

Process optimization of Venturi-based hydrodynamic cavitation for industrial azo-dye removal: Sodium chloride effect on performance, kinetics, and costs

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ARTICLE INFO

Keywords:

Textile effluent
Advanced oxidation processes
Textile dyes
Treatment economics
Nanobubble-assisted cavitation

ABSTRACT

Treatment of textile wastewater is challenging because dyes, salts, and organic matter can strongly affect advanced oxidation processes (AOPs). This study evaluated azo-dye decolorization in a 14 L hydrodynamic cavitation (HC) system previously characterized for nanobubble generation, focusing on sodium chloride (NaCl) effects on performance, kinetics, oxidant demand, and operating cost. Hydrogen peroxide (H₂O₂) and sodium persulfate (PS) were tested at pH 2–7 and oxidant-to-dye ratios of 50:1–230:1. HC was first assessed for Reactive Red 120 (RR120) and Congo Red (CR) in deionized water, while NaCl effects were investigated for RR120 at 2.5 g/L because CR precipitated under acidified saline conditions. In deionized water, RR120 decolorization reached 95% with both oxidants, whereas CR reached 94% with PS and 69% with H₂O₂. PS remained effective across the pH range, while H₂O₂ was most effective at pH 2. Concentration profiles showed an initial rapid decrease followed by one or two slower intervals, potentially reflecting reduced oxidant availability, mass-transfer limitations, competition from transformation products, and changing cavitation conditions. NaCl reduced RR120 decolorization under all investigated conditions, especially at pH 5–7, slowing down the initial and intermediate kinetic stages. Under saline conditions, H₂O₂ generally outperformed PS at equivalent oxidant-to-dye ratios. Screening-level cost analysis showed that PS-based systems were mainly constrained by oxidant cost, whereas H₂O₂-based systems were more sensitive to treatment time and energy demand. Overall, NaCl affected removal efficiency, kinetics, oxidant selection, dosage requirements, and treatment economics, identifying salinity as a key design parameter for HC treatment of textile wastewater.

1. Introduction

Over the past few decades, global freshwater withdrawal has increased significantly due to rapid population growth and rising living standards [1,2]. In particular, the industrial sector is among the largest consumers of freshwater globally [1] (e.g., ca. 215,

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000 hm³/year of water is used by the EU industrial sector), with about half of this volume eventually released back into the environment [3]. However, industrial wastewater contains a wide range of contaminants, such as organic compounds, metals, and nutrients [2], leading to negative effects on the environment and the human health in the case of improper treatment or direct discharge [2–4].

Among various industrial effluents, textile wastewater is considered a major environmental hazard due to its complex composition, which includes residual dyes, metals, surfactants, salts, chlorinated substances, and other pollutants [5,6]. In detail, textile effluents are generally characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), total dissolved solids (TDS), total nitrogen (TN), slightly alkaline pH (typically ca. 7–10) and high salinity (typically ca. 2–10 g/L) [7].

Approximately 85% of the water used in textile processes is collected as wastewater [5,8], containing up to 10 – 20% of the total dyestuff used in the dyeing process, however conventional treatment methods currently employed by the textile industries are often inadequate to effectively treat such toxic and complex wastewater [7,9], thus leading to the discharge of notable amounts of hazardous substances into the environment [10–12]. In detail, the discharge of wastewaters containing high concentrations of synthetic dyes can result in aesthetic problems, reduced light penetration, disruption of aquatic respiration, and, in some cases, mutagenic effects [6].

Azo dyes are the most widely used class of textile colorants, accounting for ca. 60–70% of the approximately 700,000 tonnes of synthetic dyes used annually in textile production [13–15]. Their colour arises from the presence of one or more azo chromophore groups (–N=N–). Owing to their low cost, ease of synthesis, vivid colours, and high chemical stability, azo dyes are widely employed in industry; however, these same properties often render them recalcitrant to conventional wastewater treatment processes [16,17]. Moreover, several azo dyes and/or their transformation products have been associated with adverse effects on ecosystems and human health [13,15].

Among anionic azo dyes, Congo Red (CR) and Reactive Red 120 (RR120) are widely used in the textile industry and are frequently investigated as representative dye pollutants in wastewater-treatment studies [16,18]. In detail, CR is a diazo dye containing two azo chromophores with both acid and basic functional groups (Fig. 1), leading to its different colours in alkaline or acidic conditions (i.e., red and blue, respectively) [13,19]. It was the first direct dye to be discovered [13], and remains widely used in the textile and plastics industries, despite its well-documented environmental hazards [20–22]. RR120 is also a diazo dye (Fig. 1) [23], widely used in fiber dyeing for its short dyeing time, strong bonds with fibers, and vivid color spectrum [16,24,25]. Although not classified as toxic [26], RR120 high water solubility and stable structure make it difficult to degrade by conventional methods, leading to concerns related to long term exposure and the generation of potentially hazardous byproducts during incomplete degradation [24].

Advanced oxidation processes (AOPs), a group of water and wastewater treatment methods employing highly reactive radicals, have gained considerable attention due to their ability to mineralize otherwise recalcitrant organic pollutants in wastewater [10,27]. They include processes like photocatalysis, Fenton and Fenton-like processes, ozone oxidation, electrochemical oxidation, ultrasound, microwaves, and cavitation. [11,28–31]. However, several of these AOPs require either high amounts of chemicals, significant amount of energy to operate, or prove challenging to be implemented at the industrial scale [10,11,32].

In particular, hydrodynamic cavitation (HC) when combined with other AOPs has emerged as a promising and efficient method for the degradation of organic compounds [27,30,33–37]. HC involves the growth and collapse of bubbles, locally reaching high temperature and pressure conditions (up to 5000–10000 K and 100–1000 bar) [32,38,39]. Moreover, several works have shown good results in applying nanobubble-based HC thanks to the higher surface-to-area ratio and half-life of nanobubbles with respect to micro-bubbles [40–42]. HC is also generally characterized by low equipment and operational costs, scalability and mild reaction conditions [43,44].

In particular, most applications focus on using microbubble-based [44–46] or nanobubble-based [47–50] HC to increase the mass transfer of oxygen and oxidating gasses (e.g., chlorine and ozone) to improve the effectiveness of chemical and biological oxidation processes. Other applications include cell wall breaking, sludge pretreatment, biodiesel synthesis, nano-emulsion preparation [51].

In the case of dye-containing wastewater, numerous researchers have shown that the combination of microbubble-based HC with other AOPs is an effective treatment method. For example, Rajioriya et al. (2017a) [52] reported high degradation of Rhodamine 6G combining HC with hydrogen peroxide or ozone. G. Li et al. (2020) [53] achieved similar degradation of Rhodamine B with HC in the presence of a Fe-doped TiO₂ catalyst. H. Sun et al. (2022) [54] demonstrated the high performance of negative pressure-assisted HC (NPA-HC) for Methylene Blue removal. Dehghani et al. (2024) [55] employed a combination of HC, UV light, and sodium persulfate to degrade CR, while Malade and Deshannavar (2018) [56] achieved high degradation of RR120 by using a combination of HC and hydrogen peroxide.

On the contrary, the use of nano-bubble based HC for textile wastewater treatment remains much less investigated. In detail, few authors have reported on the use of ozone nanobubbles for the degradation of dyes, such as Direct Blue 71, Methylene Blue [57], Green

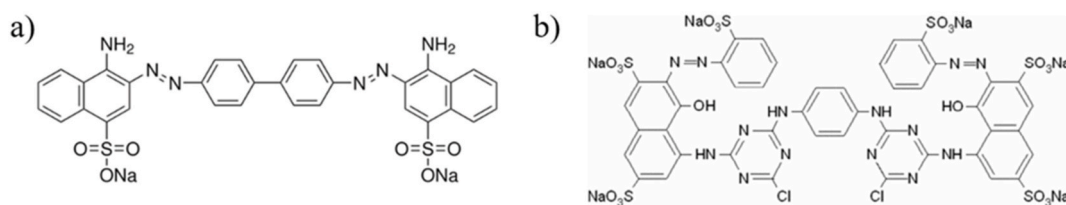


Fig. 1. Structure of Congo red (a) and reactive red 120 (b).

Rit dye [48], and Remazol Brilliant Blue R [58]. Some authors have also investigated the use of pure oxygen, as in the works by Nguyen et al. (2024) [49] and B. Wang et al. (2024) [59] on Methylene Blue and Rhodamine B, respectively.

However, there are potential risks involved in using oxidative gases such as ozone (e.g., corrosion, accidental discharge, etc.), therefore several studies have focused on investigating the use of HC induced by less reactive gasses (e.g., air or nitrogen) [59] or fluid dynamics alone [42].

Within this context, most HC studies on textile wastewater treatment have been conducted in simplified aqueous matrices and have focused primarily on endpoint decolorization under a limited set of operating conditions [10]. As a result, the factors governing HC performance in saline media remain insufficiently understood, particularly how salinity affects oxidant effectiveness and reaction kinetics. Moreover, practical design variables relevant to industrial application (e.g., oxidant type, dosage, operating pH, energy demand and overall treatment cost) have rarely been evaluated within the same experimental framework.

To address these gaps, this study used the same 14 L Venturi-based HC system characterized for nanobubble generation, described in our previous work [42] for azo-dye decolorization and process optimization under textile-wastewater-relevant conditions. CR and RR120 were first used to compare oxidant-assisted HC performance in deionized water as a function of oxidant type and pH. NaCl effects were then investigated using RR120 as the model dye, because CR precipitated in acidified saline solution, preventing safe operation of the Venturi system. The effects of oxidant type, oxidant-to-dye ratio, pH, and salinity were systematically examined, while kinetic analysis was used to identify changes in the apparent kinetic behaviour during treatment, and a screening-level operating-cost analysis was performed to compare process-selection windows at equivalent target decolorization levels.

2. Materials and methods

2.1. Materials

Congo Red (CR, dye content $\geq 35\%$, Sigma-Aldrich) and Reactive Red 120 (RR120, dye content $\geq 50\%$, Sigma-Aldrich) were used as model azo-dyes in this study. The molecular structure of CR and RR120 are reported in Fig. 1.

Sodium persulfate (PS) ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 98\%$, Sigma-Aldrich) and hydrogen peroxide (H_2O_2 , 30% w/w, Sigma-Aldrich) were used as oxidizing agents. Sodium chloride (NaCl, 99%, Carlo Erba) was used to simulate saline conditions in wastewater. Sodium sulfite (Na_2SO_3 , $\geq 98\%$, Carlo Erba) was used as a radical scavenger. Sulfuric acid (H_2SO_4 , 96% w/w, PanReac) was used for pH adjustment. All reagents were used as received without further purification.

Moreover, in order to obtain data on operating conditions more representative of a real system, we tested the effect of oxidant dosage and pH in the presence and absence of NaCl (i.e., 0 or 2.5 g/L) (HC + NaCl). It should be noted that the addition of salt to the acidified CR solution caused the immediate formation of a precipitate therefore, to avoid the risk of clogging the Venturi tube, tests in saline conditions were carried out only for RR120.

2.2. Experimental setup and procedure

2.2.1. Set-up of the HC system

The degradation of CR and RR120 was carried out at different operating conditions using a hydrodynamic cavitation setup able to treat 14 L, as described in Moftakhari Anasori Movahed et al. (2026). Briefly, this study employed the same Venturi previously characterized and optimized for nanobubble generation using a $L1 = 9.85\text{mm}$, $L2 = 72.85\text{mm}$, $\alpha = 1.96^\circ$ and 1 mm-throat geometry, whose nanobubbles were characterized by a volumetric bubble distribution in which 89.7% was below 1 μm , with a mean hydrodynamic diameter of approximately 151 nm and a zeta potential of -15.4 mV [42].

The setup consisted of a 20-liter tank connected to a centrifugal pump (1.3 kW, 6000 L/h, Sterwins) by a Venturi tube with a throat diameter of 1 mm and an immersion coil heat exchanger made of flexible PVC tubing to cool the dye solution. The Venturi outlet discharged directly into the treatment tank, 0.04 m below the water surface. The flow rate through the 1 mm throat was maintained at 80 L/h. The operating pressure of 4 bar was measured upstream of the Venturi tube before a bypass to the heat exchanger, used to regulate the system pressure. Air was not intentionally injected during treatment. The valve upstream of the pump was used only to

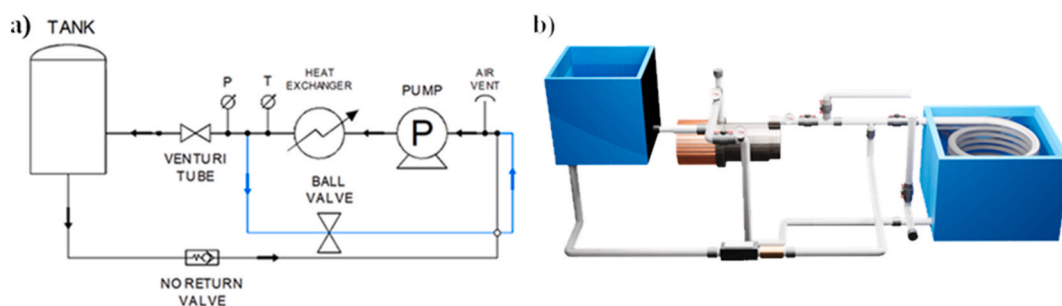


Fig. 2. Hydrodynamic cavitation setup schematic (plan view, from Moftakhari Anasori Movahed et al. (2026) (a) and the 3D representation of the system (b). The blue line in panel a) indicates the bypass flow that goes through the heat exchanger while the black line represents the HC loop.

release trapped air during system filling and was not used as an operating gas inlet. For this reason, nanobubble generation was attributed to pressure reduction, local vaporization, dissolved-gas nucleation, and hydrodynamic shear produced by passage through the Venturi. A schematic diagram of the setup is shown in Fig. 2.

In order to characterize the hydraulic operating conditions and facilitate comparison with published cavitation studies, the nominal cavitation number (σ) was calculated using Eq. (1).

$$\sigma = \frac{p_{2,abs} - p_v(T)}{\frac{1}{2}\rho u_t^2} \quad \text{Eq. 1}$$

Where, $p_{2,abs}$ is the absolute downstream receiving pressure, p_v is the water vapor pressure, ρ is the liquid density, and u_t is the mean throat velocity. This dimensionless parameter relates the difference between the downstream absolute pressure and the liquid vapor pressure to the dynamic pressure associated with the throat velocity. The flow rate of 80 L/h through the 1 mm throat corresponds to a mean velocity of 28.3 m/s. Since the outlet discharged into an atmospheric tank at a submergence depth of 0.04 m, the receiving pressure was estimated from atmospheric pressure plus the hydrostatic contribution, giving approximately 101.7 kPa absolute. Using standard atmospheric pressure and temperature-dependent pure-water properties (i.e., 21–35 °C), the effects of temperature changes during the tests were estimated as a nominal cavitation number decrease from 0.248 at 21 °C to 0.242 at 35 °C. These values are comparable in magnitude to those associated with experimentally observed Venturi cavitation. For example, Soyama et al. (2021) [60] documented vortex-cavity collapse and rebound using high-speed imaging at upstream and downstream absolute pressures of 0.6 and 0.1 MPa, respectively, corresponding to a cavitation number of approximately 0.20 according to the definition used in that study. This comparison provides context for the present operating conditions, however cavitation inception depends on device geometry, and similar cavitation numbers do not necessarily imply identical flow regimes [61]. Accordingly, the values reported here represent nominal hydraulic estimates based on the receiving pressure rather than an independently measured downstream pressure.

Prior to each experiment, the hydrodynamic cavitation (HC) system was rinsed with deionized water. Dye solutions (14 L) were prepared in deionized water at initial concentrations of 10 mg/L for CR and 15 mg/L for RR120. The pH was adjusted at the start of each test using 0.1 M sulfuric acid to the target values (i.e., 2, 5, or 7).

For each run, the dye solution was fed into the HC system, and an initial sample ($t = 0$ min) was collected from the cavitation tank. A concentrated solution of PS (100 g/L) or H_2O_2 (30% w/w) was then added to achieve the target oxidant-to-dye ratio (i.e., 50:1, 100:1, 150:1, or 230:1). Cavitation was initiated by pressurizing the system up to 4 bar, and 15 mL samples were collected after 5, 10, 15, 20, 40, 60, 80, 100, and 120 min. Treatment duration was also expressed as the nominal number of passes through the Venturi, calculated as $N = Qt/V$, where Q is the flow rate through the Venturi, t is treatment time, and V is the total circulating liquid volume [62]. With $Q = 80$ L/h and $V = 14$ L, one nominal pass corresponded to 10.5 min. Sampling times of 5, 10, 15, 20, 40, 60, 80, 100, and 120 min therefore corresponded to approximately 0.48, 0.95, 1.43, 1.90, 3.81, 5.71, 7.62, 9.52, and 11.43 passes, respectively. To quench residual oxidants and prevent further degradation after sampling, 0.5 mL of sodium sulfite solution (45 g/L in ultra-pure water (UPW)) was added to each aliquot, corresponding to a Na_2SO_3 :oxidant molar ratio of 22 for PS and of 195 for H_2O_2 [63–65]. After each experiment, the system was flushed with deionized water.

2.2.2. Pumped-loop control tests

Valve-replacement loop controls were conducted to assess decolorization during pumped circulation at the treatment pressure drop (Table S1). In detail, the Venturi was removed and replaced with a regulating valve adjusted to reproduce the pressure drop used during HC treatment (i.e., 4 bar). The corresponding dye concentration, oxidant-to-dye ratio, initial pH, NaCl concentration, and treatment duration were reproduced.

2.3. Analytical methods

Dye concentration was determined by measuring the absorbance at the characteristic wavelengths of the dyes (580 nm for CR and 520 nm for RR120) using a UV-Vis spectrophotometer (PerkinElmer Lambda2S). Calibration curves ($R^2 > 0.9998$) were prepared for each dye (i.e., between 0.5 and 8 mg/L and 0.5 to 17.5 mg/L for CR and RR120 respectively) to ensure accuracy. Decolorization (%) was calculated using Eq. (2):

$$\text{Decolorization}_{(t)} (\%) = \left(1 - \frac{C_t}{C_0}\right) \cdot 100 \quad \text{Eq. 2}$$

where C_0 and C_t are the initial and residual dye concentrations, respectively.

It should be noted that since performance was assessed by dye absorbance loss at the selected wavelength, the reported endpoint refers to decolorization rather than complete mineralization. pH was measured following the IRSA-APAT-CNR 2060 standard [66]. Furthermore, the present study was designed to quantify decolorization rather than mineralization. The commercial CR and RR120 products had stated dye contents of only $\geq 35\%$ and $\geq 50\%$, respectively, while the composition of the remaining formulation material was not specified. Consequently, bulk analysis such as TOC, COD, or BOD measurements would include contributions from both the target dyes and unidentified formulation components and could not provide a dye-specific measure of degradation. The reported endpoint is therefore limited to UV-Vis-based decolorization, and no claim of mineralization is made.

Moreover, complete UV-Vis spectra obtained for all experiments are provided in Fig. S1–S6. These spectra were used to examine the evolution of the characteristic dye absorption bands under each experimental condition, while dye concentration and

decolorization were quantified using the absorbance at the corresponding analytical wavelength.

2.4. Kinetic analysis

In this study, a kinetic regime was defined as a time interval characterized by an approximately constant slope in the concentration or logarithmically transformed concentration profile, representing an apparent stage of the observed decolorization kinetics.

For kinetic regimes containing at least three sampling points, pseudo-first-order kinetics were evaluated by linear regression of $\ln(C)$ against time, according to Eq. (3).

$$\ln\left(\frac{C_\alpha}{C_\beta}\right) = k(t_\beta - t_\alpha) \quad \text{Eq. 3}$$

where C_α and C_β are the dye concentrations at the beginning (t_α) and end (t_β) of the interval and k is the apparent pseudo-first-order rate constant (1/min). The coefficient of determination, R^2 , was reported for each pseudo-first-order regression.

For intervals containing only two consecutive measurements (e.g., 0–5 min), for which a regression and associated R^2 cannot be meaningfully determined, the average concentration loss normalized to the concentration at the beginning of the interval was calculated as:

$$s = \frac{C_\alpha - C_\beta}{C_\alpha (t_\beta - t_\alpha)} \quad \text{Eq. 4}$$

where C_α and C_β are the dye concentrations at the beginning (t_α) and end (t_β) of the interval, respectively, and (s) is the average normalized concentration-loss rate (1/min).

When the interval between two consecutive measurements encompassed an apparent transition in kinetic behaviour, the interval between them was treated as a transition window rather than being assigned to either adjacent kinetic regime. No intermediate concentration values or transition times were extrapolated, since doing so would introduce model-derived information not directly supported by the experimental sampling. Consequently, the apparent gaps between some fitted intervals do not represent missing experimental data, but rather transition windows within which the kinetic behaviour changed and for which a separate kinetic fit was not considered justified.

2.5. Screening-level operating-cost evaluation

To complement the experimental assessment of decolorization performance and reaction kinetics, a preliminary operating-cost analysis was carried out considering the contributions associated with (i) electricity consumption, (ii) acid addition, and (iii) oxidant type and dosage. Capital costs, labour, and downstream treatment requirements were not included, as a robust assessment of these items would require information beyond the scope of the present work. Accordingly, the analysis is intended as a comparative assessment of the investigated operating conditions rather than a complete techno-economic evaluation.

For each test, reagent costs were estimated using industrial prices for 96 wt% sulfuric acid (0.15 €/kg) [67], 30 wt% H_2O_2 (0.43 €/kg) [68], and sodium persulfate (PS, 0.989 €/kg) [69]. The local electricity price of 0.1902 €/kWh [70] was used for the energy-cost calculations. The centrifugal pump installed in the laboratory system was substantially oversized relative to the hydraulic duty required by the HC loop, with excess flow returned through the bypass.

Although the pump used showed an electrical draw of ca. 1.2 kW, measured using a wattmeter, this value was considered representative of the specific laboratory apparatus rather than of the power requirement of an appropriately sized HC pumping system and was therefore not used as the basis of the screening-level operating-cost calculation.

Instead, a screening-level design case estimated for an appropriately sized centrifugal pump was used in the economic analysis. In particular, we estimated energy consumption from the hydraulic duty of the HC loop according to Eq. (5), where P_h (W) is the hydraulic power, Δp is the pressure increase (Pa), and Q is the volumetric flow rate (m^3/s) [71].

$$P_h = \Delta p Q \quad \text{Eq. 5}$$

In detail, the required pump flow was taken as the 80 L/h Venturi flow plus a conservative 20 L/h allowance for the pressure-control/recirculation branch, giving a total design flow of 100 L/h. Since the bypass branches from the pressurized pump-discharge line and returns to the low-pressure tank, the bypassed flow must also be raised to the approximately 4 bar discharge pressure before this pressure is dissipated in the recirculation circuit. The 20 L/h allowance, corresponding to 20% of the total design flow, was included to represent this additional hydraulic duty and should not be interpreted as a universal minimum-flow requirement for centrifugal pumps. At an operating pressure of 4 bar, the corresponding hydraulic power requirement was 11.1 W. Assuming an overall pumping efficiency of 70% for an appropriately sized pump, the estimated input power P (W) was calculated from Eq. (6), yielding a design-basis of 15.9 W [71].

$$P = P_h / \eta \quad \text{Eq. 6}$$

Consequently, a cost of 0.00302 €/h was applied to estimate energy cost at different treatment times.

For the endpoint cost analysis, the energy cost associated with the final decolorization was calculated by considering the last

sampling time at which the increase in decolorization was at least 5 percentage points relative to the previous sampling point. This criterion was adopted to avoid attributing additional energy consumption to operating periods associated with only negligible further decolorization. Because the investigated configurations exhibited markedly different decolorization rates, their economic performance was compared at equivalent target decolorization levels rather than at a fixed treatment time. Target decolorizations from 30 to 95%, in 5-percentage-point increments where experimentally attainable, were considered. The time required to reach each target was estimated by piecewise-linear interpolation between consecutive experimental measurements. This approach was preferred over kinetic-model extrapolation because several configurations exhibited distinct reaction regimes during treatment. No extrapolation beyond the experimentally attained decolorization range was performed.

For each target, the electrical cost was calculated by multiplying the time needed to reach the target by the estimated hourly electrical cost. All costs were initially calculated for the 14 L batch and subsequently normalized to the treated-water volume and expressed as €/m³. For each target decolorization, the configuration associated with the lowest total operating cost was then identified.

For comparison with HC systems reported in the literature, the cavitation yield Y was additionally calculated using the estimated design-basis electrical input according to Eq. (7).

$$Y = \frac{(C_0 - C_t)V}{P\Delta t} \quad \text{Eq. 7}$$

where Y is expressed as mg of dye removed per J of electrical energy, C_0 is the starting concentration, C_t is the concentration at the last sampling time at which the increase in decolorization was at least 5 percentage points relative to the previous sampling point, Δt was the associated test duration, V is the treated volume (14 L), and P is the electrical power attributed to cavitation (ca. 15.9 W).

3. Results and discussion

3.1. Overall degradation after 120 min

3.1.1. HC in the absence of NaCl

3.1.1.1. HC at pH 2. The initial experiments were conducted without the addition of NaCl at pH = 2, as previous works have demonstrated that HC is most effective under acidic conditions (pH = 2-3) [51,72,73]. In these studies, pH values ranging from 2 to 10 were evaluated, with the best degradation efficiencies generally observed at the lower end of the spectrum. In detail, effect of pH has been associated with changes in aqueous-phase radical chemistry and dye behavior, rather than changes in water vapor pressure. In PS systems, pH influences the equilibria between sulfate- and hydroxyl-mediated reaction pathways [74]. pH-dependent changes in the dominant reactive species have also been demonstrated specifically in HC-activated persulfate systems [75]. Protonation of the dyes may additionally influence their reactivity and spectroscopic response, particularly for CR [76,77].

Control experiments without cavitation (Table S1) showed negligible decolorization under all tested conditions (i.e., <3%), supporting cavitation-assisted oxidant activation as a contributing mechanism, consistent with previous studies of HC-assisted oxidant activation [37,75].

For each dye and experimental condition, including oxidant type and dosage, pH, and NaCl presence or absence, the first cavitation test was performed in triplicate to assess experimental variability. Since the variability was below 5% in all cases, error bars are not

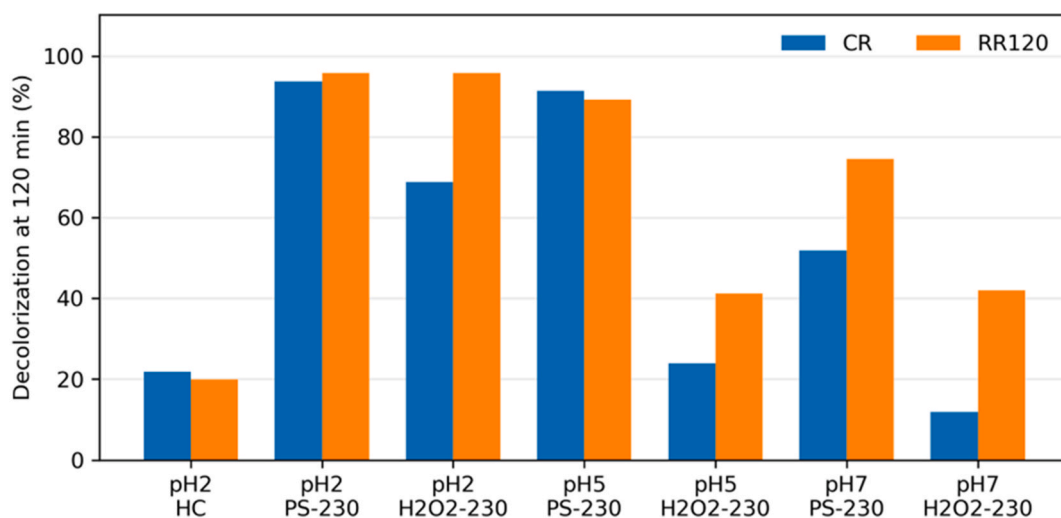


Fig. 3. Decolorization of RR120 and CR under different pH and oxidant conditions after 2 h of treatment ($C_{RR120} = 15$ mg/L, $C_{CR} = 10$ mg/L, $V = 14$ L, $P_{in} = 4$ bar, $M_{oxidant:dye} = 230:1$, $t = 2$ h).

reported in the corresponding tables and figures.

As shown in Fig. 3, when HC was used in acidic conditions ($\text{pH} = 2$), ca. 20% decolorization was reached for both dyes. The limited degradation of RR120 and CR in the absence of additional oxidants could also be linked to the presence of several polar functional groups (e.g., -OH, -COOH, -SOOH), leading these molecules to preferably remain in the liquid phase rather than in the gas phase when cavitation bubbles are formed, thus escaping from the bubbles' collapse [78].

Other studies have reported on using conventional HC systems (i.e., microbubble-based) in the absence of additional oxidants to remove the target compounds. For example, Dehghani et al. (2024) reported ca. 14% decolorization of CR in 60 min using a 4 L Venturi HC/UV system (746 W centrifugal pump) operating at 4 bar and an initial dye concentration of 20 mg/L [55]. Similarly, Saharan et al. (2011) achieved ca. 60% decolorization of RR120 in 180 min using a 6 L HC Venturi system (1.1 kW positive displacement pump) at 5 bar of pressure and $\text{pH} = 2$ with an initial dye concentration of 50 mg/L [12].

Although direct comparison is limited by differences in reactor volume, operating conditions, and reaction duration, these studies were conducted within a comparable pressure range of 4–5 bar and employed similar process configurations. Under comparable pressure conditions and without added oxidants, the present system achieved decolorization within the range reported for previous HC studies, supporting its application to oxidant-assisted azo-dye treatment.

Several literature studies have shown that both bulk nanobubbles persisting in the circulating liquid and transient cavitation cavities undergoing dynamic growth and collapse within the Venturi could contribute to radical generation. Furthermore, since the liquid repeatedly passed through the throat, persistent nanoscale gas domains could be re-exposed to pressure reduction and act as nuclei for subsequent cavitation events [79,80]. However, distinguishing the respective roles of persistent bulk nanobubbles and transient cavitation cavities would require combined bubble-population measurements (e.g., nanoparticle-tracking analysis (NTA)), high-speed visualization of cavity dynamics, and radical-dosimetry experiments under controlled cavitation-nuclei concentrations. As these mechanistic measurements were outside the scope of the present study, the observed enhancement cannot be attributed to a specific bubble-mediated mechanism.

Although degradation pathways were not explicitly investigated in the present study, several studies in literature provide insight into the radical-driven mechanisms responsible for azo dye degradation under cavitation conditions. Kim and co-workers (2024) [81] employed LC-MS to examine the degradation of CR in a hydrodynamic cavitation system dominated by hydroxyl radicals, reporting a sequential cleavage of the azo bonds leading to the formation of aromatic amines. Similarly, Zhang et al. (2007) [82] demonstrated that, in the case of RR120, hydroxyl radicals generated by cavitation not only cleave azo bonds but also attack the aromatic rings, forming hydroxylated intermediates and inducing hydrogen abstraction reactions that promote further ring-opening. In detail, the aromatic structures of RR120 can be oxidatively fragmented into smaller compounds such as catechols, phenols, and quinones, which may subsequently undergo further oxidation to short-chain carboxylic acids [83,84]. Furthermore, aromatic rings bearing -OH or -O- substituents have been shown to undergo one-electron oxidation, forming radical cations that further facilitate molecular breakdown [85].

3.1.1.2. Effects of oxidant addition on HC at pH 2. The results reported in Fig. 3 show that the addition of both H_2O_2 and PS brought a marked increase in the degradation of CR and RR120. In detail, RR120 decolorization increased markedly in the presence of either H_2O_2 (HC + H_2O_2) or PS (HC + PS), reaching approximately 95% in both cases. In contrast, CR decolorization was substantially higher with PS than with H_2O_2 , achieving about 94% and 69%, respectively. In fact, PS has been shown to better degrade organic contaminants than H_2O_2 in several water treatment processes [55,86] due to i) a slightly higher oxidation potential than hydroxyl radicals (i.e., ca. 3.1 vs. 2.8 V, respectively) [87]; ii) higher selectivity during reaction via electron transfer with organic compounds that contain unsaturated bonds or aromatic π electrons since hydroxyl radicals are non-selective radicals and may also react with other functional groups by hydrogen abstraction or electrophilic addition [88], iii) longer half-life than hydroxyl radicals (ca. 35 μs vs 20 ns, respectively), ensuring better mass transfer and higher probability to interact with the target compounds [89].

Other authors have also reported on the efficacy of oxidant-assisted HC for CR and RR120 degradation. For example, Dehghani et al. (2024) [55] reported a marked increase (i.e., from ca. 12 to 63%) when using PS for CR removal in an HC system employing a Venturi tube (i.e., $P = 4$ bar, $V = 4$ L, centrifugal 746 W pump, 20 mg/L initial concentration of CR). The effect of PS was lower than the one found in the present study (i.e., from 22 to 94%), however this could be attributed to several factors, such as the lower oxidant:target chemical ratio used with respect to our experiment (i.e., 10.5:1 vs. 230:1) and to the different scale of the cavitation system (i.e., 4 L vs. 14 L). Furthermore, Askarniya et al. (2020) [20] evaluated the effect of H_2O_2 on CR degradation in HC system (i.e., $P = 6$ bar, $\text{pH} = 3$, centrifugal 4.1 kW pump, 20 mg/L initial CR concentration) using an orifice plate. Despite employing a substantially higher oxidant:dye ratio than in the present study (530:1 versus 230:1), they reported a lower CR degradation after 60 min (35% versus 69%).

The higher decolorization observed in the present study may reflect the combined influence of reactor geometry, operating pH, scale, oxidant dosage, and the previously characterized nanobubble-generating Venturi configuration. However, because the two studies employed different reactors and operating conditions, the separate contribution of nanobubbles or oxidant-activation efficiency cannot be determined from this comparison alone.

The use of HC coupled with H_2O_2 for RR120 degradation was also investigated by Saharan et al. (2011) [12] (i.e., $P = 6$ bar, $V = 6$ L, $\text{pH} = 2$, 1.1 kW pump, 50 mg/L initial RR120 concentration). They achieved a decolorization comparable to that obtained in the present study (ca. 95%), while using a lower oxidant:dye ratio (90:1 versus 230:1).

3.1.1.3. Effects of oxidant addition on HC at pH 5 and 7. While several studies have reported that HC alone performs best under acidic conditions (pH ca. 2–3), both H_2O_2 and PS can remain effective at mildly acidic to neutral pH (ca. 5–7) [90,91]. For this reason, the

performance of the HC system was also evaluated with H_2O_2 and PS at pH = 5 and pH = 7, while maintaining a constant oxidant-to-dye ratio of 230:1.

Compared with the tests conducted at pH = 2, the results shown in Fig. 3 indicate a pronounced decline in the performance of H_2O_2 for both dyes at higher pH. For RR120, decolorization decreased to approximately 40% at both pH = 5 and pH = 7, while CR showed even lower removal, with decolorization of about 25% at pH = 5 and 15% at pH = 7. In contrast, PS maintained high decolorization efficiencies, achieving approximately 90% at pH 5 and ca. 75% decolorization at pH = 7. Similar results have also been reported by Askarniya et al. (2020) [20] for the degradation of CR in the presence of H_2O_2 (i.e., ca 40% of decolorization at P = 6 bar, pH = 6.5, 4.1 kW pump, 20 mg/L initial CR concentration, and 1000:1 oxidant:dye molar ratio).

The reduced effectiveness of H_2O_2 at higher pH is consistent with a shift in radical chemistry and oxidant speciation that limits hydroxyl-radical-driven oxidation under less acidic conditions [92]. By contrast, the limited pH dependence observed for PS is in line with the broader pH tolerance typically reported for systems based on oxidation carried out by sulfate radicals [93].

These trends, together with control experiments, are consistent with cavitation-assisted oxidant activation. However, the activation pathway and reactive-species contributions were not directly determined in this work.

3.1.2. HC in the presence of salt

3.1.2.1. Effects of oxidant addition and pH on HC. While several HC systems have shown good performance for dye degradation in simplified matrices (e.g., ultrapure water, deionized water, or tap water), real wastewater can contain substantial salt concentrations (e.g., 2.75–70 g/L) [94], which may affect oxidation processes [95].

Fig. 4 shows that adding 2.5 g/L NaCl decreased RR120 decolorization under all tested conditions. In the saline matrix, oxidant-assisted HC achieved up to approximately 85% decolorization, whereas HC without added oxidants achieved only approximately 6%.

This decrease may be partly attributed to scavenging of hydroxyl (OH) and sulfate ($SO_4^{\cdot-}$) radicals by chloride ions (Cl^-), as shown in Eqs. (8)–(12). In detail, the resulting chlorine radicals can react with chloride ions to form dichloride radical anions ($Cl_2^{\cdot-}$, $E^\circ = 2.126$ V), which may be less effective for RR120 degradation than hydroxyl and sulfate radicals [96]. Chloride-mediated radical reactions should, however, be distinguished from broader physicochemical effects of salinity, such as its effects on nanobubbles formation and characteristics [97,98].



In detail, NaCl addition may also have affected the physical characteristics of the nanobubble population and the availability of gas nuclei for subsequent cavitation events. Increasing ionic strength can screen the negative surface charge of bulk nanobubbles, shift their zeta potential toward zero, and reduce electrostatic repulsion, while strongly acidic conditions may also decrease nanobubble stability [99,100]. Changes in nanobubble stability could therefore contribute to the lower decolorization observed after NaCl addition by modifying the population of gas nuclei returning to the Venturi.

Since previous tests (Fig. 3) showed only a limited decrease in performance for both RR120 and CR when using HC + PS across

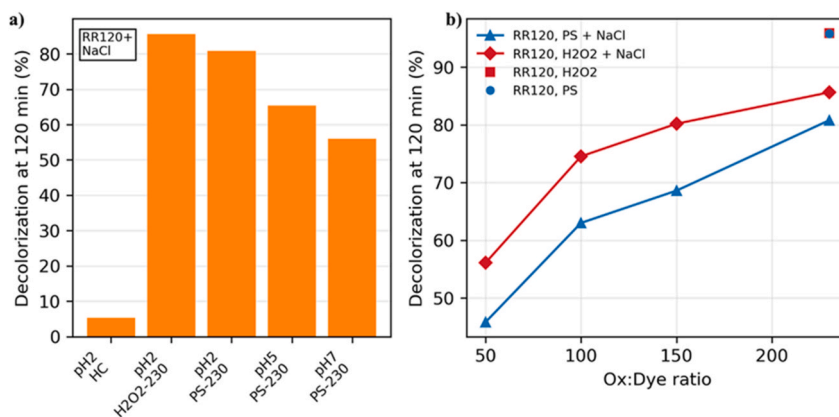


Fig. 4. Decolorization of RR120 in the presence of salt after 2 h of treatment (a); Decolorization of RR120 at different oxidant dosages in the presence of salt after 2 h of treatment (b); ($C_{RR120} = 15$ mg/L, $V = 14$ L, $P_{in} = 4$ bar, pH = 2, $C_{NaCl} = 2.5$ g/L, $t = 2$ h).

different pH values, we investigated whether acid addition could be reduced or eliminated entirely for the treatment of highly saline solutions without compromising performance. In detail, Fig. 4 shows that the effects of salinity are more pronounced under less acidic conditions, with decolorization decreasing by approximately 19% and 31% at pH = 5 and pH = 7, respectively. This trend may be attributed to the lower availability of reactive radicals compared with strongly acidic conditions, which makes scavenging reactions increasingly significant.

3.1.2.2. Effects of oxidant dosage on HC at pH 2. The addition of oxidants markedly improved decolorization performance (Fig. 3). However, because a large oxidant excess was applied (oxidant:dye ratio of 230:1), it is essential to assess whether comparable results can be achieved at lower oxidant dosages. Preliminary tests performed at pH = 2 using HC + H₂O₂ and HC + PS at an oxidant:dye ratio of 100:1 showed limited loss of performance after 2 h of treatment, achieving approximately 90% decolorization for both CR and RR120. Therefore, further experiments were conducted to optimize oxidant dosage in the presence of salt by testing oxidant:dye ratios of 50:1, 100:1, and 150:1.

Consistent with the results obtained at an oxidant:dye ratio of 230:1 (Fig. 4a), salinity effects were more pronounced for PS than for H₂O₂ (Fig. 4b) across all tested ratios. At the same oxidant:dye ratio, H₂O₂ achieved decolorization values approximately 5–20% higher than PS. Specifically, H₂O₂ maintained decolorization >80% down to a ratio of 150:1, whereas PS reached comparable performance only at the highest dosage (i.e., 230:1). In addition, both oxidants exhibited limited RR120 decolorization at a 50:1 ratio (i.e., ca. 56 and 45% for H₂O₂ and PS, respectively). This behaviour is consistent with differences in chloride scavenging chemistry for systems dominated by hydroxyl versus sulfate radicals. Chloride reacts rapidly with hydroxyl radicals to form ClOH•, but this step is reversible, allowing partial regeneration of hydroxyl radicals and producing reactive chlorine species (Cl•/Cl₂•) depending on pH and chlorine concentration. In contrast, chloride reacts rapidly with sulfate radicals to form sulfate ions and Cl•, and the reverse reaction is slow. Chlorine radicals are then rapidly converted to other reactive chlorine species (e.g., Cl₂•/ClOH•), shifting the radical distribution away from SO₄• and often lowering effective oxidation rates for dye molecules [101–103]. In fact, several studies indicate that PS-based AOPs are often more tolerant to pH variations, with a broader operational pH window than many systems dominated by hydroxyl radicals. However, this advantage does not necessarily extend to chloride-rich matrices, where chloride scavenging can substantially alter radical speciation and reduce process efficiency [90].

Several works have investigated the influence of operating conditions on dye decolorization by conventional HC [104]. For example, Innocenzi et al. (2022) [33] investigated the effects of salinity on a Venturi-based HC system for the degradation of Methyl Orange in the presence of H₂O₂ (oxidant:target ratio of 25:1, P = 5 bar, pH = 2, V = 1 L, 375 W pump, 5 mg/L initial dye concentration, 1.5–5 g/L NaCl), showing degradations ranging between ca. 53 and 66%.

3.2. Decolorization kinetics

Kinetic analysis is useful for characterizing changes in reaction behaviour and identifying distinct apparent kinetic stages in a degradation process enabling a more effective assessment of different optimization strategies [105]. In detail, the concentration profiles were evaluated using the procedure described in section 2.4. Each identified regime refers to a time interval characterized by an approximately constant slope in the concentration or logarithmically transformed concentration profile and is intended to support interpretation of changes in reaction behaviour but should not be considered to independently establish reaction mechanisms.

It should also be noted that the experiments were not run at constant temperature, as solution temperature could not be maintained constant during treatment. The temperature increased from approximately 21 to 35 °C, mainly during the first 40 min, and subsequently remained close to 35 °C. Over this temperature range, the saturation vapor pressure of water increases from approximately 2.49 to 5.63 kPa, based on established vapor-pressure data [106]. Increased vapor can modify both the pressure driving bubble collapse and the cushioning effect of vapor within the cavity, thereby changing collapse intensity [107]. Non-condensable gases within the cavities may also damp the final stage of bubble collapse [108]. Consequently, the cavitation conditions may not have remained constant throughout each run, even though the temperature profiles were similar across experiments. The reported kinetic constants should therefore be considered apparent values obtained under non-isothermal conditions.

3.2.1. HC in the absence of NaCl

The results (Table 1 and Fig. 5) show that, for HC alone (pH = 2), two distinct phases are observed for both dyes. The first phase lasts approximately 20 min, with kinetic rate constants (k) of ca. 0.0061 and ca. 0.0052 1/min for CR and RR120, respectively. After this period, the reaction slows by about a factor of 5 (k of ca. 0.001 1/min). This decrease in rate may be attributed to competition from degradation intermediates for the reactive radicals generated by cavitation [109], as well as to mass-transfer limitations associated with the lower dye concentration [110–112].

Decolorization kinetics were also investigated in deionized water in the presence of both oxidants (oxidant:dye ratio of 230:1) at pH = 2, while the use of PS was also investigated at pH = 5 and pH = 7. The results (Table 1 and Fig. 5) showed three successive kinetic intervals.

At pH = 2, the initial rapid interval lasted approximately 5 min for both dyes with either PS or H₂O₂. In detail, for CR, the initial rates were 0.1061 and 0.0534 1/min with PS and H₂O₂, respectively, whereas the corresponding rates for RR120 were 0.1138 and 0.1368 1/min. This rapid initial loss is consistent with cavitation-assisted activation of the added oxidants, although the decolorization measurements alone do not quantify oxidant activation or identify the individual reactive species involved.

Once decolorization reached approximately 30–60%, both dyes entered a slower kinetic regime. At pH = 2, this second interval

Table 1

Kinetic intervals and rate descriptors obtained for CR and RR120 decolorization under the investigated conditions. F denotes a pseudo-first-order regression based on at least three measured concentrations, for which k and R^2 are reported. L denotes an average normalized concentration-loss slope calculated between two consecutive measurements, for which s is reported without R^2 . Both k and s are expressed in (1/min).

Testing Condition	Interval 1				Interval 2				Interval 3			
	Time interval (min)	Kinetic model	Rate parameters (1/min)	R^2	Time interval (min)	Kinetic model	Rate parameters (1/min)	R^2	Time interval (min)	Kinetic model	Rate parameters (1/min)	R^2
RR120 pH2 HC	0-20	F	0.0052	0.98	20-120	F	0.0013	0.93	–	–	–	–
RR120 pH2 HC + NaCl	0-120	F	0.0005	0.96	–	–	–	–	–	–	–	–
RR120 pH2 H ₂ O ₂ -230	0-5	L	0.1368	–	5-20	F	0.1328	0.97	20-120	F	0.0012	0.96
RR120 pH2 PS-230	0-5	L	0.1138	–	5-20	F	0.1109	0.99	20-120	F	0.0014	0.98
RR120 pH5 H ₂ O ₂ -230	0-5	L	0.0377	–	5-60	F	0.0042	0.97	80-120	F	0.0010	0.98
RR120 pH5 PS-230	0-5	L	0.0865	–	5-60	F	0.015	0.99	80-120	F	0.0064	0.98
RR120 pH7 H ₂ O ₂ -230	0-5	L	0.0329	–	5-120	F	0.0034	0.99	–	–	–	–
RR120 pH7 PS-230	0-15	F	0.0410	0.99	15-120	F	0.0085	0.99	–	–	–	–
RR120 pH2 PS-230 + NaCl	0-5	L	0.0535	–	5-40	F	0.0196	0.95	40-120	F	0.0011	0.93
RR120 pH5 PS-230 + NaCl	0-20	F	0.0208	0.99	20-120	F	0.0071	0.99	–	–	–	–
RR120 pH7 PS-230 + NaCl	0-20	F	0.0085	0.98	20-120	F	0.0053	0.98	–	–	–	–
RR120 pH2 H ₂ O ₂ -50 + NaCl	0-5	L	0.0528	–	5-40	F	0.012	0.99	40-120	F	0.0004	0.99
RR120 pH2 H ₂ O ₂ -100 + NaCl	0-5	L	0.0545	–	5-40	F	0.012	0.99	40-120	F	0.0004	0.99
RR120 pH2 H ₂ O ₂ -150 + NaCl	0-5	L	0.0557	–	5-40	F	0.0254	0.99	40-120	F	0.0008	0.93
RR120 pH2 H ₂ O ₂ -230 + NaCl	0-5	L	0.0554	–	5-40	F	0.0273	0.99	40-120	F	0.0012	0.98
RR120 pH2 PS-50 + NaCl	0-5	L	0.0557	–	5-40	F	0.006	0.99	40-120	F	0.0002	0.95
RR120 pH2 PS-100 + NaCl	0-5	L	0.0570	–	5-40	F	0.0115	0.99	40-120	F	0.0004	0.93
RR120 pH2 PS-150 + NaCl	0-5	L	0.0528	–	5-40	F	0.0151	0.98	40-120	F	0.0007	0.82
CR pH2 HC	0-20	F	0.0061	0.98	20-120	F	0.0011	0.98	–	–	–	–
CR pH2 PS-230	0-5	L	0.1061	–	5-20	F	0.0141	0.96	40-120	F	0.0135	0.98
CR pH2 H ₂ O ₂ -230	0-5	L	0.0534	–	5-40	F	0.0118	0.98	40-120	F	0.0120	0.96
CR pH5 PS-230	0-20	F	0.0532	0.99	20-100	F	0.019	0.96	100-120	L	0.0016	–
CR pH5 H ₂ O ₂ -230	0-5	L	0.0183	–	5-120	F	0.0015	0.99	–	–	–	–
CR pH7 PS-230	0-20	F	0.0130	0.97	20-120	F	0.0044	0.98	–	–	–	–
CR pH7 H ₂ O ₂ -230	0-5	L	0.0095	–	10-120	F	0.0006	0.99	–	–	–	–

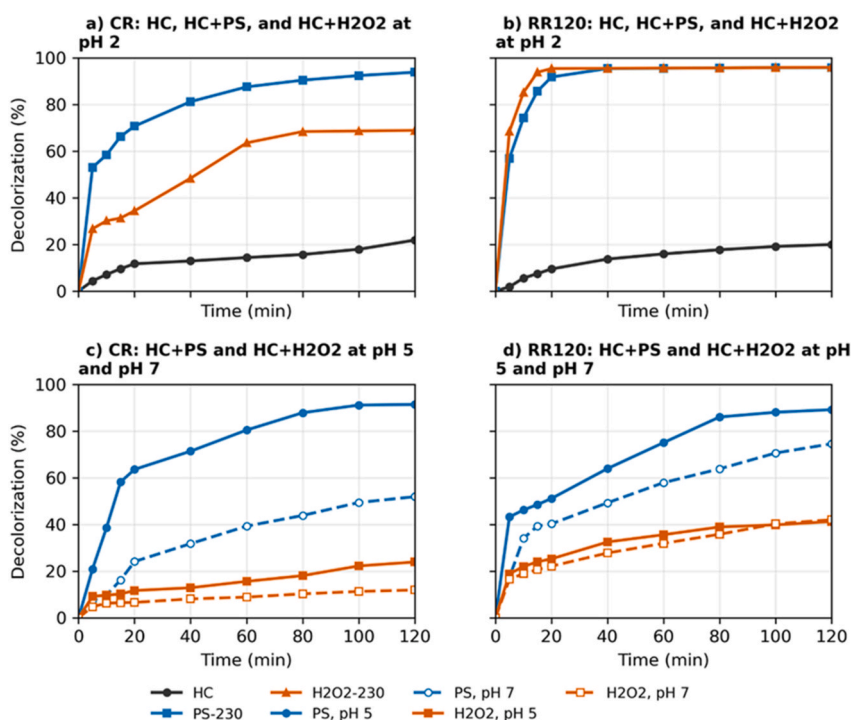


Fig. 5. Decolorization of CR and RR120 under different experimental conditions over the whole treatment: Decolorization of CR in the presence and absence of oxidants at pH = 2 (a); Decolorization of RR120 in the presence and absence of oxidants at pH = 2 (b); Decolorization of CR in the presence of PS and H₂O₂, at pH = 5 and pH = 7 (c); and Decolorization of RR120 in the presence of PS and H₂O₂, at pH = 5 and pH = 7 (d); ($C_{RR120} = 15$ mg/L, $C_{CR} = 10$ mg/L, $V = 14$ L, $P_{in} = 4$ bar, $M_{oxidant:dye} = 230:1$).

remained clearly faster than HC alone, but the apparent rate constants were lower than during the initial stage, indicating a progressive reduction in the overall decolorization rate (Table 1 and Fig. 5). A further kinetic transition was observed at longer reaction times. For RR120, the final apparent rate constants decreased to values close to those measured for HC alone, whereas CR retained a comparatively higher removal rate during the corresponding final interval. This late-stage slowdown, particularly evident for RR120, may reflect decreasing oxidant availability, competition from transformation products, mass-transfer limitations, and changes in cavitation conditions associated with the temperature increase [113,114]. Because these factors were not monitored independently, their relative contributions could not be resolved.

The final decrease in decolorization rate may therefore be associated with progressive or near-complete oxidant consumption, with the kinetics of RR120 ultimately approaching those observed for HC alone (k of ca. 0.001 1/min).

The same three-phase kinetics was observed for PS with both dyes at pH = 5, whereas for H₂O₂ this behaviour was observed only for RR120 at both pH = 5 and pH = 7. Overall, reaction rates decreased by approximately 1–2 orders of magnitude compared with those at pH = 2 (Table 1 and Fig. 5).

In contrast, PS-assisted decolorization at pH = 7 exhibited only two kinetic phases for both dyes. The initial stage lasted ca. 15–20 min, with k of ca. 0.01 and 0.04 1/min for CR and RR120, respectively. Thereafter, the reaction proceeded at a lower rate (k of ca. 0.006 1/min) until the end of the test which may reflect the accumulation of degradation intermediates [95]. Because PS activation, and thus sulfate-radical formation, is relatively slow at pH = 7 [75], these results are also consistent with the possibility that the initially added PS was not fully consumed over the duration of the experiment. A similar two-step behaviour was also observed for CR decolorization in the presence of H₂O₂ at pH = 5 and pH = 7. This may be attributed to the lower stability and reduced oxidative efficiency of H₂O₂ under near-neutral conditions [115].

3.2.2. HC in the presence of NaCl

In the absence of added oxidants, the addition of 2.5 g/L NaCl decreased the apparent pseudo-first-order rate constant for RR120 decolorization (pH = 2) from 0.0052 to 0.0005 1/min, corresponding to an approximately tenfold reduction (Table 1). The concentration profile in the NaCl-containing matrix was adequately described by a single fitted interval over 0–120 min ($R^2 = 0.96$), therefore no specific kinetic interval could be distinguished.

When oxidants were added for the degradation of RR120 in the presence of NaCl, multiple kinetic regimes could be observed. Also in this case, an initial 0–5 min concentration-loss interval was followed by two progressively slower fitted pseudo-first-order intervals. In detail, the concentration-loss rates in the presence of NaCl were approximately 0.0535 and 0.0554 1/min for PS and H₂O₂, respectively, compared with 0.1138 and 0.1368 1/min under the corresponding NaCl-free conditions. In addition, while the apparent

rate constants during the intermediate fitted interval were approximately 5-fold lower, the final fitted interval proceeded at rates comparable to those obtained without NaCl (ca. 0.001 1/min).

At pH 5 and 7, the PS-assisted experiments conducted with NaCl were each described by two fitted kinetic intervals. The results showed that the effect of NaCl varied with pH and treatment interval. At pH 7, the apparent rate constant decreased from 0.0410 to 0.0085 1/min during the initial fitted interval (i.e., 0 to 15 min without NaCl and 0 to 20 min with NaCl) and from 0.0085 to 0.0053 1/min during the subsequent interval (ca. 15–120 min without NaCl and 20–120 min with NaCl). At pH = 5, this decrease was slightly less evident, with about a 4-fold (i.e., from 0.0865 to 0.0208 1/min) decrease during the initial interval (ca. 0–5 min without NaCl and 0–20 min with NaCl) and a 2-fold (i.e., from 0.0150 to 0.0071 1/min) decrease during the second interval (ca. 5–60 min without NaCl and 20–120 min with NaCl). The later transition from the first to the second fitted regime observed with NaCl could be ascribed to several factors, including the slower accumulation of competing degradation products due to the slower decolorization. However, because these byproducts were not measured, their contribution to the observed kinetics could not be determined directly.

The effects of oxidant dosage under saline conditions on reaction kinetics were investigated for both PS and H₂O₂ (Table 1 and Fig. 6). The influence was more pronounced for PS, with a ca. 70% decrease in the second step rate when the oxidant-to-dye ratio was reduced from 230:1 to 50:1, whereas for H₂O₂ the decrease was ca. 55%. In the final stage of decolorization, when the added oxidant was largely consumed, the effect of dosage was less significant, with rate constants approaching ca. 0.001 1/min.

3.3. Screening-level operating-cost evaluation

The results of the screening-level operating-cost evaluation are shown in Figs. 7 and 8.

In detail, the endpoint cost breakdown revealed two main process-selection patterns (Fig. 7). In PS-based systems, oxidant cost generally represented the dominant contribution to the total operating cost, whereas the contribution of H₂SO₄ remained minor. By contrast, H₂O₂-based systems were more sensitive to treatment duration and, consequently, to the energy contribution. Accordingly, reducing persulfate consumption would be the main route for lowering the operating cost of PS-based treatments, whereas shortening the required treatment time would be particularly relevant for H₂O₂-based systems.

The comparison at equivalent target decolorization levels further clarified these differences (Fig. 8). For CR, the minimum-cost pathway was divided into two parts, depending on final decolorization target. Up to 65% decolorization, HC + H₂O₂ at pH = 2 was able to provide effective degradation with the lowest treatment cost (i.e., 0.241 €/m³ at 30% to 0.444 €/m³ at 65% decolorization). However, above the 65% threshold, only HC + PS at pH = 2 guaranteed the expected performance, even if at notably higher cost, reaching approximately 1.10 €/m³ at 90% decolorization.

For RR120 in the absence of NaCl, HC + H₂O₂ at pH = 2 defined the minimum-cost pathway over the complete investigated range of 30–95% decolorization (Fig. 8b). The treatment cost increased only slightly, from approximately 0.167 €/m³ at 30% to 0.227 €/m³ at 95% decolorization due to increased treatment time. Since both H₂O₂ and PS achieved similarly high final decolorization at pH = 2, the lower cost of H₂O₂ made such system the most suitable.

The presence of NaCl caused notable changes in the economic profile of each treatment option. In detail, while for RR120 the minimum-cost pathway remained entirely H₂O₂-based, the highest decolorization targets required higher dosages and longer treatment times, creating almost a 5-fold price increase from 30 to 85% decolorization (i.e., from 0.102 €/m³ at 30% to 0.443 €/m³ at 85%) (Fig. 8c). The 50:1H₂O₂:dye ratio provided the lowest cost at 30–35% decolorization, followed by 100:1 at 40–65%, 150:1 at 70–75%, and 230:1 at 80–85%. These results indicate that progressively higher oxidant dosages become economically justified only as higher decolorization targets are imposed.

For an additional energy-normalized comparison of the investigated conditions, the decolorization-based cavitation yield was calculated (Eq. (7)) as the mass of dye decolorized per unit of estimated energy input. The treatment time used for each condition corresponded to the last sampling point at which decolorization increased by at least 5 percentage points relative to the preceding measurement. When this criterion was not met, the 120 min endpoint was retained. This approach accounts for conditions in which

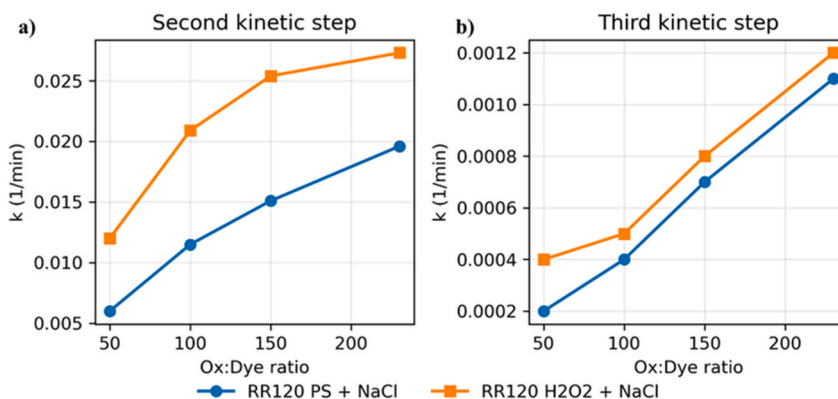


Fig. 6. Influence of Oxidant:Dye ratio on RR120 decolorization rate under saline conditions during the second (a) and third reaction steps (b). Note that the kinetic constant (k , 1/min) refer to a pseudo-first order model.

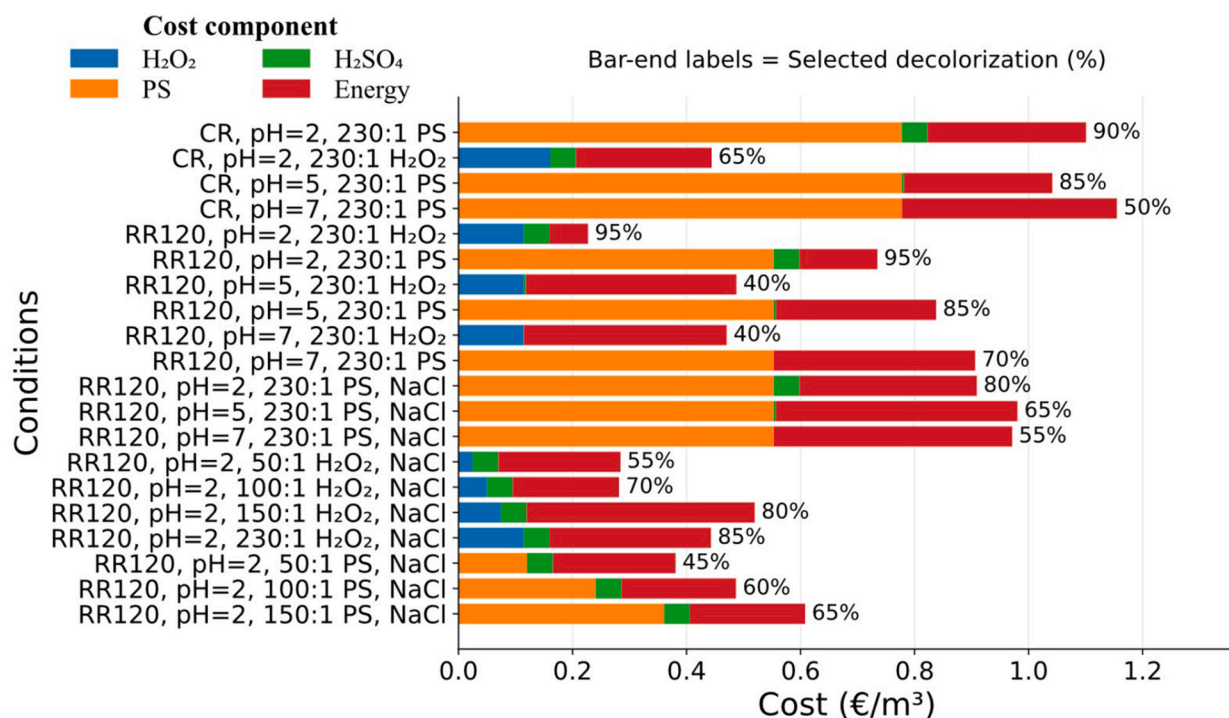


Fig. 7. Batch operating cost breakdown at the experimental endpoint for HC-assisted decolorization of CR and RR120 under different oxidant, pH and salinity conditions. Bar-end labels indicate the final decolorization (%).

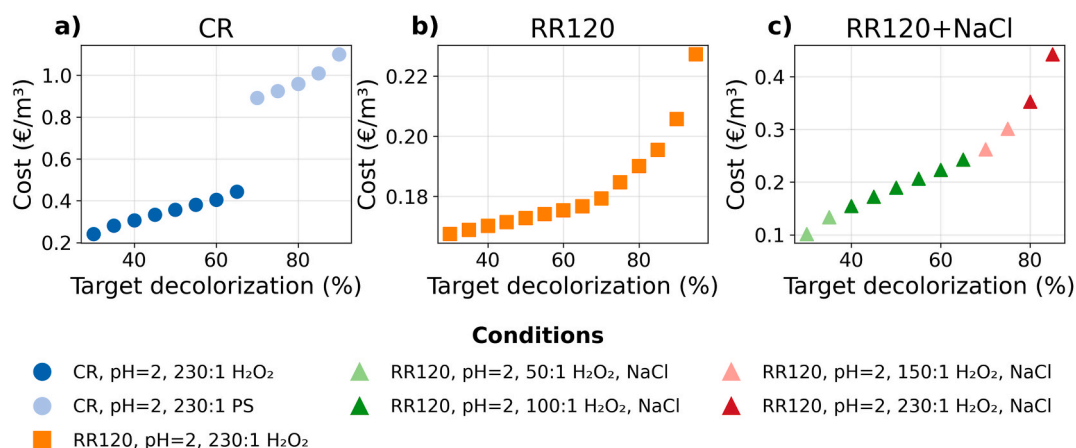


Fig. 8. Minimum treatment cost versus target decolorization for (a) CR, (b) RR120 and (c) RR120+NaCl, showing the cost-optimal HC-based configuration in each target-decolorization range.

most decolorization occurred during the early stages of treatment and avoids assigning additional energy consumption to periods with only limited further removal. Cavitation yields for all experimental conditions are reported in Table S2.

At pH = 2 and an oxidant-to-dye ratio of 230:1, CR treated with PS showed a cavitation yield of approximately 2.14×10^{-3} mg/J, compared with 1.55×10^{-3} mg/J for H₂O₂, consistent with the higher decolorization achieved with PS over the selected 60 min treatment period. For RR120 without NaCl, the highest yields were obtained under acidic conditions with H₂O₂ and PS, reaching approximately 1.38×10^{-2} and 1.01×10^{-2} mg/J, respectively. These comparatively high values resulted from the rapid initial decolorization, which gave selected treatment times of only 15 min for H₂O₂ and 20 min for PS.

These values are consistent in magnitude with cavitation yields reported for other HC-assisted dye treatments, although direct quantitative comparison is limited by differences in pollutant concentration, reactor design, treatment time, and power basis. For example, Jadhav and Gogate (2025) [116] reported cavitation yields of 8.5×10^{-4} mg/J for HC alone during Brilliant Blue degradation and 1.99×10^{-3} and 2.15×10^{-3} mg/J when HC was combined with H₂O₂ and potassium persulfate, respectively. The CR

yields obtained in the present study are therefore of the same order of magnitude, whereas the higher yields observed for RR120 without NaCl primarily reflect the rapid decolorization achieved within the first 15–20 min. More generally, previous energetic analyses of HC-based AOPs by Mukherjee et al. (2020) have shown that cavitation yield can vary by several orders of magnitude among systems and can increase substantially when process intensification reduces the treatment time required to reach a given removal target [117]. Accordingly, cavitation yield is most useful as a comparative energy-normalized indicator when differences in power accounting, reactor configuration, pollutant loading, and treatment endpoint are considered.

The presence of 2.5 g/L NaCl markedly reduced the RR120 yields to approximately 3.08×10^{-3} mg/J for H_2O_2 and 2.75×10^{-3} mg/J for PS, with both conditions requiring 60 min to reach their selected endpoints. This result shows that the effect of NaCl extended beyond the decrease in decolorization percentage and also reduced the rate at which useful decolorization was obtained per unit of estimated energy input. A negative interaction between NaCl and oxidant-assisted HC has also been reported by Innocenzi et al. (2022) for Methyl Orange [33]. In that study, NaCl concentrations of 1.5–5 g/L were investigated, and the combined presence of NaCl and H_2O_2 adversely affected decolorization compared with the corresponding individual treatments. However, NaCl alone did not produce the same response in their system, indicating that the influence of chloride is dependent on pollutant chemistry, oxidant pathway, and operating conditions rather than representing a uniform salinity effect. Overall, the present energy-normalized results support the kinetic observations and show that NaCl can reduce both treatment performance and the rate at which that performance is achieved, thereby lowering the apparent cavitation yield.

4. Conclusions

This study demonstrated that the Venturi-based HC system can effectively support azo-dye decolorization when combined with H_2O_2 or PS, whereas HC alone provided substantially lower removal. In deionized water, both oxidants achieved high RR120 decolorization at pH 2, while PS was more effective for CR and retained greater effectiveness at higher pH.

The experiments with RR120 identified NaCl as an important process variable. Addition of 2.5 g/L NaCl reduced decolorization under all investigated conditions, with stronger effects at mildly acidic and neutral pH. Under saline conditions, H_2O_2 also outperformed PS at equivalent oxidant-to-dye ratios. These effects are consistent with chloride-mediated changes in radical chemistry and may additionally involve physicochemical effects of ionic strength on nanobubbles and cavitation, although their relative contributions could not be resolved.

Kinetic analysis confirmed that NaCl affected the progression of decolorization as well as the final removal. Without added oxidants, NaCl reduced the apparent RR120 decolorization rate by approximately one order of magnitude, while oxidant-assisted treatments showed reduced initial and intermediate rates compared with the corresponding NaCl-free conditions.

The screening-level economic analysis further showed that process selection depends on dye, target decolorization, and matrix composition. H_2O_2 provided the minimum-cost pathway for RR120 both with and without NaCl, although progressively higher dosages and longer treatment times were required under saline conditions as the target decolorization increased. For CR, H_2O_2 was more economical at low-to-intermediate removal, whereas PS was required to reach the highest decolorization targets.

Overall, salt-free experiments may overestimate the performance and operational flexibility of oxidant-assisted HC for chloride-containing textile wastewaters. Matrix composition, particularly NaCl concentration, should therefore be explicitly considered when optimizing oxidant type, dosage, treatment time, and operating cost. Future studies should investigate different salt concentrations and compositions, directly characterize oxidant and reactive-species dynamics, and evaluate mineralization, transformation products, toxicity, and process performance in real textile wastewater.

CRedit authorship contribution statement

Saman Moftakhari Anasori Movahed: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Giorgos Ioannou:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Loris Calgario:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Ioannis Katsoyiannis:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis. **Antonio Marcomini:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Consent to participate

Not applicable.

Consent to publish

Not applicable.

Ethics approval

Not applicable.

Funding

This work was performed with the financial support of Ca' Foscari University of Venice.

One author (L.C) was funded by the “Interconnected Nord-Est Innovation Ecosystem (iNEST)” project and received funding from the European Union Next-GenerationEU - National Recovery and Resilience Plan (NRRP) – MISSION 4 COMPONENT 2, INVESTMENT N. ECS00000043 – CUP N. H43C22000540006. This work took place within the framework of the DoE 2023-2027 (MUR, AIS.DIP. ECCELLENZA2023_27.FF project). This work reflects only the authors' view and neither CINEA, the European Union nor the European Commission can be considered responsible for them or responsible for any use that may be made of the information it contains.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wri.2026.100404>.

Data availability

Data will be made available on request.

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