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Introduction

Water scarcity and contamination are two converging global challenges that increasingly threaten environmental and public health. By 2030, nearly two-thirds of the world's population may live under water-stressed conditions (United Nations, 2016). In Chile, over 76% of the territory is affected by drought, desertification, or land degradation (CONAF, 2021).

In parallel, emerging contaminants—such as organic dyes, endocrine-disrupting pesticides, pharmaceuticals, and personal care products—are frequently detected in surface and wastewater. These pollutants persist in the environment and are not efficiently removed by conventional treatment systems, posing significant ecological and health risks.

In this context, the development of sustainable and efficient water treatment technologies is critical. This work investigates a polymer-assisted heterogeneous Fenton system designed for the removal of emerging contaminants under mild, low-cost, and scalable conditions, supporting the advancement of accessible and environmentally responsible remediation strategies.

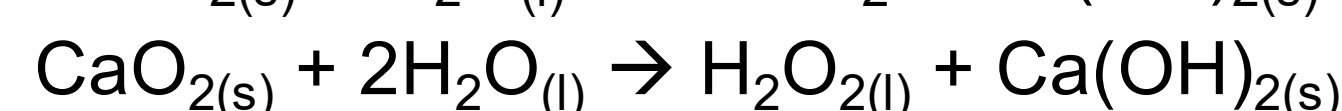
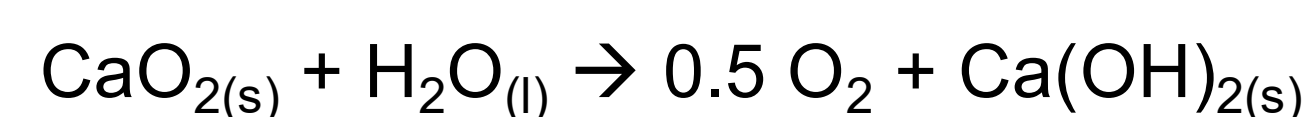


Experimental

Fenton-CaO₂ Systems:

Fenton and Fenton-like processes are widely recognized for their efficiency, low cost, and simplicity. They have been extensively applied for the degradation of various pollutants. However, their large-scale implementation is limited by the hazards and instability of H₂O₂. H₂O₂ is challenging to transport and store safely, as it gradually loses its oxidative capacity, and its handling complicates the scalability of the technology.

To overcome these limitations, this study proposes the use of solid calcium peroxide (CaO₂) as an alternative oxidant, enabling the *in situ* generation of H₂O₂ under controlled conditions:



The Fenton–CaO₂ system is highly sensitive to pH, as the hydrolysis of CaO₂ generates Ca(OH)₂, which can drastically raise the pH, especially in poorly buffered media. To ensure stable reaction conditions, this work explores the combined use of pH-regulating materials, such as commercial resins, organic acids, and tailored polymers or biopolymers, with iron-binding ligands that enhance catalytic performance. In particular, 1,2-dihydroxybenzenes (DHBs) have been shown to form iron complexes that remain reactive at pH values above 5, promoting Fenton-like activity beyond the classical acidic range. This integrated approach, combining pH buffering strategies and ligand-assisted catalysis, aims to improve the efficiency, selectivity, and scalability of Fenton–CaO₂ systems for the treatment of emerging contaminants (Fig. 1).

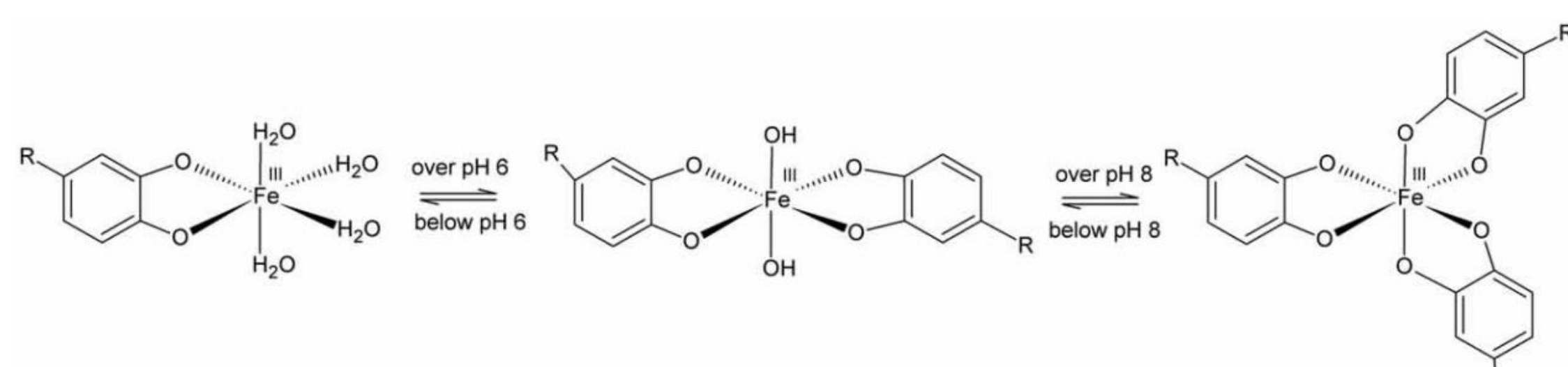


Fig. 1: Proposed mechanism for Fe–DHB complex formation.

A natural source of DHBs is the bark of *Pinus radiata*, which is highly abundant in Chile due to the country's large forestry industry (accounting for over 2% of the national GDP). According to the Chilean Forestry Institute (INFOR), *Pinus radiata* represents 56% of forest plantations, and its bark makes up about 10% of the tree's mass, resulting in an estimated 3 million m³ of bark produced annually. This bark contains high levels (12–20%) of condensed tannins, polyflavonoid compounds composed mainly of catechin or epicatechin units linked at positions 4–6 or 4–8 (see Fig. 2). These structures have an available B-ring capable of complexing metals such as iron. Recent studies have reported that this residual fraction may enhance ·OH production via the conventional Fenton reaction.

Ethylparaben was selected as a model emerging contaminant due to its environmental persistence and potential to disrupt the endocrine system. To optimize the Fenton–CaO₂ system modified with biomass-derived DHBs, a Box–Behnken design of experiments was implemented using Modde 7.0 software (Umetrics). This multivariate approach enabled the systematic evaluation of key factors and the identification of the optimal operational conditions for maximum degradation efficiency.

Under these optimized conditions, the system's performance was evaluated through multiple analytical techniques. HPLC-UV was used for the quantification of ethylparaben, while electron paramagnetic resonance (EPR) was employed to detect the generation of hydroxyl radicals (·OH). Additionally, HS-SPME-GC/MS was applied to identify the main degradation by-products. This integrated approach allowed for a comprehensive understanding of the system's reactivity and oxidative behavior under realistic and scalable conditions.

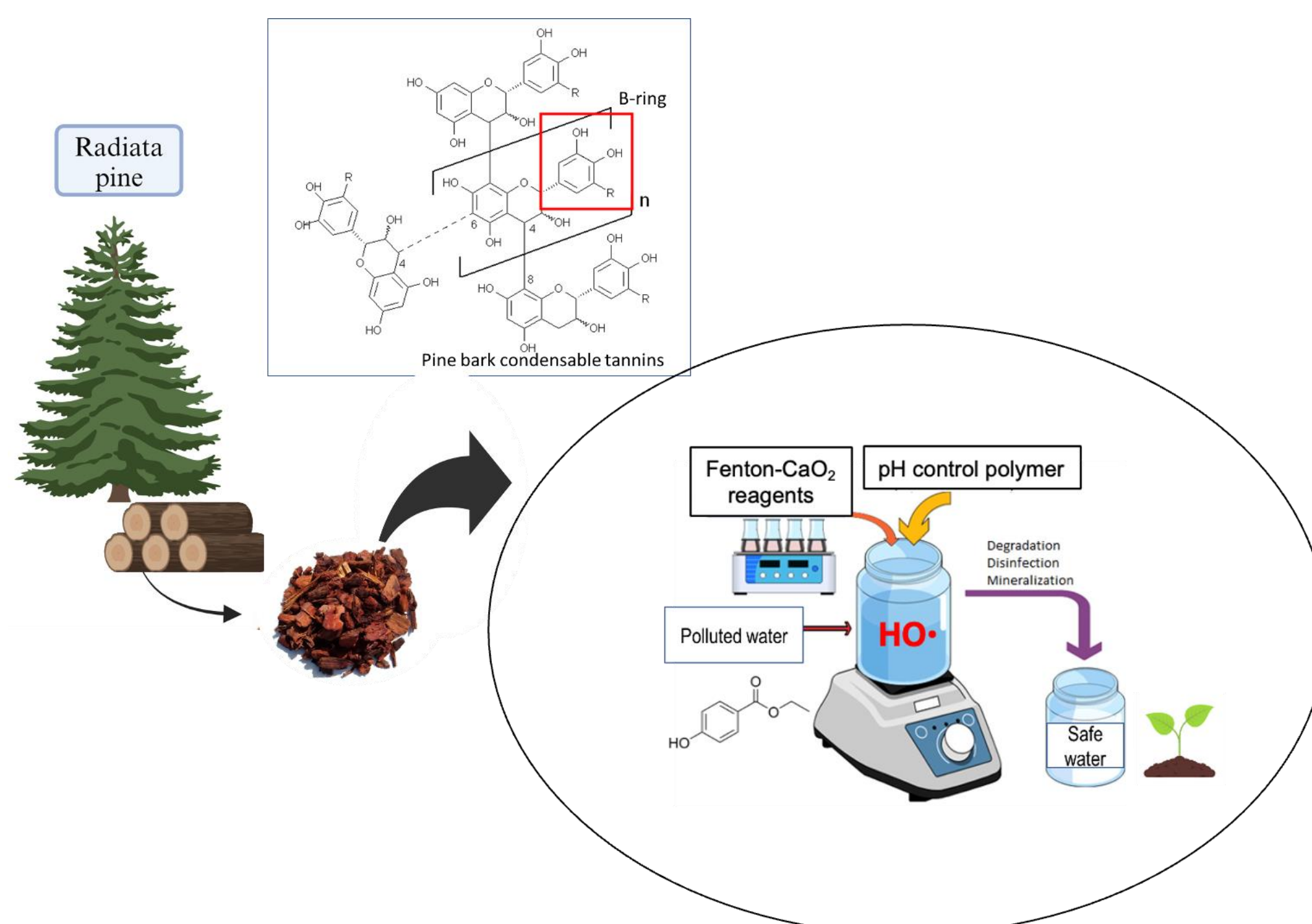


Fig. 2: Schematic representation of the experimental workflow used to evaluate ethylparaben degradation.

Results and Discussion

The following graph illustrates the effectiveness of various materials in mitigating the pH rise during CaO₂ hydrolysis. In the absence of pH control, the pH rapidly increased above 11, indicating poor buffering capacity. Commercial Resin 1 and quaternized starch exhibited strong buffering behavior, maintaining a pH below 5 throughout the reaction, which is favorable for Fenton activity. In contrast, carboxymethyl cellulose (CMC), quaternized cellulose, and Commercial Resin 2 delayed the pH rise but were unable to sustain it within the optimal acidic range over time. These results highlight the potential of quaternized starch and Commercial Resin 1 as effective pH-regulating agents for stabilizing Fenton–CaO₂ systems under near-neutral or acidic conditions.

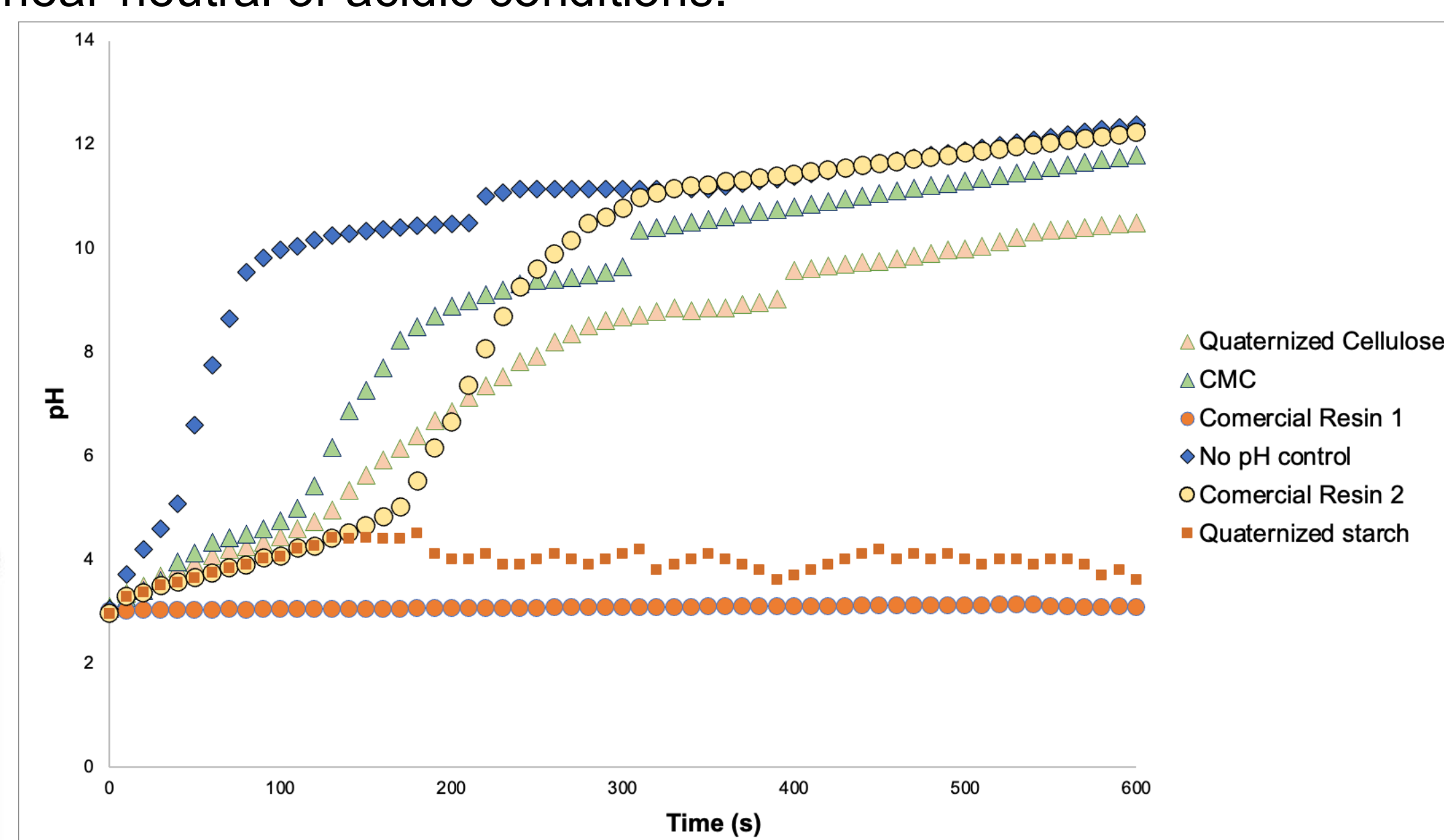


Fig. 3: Evaluation of pH-buffering performance of biopolymers and commercial resins in CaO₂ systems.

This study aimed to determine whether the Fenton–CaO₂ system, under controlled pH conditions, could effectively degrade the emerging contaminant ethylparaben. Although quaternized biopolymers showed good buffering performance, further experiments focused on a commercial ion-exchange resin due to its superior pH stabilization (Fig. 3) and simpler handling, as it requires no chemical modification or freeze-drying. The commercial resin is also reusable after proper washing. A factorial design yielded a predictive model (Eq. 1), and the corresponding response surface allowed determination of the optimal CaO₂/resin ratio of 12.5. This ratio, shown to mitigate pH rise effectively, will be applied proportionally in all Fenton–CaO₂ systems enhanced with biomass-derived condensed tannins.

$$\text{pH}_{\text{max}} = 3.544 + (-0.893 \pm 0.103) \cdot R + (0.938 \pm 0.103) \cdot \text{CaO}_2 + (-0.638 \pm 0.103) \cdot R \cdot \text{CaO}_2$$

After defining the optimal CaO₂/resin ratio for pH stabilization, an experimental design was conducted to optimize the degradation of ethylparaben. The fitted polynomial model identified key variables and interactions that influence system performance, as validated by ANOVA at a 95% confidence level. The model showed a strong correlation ($R^2 \approx 0.92$), confirming its predictive quality (Ec. 2).

$$\begin{aligned} \% \text{Deg} = & 98.043 \pm 0.784 + (2.160 \pm 0.620) \text{TAN} + (4.941 \pm 0.831) \\ & \text{CaO}_2 + (5.536 \pm 0.620) \text{Fe(III)} - (7.093 \pm 0.980) \text{TAN}^2 + (2.945 \pm 0.980) \\ & \text{Fe(II)}^2 + (4.140 \pm 0.808) \text{CaO}_2^2 - (1.628 \pm 0.679) \text{TAN} \cdot \text{Fe(III)} - \\ & (2.474 \pm 0.980) \text{TAN} \cdot \text{CaO}_2 + (5.294 \pm 0.980) \text{Fe(III)} \cdot \text{CaO}_2 \end{aligned}$$

The degradation model indicates that Fe(III), CaO₂, and tannins contribute positively in their linear form, with Fe(III) and CaO₂ being most influential. However, high tannin concentrations reduce efficiency due to possible radical scavenging or iron complexation. Positive quadratic terms for Fe(III) and CaO₂ suggest improved performance at higher levels, while negative interactions involving tannins highlight the need for balanced dosing. A strong synergistic effect was observed between Fe(III) and CaO₂. Optimal conditions were determined as 400–600 mg/L tannins, 200 μM Fe(III), and ≥2 mM CaO₂, achieving maximum ethylparaben degradation.

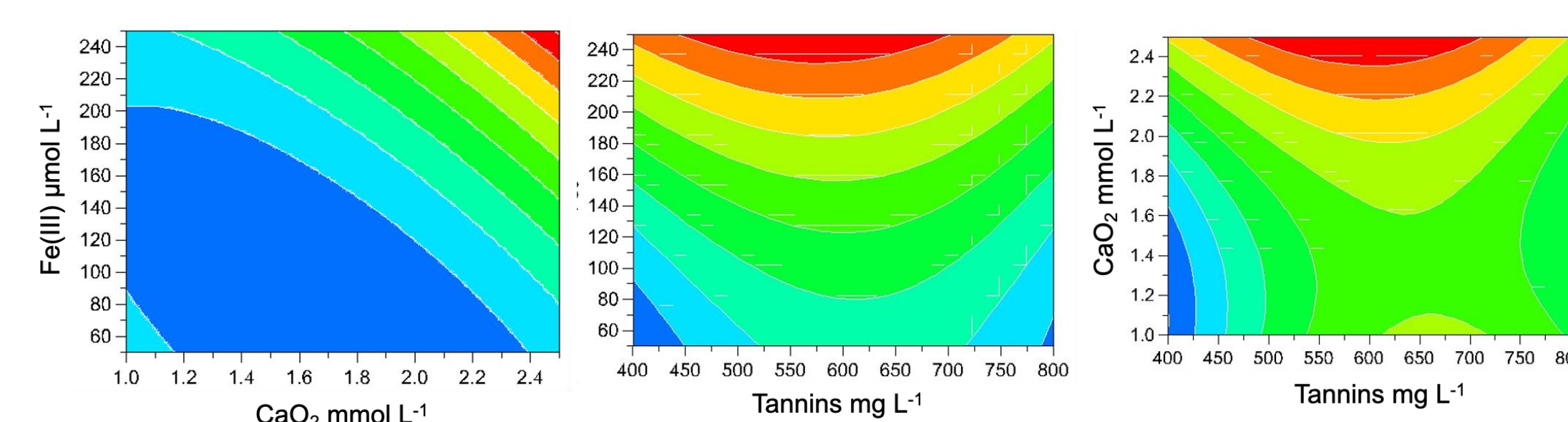


Fig. 4: RSM for different conditions in Fe–CaO₂ systems.

After, ·OH production was evaluated by EPR (Fig. 5), confirming that the systems incorporating DHB-type organic ligands under controlled pH conditions were the most efficient in generating reactive oxygen species.

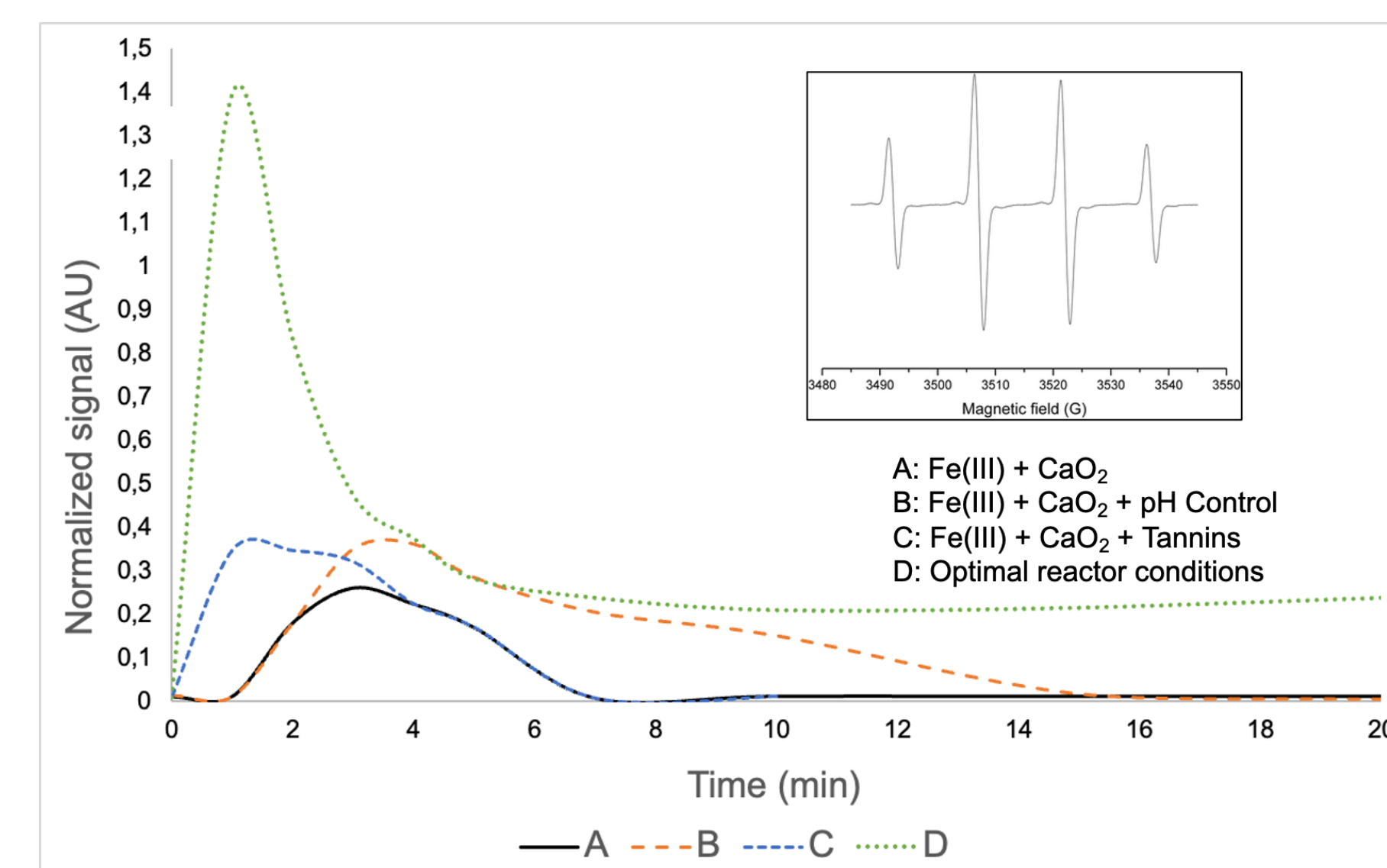


Fig. 5: ·OH production measured by spin-trapping technique in EPR for Fenton–CaO₂ systems.

Finally, three oxidation by-products were detected by HS-SPME-GC/MS at the end of the reaction: a phthalic acid derivative, phenol, and 2-methylcyclohexanol, all with very low peak areas. Their low abundance suggests limited formation or advanced degradation, supporting the high oxidative efficiency of the Fenton–CaO₂ system under optimized conditions for ethylparaben removal.

Conclusions

The optimized Fenton–CaO₂ system, enhanced by DHB-type ligands and stabilized through pH control using commercial resin 1, achieved up to 98% degradation of ethylparaben (below LOD) under mild, scalable conditions. Optimal performance was observed with 400–600 mg/L condensed tannins, 200 μM Fe(III), and ≥2 mM CaO₂, with efficient ·OH generation and strong predictive reliability ($R^2 \approx 0.92$). HS-SPME-GC/MS confirmed minimal oxidation by-products, indicating advanced degradation. Notably, the quaternized starch-based biopolymer also exhibited promising pH-regulating behavior, suggesting future potential to replace synthetic components and make the system even greener and more environmentally friendly. These results highlight the importance of integrating pH regulation with sustainable materials to enhance Fenton performance for the removal of emerging contaminants.

References

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