

SYNTHESIS AND CHARACTERIZATION OF $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ COMPOSITE AND ITS EFFECTIVENESS IN CATALYTIC DYE DEGRADATION: A COMPREHENSIVE STUDY

Síntese e Caracterização do Compósito $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ e Sua Eficácia na Degradação Catalítica de Corantes: Um Estudo Abrangente

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Abstract: The growing concern over water contamination from industrial dyes has driven the search for efficient and sustainable degradation methods. In this study, a $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ composite was synthesized through a co-precipitation method, followed by calcination and mechanochemical incorporation to investigate its potential in catalyzing the degradation of synthetic dye 1-Amino-4-[(4-anilino-9,10-dioxo-9,10-dihydroanthracen-1-yl) amino]anthraquinone-2-sulfonic acid sodium salt in aqueous solutions, commercially known as Reactive Blue 222, a reactive anthraquinone dye commonly used in the textile industry. This compound is known for its high chemical stability and resistance to biodegradation, posing significant risks to aquatic ecosystems due to its persistence and potential toxicity. Structural and morphological characteristics of the composite were thoroughly analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) techniques. These analyses confirmed the successful incorporation of Co_3O_4 particles within the ZnAl_2O_4 matrix, resulting in the coating of zinc aluminate surface by cobalt oxide. Maintenance of structures occurs after incorporation via mechanochemical method, supported by XRD and FTIR results. The catalytic performance of the $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ composite was evaluated through degradation tests of RB222 dye, and results demonstrated a high degradation efficiency, with more than 90% dye removal within 120 minutes, showcasing the composite's ability to break down dye molecules into colorless byproducts. This work highlights the potential of $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ composites as effective materials for environmental remediation, particularly in wastewater treatment. The findings suggest further research into optimizing catalyst preparation methods and exploring their application to other pollutants.

Keywords: Spinel oxide, Surface modification, Mechanochemical synthesis, Catalytic nanomaterials, Reactive dyes degradation.

Resumo: A crescente preocupação com a contaminação da água por corantes industriais tem impulsionado a busca por métodos de degradação eficientes e sustentáveis. Neste estudo, um compósito de $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ foi sintetizado por meio do método de coprecipitação, seguido de calcinação e incorporação mecanoquímica, para investigar seu potencial na catálise da degradação do corante sintético 1-Amino-4-[(4-anilino-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino]anthraquinone-2-sulfonato de sódio em solução aquosa, comercialmente conhecido como RB222, um corante antraquinônico reativo amplamente utilizado na indústria têxtil. Esse composto é conhecido por sua alta estabilidade química e resistência à biodegradação, representando riscos significativos aos ecossistemas aquáticos devido à sua persistência e potencial toxicidade. As características estruturais e morfológicas do compósito foram analisadas detalhadamente utilizando técnicas de difração de raios X (DRX), microscopia eletrônica de varredura (MEV) e espectroscopia no infravermelho por transformada de Fourier (FTIR). Essas análises confirmaram a incorporação bem-sucedida de partículas de Co_3O_4 na matriz de ZnAl_2O_4 , resultando no recobrimento da superfície do aluminato de zinco por óxido de cobalto. A manutenção das estruturas após a incorporação foi confirmada pelos resultados de DRX e FTIR. O desempenho catalítico do compósito $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ foi avaliado por meio de testes de degradação do corante RB222, demonstrando uma alta eficiência de degradação, com mais de 90% de remoção do corante em 120 minutos, destacando a capacidade do compósito em decompor moléculas de corante em subprodutos incoloros. Este trabalho destaca o potencial dos compósitos $\text{ZnAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ como materiais eficazes para a remediação ambiental, especialmente no tratamento de águas residuais. Os resultados sugerem pesquisas adicionais para otimizar os métodos de preparo do catalisador e explorar sua aplicação em outros poluentes.

Palavras-chave: Catalisadores, Compósitos, Degradação de Corantes, Remediação Ambiental, Tratamento de Águas Residuais.

INTRODUCTION

Due to its unique structural and electronic properties, cobalt oxide (Co₃O₄), which crystallizes in a cubic spinel structure, has garnered significant attention in materials science and catalysis (El-Shamy & Deyab, 2023; Medina et al., 2019). Belonging to the Fd $\bar{3}$ m space group, Co₃O₄ is composed of Co²⁺ and Co³⁺ ions distributed among tetrahedral and octahedral sites within the crystal lattice (El-Shamy & Deyab, 2023; Gerds et al., 2024). This arrangement endows the material with high thermal stability and distinctive magnetic properties, such as paramagnetic behavior at room temperature and a transition to antiferromagnetism below 40 K (Wang et al., 2018). The high conductivity of Co₃O₄, resulting from electron movement between Co²⁺ and Co³⁺ ions, makes it particularly suitable for applications in catalysts, gas sensors, electrochemical capacitors, and energy storage systems.

Another material of great interest is zinc aluminate (ZnAl₂O₄), which also possesses a cubic spinel structure and belongs to the same Fd $\bar{3}$ m space group. ZnAl₂O₄ is known for its high transparency to light with a wavelength above 320 nm, as well as its large specific surface area and chemical stability under various environmental conditions (Battiston et al., 2014; Gama et al., 2009; Kim et al., 2014). These characteristics make ZnAl₂O₄ a widely used material as a catalyst, especially in photocatalysis, where its ability to promote redox reactions on the surface is essential for the degradation of organic pollutants, such as dyes, in aqueous solutions. The photocatalytic efficiency of ZnAl₂O₄ is maximized by suppressing electron-hole pair recombination, a crucial factor in optimizing photocatalytic processes (Diaz-Torres et al., 2020; Li et al., 2011).

The combination of these two spinel phases into a Co₃O₄/ZnAl₂O₄ composite offers a promising platform for hybrid materials, uniting the complementary properties of each component. The resulting composite not only inherits the excellent thermal stability and magnetic and conductive properties of Co₃O₄ but also retains the photocatalytic properties and optical transparency of ZnAl₂O₄. This combination can lead to synergies that significantly expand the spectrum of applications, especially in areas requiring

the simultaneous interaction of electronic, magnetic, and photocatalytic properties (Ebrahimi et al., 2024; Li et al., 2020; Yin et al., 2012).

The catalytic activity of Co₃O₄ in the degradation of organic dyes has been widely explored in the literature (Zhang et al., 2021). For example, studies have demonstrated that Co₃O₄ can catalyze the degradation of dyes such as methylene blue and Congo red in aqueous solutions, using UV radiation to generate reactive oxygen species that break down dye molecules (Guo et al., 2021; Long et al., 2017; Warang et al., 2013; Zia et al., 2022). When combined with ZnAl₂O₄, this effect can be amplified, resulting in composites with greater efficiency in environmental remediation.

Among various environmental contaminants, synthetic dyes such as Reactive Blue 222 (RB222) have drawn considerable attention due to their high chemical stability, resistance to biodegradation, and toxic effects on aquatic ecosystems. RB222 (1-Amino-4-[(4-anilino-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino]anthraquinone-2-sulfonic acid sodium salt) is widely used in textile industries for dyeing cotton, wool, silk, and polyamide fibers, leading to the frequent discharge of dye-containing wastewater with concentrations ranging from 5 to 1500 mg/L (Kiran et al., 2013; Shokoohi et al., 2023). The persistence of such compounds in natural water bodies compromises light penetration, inhibits photosynthesis, and poses significant risks to aquatic organisms and human health. Therefore, the development of efficient and sustainable catalytic systems for RB222 degradation is of critical importance for wastewater treatment and environmental protection.

Furthermore, mechanochemical synthesis emerges as a promising approach for producing Co₃O₄/ZnAl₂O₄ composites, allowing precise control over particle morphology and ion distribution. This technique, which involves high-energy milling to induce solid-state reactions, has successfully synthesized materials with enhanced properties. For example, a recent study demonstrated the synthesis of Co₃O₄ nanoparticles through high-energy milling, resulting in materials with controlled particle sizes and excellent catalytic activity (Medina et al., 2019). Another work utilized mechanochemical synthesis to prepare ZnAl₂O₄ and Co₃O₄, revealing that the combination of these materials

led to a significant improvement in the photocatalytic degradation of organic dyes compared to pure materials (Fabián et al., 2015; Medina et al., 2019; Yang et al., 2004).

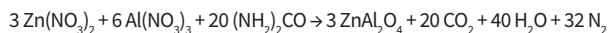
Future perspectives for the development of Co₃O₄/ZnAl₂O₄ composites include the continued exploration of new synthesis methods and a deeper understanding of the mechanisms governing interactions between the phases. Mechanochemical synthesis offers a promising pathway for developing composites with optimized structural and functional properties, capable of meeting the growing demands in areas such as energy conversion and environmental remediation.

Therefore, the present study aims to synthesize and characterize a ZnAl₂O₄-Co₃O₄ composite via mechanochemical methods and to evaluate its catalytic efficiency in the degradation of the synthetic dye Reactive Blue 222 in aqueous solution. The motivation behind this work lies in the potential synergistic effects between ZnAl₂O₄ and Co₃O₄, which could result in a multifunctional material with enhanced performance for environmental remediation applications. This work also stands out for employing a mechanochemical synthesis route, a technique still underexplored in the literature for the development of ZnAl₂O₄-Co₃O₄ composites. Moreover, the validation of the composite's catalytic performance using the complex anthraquinone-based dye Reactive Blue 222, rather than more commonly used dyes such as methylene blue or Congo red, reinforces the originality and practical relevance of the study.

MATERIALS AND METHODS

Synthesis of Zinc Aluminate (ZnAl₂O₄)

The ZnAl₂O₄ catalyst was synthesized by combustion reaction using zinc nitrate, aluminum nitrate, and urea, following the method reported by Alves et al. (2012). Zinc nitrate, aluminum nitrate, and urea were used in stoichiometric proportions according to the reaction below:



In the synthesis, 0.568 g of Zn(NO₃)₂·6H₂O (3 mmol), 2.25 g of Al(NO₃)₃·9H₂O (6 mmol), and 2.46 g of urea (20 mmol) were used. The mixture was transferred to a crucible and heated in a muffle furnace. The heating rate was set at 25°C/min until 400°C, maintained for 2 minutes. Subsequently, the temperature was increased to 500°C at 10°C/min and held for 20 minutes. After this process, the material was ground, thoroughly washed with water and ethanol, and dried in an oven at 40°C.

Synthesis of ZnAl₂O₄-Co₃O₄ Composite

This method was developed based on modifications of the synthesis methodology described by Medina et al. (2019), using a molar ratio of 1:7:1 for CoCl₂:NaBH₄:ZnAl₂O₄. The compounds were mixed in an agate mortar and milling for 5 minutes until a dark powder was obtained. The product was then transferred to 15 mL flask tubes, and distilled water was added slowly until effervescence ceased. After this process, the contents were centrifuged (6000 rpm) for 5 minutes, and the supernatant was removed after each operation, which was repeated until a neutral pH was reached. After washing, the product was dried under a vacuum at room temperature.

Characterization of ZnAl₂O₄-Co₃O₄ Composite

X-ray diffraction analyses were conducted using an X-ray diffractometer (D2 Phaser, Bruker) with a copper anode, characteristic emission line of 1.54 Å / 8.047 keV (Cu-Kα1), and a maximum power of 300W (30 kV x 10 mA). The angular range was from 5 to 60° in 2θ with an angular increment of 0.05 degrees per minute. Dynamic light scattering analyses were performed using the DLS Litesizer 500 (Anton Paar) equipment. Approximately 10 mg of the sample was added to a 3 mL glass cuvette, and the volume was completed with deionized water. The measurement temperature was 25°C, with an equilibrium time of 30 seconds, measurement angles of 173° Backscatter (NIBS default), and a duration of 10 seconds per analysis. The analyses were performed in triplicate, and the final data were obtained from a simple arithmetic mean. For the Co₃O₄ sample, an additional sonication step was applied for 15 minutes prior to measurement to assess the

effect on particle disaggregation. Fourier transform infrared spectroscopy (FTIR) analysis was performed on Vertex 70 (Bruker) equipment using an attenuated total reflectance (ATR) accessory with 2 cm⁻¹ spectra resolution and 32 scans per sample. Scanning Electron Microscopy (SEM) images were performed using the TESCAN VEGA (Tescan) equipment with integrated Energy Dispersive Spectroscopy (EDS) to identify the different inorganic elements present in the sample.

Degradation Assays of Solutions Containing Reactive Blue 222 (RB 222) Dye

A solution of RB222 dye at a concentration of 200 mg/L was prepared. In 50 mL Erlenmeyer flasks, 3 mL of this solution was mixed with 75 mg of ZnAl₂O₄-Co₃O₄ and incubated at 25 °C with orbital agitation at 150 rpm. For each time point (30, 60, 120, and 300 min), independent degradation assays were conducted in triplicate. The residual dye concentration was determined by UV-Visible spectrophotometry (Cary 60, Varian), monitoring the absorbance at 615 nm. A calibration curve was established using dye concentrations ranging from 50 to 1500 mg/L. Control samples without the catalyst were also analyzed. All assays were performed in a closed shaker to prevent evaporation and eliminate external light exposure. The experiments were conducted under complete darkness, ensuring that no photodegradation effects influenced the results. Additionally, a control assay conducted under ambient light showed no significant differences in absorbance, confirming that light did not interfere with dye degradation.

Statistical analyses were performed using OriginPro 8.5 (OriginLab Corporation, USA). The concentration data of RB222 were expressed as mean ± standard deviation from triplicate measurements. A one-way analysis of variance (ANOVA) was applied to assess the significance of differences among groups, considering both the catalyst type and the reaction time. When significant effects were observed ($P < 0.05$), Tukey's post hoc test was applied to determine statistical differences between means. Uppercase letters indicate comparisons among catalysts at the same time point, while lowercase letters denote comparisons among time intervals within the same catalyst group.

RESULTS AND DISCUSSION

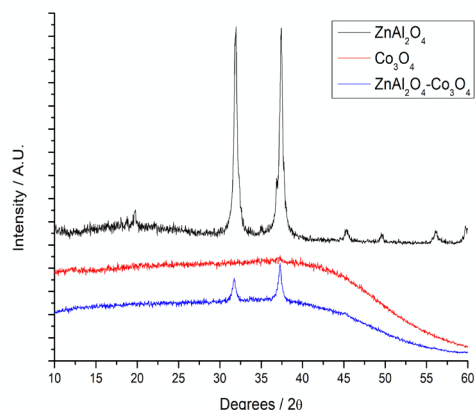
Structural and Morphological Characterization of Oxides and Composite

The ZnAl₂O₄ particles exhibit a non-uniform size distribution with an average size of 635 nm. Literature reports indicate values below 100 nm, which may be related to the synthesis method employed, calcination temperature, and sample treatment for analysis. Roudbaraki et al. (2019) synthesized ZnAl₂O₄ via the coprecipitation method with calcination at 750 °C, and for DLS analysis, the sample was diluted in ethanol (1 g/L) and sonicated for 2 hours. The result revealed a particle size of around 55 nm. In the present study, ZnAl₂O₄ was produced by combustion at 500 °C, and the sample was dispersed in water for DLS analysis. The particle distribution of the ZnAl₂O₄-Co₃O₄ composite indicated an increase in the average size (1037 nm), likely due to particle agglomeration, suggesting that there is no adsorption or incorporation of particles into the superficial or lamellar positions of the zinc particle structure. The average particle size of Co₃O₄ obtained in this work was 878 nm, corresponding to a significant increase in size. Medina et al. (2019) synthesized Co₃O₄ using the same mechanochemical method and reported an average particle size of 120 ± 40 nm. Notably, the DLS analyses allowed the observation of the diameter of hydrated particles, which may explain this size increase. In the present study, ultrasonication of the Co₃O₄ sample for 15 minutes resulted in particle disaggregation, with a small peak observed at 185 nm. This finding is consistent with the particle size distribution reported by Medina et al. (2019).

The diffractograms of the samples ZnAl₂O₄, Co₃O₄, and composite ZnAl₂O₄-Co₃O₄ can be seen in Figure 1. When analyzed individually, the Co₃O₄ diffractogram shows a significantly broadened signal, typical of amorphous material. This result was expected, as milling greatly reduces the crystallinity of the particles. Additionally, due to the particle size, CuKα radiation (1.5406 Å) does not penetrate sufficiently into the sample to characterize reflection planes in more internal and likely more crystalline regions, necessitating the use of a shorter wavelength radiation source, such as

MoK α (0.71073 Å), for better sample penetration (Medina et al., 2019). The ZnAl₂O₄ diffractogram aligns with the data obtained by Du et al. (2015). The 2 θ values of 31.22°, 36.77°, 44.69°, 48.98°, 55.52°, and 59.27° correspond to the reflection planes (220), (311), (400), (331), (442), and (511), respectively. Regarding the ZnAl₂O₄-Co₃O₄ composite diffractogram, the coexistence of the two phases is observable. The signal broadening, as seen in the Co₃O₄ diffractogram, indicates the presence of an amorphous cobalt oxide phase. However, two typical diffraction peaks of zinc aluminate are also visible with higher intensity at 31.22° and 36.77° and a smaller peak with lower intensity at 44.69°. There are no shifts in the 2 θ values when cobalt oxide is incorporated into the spinel structure. This indicates no structural alteration in the zinc aluminate, only the incorporation of cobalt oxide on the surface.

Figure 1
XRD patterns of ZnAl₂O₄, Co₃O₄, and composite ZnAl₂O₄-Co₃O₄



Images of electronic microscopy samples were observed in Figure 2, and Table 1 shows the atomic weight of principal components. The cobalt oxide image (Fig 2A) presents non-shape particles, corroborating the XRD results for the amorphous cobalt oxide phase. Large particles with aggregation can be observed as indicated at DLS characterization. However, it is possible to see that aggregation is created from slight particles in agreement with DLS data after sonication. ZnAl₂O₄ image (Fig 2B) shows a roughened surface morphology formed by the aggregation of smaller oxide particles. The figure scale indicates particle size close to 1 μ m, which corroborates the DLS data. Similar morphological features, including particle coalescence and aggregation, have also been

reported in ZnO/ZnAl₂O₄ composites (Chen et al., 2021). ZnAl₂O₄-Co₃O₄ image (Fig 2C) is morphologically similar to the Co₃O₄ image and indicates that the ZnAl₂O₄ surface is coated with cobalt oxide. This supports the effectiveness of the mechanochemical incorporation. Surface modifications of this type, caused by heterojunction formation, have also been observed in similar systems (Chen et al., 2021). This image proves that the experimental technique is successful for composite preparation.

EDS was used to identify the atomic weight composition using the entire image map. The average composition data of the samples can be viewed in Table 1. Atomic weight distribution for Cobalt oxide presents a similar composition between theoretical and experimental atomic percentages. The most significant deviation is found for oxygen. It can be understood as the formation of oxides of impurities present in the sample, as shown in the EDS graphs in Figure 2. For zinc aluminate, the experimental and theoretical values are also close, and the ratio between the proportions of zinc and aluminum is less than 2, indicating that the reaction stoichiometry is maintained. The experimental values indicate a lower concentration of zinc than expected, which may have been caused by the technique used in the synthesis or leaching after washing. However, the literature shows that the XRD data agree with the spinel structure. These deviations, especially the elevated surface cobalt content, are consistent with EDS limitations and surface-dominated structures previously described in nanocomposites synthesized via similar methods (Chen et al., 2021). However, the Zn/Al ratio is maintained in the formation of the composite, indicating conservation of the structure, which also corroborates the XRD data. The higher-than-expected cobalt ratio is probably due to the coating of the zinc aluminate surface by cobalt oxide. Since the radiation used in EDS is not penetrating, analyzing only the surface, it can be understood that what occurred was an impregnation of cobalt oxide on the surface of the spinel, indicating that the technique used was interesting in terms of improving the surface of the spinel. It is worth noting that no boron and nitrogen impurities were found, which indicates that the reagents were consumed in the syntheses and will not interfere with the interpretation of the dye degradation results.

Figure 2
Images of scanning electronic microscopy (SEM) of (A) ZnAl₂O₄, (B) Co₃O₄, and composite (C) ZnAl₂O₄-Co₃O₄

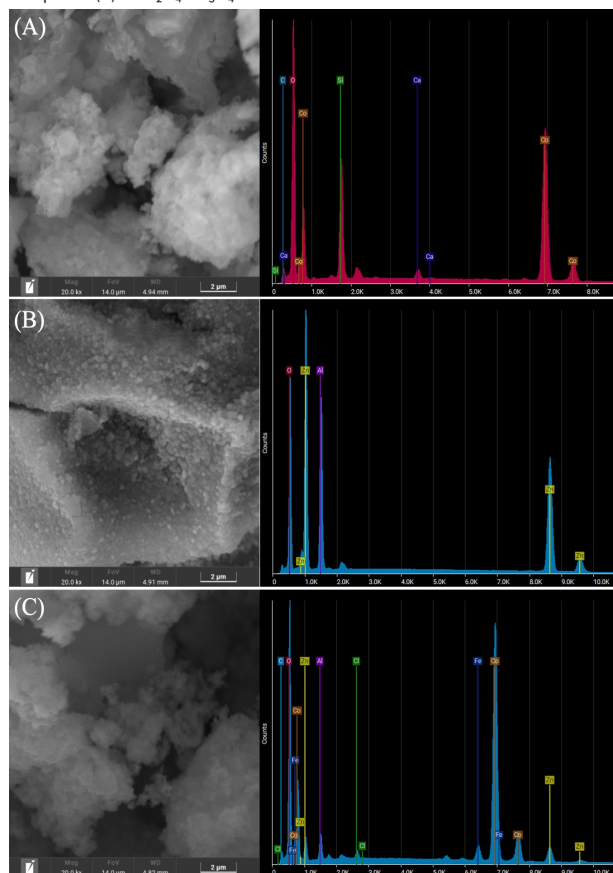


Table 1
The atomic weight of selected atoms by energy-dispersive X ray spectroscopy. (Other atoms: C from conductive tape, Cu from sampler, Si/Fe/Ca/Cl as impurities were disregarded for calculation)

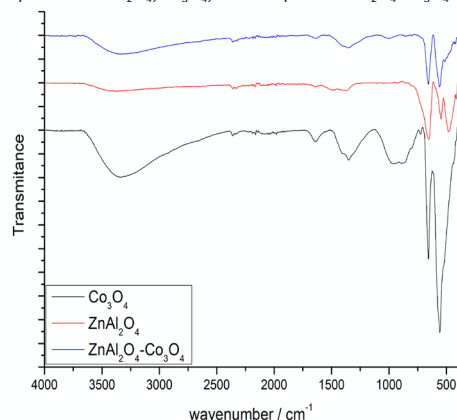
Element	Atomic weight (Theoretical / Experimental) / %		
	Co ₃ O ₄	ZnAl ₂ O ₄	ZnAl ₂ O ₄ -Co ₃ O ₄
Co	73.44 / 60.23	-	20.70 / 55.59
Zn	-	35.66 / 45.62	22.92 / 5.85
Al	-	29.44 / 25.75	18.94 / 3.27
O	26.55 / 39.77	34.96 / 28.62	37.44 / 35.28

FTIR ANALYSIS OF SYNTHESIZED MATERIALS

Figure 3 shows FTIR-ATR spectra for oxides and composite samples. The FTIR spectrum of Co₃O₄ exhibits multiple absorption bands, with the most prominent located at approximately 575 cm⁻¹ and 666 cm⁻¹. These bands are attributed to Co³⁺-O stretching in tetrahedral

sites and Co²⁺-O stretching in octahedral sites, respectively, and are characteristic of the normal spinel structure of Co₃O₄ (Karthikeyan et al., 2023; Medina et al., 2019). In addition to these, weaker bands were observed around 1635 cm⁻¹ and 3426 cm⁻¹, which are commonly associated with H-O-H bending and O-H stretching modes from adsorbed water and surface hydroxyl groups, especially in samples obtained via precipitation or aqueous routes (Medina et al., 2019; Rabee et al., 2022). In the Co₃O₄ spectrum, absorption bands were detected between 878 and 1350 cm⁻¹. As previously reported by Medina et al. (2019), these bands can be attributed to B-O stretching vibrations of surface boron-containing species formed during the hydrolysis of sodium borohydride. Despite washing, these species appear to remain partially adsorbed onto the oxide surface as residues from the mechanochemical synthesis process. The FTIR spectrum of ZnAl₂O₄ displays three characteristic absorption bands located at approximately 670, 590, and 500 cm⁻¹. These bands are typically attributed to Al-O and Zn-O stretching vibrations in the spinel framework. A shoulder near 750 cm⁻¹ is also observed, which may correspond to lattice deformation or structural distortion modes. These vibrational features are consistent with those reported for spinel-type ZnAl₂O₄ materials synthesized by similar methods (Chen et al., 2021; Du et al., 2015). The FTIR spectrum of the ZnAl₂O₄-Co₃O₄ composite does not represent a simple linear combination of the spectra of the two isolated oxides. Instead, shifts in band positions and variations in intensities were observed, suggesting interactions between the ZnAl₂O₄ and Co₃O₄ phases. These spectral changes may be attributed to surface coverage effects, partial substitution of lattice ions, or the formation of interfacial bonds during the mechanochemical synthesis. Such phenomena are commonly reported in nanocomposites where chemical interactions alter the local bonding environment (Chen et al., 2021). The FTIR spectrum of the composite reveals more intense Co₃O₄ absorption bands, which is consistent with the dispersion of cobalt oxide over the ZnAl₂O₄ surface, as also evidenced by the SEM images. This spectral behavior supports the conclusion that Co₃O₄ predominantly covers the surface of the spinel phase as a result of the mechanochemical synthesis of the ZnAl₂O₄-Co₃O₄ composite.

Figure 3
FTIR-ART spectra of ZnAl₂O₄, Co₃O₄, and composite ZnAl₂O₄-Co₃O₄



CATALYTIC PERFORMANCE IN DYE DEGRADATION

A spectroscopy technique in the visible region was used to monitor the absorbance of the band at 615 nm, which is typical of the RB222 dye, to measure the degradation of the dye. Table 2 presents the data on the dye concentration and % of discoloration from a standard solution of 200 ppm of the dye.

Table 2
RB222 colorant concentration and percentage of discoloration after respective time. Values represent the triplicate mean

Time / min	[RB222] / ppm			Discoloration / %		
	Co ₃ O ₄	ZnAl ₂ O ₄	ZnAl ₂ O ₄ -Co ₃ O ₄	Co ₃ O ₄	ZnAl ₂ O ₄	ZnAl ₂ O ₄ -Co ₃ O ₄
0	200 ± 0.32			0		
15	24.1±0.06 ^{A,b}	172±0.16 ^{C,c}	38.3±0.10 ^{B,c}	87.8	14	80.9
30	19.3±0.13 ^{A,b}	136±0.01 ^{C,b}	13.33±0.12 ^{B,b}	87.9	31.8	93.55
60	19.3±0.13 ^{A,b}	148±0.21 ^{C,b}	5.71±0.15 ^{B,b}	87.9	8.44	97.24
120	14.2±0.14 ^{A,a}	135±0.08 ^{C,b}	4.76±0.21 ^{B,b}	91.1	16.5	97.70
300	11.6±0.02 ^{A,a}	112±0.09 ^{C,a}	3.61±0.08 ^{B,a}	94.22	30.8	98.25

Note: Values are expressed as mean ± standard deviation of three replicates. Means followed by the same uppercase letter in the same row do not differ significantly from each other, indicating no statistical difference between catalysts at the same reaction time. Means followed by the same lowercase letter in the same column do not differ significantly from each other, indicating no statistical difference among reaction times for the same catalyst. Statistical differences were determined by one-way ANOVA followed by Tukey's post hoc test ($P < 0.05$).

The dye degradation results show that the isolated zinc aluminate presents slight degradation of the azo dye, with a maximum percentage of discoloration close to 30% after 300 minutes of experiment. In previous studies, Stringhini et al. (2015) achieved 100% degradation of the dye Procion Red H-E7B at a concentration of 130 ppm using ZnAl₂O₄ under UV

irradiation for 120 minutes. Battiston et al. (2014) achieved 100% degradation of the dye Direct Black 38 at a concentration of 80 ppm using ZnAl₂O₄ under solar light irradiation. The data cited in the literature show high degradation if the incidence of ultraviolet radiation activates zinc aluminate. Since the idea of this study is to make a comparison with the composite, experiments were not carried out in the presence of ultraviolet radiation.

Cobalt oxide is already known for its power to degrade dyes. The discoloration results of the RB222 dye solution using only the oxide were almost 90% degradation after 300 minutes of the experiment (Guo et al., 2021; Long et al., 2017; Warang et al., 2013; Zhang et al., 2021; Zia et al., 2022). The statistical analysis of the degradation data confirmed that the observed differences among the catalysts were significant. According to one-way ANOVA followed by Tukey's test ($P < 0.05$), the ZnAl₂O₄-Co₃O₄ composite presented statistically lower residual concentrations of RB222 at all time points when compared to the isolated oxides. Additionally, differences between Co₃O₄ and ZnAl₂O₄ were also significant, with the latter consistently showing inferior catalytic performance. The use of both uppercase and lowercase letters in Table 2 denotes these distinctions: uppercase letters compare catalyst types at the same time point, and lowercase letters compare degradation efficiency across time within each catalyst group. These results reinforce the superior and consistent performance of the composite material. The experimental data for the composite indicate an excellent percentage of dye degradation after 30 minutes of experimentation, with approximately 90% discoloration. For the 300 minutes used in the experiments, it was possible to observe 98.25% dye degradation, a value higher than that found for isolated cobalt oxide. It is possible to notice that there was synergy in dye degradation in the composite results since the values were higher even for isolated cobalt oxide. Although they present similar values, the results are higher for the composite. This may be linked to how the cobalt oxide is distributed on the surface of the zinc aluminate, as observed in Figure 2 (Adekunle et al., 2020; Luo et al., 2019; Warang et al., 2013).

It is important to note that all degradation experiments were conducted under dark conditions, without UV irradiation, to eliminate any contribution from photodegradation.

Furthermore, control experiments conducted in the absence of the ZnAl₂O₄-Co₃O₄ composite showed no significant reduction in dye concentration over time, indicating that neither photodegradation nor adsorption significantly contributed to the observed dye removal. These findings confirm that the decrease in absorbance is predominantly due to the catalytic degradation promoted by the composite.

CONCLUSION

The present study successfully demonstrated the synthesis and characterization of the ZnAl₂O₄-Co₃O₄ composite, combining the catalytic properties of ZnAl₂O₄ with the electronic and magnetic characteristics of Co₃O₄. The adopted synthesis methodology allowed for producing particles of suitable sizes for dye degradation applications, with the material characterization confirming the presence of the desired phases without significant structural alterations. The catalytic activity was evidenced in the degradation tests of the RB222 dye, where the composite exhibited synergy, surpassing the degradation rates of the isolated materials. The ZnAl₂O₄-Co₃O₄ composite achieved 98.25% dye degradation after 300 minutes, surpassing both individual oxides in efficiency. These differences were statistically significant, confirming that the superior performance of the composite is not only evident in practical terms, but also supported by rigorous analysis. The results validate the synergistic effect between the two spinel phases and reinforce the potential of this material for environmental remediation applications, especially in the treatment of recalcitrant organic pollutants such as reactive dyes. These results indicate that integrating zinc and cobalt oxides could be a promising approach for developing materials with advanced functionalities, particularly in pollutant degradation processes in aqueous solutions. Further studies are suggested, exploring new synthesis methodologies and applying the composite under more varied conditions, such as ultraviolet radiation, to maximize its photocatalytic potential.

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