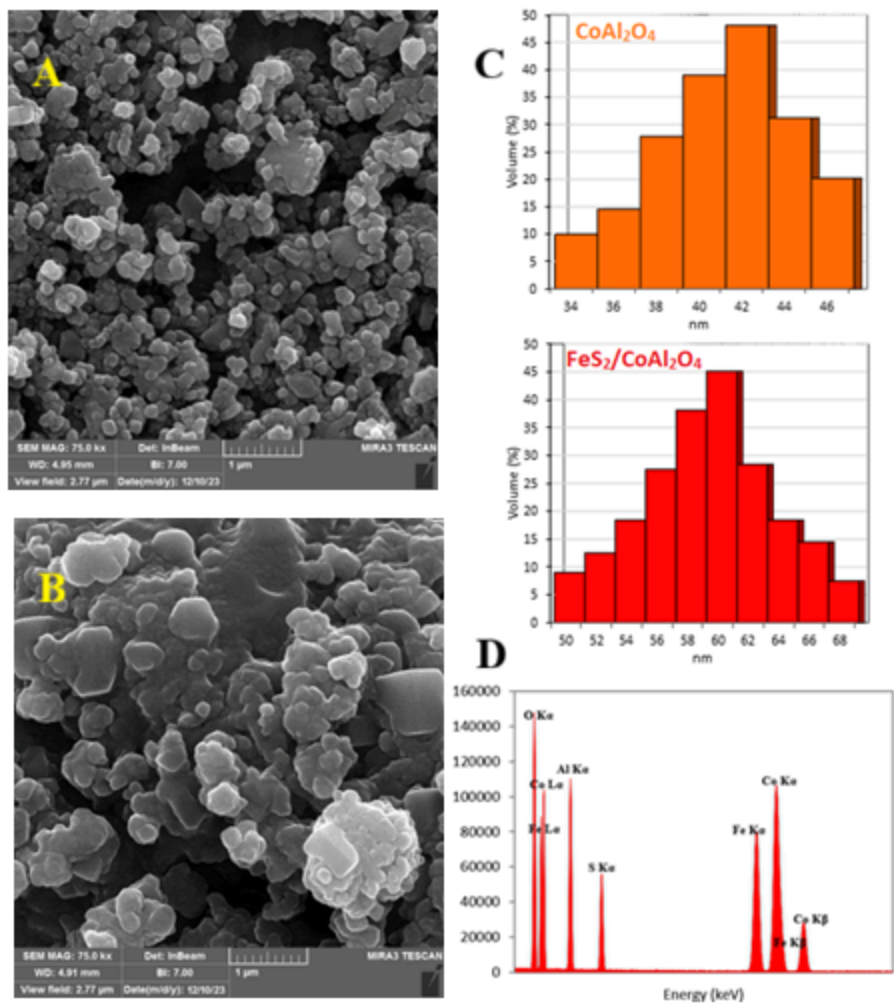


Figure 5

The FESEM images of the CoAl_2O_4 (A), $\text{FeS}_2/\text{CoAl}_2\text{O}_4$ (B), The DLS plots of the prepared samples (C), and EDS spectrum of the $\text{FeS}_2/\text{CoAl}_2\text{O}_4$

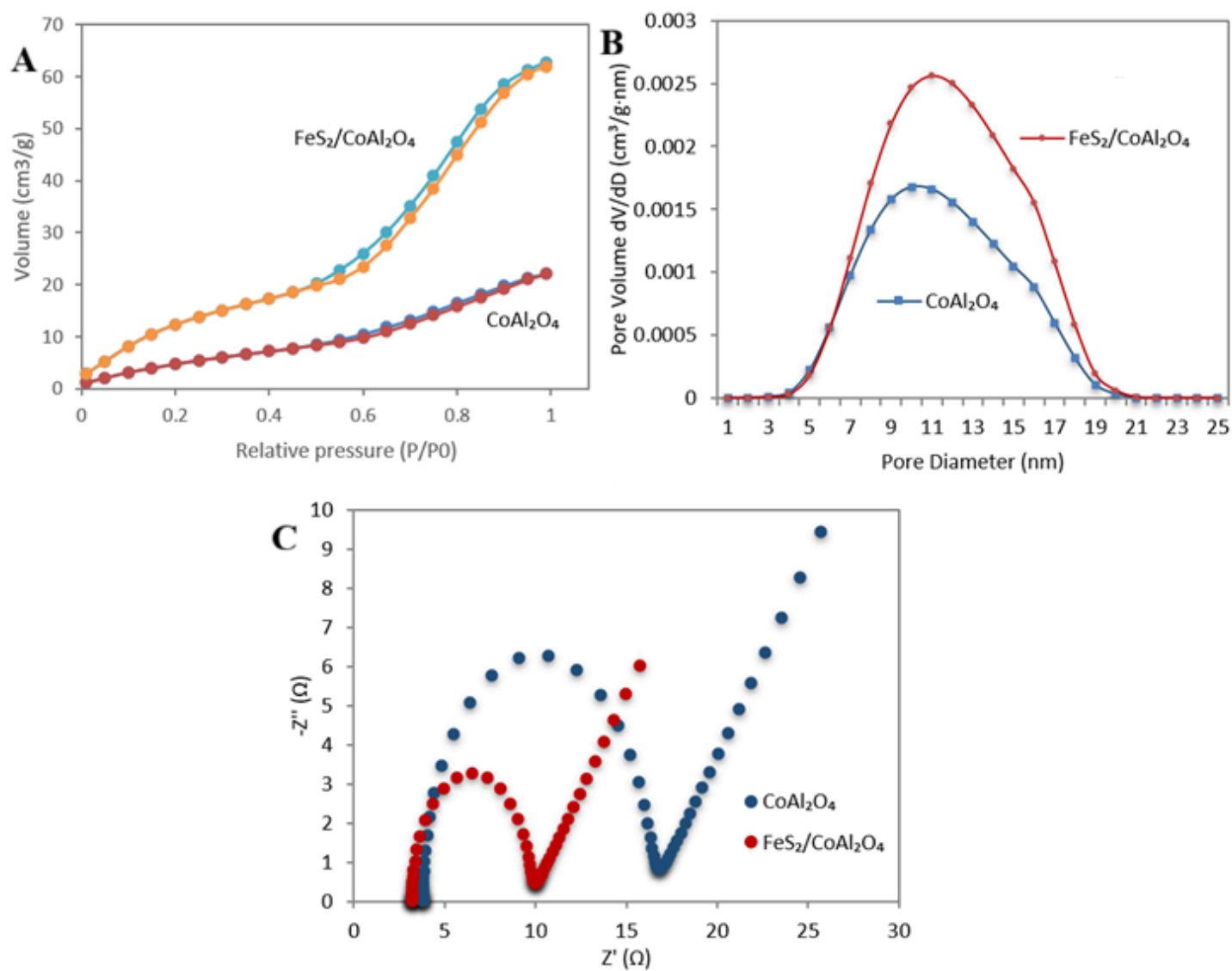


Figure 6

The BET (A), BJH (C), EIS Nyquist (C) plots of the prepared samples

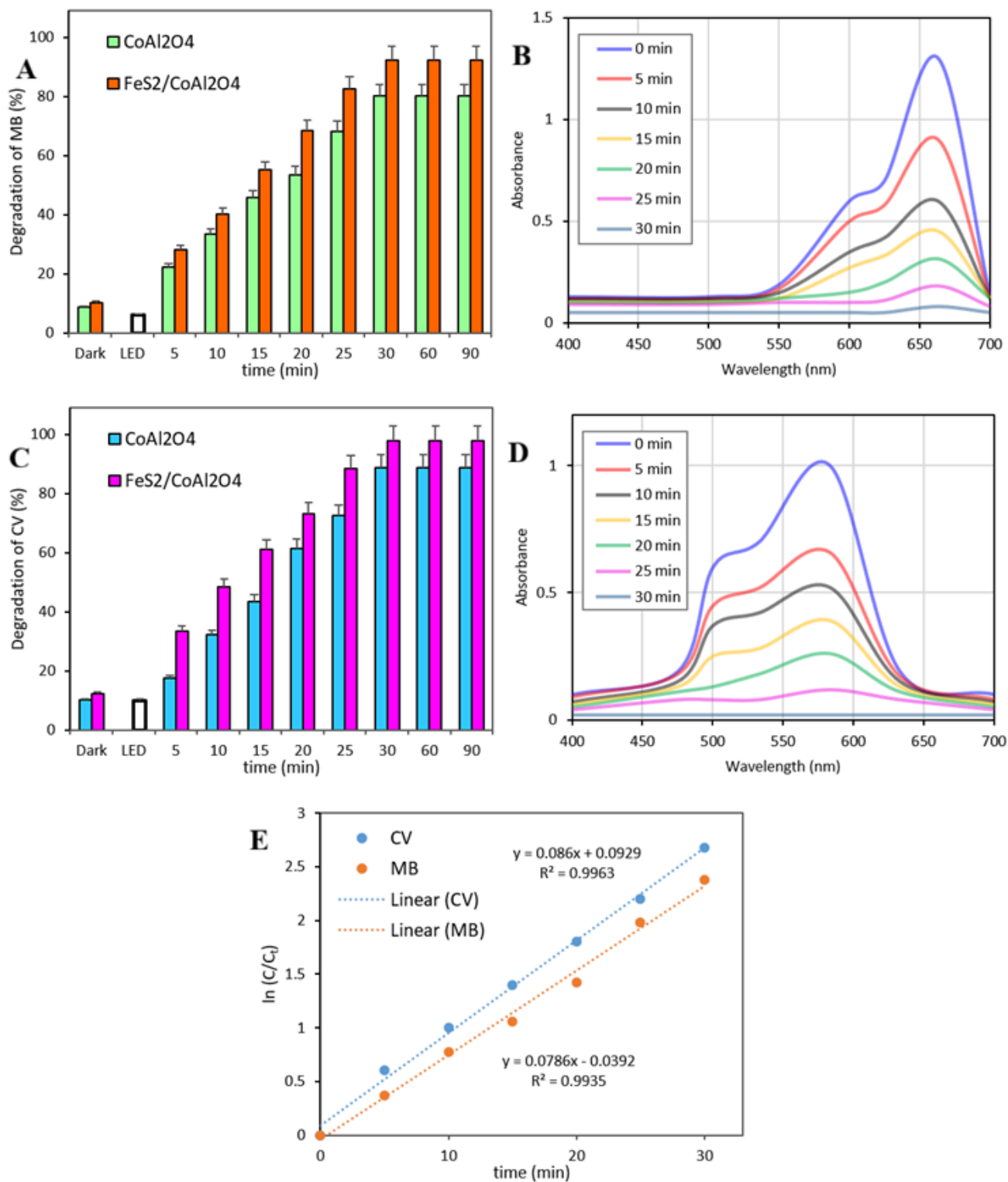


Figure 7

The degradation of MB by the prepared samples (A), the UV-vis spectrum of MB degradation by FeS₂/CoAl₂O₄ (B), The degradation of CV by the prepared samples (C), the UV-vis spectrum of CV degradation by FeS₂/CoAl₂O₄ (D), the kinetic plot of the FeS₂/CoAl₂O₄ activity for degradation of MB, and CV dyes (E)

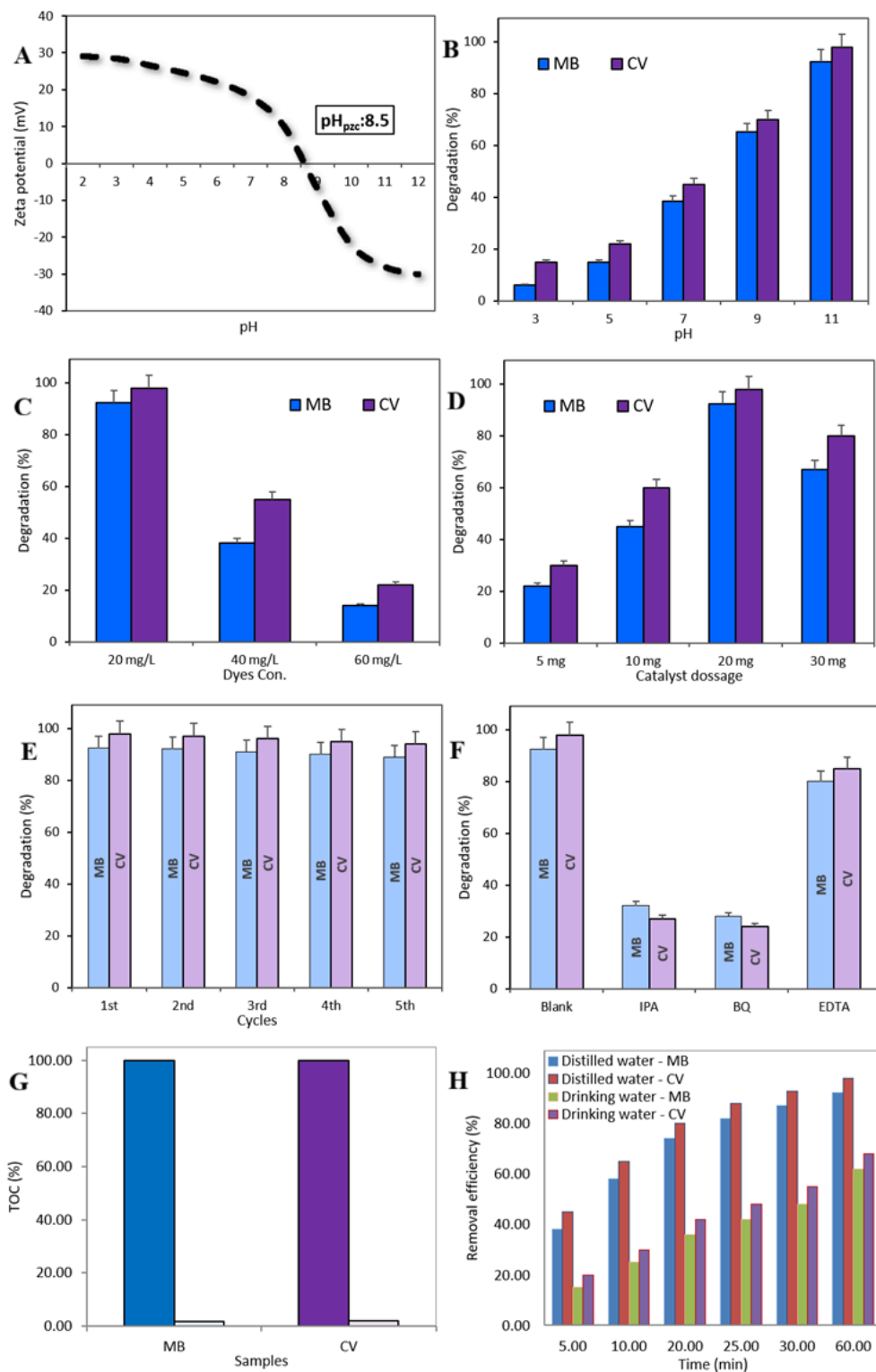


Figure 8

The pH_{zpc} of the prepared $FeS_2/CoAl_2O_4$ nanocomposites (A), the effect of pH (B), dye concentration (C), catalyst dosage (D), on degradation of dyes, the reusability test (E), the scavenging test (G) of the $FeS_2/CoAl_2O_4$ nanocomposites, the TOC response (G) by the $FeS_2/CoAl_2O_4$ nanocomposites, and the removal response of the $FeS_2/CoAl_2O_4$ nanocomposites in two real water samples for MB, and CV degradation under LED irradiation (H)

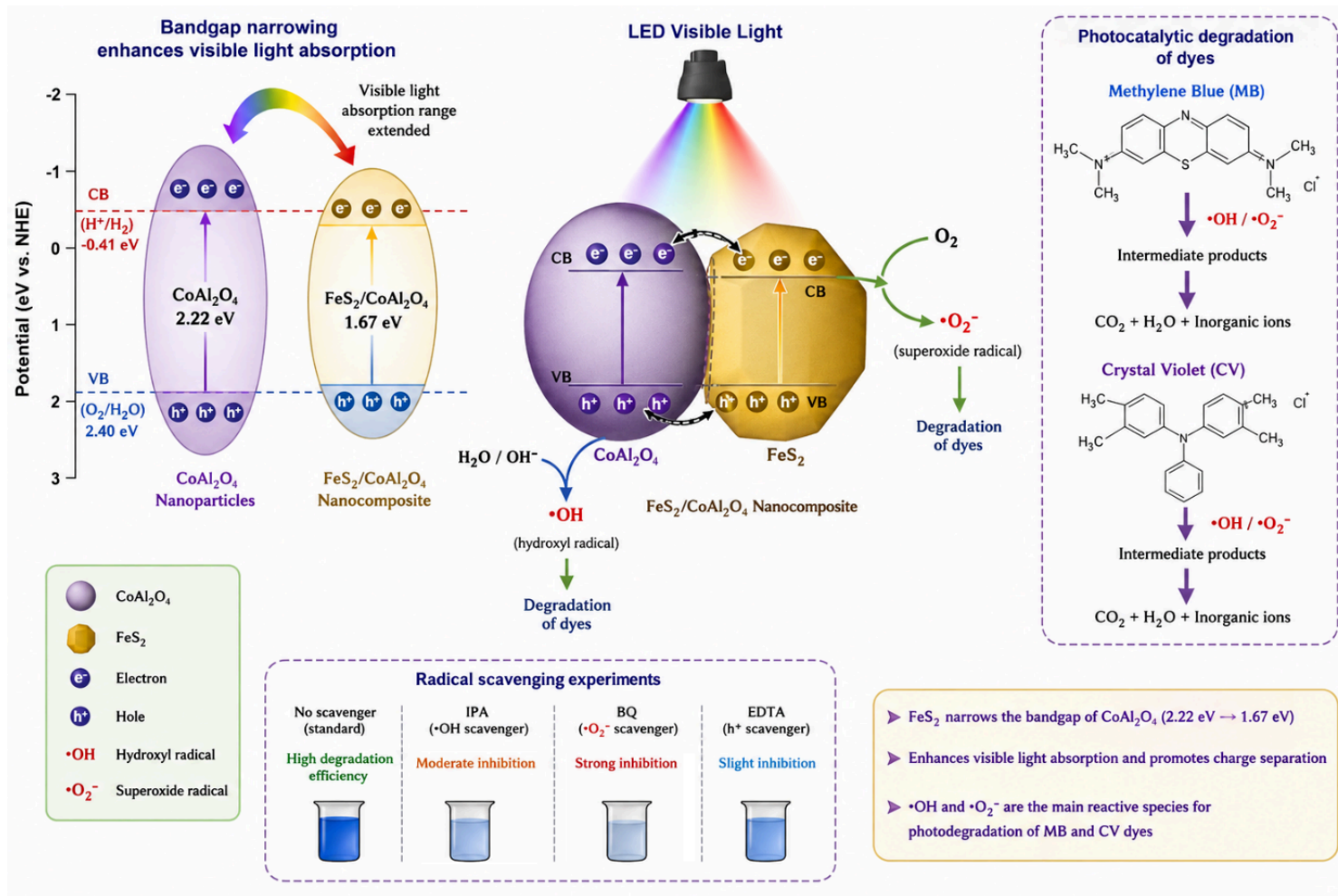


Figure 9

The mechanism of the degradation of MB, and CV by the prepared $FeS_2/CoAl_2O_4$ nanocomposites under LED irradiation