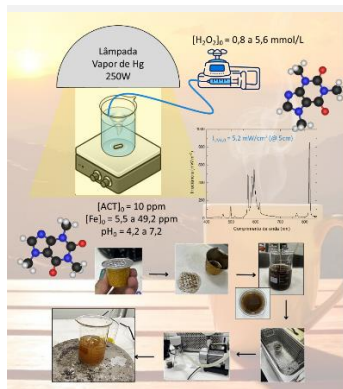




Solar Photo-Fenton Degradation of Caffeine from Coffee Capsule Washing Waters: An integrated experimental, modelling, and Techno-Economic Assessment study

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The recycling of coffee capsules are increasingly becoming a social and technical issue in Latin America. In this work, solar photo-Fenton (SPF) was evaluated for caffeine removal from synthetic and real coffee-capsule washing waters. A Doehlert design evaluated the effect of $\text{H}_2\text{O}_2/\text{COD}$ (1-7) and $\text{Fe}/\text{H}_2\text{O}_2$ (0.05-0.20) ratios. Optimal SPF conditions ($\text{H}_2\text{O}_2/\text{COD} = 7.30$, $\text{Fe}/\text{H}_2\text{O}_2 = 0.050$) resulted in an apparent removal kinetics of $4.21 \times 10^{-3} \text{ min}^{-1}$ (1.45x faster than dark Fenton). Scale-up modelling (PFR, SBR, CSTR) and techno-economic analysis (TEA) of six configurations showed SBR-SPF as optimal: CAPEX R\$ 125,417, OPEX R\$3,678/yr, GWP = 0.381 kg $\text{CO}_2\text{-eq}/\text{m}^3$. The study demonstrates technical feasibility for caffeine-rich industrial effluent treatment at regional scale.

Introduction

Single-use aluminium coffee capsules represent a rapidly growing waste stream: Brazil generates an estimated 39,060 t/yr of capsule waste, with the São Paulo metropolitan region (RMSP) alone producing 34.2 t/day [1]. Industrial recycling of capsules requires washing with water (Figure 1), generating effluents containing 20-40 mg/L caffeine, a recalcitrant micro-pollutant classified as an emerging contaminant.

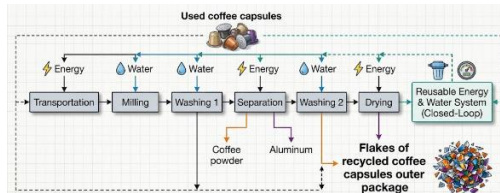


Figure 1. Coffee capsule recycling process

Caffeine has been detected in Brazilian surface waters at up to 127,000 ng/L (mean 4,823 ng/L [2]), where it disrupts aquatic endocrine systems and reproductive behaviour. Conventional biological treatment is ineffective for caffeine due to its structural stability (trimethylxanthine ring); advanced oxidation processes (AOPs) that generate hydroxyl radicals ($\cdot\text{OH}$) capable of non-selective mineralisation are required [3].

The Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) and its solar-assisted variant, solar photo-Fenton (SPF), regenerate Fe^{2+} photocatalytically under visible irradiation ($\lambda < 450 \text{ nm}$), sustaining the catalytic cycle at lower H_2O_2 doses compared with dark Fenton [4]. Despite extensive literature on Fenton treatment of pharmaceuticals, rigorous comparative studies quantifying kinetics, reactor

design, CAPEX, OPEX and carbon footprint for caffeine-rich coffee-capsule effluents are lacking.

This work addresses this gap by applying a Doehlert experimental design to optimise Fenton and SPF reagent ratios, deriving pseudo-first-order kinetic constants, modelling three reactor configurations (PFR, SBR, CSTR) for each process, and performing comparative TEA and GWP estimation for all six process-reactor combinations.

Material and Methods

Bench-scale experiments were conducted using model caffeine solutions (10 mg/L in deionized water) and a real matrix consisting of coffee capsule washing water (approx. 30 mg/L of caffeine). Photocatalytic runs were performed in 500 mL reactors maintained under a solar simulating lamp. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ served as the Fe^{2+} source, with H_2O_2 delivered via a syringe pump over a 5-minute interval. Aliquots were quenched with methanol at specific intervals to halt the reaction. Caffeine concentration was quantified via HPLC using a C18 column (4.6 x 150 mm, 5 μm) with a $\text{MeOH}:\text{H}_2\text{O}$ (30:70 v/v) mobile phase at 1.0 mL/min and 35 degrees °C. Detection was performed at 273 nm (Rt approx. 7.3 min, LOD = 0.1 mg/L, $R^2 > 0.999$).

A Doehlert matrix was employed to optimize the process across 9 experimental runs, including three center-point replicates. The variables investigated included the $\text{H}_2\text{O}_2/\text{COD}$ molar ratio (1-7) and the $\text{Fe}/\text{H}_2\text{O}_2$ molar ratio (0.05-0.20), corresponding to concentration ranges of 0.8-5.6 mmol/L for H_2O_2 and 5.5-49.2 mg/L for Fe. The target response was the percentage of caffeine removal at 60 minutes, with optimization achieved via desirability function maximization. Solar irradiation was simulated using a metal halide reflector providing a total irradiance of



approx. 500 W/m² with a UV-A irradiance (I_{UVA}) of 5.2 mW/cm² at 5 cm.

Degradation kinetics were described by a pseudo-first-order model: $\ln(C/C_0) = -k_{\text{app}} t$. The apparent rate constants (k_{app}) were determined by non-linear least squares fitting for both deionized and real matrices. For the full-scale treatment of 1.0 m³/h, three reactor configurations were modeled: (a) Plug Flow Reactor (PFR), (b) Sequencing Batch Reactor (SBR), and (c) Continuous Stirred-Tank Reactor (CSTR). Reactor volumes were sized to achieve 90% caffeine removal based on the respective k_{app} values obtained experimentally.

The Techno-Economic Assessment (TEA) calculated CAPEX based on tank costs (R\$ 3,800/m³), solar CPC collectors (R\$ 1,500/m²), and a 50% installation factor. OPEX was estimated considering reagents (H₂O₂ at R\$ 6.5/kg and FeSO₄ at R\$ 2.8/kg) and electricity (R\$ 0.82/kWh) for 8,000 h/yr of operation. The Life Cycle Assessment (LCA) focused on Global Warming Potential (GWP), utilizing emission factors of 0.15 kg CO₂-eq/kWh for the electricity grid, 1.5 kg CO₂-eq/kg for H₂O₂ manufacture, and 0.5 kg CO₂-eq/kg for FeSO₄ production.

Results and Discussion

The response surface for % caffeine removal showed a maximum in the high-H₂O₂/COD, low-Fe/H₂O₂ region for SPF, and high H₂O₂/COD, high Fe/H₂O₂ for dark Fenton. The optimal Fenton point was H₂O₂/COD = 7.30, Fe/H₂O₂ = 0.20; and for SPF: H₂O₂/COD = 7.30, Fe/H₂O₂ = 0.050, confirming UV-driven Fe²⁺ regeneration reduces Fe demand 4-fold. The comparison of kinetics in deionised water were $k_{\text{app}} = 4.21$ vs $2.89 \times 10^{-3} \text{ min}^{-1}$ (SPF 1.45x faster); in real matrix 3.04 vs $2.25 \times 10^{-3} \text{ min}^{-1}$. Overall caffeine removal in real matrix at 60 min ~13.5% (vs. >90% in deionised water) due to OH-radical scavenging by co-dissolved organics, and the time for 90% removal was, in SBR-Fenton, 27.1 h and in SBR-SPF = 17.6 h (-35%).

The PFR-SPF volume was found to be 43%

smaller than PFR-Fenton at equal conversion; CSTR configurations required the largest volumes.

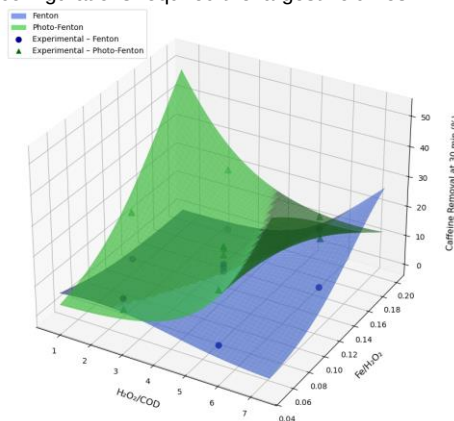


Figure 2. Response surface of Fenton and SPR for caffeine removal in 30 min

The TEA and GWP are shown in Table 1. At RMSP scale (34.2 t/day capsule waste, ~4,700 m³/day washwater), the SBR-SPF reagent cost is R\$0.78 per m³ treated.

Table 1. Economic analysis

Reator	CAPEX (R\$)	OPEX Annual (R\$)	GWP TOTAL (kg CO ₂ /m ³)
PFR Fenton	24,000	14,452	1.024
PFR foto-Fenton	79,301	6,137	0.487
SBR Fenton	42,750	3,677	0.304
SBR foto-Fenton	125,416	3,677	0.381
CSTR Fenton	129,810	14,452	1.024
CSTR foto-Fenton	262,820	6,137	0.614

Conclusions

The key outcomes of this work were (i) SPF is 1.45x faster than dark Fenton and requires 4x less iron at the optimised condition; (ii) the real capsule matrix reduces k_{app} by ~28% vs. deionised water due to OH-radical competition, requiring extended residence times or pre-treatment; (iii) among six reactor-process configurations, SBR-SPF provides the best balance: 17.6 h for 90% removal, CAPEX R\$125,417, OPEX R\$3,678/yr, GWP = 0.381 kg CO₂-eq/m³; (iv) SBR-Fenton has lower CAPEX (R\$42,750) and lower GWP (0.304 kg CO₂-eq/m³) but requires 54% more treatment time; (v) scale-up to RMSP demand is technically achievable with SBR-SPF at R\$ 0.78/m³ reagent cost. This study provides a complete engineering basis for implementing solar photo-Fenton in industrial coffee-capsule recycling facilities.

Acknowledgments

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