



Calcium Ferrites: Sol-Gel Synthesis for Photocatalysis Dye Degradation

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ABSTRACT

This study describes the facile sol-gel synthesis of non-toxic calcium ferrites, which are applied in the degradation of dyes in water and align with SDG 6. We demonstrate that control of calcination temperature governs crystallographic phase formation, particularly the critical formation of the cubic spinel (C-CaFe₂O₄) and its influence on the magnetic and morphological properties. This phase, whether isolated or synergistic with orthorhombic Ca₂Fe₂O₅, enables exceptional photocatalytic degradation of methylene blue (up to 99% removal) while facilitating magnetic recovery. Our findings offer a compelling pathway for developing sustainable, economically viable, and highly efficient ferrite-based photocatalysts for robust wastewater treatment.

Keywords: calcium ferrites, water remediation, photocatalysis, dyes degradation

Introdução

Global water scarcity and inadequate wastewater treatment pose critical challenges, necessitating innovative materials for contaminant removal in line with SDG 6 (1). While traditional ferrites offer advantageous magnetic properties for easy recovery, their potential toxicity due to the inclusion of transition metals (e.g. Co, Cu, Ni) is a concern (2). This work addresses this by synthesising non-toxic calcium ferrites via a sol-gel method, comprehensively characterising their structural, morphological, and magnetic properties, and critically evaluating their photocatalytic degradation efficiency against organic dyes to develop safe, cost-effective water remediation solutions.

Experimental

Material synthesis and characterisation

The SG method involved calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O) supplemented with citric acid (CA), maintaining Ca:Fe:CA molar ratios of 1:2:2. The pH of the solution was adjusted to 7 using ammonium hydroxide (30% wt) all reactants from (Merck KGaA). After which the mixture was stirred and heated at 100 °C until a viscous gel was formed. After a dry, SG-derived gel was subjected to calcination in a muffle furnace at temperatures ranging from 20 °C to 1200 °C for 1 h, employing a heating rate of 2.5 °C min⁻¹. Crystalline phases were analysed by XRD, surface images obtained via SEM, and magnetic properties measured with a vibrating sample magnetometer (VSM).

Photocatalytic experiments

We assessed the photocatalytic degradation efficiency of ferrite suspensions (1 g L⁻¹) on methyleneblue (MB) and

methylorange (MO) (5 mg L⁻¹) under 60 W m⁻² UV-A irradiation for 2 h. Before irradiation, suspensions were stirred in the dark for 2 hours to establish adsorption equilibrium. Post-irradiation, samples were centrifuged (4500 rpm, 10 min), and dye removal was quantified via UV/Vis spectrophotometry (MB: 664 nm; MO: 464 nm). The percentage of dye removed was determined using Equation 1.

$$\text{Dye removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Results e Discussion

X-ray diffraction analysis shows brownmillerite Ca₂Fe₂O₅ (orthorhombic ferrite) as the predominant phase in SG samples temperatures above 500 °C, which progressively evolved into O - CaFe₂O₄, the phase of orthorhombic calcium ferrite (**Figure 1**). It is possible to observe brownmillerite already in calcination at 300 °C, accompanied by the formation of cubic spinel (C-CaFe₂O₄). This phase is difficult to isolate because the relatively large ionic radius of Ca²⁺ hinders its incorporation into the tetrahedral sites of the spinel structure, thereby necessitating higher temperatures or a prolonged calcination period for phase formation (3).

The magnetic properties, as determined by VSM, indicate that the saturation magnetisation (Ms) decreases with increasing temperature (**Figure 2**). Remanent magnetisation (Mr) significantly declines from ±17 to ±0.4 Am² kgFe⁻¹ as the calcination temperature rises, accompanied by a reduction in coercivity (Hc) from 3 × 10⁻² T at lower temperatures to 9 × 10⁻³ T at higher calcination temperatures.



The decrease in M_s observed with increasing temperature for $\text{CaFe}_{1:2}\text{SG}$ samples can be ascribed to thermally induced structural transitions, notably the gradual transformation of the C- CaFe_2O_4 phase into the O- CaFe_2O_4 phase. The latter is inherently less magnetic than the Fe_3O_4 -like cubic structure (4).

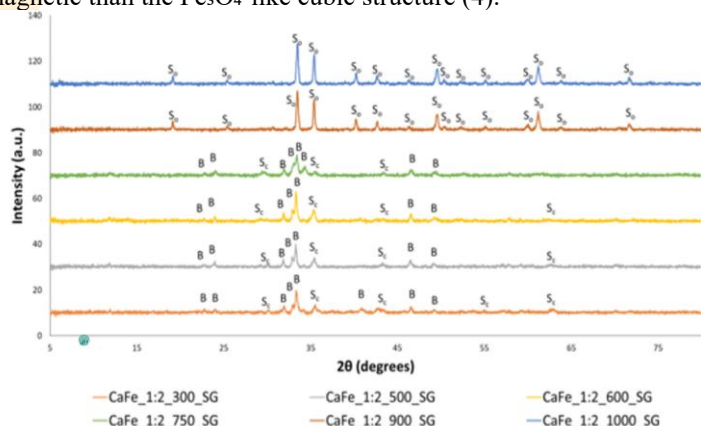


Figure 1: XRD pattern for $\text{CaFe}_{1:2}\text{SG}$ samples. B: $\text{Ca}_2\text{Fe}_2\text{O}_5$ (Brownmillerite); So: CaFe_2O_4 (Spinel-orthorhombic); Sc: CaFe_2O_4 (Spinel-cubic).

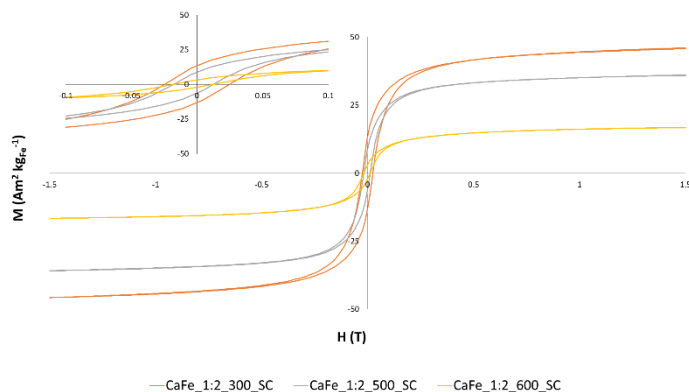


Figure 2: Hysteresis loops for CaFe_{SC} samples after calcination at different temperatures for 1h in air.

SEM shows that $\text{CaFe}_{1:2}$ samples have a rod-like shape below 600°C , but develop irregular, less porous structures above 900°C . EDX confirmed calcium and iron presence, with a measured Ca:Fe ratio of 1:2.05 for $\text{CaFe}_{1:2}\text{SC}$ samples (**Figure 3**).

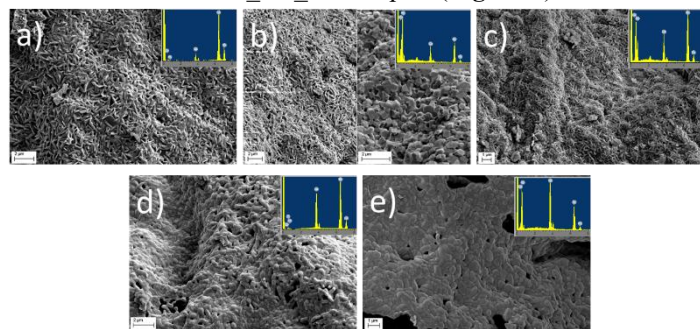


Figure 3: Morphological characterisation of $\text{CaFe}_{1:2}\text{SC}$ calcined samples at: a) 300°C , b) 500°C , c) 600°C , d) 900°C and e) 1000°C with the respective EDX maps.

The SG $\text{CaFe}_{1:2}$ samples, which contained the cubic spinel phase, demonstrated high photocatalytic activity in degrading MB, achieving degradation rates of up to 99% (**Table 1**).

At calcination temperatures above 900°C , orthorhombic ferrite became the predominant phase, and performance decreased. The coexistence of both orthorhombic $\text{Ca}_2\text{Fe}_2\text{O}_5$ and cubic CaFe_2O_4 ($\text{CaFe}_{1:2_300-750}$) may contribute to MB removal by facilitating charge separation and increasing carrier lifetime. In contrast, the photocatalytic activity against MO was relatively low, with maximum conversions reaching only 10% for the $\text{CaFe}_{1:2_500_SC}$ sample.

Table 1: Photocatalytic features of CaFe_{SC} against MB and MO at specific pH values.

Sample name	MB removal (%)	MO removal (%)	pH
$\text{CaFe}_{1:2_300_SC}$	86.6	1.5	6
$\text{CaFe}_{1:2_500_SC}$	94	9.1	6
$\text{CaFe}_{1:2_600_SC}$	86.6	1.3	7
$\text{CaFe}_{1:2_900_SC}$	28.3	-	6
$\text{CaFe}_{1:2_1000_SC}$	25.5	-	6

Conclusion

Our investigation demonstrates the successful sol-gel synthesis of expected non-toxic calcium ferrites, strategically designed to address pressing global wastewater challenges and support SDG 6. Comprehensive material characterisation revealed a strong correlation between calcination temperature, magnetic properties, crystallographic phase evolution (specifically the prevalence of cubic spinel C- CaFe_2O_4), and resultant photocatalytic efficiency. Notably, the C- CaFe_2O_4 phase proved exceptionally effective in methylene blue degradation, achieving remarkable removal rates up to 99%, underscoring its significant potential as an easily recoverable and environmentally benign material for advanced water purification.

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