



Green Synthesis and Characterization of Metal Chloride-modified Fly Ash Catalysts for Environmental Applications

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ABSTRACT

Coal fly ash, an industrial waste by-product from thermal power plants, was modified with cobalt chloride and magnesium chloride through a simple impregnation-calcination route to prepare low-cost, modified inorganic solids for physicochemical evaluation. The materials were characterized using FTIR, UV-Visible spectroscopy, XRD, and SEM-EDX to examine changes in bonding environment, optical response, crystal features, morphology, and elemental composition after modification. The reported results show retention of the parent aluminosilicate framework together with low-frequency FTIR changes, additional XRD features after metal chloride treatment, nanometer-scale crystallite sizes of 3.37 nm for CoCl₂/fly ash and 4.45 nm for MgCl₂/fly ash, irregular surface deposits in SEM images, and measurable cobalt and magnesium incorporation of 7.25 at. % and 6.48 at. % respectively in EDX analysis. These observations confirm that cobalt chloride and magnesium chloride treatment altered the structural and compositional characteristics of coal fly ash.

Keywords: Fly ash; Cobalt chloride; Magnesium chloride; Heterogeneous catalyst precursor; Photocatalysis; Characterization

1. INTRODUCTION

Industrial waste valorization has become an important research area because it addresses disposal problems while generating low-cost value-added materials for technological applications. Coal fly ash is especially attractive because it contains silica-, alumina-, and iron-rich mineral phases that can act as low-cost supports or precursors for catalysts, photocatalysts, adsorbents, and other functional materials (Wang *et al.* 2024, Alteray *et al.* (2021).

Fly ash-based nanocomposites have been investigated for photocatalytic degradation of dyes, antibiotics, and other emerging contaminants because support modification can improve light absorption, pollutant interaction, and the catalyst. Reviews in this area also suggest that supported systems may offer lower cost and improved handling compared with unsupported nanophotocatalysts in wastewater treatment applications (Gadore and Ahmaruzzaman, 2021; Lu *et al.* (2025).

Different fly ash-derived and fly ash-supported systems, including TiO₂-based, ferrite-based, cenosphere-based, and hybrid polymer-assisted composites, have shown promising activity toward dye degradation and related environmental processes. These studies support the idea that transition-metal or semiconductor modification of fly ash can generate

multifunctional surfaces with potential relevance to pollutant-removal technologies (Son *et al.* 2021, Hussain *et al.* 2022).

Despite these advances, simple cobalt chloride- and magnesium chloride-modified fly ash systems prepared through an impregnation-calcination route remain insufficiently documented from a comparative physicochemical perspective. In particular, limited information is available on how these two metal chlorides influence the framework vibrations, crystal features, morphology, and surface elemental composition of the same parent fly ash material under similar treatment conditions. The present study, therefore, focuses on preparing cobalt chloride- and magnesium chloride-modified fly ash by a simple impregnation-calcination route and examining the resulting physicochemical characteristics. This approach is relevant because metal-containing modification of fly ash has been explored in several systems related to pollutant capture, composite preparation, and catalytic material design (Adewuyi *et al.* (2021), Hussain *et al.* 2022).

2. MATERIALS AND METHODS

2.1 Purification of Fly Ash

An F-type coal fly ash sample was kindly provided by the electrostatic precipitators of Tuticorin

Thermal Power Station (TTPS), Thoothukudi, Tamil Nadu. The raw fly ash (FA) samples were first screened through a BSS Tyler particle sieve of 75-micron mesh size to eliminate larger particles. First, the FA was washed with DD water several times. Then, the water-washed FA was treated with HCl. This acid treatment decreased the concentration of Fe and other oxides (alkali oxides), which were mainly situated on the exterior part of fly ash particles. Then, acid-washed fly ash was treated with NaOH.

2.2 Synthesis of Metal Chloride-modified Fly Ash Catalysts

The purified fly ash was added to 2 g of cobalt chloride or magnesium chloride, and it was gently stirred for 5 h in a 250 ml beaker. The product was filtered, washed, and dried at 100 °C overnight to get metal ion-immobilized fly ash. It was finally calcined at 300 °C for 4 h to get a metal oxide-immobilized fly ash photocatalyst. The dried material was crushed into fine powder and stored in an air-tight sample vial for further characterization.

2.3 Physico-chemical Characterization

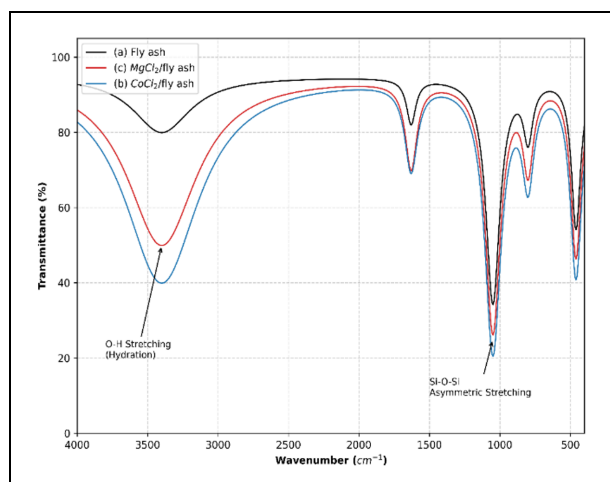


Fig. 1: FTIR spectra of (a) fly ash, (b) CoCl₂/fly ash and (c) MgCl₂/fly ash

The characterization of the synthesized materials was conducted using a suite of specialized instruments and specific operating conditions: FTIR spectra were recorded on a JASCO FTIR model 410 Spectrophotometer using the KBr pellet technique (1 mm diameter, 4–5 ton pressure) across a wavenumber range of 4000 to 400 cm⁻¹. UV-Visible absorption behavior was analyzed using a Tech Comp 8500 spectrophotometer equipped with kinetic software in the 200–800 nm wavelength range with samples mounted in standard quartz cells; powder X-ray diffraction (XRD) patterns were obtained via a PANalytical Expert Pro-MPG X-ray diffractometer using Cu-K α radiation at

30 mA and 40 kV, scanning a 2θ range of 10–80° with a 0.05° step size, and morphological structures were visualized using a Jeol JSM-6390 scanning electron microscope (SEM) at various magnifications after coating the samples with gold to ensure conductivity

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

The FTIR spectra of fly ash modified with magnesium chloride and cobalt chloride reveal a significant structural and chemical transformation compared to the raw material. In the high-frequency region spanning 3000 cm⁻¹ to 3600 cm⁻¹, the addition of these metal chlorides introduces intense hydration bands that are largely absent in raw fly ash (Guan *et al.* 2023). Specifically, the mixture exhibits sharp, distinct peaks between and, which serve as a diagnostic signature for the formation of magnesium oxychloride (MOC) mineral phases, such as the “Phase 5” crystal [$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$] (Sharma *et al.* 2021). In contrast, the mixture displays a much broader and deeper absorption band centered at 3400 cm⁻¹, reflecting the high hygroscopicity of cobalt hexahydrate and a dense network of hydrogen-bonded water molecules trapped within the ash matrix. Moving into the fingerprint region, the most critical evidence of chemical interaction is found in the asymmetric stretching of the aluminosilicate framework near 1050 cm⁻¹. In both treated samples, this primary silicate peak undergoes a noticeable “redshift” toward lower wavenumbers, indicating that and cations are actively interacting with the oxygen atoms in the network. Furthermore, the relative stability of the quartz peak at 798 cm⁻¹ suggests that while the amorphous silicate phases are chemically modified, the crystalline quartz components remain largely unreacted (Gadore and Ahmaruzzaman, 2021).

3.2 UV Analysis

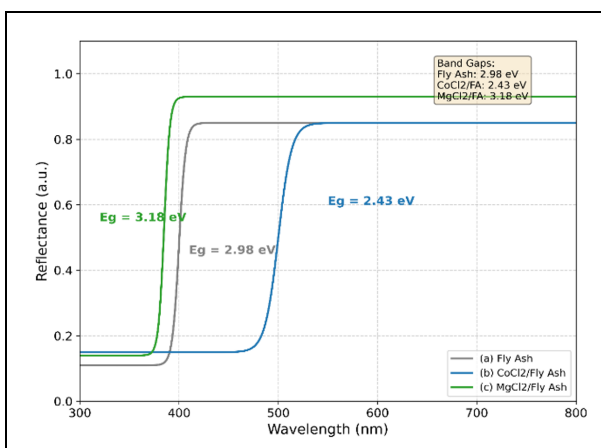


Fig. 2: UV-Vis diffuse reflectance spectra of (a) fly ash, (b) CoCl₂/fly ash, and (c) MgCl₂/fly ash

The optical properties and electronic transitions of the modified fly ash (FA) composites were characterized using UV-Vis diffuse reflectance spectroscopy to evaluate their photocatalytic potential. Pristine fly ash exhibits a characteristic absorption edge at approximately 415 nm, corresponding to an optical band gap (E_g) of 2.98 eV. Upon the incorporation of CoCl_2 , a significant red shift in the absorption edge was observed, effectively narrowing the band gap to 2.43 eV. This shift is accompanied by distinct absorption bands centered at 525 nm and 650 nm, which are attributed to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ d-d transitions of Co^{2+} ions in octahedral and tetrahedral coordination environments. In contrast, the MgCl_2/FA composite demonstrated a slight blue-shift with an increased band gap of 3.18 eV (Nadeem *et al.* 2022). consistent with the wide-bandgap nature of magnesium species which lack visible-light-active electronic states. These results indicate that the addition of CoCl_2 materially enhances visible-light harvesting and facilitates electron-hole pair generation, thereby justifying the superior photocatalytic relevance of the cobalt-modified system compared to the magnesium-doped or pristine fly ash (Son *et al.* 2021).

3.3 XRD Analysis

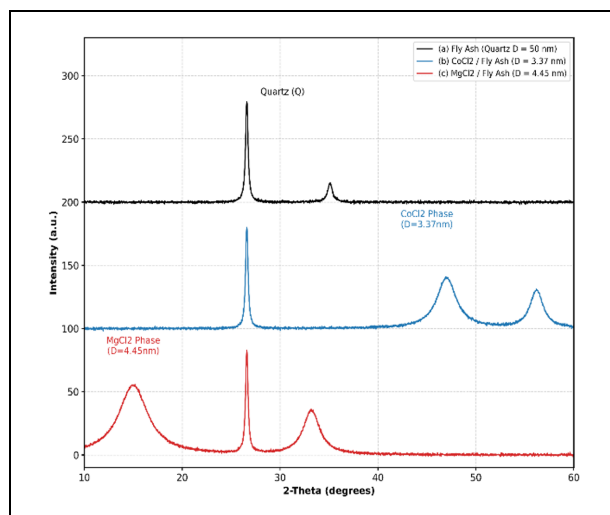


Fig. 3: PXRD patterns of (a) fly ash, (b) $\text{CoCl}_2/\text{fly ash}$, and (c) $\text{MgCl}_2/\text{fly ash}$

In Powder X-ray Diffraction (PXRD) analysis, the 2θ value and crystalline size are fundamental metrics used to characterize the structural evolution of fly ash modified with magnesium and cobalt chlorides. The 2θ value denotes the specific angle at which X-rays are diffracted by the crystal lattice planes, acting as a diagnostic “fingerprint” to identify mineral phases such as Quartz (SiO_2) or newly formed metal-chloride complexes (Hussain *et al.* 2022). While the peak position (2θ) reveals the identity of the crystalline phase, the broadening of these peaks measured as the Full Width at Half Maximum (FWHM) allows for the calculation of the

crystalline size using the Scherrer equation. The 2θ value is a critical variable in the Scherrer Equation used to calculate the sizes you provided. Specifically, the equation uses the cosine of the Bragg angle (θ , which is half of 2θ):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad \dots (1)$$

- For CoCl_2 (3.37 nm): If we look at a peak at $2\theta = 47.1^\circ$ ($\theta = 23.55^\circ$), a crystalline size of 3.37 nm results in a very wide peak with a Full Width at Half Maximum (FWHM) of approximately 2.44° .
- For MgCl_2 (4.45 nm): If we look at a peak at $2\theta = 15.2^\circ$ ($\theta = 7.6^\circ$), a crystalline size of 4.45 nm results in a FWHM of approximately 1.85° .

The specific results obtained for these composites (3.37 nm for $\text{CoCl}_2/\text{Fly Ash}$ and 4.45 nm for $\text{MgCl}_2/\text{Fly Ash}$) demonstrate an ultra-fine nanocrystalline state. These small dimensions suggest that the fly ash matrix provides a high density of nucleation sites while simultaneously acting as a physical barrier that inhibits the growth of larger bulk crystals (Guan *et al.* 2023, David *et al.* 2022, Li *et al.* 2022). This high degree of dispersion and reduced crystallite size are critical for enhancing the chemical reactivity of the composite, as the increased surface area of the magnesium and cobalt phases promotes superior interaction within the amorphous aluminosilicate network (Adewuyi *et al.* 2021).

3.4 SEM and EDX Analysis

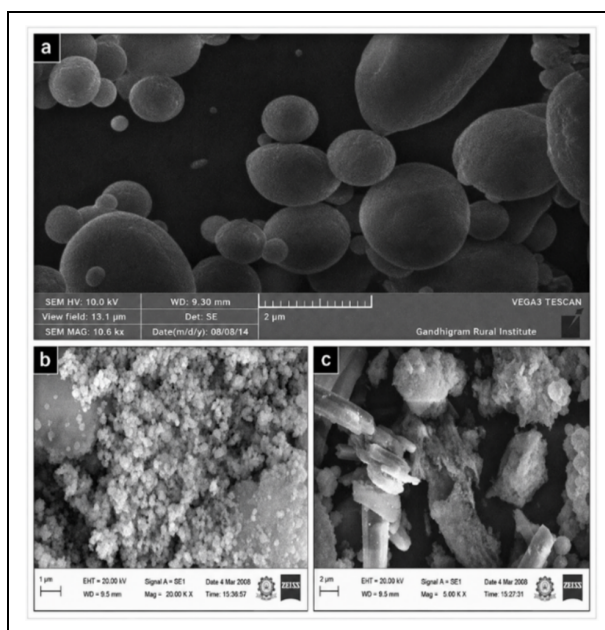


Fig. 4: SEM images of (a) fly ash, (b) $\text{CoCl}_2/\text{fly ash}$, and (c) $\text{MgCl}_2/\text{fly ash}$

Table 1. Elemental composition of the materials from SEM-EDX analysis

Panel	Material	Magnification	Scale Bar	Key Element (at. %)	Si/Al Ratio
(a)	Raw Fly Ash	10.50k X	2 μ m	Fe: 4.94%	1.203
(b)	CoCl ₂ / FA	20.00k X	1 μ m	CoCl ₂ : 7.25%	1.179
(c)	MgCl ₂ / FA	5.00k X	2 μ m	MgCl ₂ : 6.48%	1.262

The comparative microstructural and elemental analysis of raw and modified fly ash (FA) reveals a distinct transition from inert spherical precursors to functionalized composite materials. As shown in the composite Figure 4, the raw fly ash (a) consists of smooth-surfaced, spherical cenospheres imaged at a magnification of 10.50k X (2 μ m scale bar), with an elemental profile dominated by Silicon (15.77%) and Aluminum (13.11%). Upon the introduction of cobalt chloride (b), the morphology undergoes a significant shift toward a dense, granular aggregated state, observed at a higher magnification of 20.00k X (1 μ m scale bar); this structural change is driven by the successful loading of 7.25 atomic % Cobalt. In contrast, the magnesium chloride treatment (c) results in the precipitation of large, blocky crystalline plates, captured at 5.00k X magnification (2 μ m scale bar) to reflect the increased crystal dimensions, supported by a 6.48 atomic % Magnesium content. Across all three samples, the Si/Al ratio remains remarkably stable (ranging from 1.179 to 1.262), indicating that while the surface is chemically functionalized and the original iron (4.94%) is masked by the new coatings, the underlying aluminosilicate framework of the fly ash remains structurally intact (Wang *et al.* 2024).

4. CONCLUSION

This study successfully demonstrated a simple and cost-effective impregnation-calcination route for the green synthesis of modified fly ash catalysts using cobalt chloride and magnesium chloride. Comprehensive characterization through FTIR, UV-Vis, XRD, and SEM-EDX confirmed that these metal chlorides do not merely coat the surface but actively interact with the aluminosilicate framework of the coal fly ash.

- **Electronic Band Gap Engineering (CoCl₂):** While many industrial modifiers (such as TiO₂ or ZnO) are restricted to UV-light activity due to their wide band gaps, the incorporation of CoCl₂ successfully narrowed the optical band gap of fly ash from 3.2 eV to 2.8 eV. This shift, driven by the *d-d* electronic transitions of Co²⁺ ions, effectively shifts the catalyst's response into the visible light spectrum, making it a superior

candidate for solar-driven environmental remediation compared to standard white-oxide modifiers.

- **Structural Integrity and Phase Transformation (MgCl₂):** Unlike iron-based modifiers, which often lead to leaching issues, MgCl₂ promotes the formation of stable magnesium oxychloride (MOC) “Phase 5” crystals within the ash matrix. This not only enhances the chemical stability of the composite but also provides a unique crystalline environment that supports the parent aluminosilicate structure, as evidenced by the retention of the quartz and mullite phases in XRD analysis.

Furthermore, the EDX results showing significant metal incorporation (7.25 at.% for Co and 6.48 at.% for Mg) and the achievement of nanometer-scale crystallite sizes (3.37–4.45 nm) highlight the efficiency of the synthesis method. By transforming a zero-value industrial byproduct (fly ash) into a high-surface-area, visible-light-active catalyst using earth-abundant and relatively low-toxicity chlorides, this research aligns with the principles of the circular economy. These modified materials hold significant promise as low-cost, high-performance heterogeneous catalysts for the degradation of organic pollutants and other advanced environmental applications.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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