



Decolorization of Reactive Red 120 in a micro-reactor by linking chemical effects with cavitation dynamics through data-driven analysis

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ABSTRACT

Textile wastewater containing azo dyes is difficult to treat due to their poor biodegradability, and although hydrodynamic cavitation has shown potential for their removal, the effect of microfluidic systems remains to be investigated. In this study, a Venturi-type cavitation micro-reactor was evaluated for the decolorization of Reactive Red 120 by systematically investigating the effects of initial dye concentration, solution's pH, H₂O₂ addition, inlet pressure, and sample volume. Cavitation dynamics were characterized by visualization and pressure measurements, •OH generation was assessed by salicylic acid dosimetry, and most important process parameters were identified by statistical analysis and machine learning. Decolorization increased with the number of cavitation passes under all conditions. Acidic conditions (pH = 2) resulted in the highest observed removal. The addition of 1700 µM H₂O₂ into 250 mL samples further improved decolorization and resulted in removal of 6.2 ± 1.2 mg after 35 cavitation passes. Pressure difference at 700 kPa showed maximum decolorization (10.2 ± 2.5 mg in 250 mL), whereas •OH generation increased up to 900 kPa (2.53 ± 0.4 µg/mL). Sample volume had the strongest effect where dye removal increased from 1.7 mg at 125 mL to 55.3 mg at 1000 mL after 35 cavitation passes at 100 mg/L. Statistical analysis confirmed that initial dye concentration, cavitation passes, pH, and H₂O₂ affected decolorization. Machine learning analysis further showed that in this study dye removal could be predicted from operating conditions with $R^2 = 0.84$, with sample volume and initial dye concentration identified as the most important variables.

1. Introduction

Besides consuming large amounts of water, the textile industry wastewater (WW) discharges represent a major source of environmental pollution as they contain large amounts of synthetic dyes, up to 20% of which are lost during processing [1–3]. One of the most worrying negative impacts of this coloured WW is related to the reduced penetration of sunlight into water bodies, which has a negative impact on aquatic life and ecosystem stability due to impaired photosynthesis and lower dissolved oxygen levels [1,3,4]. Another major environmental problem associated with textile WW is the high prevalence of azo dyes, a class of synthetic dyes known for their structural diversity, low cost, high stability, and broad color range [1,5]. These compounds are usually large, complex molecules with a molecular weight often exceeding 600 g/mol, containing one or more azo groups (-N=N-) linking aromatic

rings. This chemical structure contributes to their resistance to aerobic biodegradation [6]. Numerous review studies have emphasized their toxicity [1,7,8], which is primarily due to the formation of aromatic amines after cleavage of the central azo bond [1,8]. For this reason, many efforts have been directed towards effective decolourisation of textile WW in recent years [2,4,8]. The conventional solutions such as biological oxidation, adsorption, coagulation/flocculation and membrane separation all have limitations including incomplete degradation, long treatment times, inefficiency, sludge production, high treatment costs, membrane fouling and most importantly secondary pollution [3,9–11]. As a result, attention has shifted to advanced oxidation processes (AOPs), where reactive species like hydroxyl and sulphate radical, are exploited in the dye decolourisation [2,3]. AOPs, including ozonation [12], photocatalysis [13], atmospheric non-thermal plasma [14] and cavitation [5,15], have all been shown as very effective in degrading

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different synthetic dyes. As the effectiveness of treatment processes in many cases depends on the characteristics of the treated samples none of the investigated methods has yet proved to be economically attractive [8]. For this reason, further investigation is warranted and hydrodynamic cavitation (HC) has proven to be a promising technology with considerable untapped potential. The effects of HC are manifested after the collapse of symmetric or asymmetric bubbles, releasing the stored energy in the form of high pressures and temperatures, the formation of radicals (primarily hydroxyl radicals - $\cdot\text{OH}$) and mechanical forces such as fast jets, microstreaming, shear forces and shock waves [16]. The fact that either chemical or mechanical effects can be used to break bonds of large synthetic or natural molecules [17,18] makes HC especially attractive. Another notable advantage is its versatility, as it can be integrated with different processes to make hybrid AOPs, often leading to synergistic effects that enhance performance beyond that of a single process [5,6,9,19–21]. Most of these studies have been conducted at a macro-scale, usually involving static devices such as orifices or Venturi constrictions [3,20,21], or dynamic systems like rotating generators of HC [22]. However, the recent emergence of nano- and micro-fluidics [23,24] along with advancements in micro-reactor fabrication, has sparked growing interest in studying bubble dynamics and cavitating flows within confined micro-scale geometries [25–27]. This interest has resulted in widespread use and investigations of micro-reactors in various scientific fields from chemical, medical, biotechnological to pharmaceutical. Advantages such as small size, high area to volume ratio, precise temperature and pressures control and excellent mixing efficiency, have made them more desirable than macro-scale reactors. These properties enable significantly higher reaction rates, yields and selectivity and contribute to intensification of processes [28]. At the microscale, cavitation behaviour can differ substantially from macro-scale systems because confinement, reduced availability of free-stream nuclei, shorter residence times in low-pressure regions, and increased liquid metastability influence cavitation inception and bubble dynamics [29,30]. Recent microfluidic HC studies have demonstrated that these confined geometries can be used to investigate pollutant removal, reactive oxygen species formation, and cavitation-cloud dynamics under well-controlled conditions [25,27,31,32]. Scaling down classical Venturi and orifice geometries also enables more direct observation of cavitation structures and their interaction with the channel walls, providing a useful platform for linking local hydrodynamics with mechanical and chemical effects. Furthermore, scaling down HC devices (Venturi constrictions or orifices) converts highly turbulent 3D cavitating flow towards more controllable 2D flow, allowing researchers to study fundamental cavitation mechanisms more precisely. The confined geometry in the micro-reactors allows better control of bubble dynamics, and higher bubble density, which all results in improved mechanical and chemical effects.

Despite the growing interest in cavitation and microfluidics, to the authors' knowledge, no study has yet investigated the decolorization of azo dyes using a HC microfluidic reactor. Moreover, the relationships between operating conditions, cavitation dynamics, cavitation-induced chemical effects, and azo-dye removal at the microscale remain largely unexplored. Consequently, there is currently a lack of systematic understanding of how these interconnected phenomena determine treatment performance in HC micro-reactors. To address this gap, a Venturi-type micro-reactor was employed as a controlled laboratory platform to relate cavitation behaviour and the resulting mechanical and chemical effects to RR120 decolorization. RR120 was selected as a representative azo dye because of the limited existing HC literature and its suitability for controlled laboratory investigations. The effects of initial dye concentration, solution pH, H_2O_2 concentration, pressure difference across the Venturi constriction, and sample volume were systematically investigated. To enable a more meaningful comparison between the investigated operating conditions, the decolorization performance is presented as the absolute amount of dye removed rather than the conventional percentage removal. Selected experiments were

performed in triplicate and analysed using ANOVA. Finally, machine learning (ML) algorithms were applied to identify relationships between the operating conditions, HC-induced chemical effects, and decolorization performance.

2. Materials and methods

2.1. Chemicals

Reactive Red 120 (CAS No. 61951-82-4), high-purity salicylic acid (SA $\geq 99\%$) and the two SA products 2,3-dihydroxybenzoic acid (2,3-DHBA, 99%), and 2,5-dihydroxybenzoic acid (2,5-DHBA, $\geq 97.5\%$) were purchased from Sigma-Aldrich. 30% (v/v) H_2O_2 was purchased from Roth, while 1 M HCl was purchased from Honeywell Fluka.

2.2. Experimental hydrodynamic cavitation micro-reactor set-up

Experimental setup, as shown on Fig. 1a, consists of a Venturi shape micro-reactor (1), connected into a closed loop circuit with a reservoir (2) of a 1 L volume and a microfluidic vane pump (TCS Micropumps V4000) (3). Micro-reactor in a shape of a convergent - divergent (18° - 10°) nozzle was laser cut out of 450 μm thick stainless-steel plate, with a height of a 225 μm at the throat. The plate was sandwiched between two acrylic plates to provide transparency for visualization of cavitation phenomena generated downstream the constriction. Inlet and outlet holes are drilled into the back layer of the acrylic glass plate to allow for the connecting tubes to feed the liquid into and out of the channel. The channel geometry was adopted from the study of Podbevšek et al. [27] as the most efficient in terms of chemical effect. It was kept constant throughout the study to isolate the effects of operating conditions without introducing geometry as an additional experimental factor. Pressure was measured at the inlet and outlet of the test section with a gauge pressure transducers (WIKA A-10, measuring range: 0–10 bar). During the experiments, the temperature was maintained at $25.0 \pm 0.5^\circ\text{C}$ using a cooling coil (4) immersed in the reservoir and connected to a DuraChill CA03 recirculating chiller (cooling capacity: 1.28 kW). The temperature was continuously monitored via a K-type thermocouple (5). Detailed experimental conditions in the Venturi-type micro-reactor are listed in Fig. 1b. To ensure a fair comparison, all experiments were assessed at identical numbers of cavitation passes (CP), meaning that each sample, regardless of experimental conditions (Table 1: volume, pressure difference (Δp)) passed through the cavitation zone the same number of times, based on flowrate measurements.

2.3. Cavitation characterization

Cavitation downstream of the Venturi constriction (divergent part – Fig. 1) was characterized by combining high-speed visualization and high-frequency pressure pulsation measurements. The objective was to simultaneously record images of the cavitation structures and the corresponding pressure signals, enabling a detailed comparison of cavitation behaviour under different experimental conditions based on critical features of the signals. Precise synchronization of the two signals was crucial to correlate bubble shedding events with pressure oscillations. High-speed imaging was performed using a Photron FastCam SA-Z camera with resolution of 640×280 pixels (corresponding to 16×7 mm) at 100,000 fps and 0.25 μs shutter speed. The camera was positioned perpendicular to the Venturi section plane on the front side of the test section. Backlight illumination was used to achieve clear visualization of the bubbles structure. Particular care was taken to maintain consistent camera and light positioning and recording conditions throughout all experiments. Pressure pulsations were measured using high-frequency pressure transducer PCB 113B26 with a sampling frequency of 400 kHz installed at 25 mm downstream the Venturi throat. Signal was captured via National Instruments measurement card NI-9222.

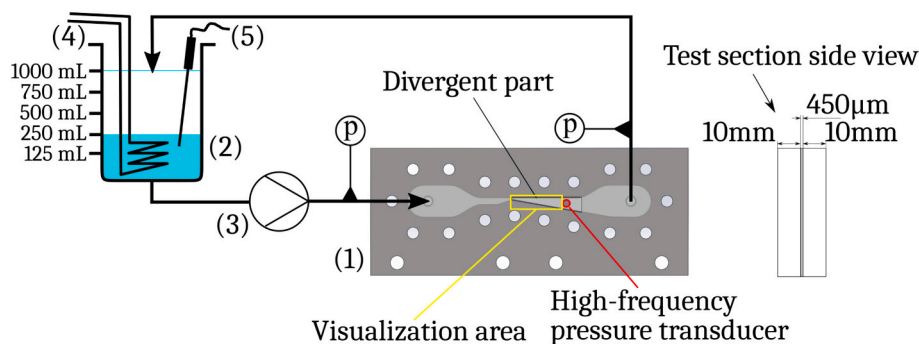


Fig. 1. Experimental setup scheme with side test section view.

Table 1

Selected experimental conditions. Equations used for the calculation of Cavitation and Reynolds number are given in the Supplementary material, Suppl. 1. The rated power of the microfluidic pump was determined from the manufacturer's performance curve.

Cross section [$\mu\text{m} \times \mu\text{m}$]	225 $\times$ 450		
Pressure difference (Δp) [kPa]	500	700	900
Flowrate (Q) [mL/s]	3.7	4.4	4.9
Time per CP [s]*	68	57	51
Cavitation number [–]	0.89	0.84	0.85
Reynolds number [–]	12,300	14,600	16,300
Rated pump power [W]	70	90	105

* for $V = 250$ mL.

2.4. Post-processing of the cavitation visualization and pressure signals

Cavity length was evaluated by mean of representations as the one in Fig. 5b. For continuous time instants images are analysed, quantifying mean levels of white in each column of pixel. In this way length of vapor shedding is compared in terms of pixel, as camera distance from the test section is maintained constant. The measured pixel size was then converted into physical size using a calibration factor of 1 pixel = 0.025 mm.

Cavity dispersion is demonstrated according to evaluation of fractal dimension D . This parameter quantifies how complex and irregular, space filling of a geometric object or pattern is, based on how details change with scale. Definition of this parameter is given in the following equation:

$$D = \frac{\log(Nr)}{\log\left(\frac{1}{r}\right)} \quad (1)$$

where Nr stands for number of segments in a unit, and r stands for the scaling factor (length).

Pressure peak mean was determined based on high-frequency pressure measurements. Pressure analysis relies on the mean of the 50 highest recorded peaks, balancing the need to capture rare but extreme events without overestimation, and the predominance of lower-amplitude pulses.

Shedding frequency was determined based on high-frequency pressure measurements and compared with visualization observation. The Fourier transform is utilized to convert the time-based signal of the shedding events into the frequency domain (Suppl. 2). The two-time signals that are taken into consideration are the pressure signal detected from pressure transducers and the instantaneous amount of vapor in the channel evaluated from high-speed imaging. The two analyses yielded almost perfectly matching results, allowing the identification of the dominant shedding frequency as a peak in the spectrum.

2.5. Experimental conditions and design

Overview of the investigated experimental conditions is presented in Table 2. Exps. 1–38 systematically evaluated the influence of key experimental conditions on the decolorization of RR120. The investigated variables included initial RR120 concentration (6.25, 12.5, 25, 50 and 100 mg/L), solution pH (2, 3.5, 5 and neutral), H_2O_2 concentration (0, 850, 1700 and 3400 μM), pressure difference (500, 700 and 900 kPa) across the Venturi constriction of the micro-reactor, and sample volume (125, 250, 500, 750 and 1000 mL). The selected RR120 concentration range reflects typical dye concentrations found in textile WW effluents, which may reach up to 250 mg/L [2]. The chosen pH values were based on previous studies [5,6] and were selected to cover both acidic (Exps. 6–8) and neutral conditions (Exp. 3). For experiments involving H_2O_2 addition, a RR120 concentration of 25 mg/L was used to evaluate different molar ratios of dye to H_2O_2 , 1:50, 1:100 and 1:200 (Exps. 14–16). Based on these results, the optimal concentration was selected for subsequent experiments (Exps. 17–26). The selected Δp (Exps. 27–28) represented different cavitating regimes, while the influence of sample volume was studied at two initial dye concentrations (100 and 25 mg/L) under optimal pH and H_2O_2 conditions (Exps. 29–38). To enable meaningful comparisons between experiments, sampling times in the latter experiments were adjusted to account for increased duration of a single CP at lower Δp and larger sample volumes. Even though sampling times differed, all samples passed through the cavitation zone the same number of times (35 CP by the end of the sampling period). For selected representative experiments (Table 2), cavitation visualization and pressure pulsation measurements were performed to support the interpretation of decolorization results. Additionally, to assess the role of RR120 in cavitation dynamics, measurements were conducted also in deionized water (DW) alone at three Δp (Exp. X) and in DW with H_2O_2 addition (Exp. Y). $\cdot\text{OH}$ formation was evaluated at three Δp (Exps. SA1–SA3) and sampling times were again adjusted to account for changes in CP duration at lower Δp .

Experiments marked with an asterisk in Table 2 were performed as three independent experimental runs, whereas the remaining conditions were evaluated in a single experimental run. Measurements obtained at successive sampling times within the same run represent repeated measurements of the same experimental unit and do not constitute independent replicates. Consequently, between-run variability could not be estimated directly for the unreplicated conditions, including the neutral-pH experiments and parts of the H_2O_2 concentration series. Comparisons involving these conditions should therefore be regarded as exploratory rather than confirmatory.

2.6. Sample preparation and analyses

RR120 solutions were prepared immediately prior to each experiment. Samples collected before, during, and after treatment were analysed using a DR3900 spectrophotometer (Hach). RR120 concentration

Table 2

Overview of experiments and experimental conditions performed for the purposes of this study.

Exp.	Sampling time (min)	V (ml)	c_i RR120 (mg/L)	pH	H ₂ O ₂ (μM)	Δp (kPa)
X†	–	250	–	Neutral	–	900
Y	–	250	–	Neutral	1700	900
1	–	250	100	–	–	–
2	–	250	50	–	–	–
3	0, 5, 10, 15, 30	250	25	Neutral	–	900
4	–	250	12.5	–	–	–
5	–	250	6.25	–	–	–
6	–	250	–	5	–	–
7	0, 5, 10, 15, 30	250	25	3.5	–	900
8	–	250	–	2	–	–
9*	–	250	100	–	–	–
10*	–	250	50	–	–	–
11*	0, 5, 10, 15, 30	250	25	2	–	900
12*	–	250	12.5	–	–	–
13*	–	250	6.25	–	–	–
14	–	250	–	–	850	–
15	0, 5, 10, 15, 30	250	25	2	1700	900
16	–	250	–	–	3400	–
17*	–	250	100	–	–	–
18*	–	250	50	–	–	–
19*	0, 5, 10, 15, 30	250	25	2	1700	900
20*	–	250	12.5	–	–	–
21*	–	250	6.25	–	–	–
22	–	250	100	–	–	–
23	–	250	50	–	–	–
24	0, 5, 10, 15, 30	250	25	Neutral	1700	900
25	–	250	12.5	–	–	–
26	–	250	6.25	–	–	–
27*	0, 6, 11, 17, 34	250	100	2	1700	700
28*	0, 6, 13, 20, 40	250	100	2	1700	500
29	0, 5, 10, 15	250	125	–	–	–
30*	0, 5, 10, 15, 30	250	25	–	–	–
31	0, 5, 10, 15, 30, 45, 60	500	100	2	1700	900
32	0, 5, 10, 15, 30, 45, 60, 75, 90	750	100	2	1700	900
33	0, 5, 10, 15, 30, 45, 60, 75, 90, 105, 120	1000	100	2	1700	900
34	0, 5, 7.5, 10, 15	125	–	–	–	–
35	0, 5, 7.5, 10, 15, 20, 30	250	–	–	–	–
36	0, 5, 7.5, 10, 15, 20, 30, 40, 45, 60	500	–	–	–	–
37	0, 5, 7.5, 10, 15, 20, 30, 40, 45, 60, 75, 80, 90	750	25	2	1700	900
38	0, 5, 7.5, 10, 15, 20, 30, 40, 45, 60, 75, 80, 90, 105, 120	1000	25	2	1700	900
SA1*	0, 5, 10, 15, 30	250	–	–	–	900
SA2*	0, 6, 11, 17, 34	250	–	< 3	–	700
SA3*	0, 6, 13, 20, 40	250	–	< 3	–	500

†: experiment X also performed at Δp 500 and 700 kPa (see Fig. 5b); *: experiments were repeated three times to assess repeatability; Δp: pressure difference between the inlet and outlet of the Venturi constriction of the micro-reactor; c_i : initial dye concentration; neutral: signifying that the pH after the dissolution of the dye and addition of H₂O₂ was not adjusted and remained at its initial value (from 5.9 to 7.3).

was determined by measuring absorbance at 513 nm and applying a calibration curve in the concentration range of 0.782–100 mg/L. The high correlation coefficient ($R^2 = 0.9999$) confirmed excellent linearity within this range. It should be noted that the spectrophotometric analysis quantifies only the concentration of the parent RR120 molecule. Therefore, the reported decolorization (or RR120 removal) reflects only the reduction in the concentration of the parent dye and does not provide information on the formation of degradation intermediates, the extent of mineralization, or the toxicity of the treated solution. To investigate whether H₂O₂ alone contributed to dye decolorization, a control experiment without cavitation was conducted. The test was

performed for 30 min at 25 °C under magnetic stirring in 250 mL of DW containing 100 mg/L of RR120 and 1700 μM H₂O₂. Only minimal decolorization (< 1%) was observed under these conditions.

To confirm the chemical effects of cavitation, particularly •OH formation, salicylic acid (SA) dosimetry was applied. The method is based on the reaction between •OH generated during cavitation and SA, resulting in the formation of two hydroxylated products, 2,3- and 2,5-DHBA. A detailed description of the method is provided elsewhere [33]. Briefly, a 300 mg/L SA solution was prepared and acidified with HCl prior to HC experiments to obtain a pH < 3. SA experiments were performed separately in dye-free solutions and used to compare the formation of DHBA products under different HC operating conditions, particularly at different pressure differences (Table 2, Exps. SA1–SA3). These experiments were used to support the discussion of RR120 decolorization obtained under the same hydrodynamic conditions (Table 2, Exps. 17, 27–28) and to see whether similar trends could be observed between the chemical effects of cavitation and dye removal. However, since the SA and RR120 samples differ in chemical composition, the absolute concentrations of SA products measured in the dosimetry experiments should not be considered representative of the values that would be obtained in the RR120 samples under the same operating conditions. The formed products were analysed using a high-performance liquid chromatography system (HPLC Agilent Infinity 1260) equipped with a diode array detector and a LiChrospher® 60 RP-Select B column (MZ-Analysentechnik GmbH, Germany). For these analyses, 1 mL samples were collected.

2.7. Statistical analysis

Statistical analyses were performed in R using linear mixed-effects models. Because RR120 decolorization was measured repeatedly in the same samples, experimental unit was included as a random intercept to account for within-sample correlation. Fixed effects were tested by Type III analysis of variance with Satterthwaite's approximation for denominator degrees of freedom. Where appropriate, post hoc pairwise comparisons of estimated marginal means were performed with Holm adjustment for multiple testing. Statistical significance was set at $p < 0.05$. For the experiments evaluating the effects of solution pH on RR120 decolorization, initial RR120 concentration, number of CP, and pH were included as fixed factors, along with all interaction terms. For the experiments evaluating the effects of H₂O₂ addition, initial RR120 concentration, number of CP, and H₂O₂ addition were included as fixed factors, together with all interaction terms. In both cases, number of CP was analysed as a categorical variable to account for non-linear temporal effects across the four sampling points. The experimental unit was defined as the unique replicate within each treatment-by-concentration combination. For the experiments evaluating the effects of pressure difference, number of CP, and their interaction were fitted as fixed effects, and the experimental unit was included as a random intercept. This model structure was used to determine whether RR120 decolorization differed among pressure conditions overall and whether the pressure effect changed over time. When appropriate, pairwise comparisons among pressure levels were performed separately for each sampling time. In experiments with a balanced design, all treatments were performed in triplicate unless otherwise stated. For unbalanced datasets in which one experimental condition was represented by a single independent experimental run, the same model structure was retained. However, estimates and p -values involving the unreplicated condition rely on variance information obtained from the replicated conditions and on the assumptions of the mixed-effects model. They consequently have reduced precision and inferential reliability and were interpreted as exploratory rather than confirmatory. Data are shown as mean ± SD; $n = 3$ unless otherwise stated in the corresponding figure legends.

2.8. Design of ML analysis

In the experimentally obtained dataset (Table 2: Exps. 1–38) of measured values of the removed amount of RR120 based on different combinations of input parameters (e.g., volume, pH, pressure difference) the patterns that explain the behaviour of the cavitation phenomena of removing RR120 might be non-trivial and even impossible to detect by traditional domain-knowledge-based analysis through, e.g., simply plotting 2D or 3D plots that show how individual (pairs) of input parameters affect the removed amount of RR120. For this reason, ML-based analysis was employed in this study to reveal possible more intricate patterns in the experimentally obtained dataset and to better understand the phenomena investigated. The goal of ML analysis was thus: 1) to verify if patterns exist in input parameters that can be used to predict the removed amount of RR120, and 2) to determine which are the most important parameters that influence the removed amount of RR120.

The first step of the procedure is to generate a supervised ML regression model, which can, based on input parameters, predict the removed amount of RR120. The model is then tested to see if it achieves sufficient prediction performance, and if sufficient performance is achieved, the model is analysed through feature importance analysis to determine which features (i.e., input parameters) are the most important for the model to make the predictions. Two different models in terms of input parameters were generated and tested in this study:

- Model 1: predicts the removed amount of RR120 based on the following parameters: volume, RR120 concentration, pH, H_2O_2 , and pressure difference.
- Model 2: predicts the removed amount of RR120 based on the cavitation characterization: cavity length, fractal dimension, mean pressure peak and shedding frequency.

For generating prediction models and feature importance analysis, programming library Scikit-learn was used [34]. In the preparation of a dataset for ML analysis, experiments that were repeated more than once for the same combination of values of input parameters were merged in a single instance in the dataset. The values of parameters and the target value of these merged experiments were averaged. The size of the final dataset for ML analysis is thus:

- 39 instances with 5 input parameters and one target variable for Model 1,
- 39 instances with 4 input parameters and one target variable for Model 2.

2.8.1. Generating supervised ML-based prediction models

For both types of models (i.e., Model 1 and Model 2), five different supervised ML algorithms were tested and compared. Hyperparameters of each tested algorithm were tuned through 10-fold cross-validation to find the best algorithm with the highest prediction performance. The five tested algorithms and their hyperparameters candidate values are:

- ElasticNet (α : 0.01, 0.1, 1.0; l1 ratio: 0.3, 0.5, 0.7, 1.0),
- SVR RBF (C: 1, 10, 100; ϵ : 0.05, 0.1, 0.2; γ : scale, 0.1, 1.0),
- KNN (η : 3, 5, 7; weights: uniform, distance; p : 1, 2),
- Random Forest ($\eta_{\text{estimators}}$: 100, 300; max. Depth: None, 5; min. Samples leaf: 1, 2),
- Gradient Boosting ($\eta_{\text{estimators}}$: 100, 200; learning rate: 0.05, 0.1; max. Depth: 2, 3).

The performance metric to tune hyperparameters of individual tested supervised ML algorithms and to select the best algorithm for feature analysis is R^2 (coefficient of determination). The model testing strategy to select the best algorithm is *Leave-one-out-cross-validation*

(LOOCV). The best algorithm, if the performance of the corresponding generated prediction model is sufficient ($R^2 \gg 0$), is then used in the following feature importance analysis.

2.8.2. Feature importance analysis

To identify which are the most important parameters that determine the removed amount of RR120, permutation-based feature importance analysis [34] is employed. The number of times to permute a feature was set to 200 permutations. The scoring metric is R^2 .

3. Results and discussion

3.1. Cavitation characterization via visualization and pressure measurements

Based on our previous findings [33], demonstrating that even small additions of chemicals or their combinations can alter cavitation dynamics, a detailed analysis of the chemicals used in this study was performed. Cavitation patterns shown in Fig. 2 represents five distinct cases observed downstream of the Venturi constriction at a pressure difference of 900 kPa and a constant temperature of 25 °C. Cavitation in DW (Fig. 2a) serves as a reference for comparison with the other used cases (Fig. 2b–e), where addition of H_2O_2 , RR120 and SA on cavitation dynamics are investigated. In general, cavitation develops and grows downstream of the constriction under well-defined re-entrant flow, which constitute the primary mechanism responsible for cloud shedding. As clearly visible in Suppl. 3 (Video #1), the upper part of the cavitation structure is characterized by velocities considerably higher than those of the mainstream flow, which gives a potential for development of a Kelvin-Helmholtz instabilities [35]. In contrast, the lower region generates a reverse flow that extends almost to the throat, promoting detachment of the cavitation cloud from the attached cavity and its subsequent downstream shedding. The collapse of the detached cloud generates a shock wave that propagates omnidirectionally and further promotes the shedding process, in addition to the primary mechanism driven by the re-entrant jet. Regarding the effect of H_2O_2 addition (Fig. 2b), vapor shedding appears to be more unstable and fragmented. This effect is particularly enhanced as a sort of partial division of the vapor structures commonly appears. Those instabilities anyway are not strong enough to cause complete break from the cavity, but what is observed is a partial separation of the overall vapor structure during growth step, giving rise to a non-continuous or weakly-joined structure (Fig. 2b – 1.3 ms). Structure compactness is then recovered before reaching maximum length (Fig. 2b – 2.7 ms) and a consequential full detachment of the cavity (Fig. 2b – 4.7 ms). The cavity length decreased, while the shedding frequency and fragmentation index D increased (Table 3). With presence of dye (Fig. 2c) and combination of dye and H_2O_2 (Fig. 2d) a tendency towards individual bubble creation is observed. This is particularly evident at the bottom wall of the divergent channel section, under the cavity shedding from the main structure (Fig. 2c – 4.6 ms). Even stronger individual bubble generation also appears after the implosion of the shed cavitation cloud in the far downstream region (Fig. 2c – 7 ms; Fig. 2d – 6 ms). What is crucial to be observed is that dye addition strongly influences cavity length, causing a clear reduction with respect to DW case. A discernible dependence on concentration emerges when cases with varying dye concentrations are compared, with a concomitant decrease in length reduction as the concentration is reduced (Table 3). An observation of a frequent cavity rebound is noted in case of combination of dye and H_2O_2 (Fig. 2d – 6.4 ms). The incorporation of SA has been demonstrated to induce a substantial modification in the vapor structure [33], leading to the formation of numerous individual small vapor bubbles in the main shedding area (Fig. 2e – 3.6 ms) in the cavitation downstream region, and in the re-entrant jet area (Fig. 2e – 5.4 ms). Moreover, in general cavity formed consists of smaller individual bubbles which have smaller size and thus larger structures with high void fraction are harder to form (Fig. 2e – 3.6

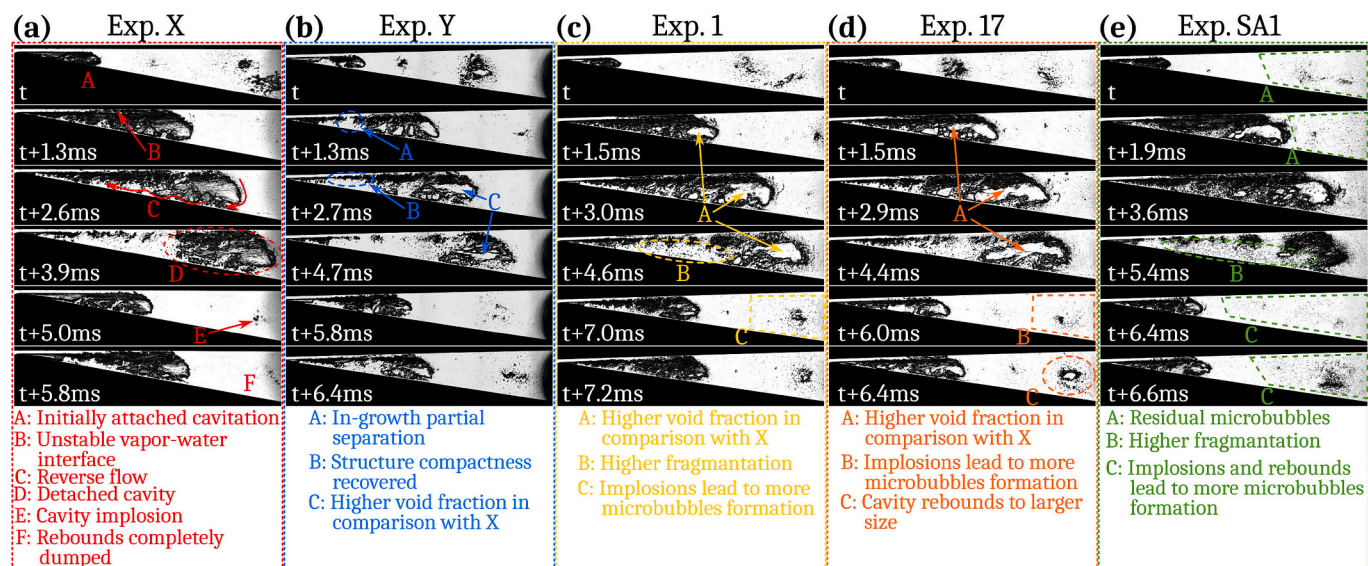


Fig. 2. Appearance of cavitation dynamics under selected operating conditions: a) DW - Exp. X; b) DW + H₂O₂ - Exp. Y; c) DW + RR120 (100 mg/L) - Exp. 1; d) DW + RR120 (100 mg/L) + H₂O₂ (1700 μM) - Exp. 17; e) DW + SA - Exp. SA1.

Table 3

Summary of the key visualization and pressure measurement results for selected experiments.

Exp.	c _i RR120 (mg/L)	pH	Δp (kPa)	H ₂ O ₂ (μM)	SA (mg/L)	Visualization		Pressure measurements	
						Cavity length (mm)	D	Pressure peak mean (Mpa)	Frequency (Hz)
X	0	Neutral	900	0	0	16	1.4881	0.9702	141
Y	0	Neutral	900	1700	0	13.9	1.5234	0.9256	160
27	100	2	700	1700	0	12.5	1.4109	0.6328	181
28	100	2	500	1700	0	10.1	1.3123	0.3768	214
17	100	2	900	1700	0	13.8	1.4705	0.6954	150
18	50	2	900	1700	0	14.3	1.4729	0.6651	161
19	25	2	900	1700	0	14	1.4757	0.6426	170
20	12.5	2	900	1700	0	14.3	1.5069	0.6253	164
21	6.25	2	900	1700	0	15	1.5114	0.6408	163
1	100	Neutral	900	0	0	14	1.4958	0.6519	150
2	50	Neutral	900	0	0	13.8	1.4781	0.6686	151
3	25	Neutral	900	0	0	13.8	1.4722	0.6973	141
4	12.5	Neutral	900	0	0	14.8	1.5124	0.6123	163
5	6.25	Neutral	900	0	0	15.3	1.5215	0.6620	155
SA1	0	< 3	900	0	300	15.5	1.5215	0.7155	137
SA2	0	< 3	700	0	300	12.3	1.4411	0.7030	170
SA3	0	< 3	500	0	300	9.8	1.3454	0.4921	210

ms), like in other cases (Fig. 2b, c, d). All these effects result in an increased *D* index with respect to DW, but lower cavitation length (Table 3).

Analysis of implosion dynamics further reveals distinct behavioural patterns which could be linked to the overlying effect. Putting now the focus on the last instants of the five different cases (Fig. 2), we can compare large bubble structures implosion and consequent rebound phases. What was noticed is that pure DW shedding (Fig. 2a) after first cavitation cloud collapse (Fig. 2a – 5 ms) is characterized by almost complete dissipation of cloud rebound (Fig. 2a – 5.8 ms), leading to strong pressure waves that are clearly visible by the compression effect generated in other small bubbles in the surrounding (Suppl. 3, Video #1). Similar effect is observed in case of H₂O₂ addition (Fig. 2b), while different behaviour is observed in case of dye addition (Fig. 2c, d). A commonly observed effect in these cases is that after the first collapse (Fig. 2c – 7 ms, Fig. 2d – 6 ms) and consequent bubble rebound (Fig. 2c – 7.2 ms, Fig. 2d – 6.4 ms), a big core bubble with high volume fraction and smaller nuclei are maintained, flowing downstream and inevitably facing following rebound implosions. Further difference can be observed when comparing these data with those obtained after SA addition

(Fig. 2e – 5.4 ms). In this instance, the process of bubble implosion gives rise to a consistent number of isolated bubbles in the flow, comparable to those formed even during the shedding process.

The results summarized in Table 3 combine flow visualization and pressure measurements for the selected experiments and provide additional insight into how solution composition affects cavitation behaviour in the micro-reactor. The cavity length generally decreased with increasing RR120 concentration, from 16 mm in pure DW to about 13.8 mm at the highest RR120 concentration, both at neutral pH and at pH = 2 in the presence of H₂O₂. As expected, increasing the Δ*p* resulted in longer cavities, regardless of the chemical composition of the treated samples. At the same time, comparison of the *D* index shows that cavitation fragmentation increased in the presence of H₂O₂ (Exp. Y) relative to pure water (Exp. X), indicating that H₂O₂ alone influenced cavity structures. In contrast, comparison across the c_i RR120 (Exps. 1–5 and 17–21) revealed that the relationship between cavity length and *D* remained broadly similar irrespective of H₂O₂ addition or pH adjustment. This means that the clear H₂O₂ effect observed in the least complex systems (Exps. X and Y) was not reproduced to the same extent once dye, acid, or H₂O₂ were present simultaneously. In our previous study on

macro-scale reactors [33], we showed that combining SA and HCl significantly affected both cavitation visualization and pressure pulsations, whereas HCl alone or SA alone did not induce substantial changes. The distinct differences appeared only when the two compounds were present together in a suitable concentration range. The present results suggest that, although water matrix complexity affects cavitation dynamics in both macro- and micro-reactors, the effects in the micro-reactor are less pronounced. This may be attributed to the geometric confinement of the micro-reactor, which promotes a more quasi-two-dimensional flow field, in contrast to the fully three-dimensional flow structures that develop in larger macro-scale reactors. Another possible explanation for the observed effects under the investigated experimental conditions could be due to the chemical structure of RR120.

Following a precise alignment between the visualised and pressure signals, it was observed in our experiments that the proximity of neighboring vapor structures resulted in an attenuation of pressure propagation, leading to a reduction in the peak values detected between Exps. X & Y and other experiments (Table 3 – Pressure Peak Mean).

Experimental comparison between Exps. X and Y demonstrates that the addition of H_2O_2 exerts minimal influence on implosion intensity. In pure DW, mean peak pressures reached 0.9702 MPa, while Exp. Y yielded a comparable mean of 0.9256 MPa. Conversely, vapor structures that can detach and flow downstream, imploding partially isolated, have the capacity to express their full potential, resulting in the generation of the highest-pressure peaks. In contrast, the introduction of c_i RR120 or SA consistently reduced implosion strength. For all Exps. 17–21 and 1–5, mean peak pressures stabilized around 0.64 MPa, largely independent of RR120 concentration. Pairwise comparisons (e.g., 1–17, 2–18) confirmed only minor differences when H_2O_2 was combined with these additives. A preliminary study of frequency characterization by the mean of Fourier transformed analysis highlighted a main component for the shedding around 140 Hz for pure DW (Exp. X), considering Δp equals to 900 kPa (Table 3). These value increase with inlet pressure reduction, giving rise to faster shedding, characterized by lower cavity extension and lower mean peak pressure observed, with frequency reaching 150 Hz at 700 kPa, and 220 Hz in case of 500 kPa Δp . A tendency to decrease

shedding time is observed with the addition of H_2O_2 , with a slight increase of frequency in case of both pure DW (Exp. X), and dye addition in different concentrations (Exps. 17–21), comparing corresponding couples of tests. This observation aligns with the findings from the visualization phase, which indicated an enhancement in the instability of the vapor structures which inherently favour the detachment of the vapor region. Consequently, this effect would be responsible for the recognized acceleration of the detachment process. Further considerations can be made by considering the differences that become evident once the dye is in the solution. Comparison of baseline case Exp. X to Exps. 17–21 and 1–5, highlights a systematic increase of frequency for these second conditions, introducing a change of about 10–20 Hz. These considerations, together with those previously discussed, highlight how the introduction of the dye leads to substantial differences in the measured quantities, including a reduction in the mean peak pressure and cavity length, but an increase in both frequency and dispersion. This allows us to infer that variations in the relevant physical and chemical properties, such as surface tension and viscosity, as well as the amount of dissolved gas, may play a key role in understanding the observed changes in the dynamics.

3.2. The effect of initial RR120 concentration

The results of RR120 decolorization at different initial dye concentrations (c_i) and neutral pH are shown in Fig. 3 (main graph). The results demonstrated that decolorization increases with the number of CP for all investigated concentrations, and a pronounced increase is observed between 18 and 35 CP for all cases except 6.25 mg/L. This discrepancy could be attributed to the relatively short treatment time and low initial amount of RR120, which reduces the probability of interaction with $\cdot\text{OH}$ as the dye concentration decreases with longer treatment time. In general, the results show that the percentage of decolorization decreases with increasing initial dye concentration (Suppl. 4). These findings are consistent with literature reports on the decolorization of RR120 at comparable concentrations using cavitation [5,6,36,37] or other AOPs [13,38], as well as studies involving other azo dyes treated by cavitation

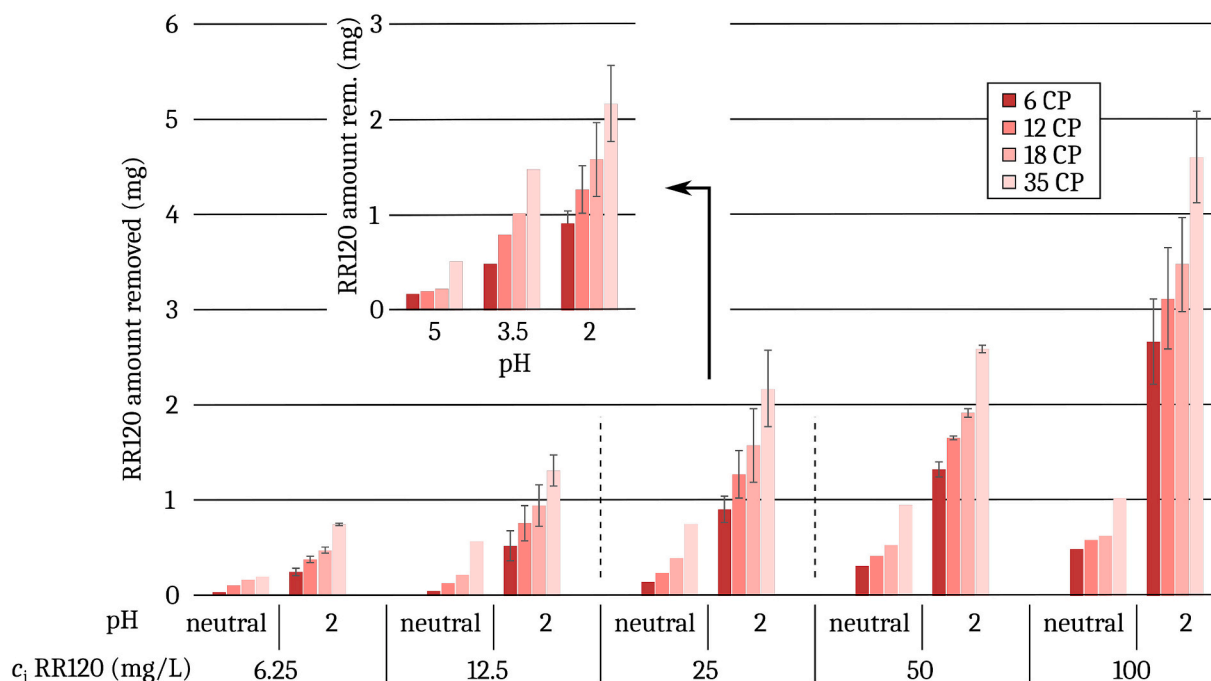


Fig. 3. Effect of solution's pH on decolorization of 25 mg/L RR120 (inset) and effect of initial RR120 concentration on decolorization at neutral pH and pH = 2 (main graph). Experiments were performed in 250 mL DW samples at pressure difference of 900 kPa (Table 2: Exps. 1–13). Experiments at neutral pH and pH 3.5 and 5 were performed only once, therefore no error bars are shown for these conditions. Experiments at pH 2 were performed in triplicates, therefore data are presented as mean $\pm$ standard deviation. CP represents cavitation passes.

[9,19,39] or alternative AOPs [3,21]. For example, Khorshidi and Mohammadidoust, reported a decrease in RR120 removal efficiency from 56 to 44% as the concentration increased from 11 to 21 mg/L [37]. Rajoriya et al. similarly reported a decline from 47 to 19% when the concentration of Reactive Blue 13 increased from 30 to 60 mg/L [9], while Noori et al. showed that Direct Red 16 removal dropped from 88 to 75% when the concentration was doubled from 20 to 40 mg/L [19]. However, it is important to distinguish between relative and absolute removal. While the percentage removal decreases, the absolute amount of original RR120 molecule removed (mg in 250 mL in our study) increases with higher initial dye concentration (Fig. 3). Increasing the initial RR120 concentration enhances the probability of $\bullet\text{OH}$ -dye interactions, resulting in a greater absolute amount of dye removed, even though the overall percentage removal declines. Similar observations have been made for the azo dyes K-2BP [39] and ReD-G [21].

3.3. The effect of solution pH

For the initial evaluation of the effect of solution pH, an initial dye concentration of 25 mg/L was selected. Fig. 3 (inset) demonstrates that the initial solution pH influences RR120 decolorization, with the highest removal of RR120 (2.2 mg in 250 mL) observed at pH = 2 (Table 2: Exps. 6–8). This pH dependence may be related to both the acid-base properties of the RR120 molecule and to the influence of acidic conditions on $\bullet\text{OH}$ chemistry. RR120 contains three ionizable functional groups, namely six sulfonic acid groups, two phenolic -OH groups adjacent to the azo bond, and two diaminochlorotriazine groups [40,41]. Using potentiometric titration four distinct pKa values of <2, 4.4, 9.38 and 11.54 have been identified [41], where lower pKa values were attributed to the ionization of amino groups and higher values correspond to the dissociation of phenolic -OH groups. The dissociation of sulfonic acid groups is believed to occur at pH values below 1 [40]. These changes modify the molecular speciation of the dye and may contribute to the observed pH dependence which is also consistent with observations of previous studies [5,6,37]. Malade et al. [5] reported on an increase of RR120 decolourisation from 45 to 75%, when decreasing pH from 10 to 2, respectively. Similarly, higher reaction rate constant ($7.5 \times 10^{-3} \text{ min}^{-1}$ at pH = 2 compared to $2 \times 10^{-3} \text{ min}^{-1}$ at pH = 9) was reported by Saharan et al. [6].

Similar trends have been described for other azo dyes treated by various AOPs, where the optimal working pH plays a crucial role in achieving maximum degradation efficiency [12,19,39]. Wang et al. showed that the decolorization of Reactive Brilliant Red K-2BP increased from 75 to 97% when pH was lowered from 5.5 to 2 [39]. Similarly, Thi Dang et al. reported on an increase in removal efficiency of RR120 from around 50 to 70% when pH decreased from 11 to 3 [12]. Although changes in the ionization state of RR120 may contribute to the observed pH dependence, previous studies have also suggested that acidic conditions could favour $\bullet\text{OH}$ mediated oxidation during AOPs, thereby contributing to higher decolorization effectiveness [5,9,21,39]. Furthermore, the same concentration-dependent trend as observed at neutral pH is evident at pH = 2 (Fig. 3), with the highest absolute removal of the parent compound determined at 100 mg/L ($4.6 \pm 0.5 \text{ mg}$ in 250 mL) after 35 CP (Table 2: Exps. 9–13). For comparison, it can be observed that the removal of RR120 is consistently lower under neutral pH conditions than at pH = 2 across the investigated concentrations (Fig. 3, main graph). In the linear mixed-effects model, RR120 decolorization was associated with the initial concentration ($p < 0.001$), number of CP ($p < 0.001$), and pH ($p < 0.001$), and the significant interaction between these variables ($p = 0.018$) indicates that the effect of pH depends on both initial RR120 concentration and number of CP. Detailed model results are presented in Suppl. 5a and 5b. Pairwise model-based comparisons (Suppl. 5b) showed no significant difference between neutral pH and pH = 2 at 6.25 mg/L. At 12.5 mg/L greater decolorization was estimated at pH = 2 after 18 ($p = 0.0418$) and 35 CP ($p = 0.0379$). At 25, 50, and 100 mg/L, the model estimated greater

decolorization at pH = 2 at all sampling times, with the largest differences observed at 100 mg/L (all $p < 0.0001$). These results suggest that acidic conditions may enhance RR120 decolorization and that the magnitude of this effect may increase with initial concentration and number of CP. However, because the neutral-pH conditions were represented by single experimental runs, the corresponding pH estimates and p -values rely on variance information from the replicated pH = 2 conditions and on the assumptions of the mixed-effects model. These comparisons should therefore be regarded as exploratory rather than confirmatory and require validation in independently replicated experiments.

3.4. The effect of H_2O_2 addition

To enhance RR120 decolorization, the role of an external oxidant was evaluated. H_2O_2 , which dissociates under cavitation into $\bullet\text{OH}$ radicals, can therefore act as an additional source of reactive species [42]. For the initial evaluation of its effects, experiments were performed at an initial dye concentration of 25 mg/L using different dye-to- H_2O_2 molar ratio (1:50, 1:100 and 1:200) to determine the optimal H_2O_2 dosage (Fig. 4: inset, Exps. 14–16). The results indicate that increasing the H_2O_2 concentration improves RR120 removal, but only up to 1700 μM . At this concentration, the highest RR120 removal after 35 CP was achieved ($3.3 \pm 0.5 \text{ mg}$ in 250 mL). Further increasing the H_2O_2 dose up to 3400 μM reduced decolorization by 12%. This decline can be attributed to the scavenging effect of excess H_2O_2 , which competes with the dye for $\bullet\text{OH}$, decreasing their availability for dye decolorization. Similar trend has been reported for other azo dyes treated by HC and H_2O_2 [9,11,20]. The control experiments (see Chapter 2.6) confirmed that the observed decolorization results from radicals generated by HC from water and H_2O_2 , rather than from H_2O_2 alone thereby confirming the synergistic interaction between HC and H_2O_2 . In the absence of cavitation, H_2O_2 alone resulted in negligible RR120 decolorization (<1%), demonstrating that it is ineffective under the investigated conditions without activation. During cavitation bubble collapse, the extreme local temperatures and pressures promote the cleavage of H_2O_2 into additional $\bullet\text{OH}$ radicals, thereby increasing the concentration of reactive species available for RR120 oxidation. Minimal degradation of RR120 by H_2O_2 alone has also been reported in other studies [6,13]. Based on these findings, 1700 μM of H_2O_2 was selected as the optimal concentration and all subsequent experiments were performed for all 5 initial concentrations investigated (Table 2: Exps. 9–13 and 17–21).

When applied across different initial dye concentrations (Fig. 4: main graph), the addition of H_2O_2 consistently improved decolorization compared to HC alone, with removal increasing progressively with the number of CP. The enhancement can be attributed not only to additional $\bullet\text{OH}$ generation from H_2O_2 but also to the intense micro-mixing induced by cavitation bubble collapse, which improves mass transfer and facilitates the transport of reactive species from the cavitation zone into the bulk solution. This increases the probability of contact between radicals and RR120 molecules. Furthermore, H_2O_2 may act as cavitation nuclei, promoting bubble formation and potentially increasing cavitation intensity and oxidation efficiency [15].

The highest removal of the parent dye molecule was obtained at an initial RR120 concentration of 100 mg/L, reaching $6.2 \pm 1.2 \text{ mg}$ in 250 mL after 35 CP. Notably, this concentration also exhibited the lowest repeatability, as reflected by the larger standard deviation. This may be attributed to the increased complexity of the system when both dye and H_2O_2 are present at high concentrations, leading to more chaotic hydrodynamic conditions (Table 3: visualization and pressure measurements results). Mixed-effects ANOVA (Suppl. 6a) showed significant main effects of starting dye concentration ($p < 0.001$), number of CP ($p < 0.001$), and H_2O_2 ($p = 0.020$) on decolorization of RR120. Significant interactions between studied factors indicate that temporal changes in RR120 decolorization depend on initial dye concentration ($p = 0.00121$) and that the effect of H_2O_2 varies across both number of CP and starting

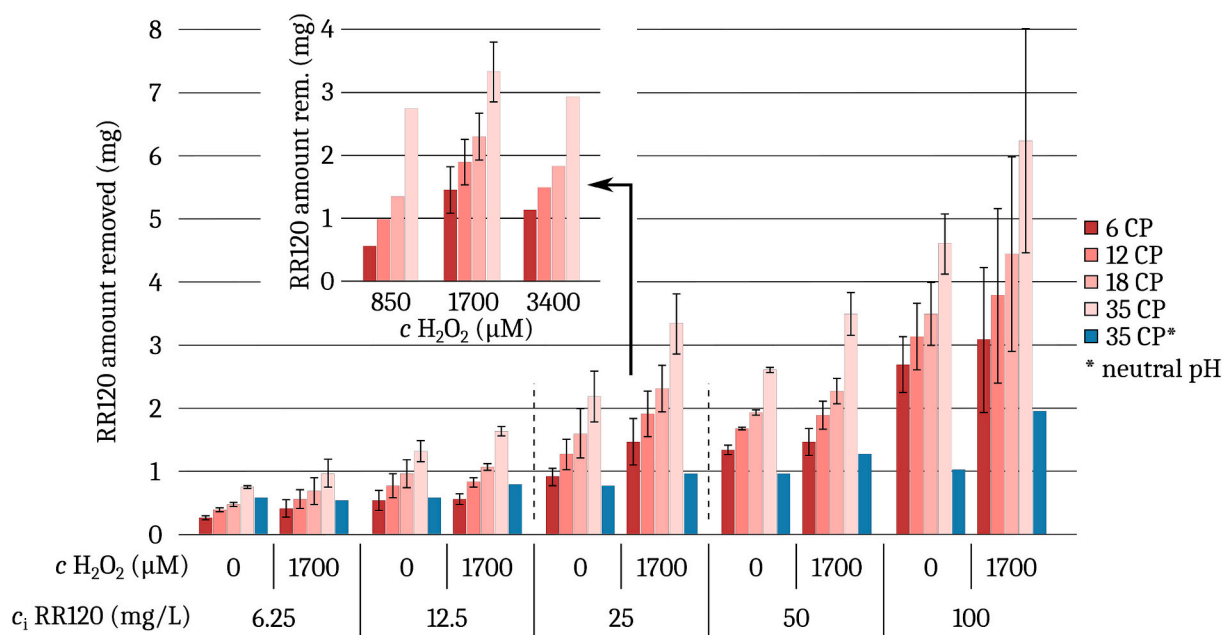


Fig. 4. Effect of different concentrations of H₂O₂ on decolorization of 25 mg/L RR120 (inset) and the effect of 1700 μM H₂O₂ on the decolorization of RR120 at the five selected initial concentrations (main graph). Experiments were performed in 250 mL DW samples at pH = 2 (red columns) or neutral pH (blue columns) and a Δp of 900 kPa (Table 2: Exps. 14–16, Exps. 9–13 and Exps. 17–21). All experiments performed at pH 2 without H₂O₂ and with 1700 μM H₂O₂ were performed in triplicates; these data are therefore presented as mean $\pm$ standard deviation. Experiments at neutral pH and those with 850 μM H₂O₂ or 3400 μM H₂O₂ were performed only once, therefore no error bars are shown for these conditions. CP represents cavitation passes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dye concentration. Post hoc pairwise comparisons (Suppl. 6b) showed that H₂O₂ did not significantly affect RR120 decolorization at early sampling times but significantly increased it at 100 mg/L after 18 CP ($p = 0.0385$), at 25 mg/L after 35 CP ($p = 0.0121$) and at 100 mg/L after 35 CP ($p = 0.0012$), with a near-significant increase at 50 mg/L after 35 CP ($p = 0.0525$).

Comparable findings have been reported in previous studies investigating RR120 removal by HC. Malade et al. achieved 97.5% decolorization after 120 min using an orifice-type HC device (tap water, 10 mg/L RR120, 3517 μM or 120 mg/L H₂O₂, pH = 2), compared to 74% removal without oxidant addition [5]. Similarly, Saharan et al. reported 100% removal after 180 min (tap water, 50 mg/L RR120, 2040 μM H₂O₂, and pH = 2), using an orifice-type HC device, whereas HC alone resulted in only 60% removal [6]. Although higher overall decolorization efficiencies (%) were achieved in these macro-scale orifice HC systems compared to the present study, it is important to note that the treatment times in those studies were substantially longer than in the present study. In our case, the highest removal (61.2%, Suppl. 7) was obtained at an initial RR120 concentration of 6.25 mg/L with the addition of 1700 μM H₂O₂. Similar synergistic effects between HC and external oxidant at acidic pH have been reported for other azo dyes. For example, Askarniya et al. reported 41% decolorization of 20 mg/L Congo Red after 60 min combining single orifice HC with 1000 mg/L of H₂O₂ [15]. On the other hand, Rajoriya et al. achieved 91% degradation of 30 mg/L of Reactive Blue 13 after 120 min using slit Venturi HC [9]. Innocenzi et al. observed 53% of 5 mg/L Methyl Orange after 60 min using Venturi HC and 16.5 mg/L H₂O₂, compared to 31% with HC alone [20]. Wang et al. reported 97% degradation of 20 mg/L Reactive Brilliant Red K-2BP after 120 min using swirling jet-induced HC with 300 mg/L H₂O₂, compared to only 32% using HC alone [39].

Together, these findings confirm that combining various scale HC reactors with an optimized dose of external oxidant predominately under acidic conditions significantly enhances azo dye removal, while highlighting that experimental conditions (Δp and sample volume) can be further investigated to improve overall efficiency.

3.5. The effect of pressure difference

The effect of Δp on RR120 decolorization in the presence of the optimal H₂O₂ dose is shown in Fig. 5a. To obtain a more clearly detectable difference between the tested conditions, a higher initial concentration (100 mg/L) was chosen. As shown in Fig. 5a decolorization efficiency increased (based on the average values) as the Δp was raised from 500 to 700 kPa, reaching a maximum removal of 10.2 ± 2.5 mg in 250 mL at 700 kPa. However, a further increase to 900 kPa resulted in a decline in decolorization efficiency, with removal dropping below the level achieved at 500 kPa. These results indicate the existence of an optimal pressure at which bubble generation, bubble collapse intensity, and mass transfer conditions are most favourable for RR120 removal. At Δp 700 kPa, cavitation in the investigated Venturi HC micro-reactor seems to be intense enough to promote efficient formation of $\cdot\text{OH}$ radicals from both water and H₂O₂, leading to the highest observed decolorization. Results were analysed using a linear mixed-effects model with pressure and CP number as fixed effects (Suppl. 8a). Number of CP had a significant effect on decolorization ($p < 0.001$), while the overall main effect of pressure was not significant ($p = 0.260$). However, the significant interaction between pressure and CP ($p = 0.00543$) indicates that the effect of pressure was not constant over time. Pressure-related differences became more apparent after 35 CP, with decolorization tending to be higher at 700 than at 900 kPa, although pairwise comparisons at individual time points were not significant after Holm adjustment (Suppl. 8b). Comparing cavitation numbers (Fig. 1b) shows that Δp of 700 kPa results in the lowest value, indicating favourable conditions for cavity development. Although decreasing cavitation number generally enhances cavitation activity, this trend holds only until an optimal regime is reached (Malade and Deshannavar 2018).

Spatial-temporal evolution of cavitation dynamics presented on Fig. 5b for DW and DW + c_i RR120 (100 mg/L) + H₂O₂ at pH = 2 reveals differences between cavity extent and shedding frequencies. The increase in cavity length is more prominent between 500 and 700 kPa in

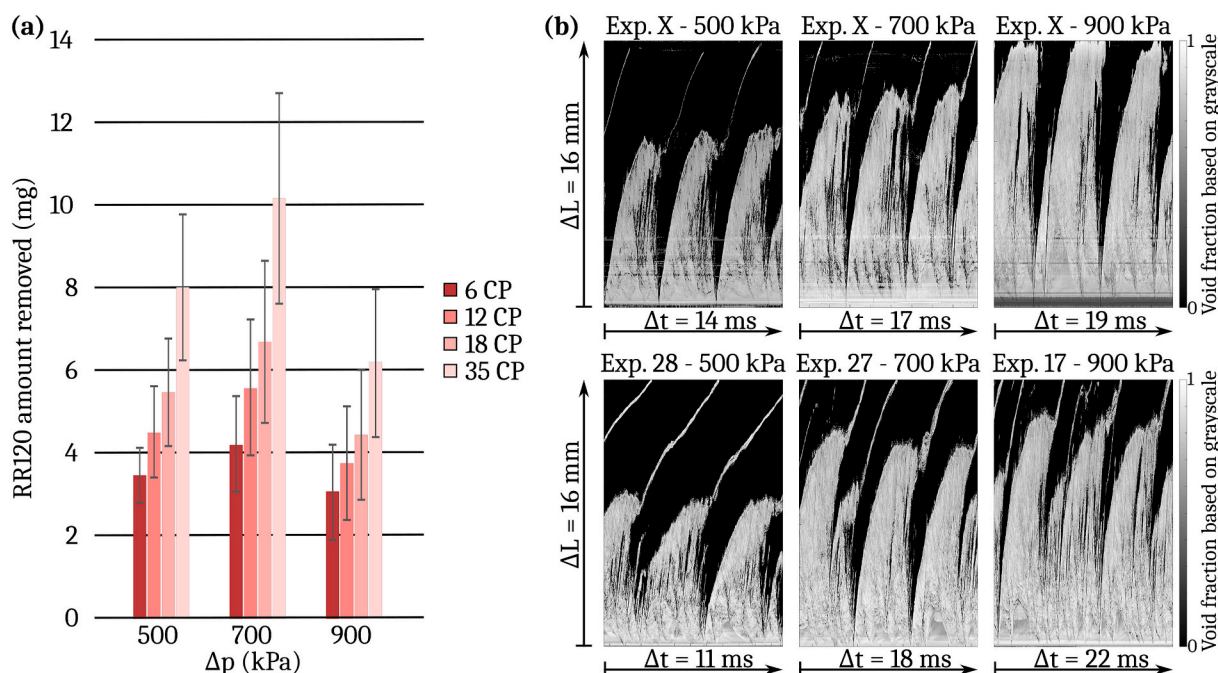


Fig. 5. a) Effect of Δp on the decolorization of RR120. Experiments were performed in 250 mL DW samples at pH = 2, with an initial RR120 concentration of 100 mg/L and the addition of 1700 μM H_2O_2 (Table 2: Exps. 17, 27 and 28). All experiments were performed in triplicates, therefore data are presented as mean $\pm$ standard deviation; CP represents cavitation passes; b) Spatial-temporal presentation of cavitation dynamics for cases with different Δp in DW (Exp. X) and DW + c_1 RR120 100 mg/L + H_2O_2 at pH = 2 (Exps. 17, 27 and 28).

comparison with the 700 and 900 kPa step (Exps. 28, 27 and 17). At lower Δp , the vapor structure is shorter and exhibits a higher oscillation frequency, whereas the transition from 500 to 900 kPa leads to substantial changes in the cavitating flow. However, the relatively small difference between 700 and 900 kPa suggests that the micro-reactor is already approaching choked cavitation conditions at the highest Δp , which suggest that the cavitating region becomes more extended at higher pressure, but not necessarily more effective in terms of productive collapses associated with dye removal. Shedding frequency decreases with higher Δp , which could be an explanation for optimal ratio between cavitation extent and frequency of cavitation structure collapses. At 500 kPa the cavitation extent is the smallest, but with highest shedding dynamics, while at 900 kPa, excessive vapor generation likely promotes the formation of larger vapor clouds and partial coalescence of individual cavities into bigger vaporous structures, which collapse less violently or are transferred downstream without effective collapse and with lower frequency. As a result, the local collapse pressure and temperature decrease, lowering radical generation and overall oxidation efficiency, as also described in other studies [6,20]. This may also indicate that, at lower Δp and consequently lower liquid velocities, interfacial transport conditions are more favourable, enabling more effective diffusion of dye molecules and their accumulation at the bubble surface, where oxidative reactions are expected to occur. Thus, while increasing Δp initially enhances cavitation intensity, further increases may suppress effective bubble collapse and reduce decolorization.

A similar trend was reported by Saharan et al. for the decolorization of 50 mg/L RR120 [6]. In their study, dye removal increased with inlet pressure up to 500 kPa but decreased when the pressure was further raised to 1000 kPa. They correlated degradation efficiency with the cavitation number, observing higher decolorization at lower cavitation numbers until the onset of choked cavitation conditions. Comparable behaviour has also been observed for other azo dyes treated by HC. Innocenzi et al. reported that Methyl Orange removal increased as inlet pressure rose from 84 to 400 kPa (maximum 31.6%) but decreased to approximately 10% at 600 kPa due to choked cavitation [20]. Similarly, Gore et al. showed that decolorization of 40 mg/L Reactive Orange 4

increased up to 500 kPa (37%) and declined at higher pressures [11]. Under choked cavitation conditions, the formation of many cavities at elevated pressures causes coalescence into larger vapor bubbles that no longer behave as individual collapsing cavities, thereby reducing degradation efficiency [11]. Wang et al. observed a similar pressure-dependent trend during degradation of Reactive Brilliant Red K-2BP with 300 mg/L H_2O_2 , where removal increased as pressure rose from 200 to 600 kPa (up to 97%), due to increased pressure drop and bubble formation intensity [39]. Likewise, increasing inlet pressure from 200 to 400 kPa improved Congo Red degradation in the presence of persulfate, which was attributed to higher energy input, greater turbulence, and increased radical formation [3]. In general, increasing inlet pressure enhances energy dissipation, turbulence intensity, and pressure drop across the reactor, all of which promote cavitation intensity and radical generation but only up to an optimal threshold as shown in all the above-mentioned studies.

Finally, when comparing decolorization performance at different Δp , it is essential to ensure that the comparison is made on a consistent basis. Increasing inlet pressure increases the liquid flow rate and therefore the number of passes through the cavitation zone per unit of time. If results are compared solely based on treatment time, higher pressures may appear more effective simply because the liquid is affected by more cavitation events. For this reason, in the present study, performance comparison was based on the number of CP rather than sampling time (Table 2), as also emphasized by [3,11,19]. This approach allows for a more accurate evaluation of the intrinsic effect of inlet pressure on cavitation intensity and removal efficiency.

3.6. The effect of sample volume

The effect of sample volume was evaluated at two initial RR120 concentrations (25 and 100 mg/L), and the results are presented as the absolute amount removed within the treated volume (Fig. 6a and b) and amount removed per CP (Fig. 6c and d). To ensure a fair comparison, all experiments were assessed at identical numbers of CP (up to 35 CP), meaning that each sample, regardless of volume, passed through the

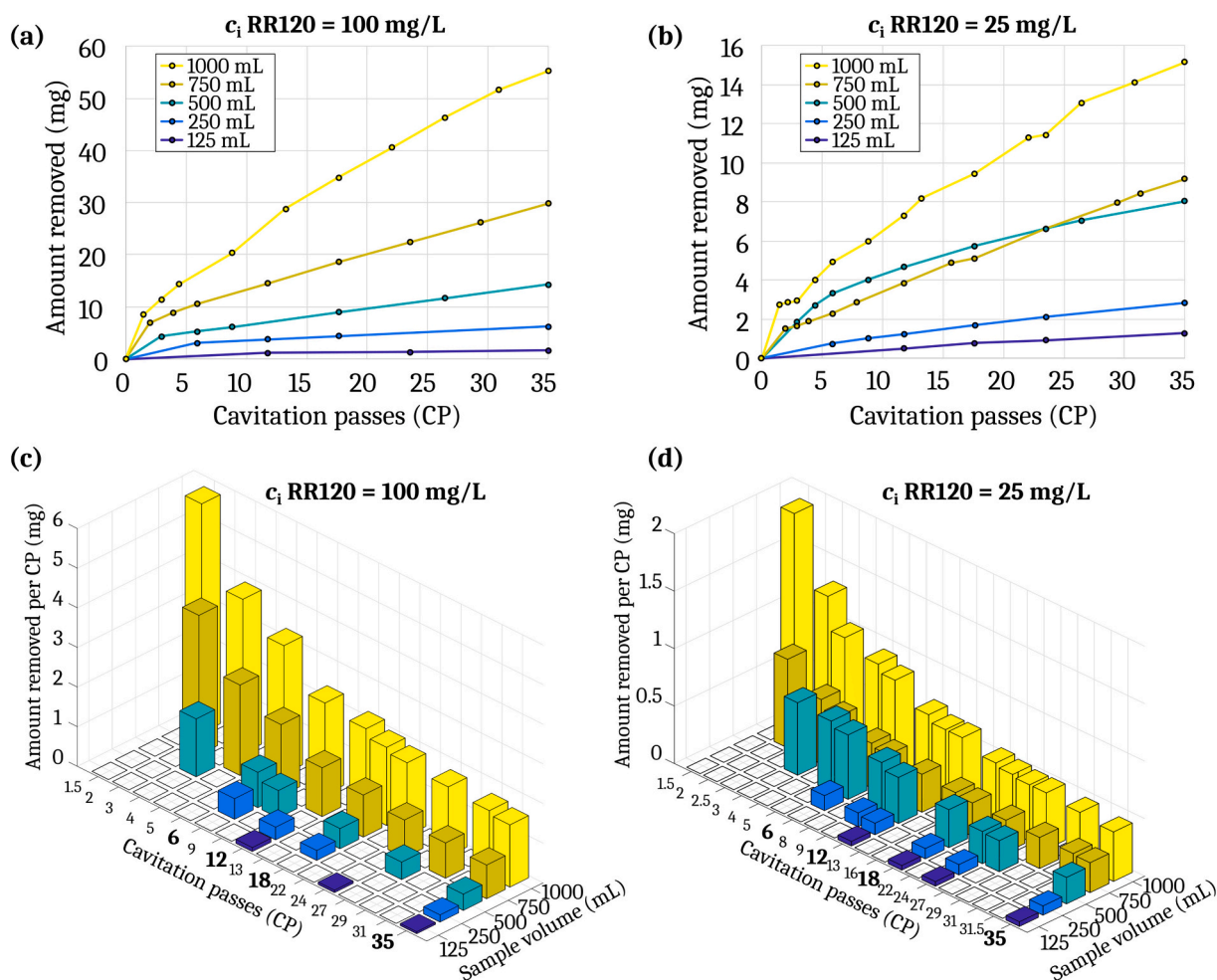


Fig. 6. Effect of sample volume on RR120 removal: a) Amount removed as a function of CP at an initial RR120 concentration of 100 mg/L; b) Amount removed as a function of CP at an initial RR120 concentration of 25 mg/L; c) Amount removed per CP as a function of both, sample volume and CP, at an initial RR120 concentration of 100 mg/L and d) Amount removed per CP as a function of both, sample volume and CP, at an initial RR120 concentration of 25 mg/L. Experiments were performed at pH = 2, Δp of 900 kPa, $Q = 4.9$ mL/s and with 1700 μM of H_2O_2 (Table 2: Exps. 29–38).

cavitation zone the same number of times, based on flowrate measurements (flowrate of 4.9 mL/s at Δp 900 kPa – Fig. 1). For both concentrations, the results show a strong dependence on sample volume, with the highest amount removal observed at 1000 mL (55.3 mg and 15.2 mg for 100 and 25 mg/L, respectively). At 100 mg/L (Fig. 6a), a clear and consistent trend is evident, with RR120 removal increasing proportionally with volume across all treatment times, accompanied by progressively steeper slopes of the curves. A substantial difference was observed between the smallest and largest treated volumes, with 1.7 mg removed at 125 mL compared to 55.3 mg at 1000 mL after 35 CP. This corresponds to a 32-fold increase in removal, far exceeding the 8-fold increase expected from simple linear scaling with volume. In contrast, at 25 mg/L (Fig. 6b), the trend is less pronounced but still evident. After 35 CP, the largest treated volume showed approx. 12 times higher RR120 removal compared to the smallest one (1.3 mg vs. 15.2 mg for 125 and 1000 mL, respectively), instead of expected 8-fold increase.

The comparison of the amount of RR120 removed per CP at the two investigated initial dye concentrations is shown in Fig. 6c and d. In both cases, the highest amount of dye was removed after the first sampling time, regardless of the treated volume, reaching 5.78 mg at 100 mg/L and 1.87 mg at 25 mg/L in the 1000 mL sample. Thereafter, the amount removed per CP decreased with increasing treatment time, which is consistent with the gradual depletion of the parent RR120 molecules after each CP. A clear volume-dependent trend was observed at both initial concentrations, with the highest effectiveness consistently

achieved for the largest treated volume and the lowest for the smallest one. At 100 mg/L, the amount removed per CP decreased from 5.78 mg in 1000 mL to 0.10 mg in 125 mL, whereas at 25 mg/L it decreased from 1.87 mg to 0.04 mg, respectively. For the largest treated volume, the amount removed per CP was therefore approximately three times higher at 100 mg/L than at 25 mg/L. These results indicate that the effect of treated volume is not limited to the total amount of dye present but also influences how effectively each CP contributes to RR120 removal. This is particularly evident at higher initial concentration, where the beneficial effect of increasing volume becomes much more pronounced.

The pronounced differences observed between the treated volumes (Fig. 6) are particularly interesting and suggest that the process may not be governed solely by cavitation. One possible explanation is the contribution of longer-lived reactive oxygen species, which persist for milliseconds to seconds and are less reactive than short-lived $\cdot\text{OH}$ radicals, whose lifetime is typically in the nanosecond range [43,44]. Species such as superoxide anion ($\text{O}_2^{\cdot-}$), hydroperoxyl ($\text{HOO}^\bullet$), and peroxy radicals ($\text{ROO}^\bullet$) may remain active or further react with H_2O_2 after leaving the cavitation zone and continue circulating through the setup. As a result, additional oxidation may occur in the reservoir and along the recirculation loop, extending the effective treatment beyond the cavitation zone itself. This effect is expected to become more important at larger treated volumes, where the overall residence time in the system is longer and these species have more opportunity to react with RR120 for the same number of CP. Although $\cdot\text{OH}$ are generally regarded as the

primary oxidizing species in cavitation-based systems, studies have shown that the above-mentioned longer-lived species can also form in various macro-HC and HC/H₂O₂ systems [45,46]. In addition, azo dyes have been reported to undergo degradation not only by $\bullet\text{OH}$, but also by these reactive species through azo-bond cleavage [47,48]. Therefore, it could be that the improved performance observed at larger treated volumes arises not only from the direct action of $\bullet\text{OH}$ generated during the collapse of cavitation bubbles, but also from the continued oxidation by longer-lived reactive species transported throughout the system. However, it must be pointed out that this explanation is only a hypothesis, and further experiments are needed to determine whether long-lived oxygen reactive species are indeed responsible for the observed sample volume effect. Another possible explanation is that, at higher volumes, the increased total amount of RR120 molecules also increases the probability of their interaction with $\bullet\text{OH}$ because of the prolonged treatment (up to 120 min corresponding to 35 CP), thereby promoting more effective decolorization. In contrast, at lower sample volumes, a fraction of the generated radicals may remain unused due to a lower probability of RR120-radical interaction. These two possible mechanisms may help explain why RR120 removal increases with volume more strongly than would be expected from simple linear scaling alone. Relatively few studies have investigated the effect of sample volume in flow-through HC systems. However, some insights can be drawn from related AOP studies. In a batch-mode cold plasma study on dye degradation, process effectiveness decreased with increasing volume due to dilution of reactive species, which reduced degradation performance [49]. In contrast, opposite behaviour was reported for batch-mode acoustic cavitation, where $\bullet\text{OH}$ formation (assessed via SA dosimetry) increased with volume [50]. This was attributed to improved availability of scavengers under sufficient ultrasonic agitation, enhancing radical use. Results consistent with the present study were reported for a flow-through Venturi HC system combined with plasma-activated water [51]. Increasing the treated volume from 2 to 10 and 20 L led to higher absolute removal of methylene blue at constant initial concentration. Furthermore, when comparing different initial concentrations (0.1 and 0.5 mg/L at 10 and 20 L), higher removals were observed at higher dye concentrations, in agreement with the trends identified in this work.

These findings have important implications for the scale-up of HC treatment systems. Together with our previous observation that micro-scale HC reactors produce stronger chemical effects than conventional macro-scale reactors [26], the present results demonstrate that the enhanced performance of micro-scale HC is maintained, and even improved in terms of energy efficiency, when treating larger liquid volumes. The highest energy yield Y_{RR120} (definition given in Suppl. 9) was achieved at an initial concentration of 100 mg/L and a treated volume of 1000 mL, reaching 0.263 mg/Wh, which is approximately 3.6 times higher than that obtained at an initial concentration of 25 mg/L under the same treatment volume (0.072 mg/Wh). Moreover, increasing the treated volume from 250 mL to 1000 mL increased the energy yield by approximately 5 and 9-fold for c_i of 25 and 100 mg/L, respectively, demonstrating the clear energy advantage of processing larger solution volumes. Because energy yield strongly depends on reactor design, operating conditions, pollutant concentration, treatment time, and the applied oxidation process, direct comparison between different HC studies is difficult and should be interpreted with caution. Nevertheless, Askarniya et al. reported an energy yield of approximately 0.030 mg/Wh for Congo Red decolorization using macro-scale HC combined with Fenton's reagent (1000 mg/L H₂O₂, 25 mg/L Fe₂SO₄) at an initial dye concentration of 20 mg/L, pH = 3, 6 bar, and a treatment time of 60 min [15]. These findings suggest that arrays of micro-reactors operated in parallel or in series could provide a potential route towards process scale-up while preserving the hydrodynamic characteristics of individual micro-reactors. However, further research is needed to better understand the observed volume effect and evaluate whether this approach remains effective at larger treatment capacities and with more

complex water matrices.

3.7. Radical production using SA dosimetry

The results presented in Fig. 7a show the formation of the most representative oxidation product of SA (2,3-DHBA) under acidic conditions (pH < pK_a), whereas the results of the 2,5-DHBA products are shown in Suppl. 10. These products are generated via electrophilic hydroxylation of SA by $\bullet\text{OH}$ produced in the HC micro-reactor. Due to its high reaction rate constant with $\bullet\text{OH}$, the formation of stable hydroxylated products, and its selectivity towards $\bullet\text{OH}$, SA dosimetry is widely employed as a reliable method for indirect quantification and comparative assessment of $\bullet\text{OH}$ generation in AOPs, including HC, under varying experimental conditions [33]. The results show that the concentrations of both products increase with the number of CP, reaching maximum values after 35 CP. For both products the most pronounced increase occurs between 18 and 35 CP, reflecting a longer treatment period compared to earlier intervals. Furthermore, 2,3-DHBA is consistently formed in greater amounts than 2,5-DHBA. This preferential formation has also been observed in our previous investigations using a macro-scale Venturi and orifice HC reactor [33,52] and three different micro-scale HC reactors [26]. In SA molecules, the -OH and -COOH functional groups influence the electron-density distribution within the aromatic ring and consequently determine the preferred sites of electrophilic $\bullet\text{OH}$ attack, particularly at positions ortho and para to the phenolic -OH group. The relative formation of 2,3-DHBA and 2,5-DHBA was shown to depend on the specific AOP, reaction conditions, and the presence of catalysts, metals, or other additives. Chakinala et al. [53] demonstrated that, under acoustic cavitation, the 2,3-DHBA/2,5-DHBA ratio changed with the addition of different substances and under conditions of enhanced oxidative activity. They proposed that adsorption of SA on a solid catalyst surface may favour hydroxylation at the 5-position because attack at the neighboring 3-position may be sterically hindered by the carboxyl group. Gruber et al. [54] likewise showed that the formation of both DHBA isomers is sensitive to the surrounding reaction environment, with oxygen concentration, metal catalysis, and ultrasonic irradiation affecting their concentrations. Moreover, Arrojo et al. [55] reported a different product distribution in a Venturi-type HC system, where 2,5-DHBA predominated over 2,3-DHBA. These findings suggest that the relative distribution of the two DHBA isomers is strongly influenced by the physicochemical environment and cavitation conditions. The highest concentrations of SA products after 35 CP (2.53 ± 0.4 µg/mL for 2,3-DHBA and 0.33 ± 0.13 µg/mL for 2,5-DHBA) were obtained at an inlet pressure of 900 kPa. For 2,3-DHBA, the mean concentration appears noticeably elevated at 900 kPa compared to lower Δp , whereas no statistically meaningful difference is evident for 2,5-DHBA across the investigated pressure range. The statistical analysis using ANOVA (Suppl. 11a) shows that number of CP strongly affected formation of 2,3-DHBA ($p = 2.578 \cdot 10^{-12}$), while the overall main effect of Δp was not significant ($p = 0.160$). However, post hoc comparisons (Suppl. 11b) indicated that pressure influenced 2,3-DHBA formation at the final sampling time (after 35 CP), with higher values formed at 900 kPa than at 500 or 700 kPa. No significant differences among pressures were observed at earlier sampling times.

It is interesting to note that $\bullet\text{OH}$ production increases with increasing Δp , whereas RR120 decolorization improved only up to 700 kPa and then decreased (Fig. 5a). It should be pointed out that the two investigated solutions (RR120 with H₂O₂ and SA without H₂O₂) differed in their physicochemical properties, consequently, the cavitation dynamics were not identical despite same operating conditions. As shown in Figs. 2d, e and 7b, cavitation generated at $\Delta p = 900$ kPa exhibited a comparable overall cavity length in both cases. However, the morphology of the cavitation structures differed considerably. In particular, the cavitation cloud observed for the SA solution (Exp. SA1) appeared to undergo more extensive fragmentation, resulting in the formation of a higher number of microbubbles than in Exp. 17 (RR120

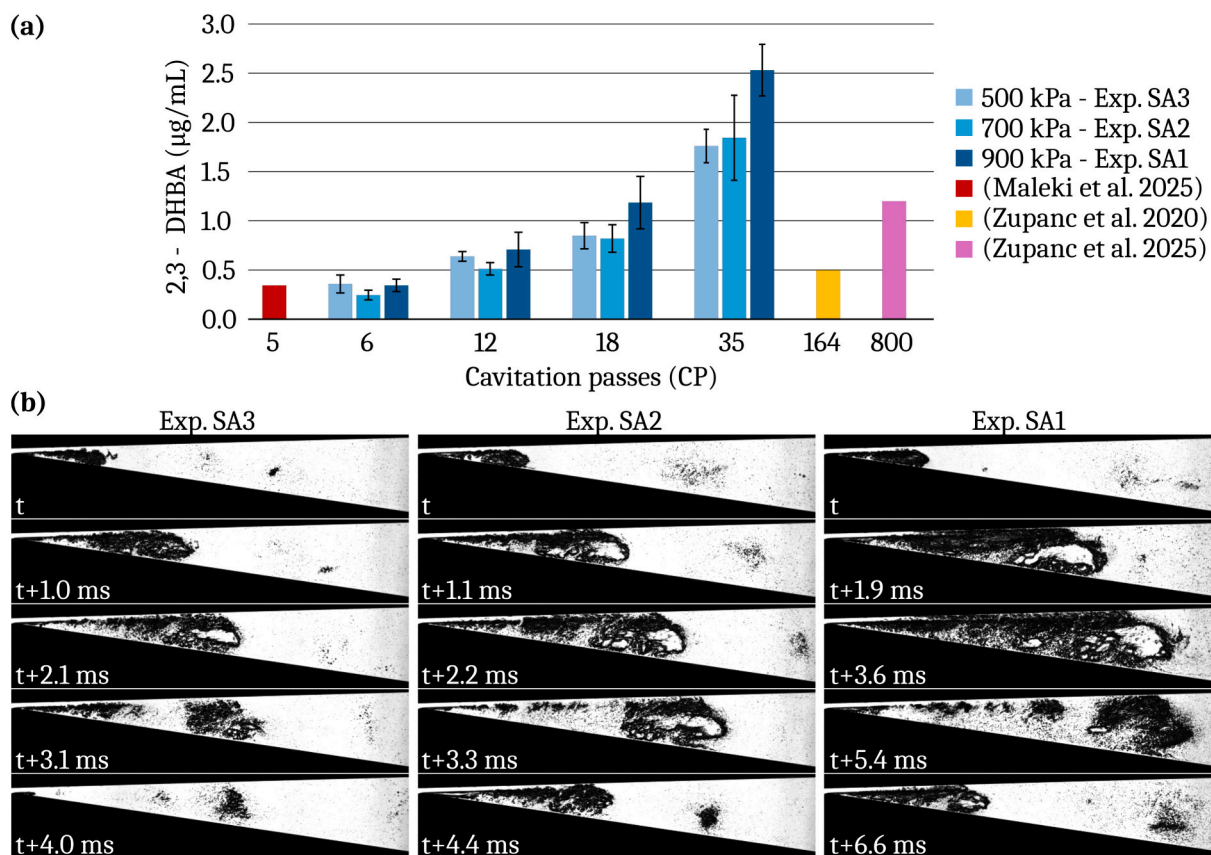


Fig. 7. a) Concentrations (µg/mL) of the main SA product formed in a Venturi HC micro-reactor at three Δp (500, 700 and 900 kPa) using 300 mg/L SA. Experiments were performed in 250 mL DW samples at pH < 3 (Table 2; Exps. SA1–SA3). All experiments were performed in triplicates, therefore data are presented as mean $\pm$ standard deviation; b) Visualization under selected experimental conditions (Exps. SA1–SA3).

with H_2O_2). Since microbubble collapse is closely associated with $\cdot\text{OH}$ generation, this difference may have contributed to the higher reactor effectiveness for radical production measured by SA dosimetry [31]. At the same time, the relatively small increase in cavity length and the lower shedding frequency between 700 and 900 kPa suggest that the micro-reactor may be approaching choked cavitation conditions at the highest Δp , although this cannot be considered direct proof of fully developed choking. Unlike SA, RR120 is a substantially larger and more complex molecule. During its oxidation, numerous intermediate products are formed, many of which are also susceptible to reactions with $\cdot\text{OH}$ radicals. These intermediates therefore compete with the parent dye for the available reactive oxidizing species, reducing the fraction of radicals available for RR120 decolorization. In combination with the observed differences in cavitation dynamics, this competitive radical consumption may explain the lower decolorization efficiency at $\Delta p = 900$ kPa, despite the higher $\cdot\text{OH}$ yield determined by SA dosimetry (Fig. 7). Similar pressure-dependent behaviour has also been reported for macro-scale HC systems, where dye removal decreased above an optimum pressure and was associated with the onset of choked cavitation [6,11,20].

When comparing the chemical effects of cavitation in micro-reactors under different operating conditions (e.g., Δp), the spatial distribution, size, and collapse dynamics of individual cavitation bubbles are critical parameters [26]. The formation of $\cdot\text{OH}$, determined via SA hydroxylation, is directly governed by the number of cavitation events and the intensity of bubble collapse. In general, increasing inlet pressure enhances the pressure drop across the constriction, reduces cavitation number, and promotes the formation of a greater number of vapor cavities. This typically leads to a higher density of localized hot spots upon collapse and, consequently, stronger chemical effects, as reflected

in Fig. 7a after 35 CP. In our previous study [26], it was demonstrated that both micro-reactor geometry and inlet pressure significantly influence the magnitude of chemical effects. Specifically, inlet pressures of 900 and 1300 kPa in a micro-orifice design produced more radicals compared to 1100 kPa in a micro-Venturi and 11,500 kPa in a long diaphragm reactor. Flow visualization (Fig. 7b) and pressure pulsation analyses further support these observations (Table 3). At lower pressure difference, fewer cavitation bubbles are formed, and their collapses are less intense, resulting in weaker chemical effects. In contrast, higher pressure difference generates a more turbulent and spatially extended cavitating flow field, increase both frequency and intensity of collapse events. Enhanced turbulence improves mass transfer between gas and bulk liquid phase, thereby increasing the probability of interactions between SA molecules and $\cdot\text{OH}$. Moreover, the development of shear layers downstream of the constriction promotes additional cavitation events and improved dispersion of individual vapor structures, further contributing to chemical activity. In micro-scale HC reactors, the cavitating flow may also exhibit Kelvin-Helmholtz instabilities at liquid-vapor interfaces, more pronounced at higher flow velocities, which could further enhance interfacial mixing [35]. These hydrodynamic features collectively explain the pressure-dependent increase in SA hydroxylation at higher Δp observed in the present study.

When the present results (Fig. 7a, red and dark blue column) are compared with those obtained in a macro-scale system (Fig. 7a, yellow and violet column), a pronounced difference in chemical effects between macro- and micro-scale reactors becomes evident, whereas the difference between the two micro-reactor designs is negligible. In a macro-scale Venturi reactor [33], the concentration of 2,3-DHBA reached 0.49 ± 0.0 µg/mL after 164 CP at the pressure difference of 700 kPa, whereas in a macro-scale orifice reactor [52] 1.2 µg/L concentration was

reached after 800 CP at 700 kPa. In contrast, comparable concentrations were achieved in micro-scale systems after only a few passes: 0.34 ± 0.1 $\mu\text{g/mL}$ after 5 CP in our previous study [26] and 0.34 ± 0.07 $\mu\text{g/mL}$ at 900 kPa after 6 CP in the present study. As discussed in this work, the enhanced chemical effects of micro-scale reactors can be attributed to their higher surface-area-to-volume ratio, improved mixing, and shorter diffusion pathways, which together promote higher mass transfer rates. Additionally, micro-reactors tend to generate more stable and spatially uniform cavitating flow structures, leading to more efficient and reproducible bubble collapse events and, consequently, increased radical formation per CP.

3.8. Results of ML analysis

3.8.1. Prediction models performance

A sufficient prediction performance was achieved only for Model 1. Model 1 can predict the removed amount of RR120 based on the volume, RR120 concentration, pH, H_2O_2 , and Δp with the coefficient of determination (R^2) value of 0.84, while Model 2 failed to predict the removed amount of RR120 based on the cavitation descriptors: frequency, pressure peak mean, D , and cavity length ($R^2 = 0.09$). Table 4 shows the best algorithms and their prediction performances, while Fig. 8a shows predicted vs. actual removed amount of RR120 for Model 1 and the corresponding best algorithm, i.e. SVR RBF (C: 100; ϵ : 0.05; γ : 0.1). The low predictive performance of Model 2 ($R^2 = 0.09$) may originate from two related factors: insufficient information contained in the selected cavitation features and/or a complex nonlinear relationship between cavitation behaviour and RR120 oxidation. To investigate the latter possibility, both linear and machine-learning algorithms capable of capturing nonlinear relationships and based on different modelling principles were evaluated. However, none of the tested approaches resulted in satisfactory predictive performance for Model 2. This suggests that increasing model complexity alone is insufficient to adequately predict the removed amount of RR120 from the currently available features. Therefore, the poor performance of Model 2 is likely at least partly related to limitations in the available predictor set. The selected cavitation features may not fully represent the physical and chemical processes governing RR120 oxidation. More flexible approaches such as deep-learning models could, in principle, capture higher-order nonlinear interactions. However, the number of available experimental observations in the present study is insufficient for reliable training of such models and would result in a high risk of overfitting. Consequently, the low R^2 of Model 2 should primarily be interpreted as indicating that the currently available cavitation-related features do not contain sufficient predictive information to accurately estimate RR120 removal, rather than simply as a limitation of the particular regression algorithm used. Future studies should combine the present measurements with more spatially and temporally resolved descriptors of bubble collapse, direct radical measurements in the RR120 reaction matrix, and a larger dataset covering a broader operating range. In addition, all measurements were obtained using a single micro-reactor geometry. Systematic variation of the throat dimensions, channel aspect ratio, convergent and divergent angles could generate a broader range of cavitation regimes and may help determine whether these descriptors contain stronger predictive information. However, improved predictive performance cannot be assumed without testing a larger and more

balanced dataset covering multiple geometries.

The above results show that the patterns from which the removed amount of RR120 can be predicted exist only in the first set of parameters, i.e., volume, RR120 concentration, pH, H_2O_2 , and Δp . In the parameters that were used in Model 2 (cavitation description parameters of frequency, pressure peak mean, D , and cavity length), at least the tested algorithms and the tested hyperparameter combinations cannot reveal patterns for sufficient prediction performance. Because only Model 1 achieves sufficient performance, only Model 1 was used in further feature importance analysis.

3.8.2. Feature importance analysis results

Fig. 8b shows results of permutation-based feature importance analysis. Within the investigated dataset, sample volume and initial RR120 concentration were identified as the most important parameters, whereas pH, H_2O_2 concentration, and Δp showed lower importance. It should be emphasized that permutation-based feature importance is inherently dataset-specific and depends strongly on both the range and combination of feature values represented in the experimental dataset. Consequently, the obtained feature-importance ranking should be interpreted as applying to the investigated operating window and water matrix rather than as a universally applicable ranking of the governing process parameters. In other operating ranges, or in more complex water matrices such as real textile wastewater, the relative importance of these parameters may differ due to additional constituents and interactions not represented in the present dataset. Likewise, insufficient variation of a particular feature within the dataset may result in a low estimated importance even when that parameter may exert an important effect under other conditions.

Possible correlations among the input features were additionally evaluated because strongly correlated predictors can affect the interpretation of feature-importance results. Pearson and Spearman correlation coefficients were calculated for all pairwise combinations of the Model 1 input parameters (sample volume, initial RR120 concentration, pH, H_2O_2 concentration, and Δp). No significant correlations between the input parameters were detected in the experimental dataset, reducing the likelihood that the identified feature-importance ranking primarily reflects correlations among the model inputs.

4. Conclusions

This study demonstrated that a Venturi-type hydrodynamic cavitation micro-reactor can effectively decolorize Reactive Red 120, with performance strongly influenced by operating conditions and solution composition. Acidic conditions significantly enhanced decolorization, with the best performance at $\text{pH} = 2$, while H_2O_2 further improved removal up to an optimum concentration, above which radical scavenging most likely reduced efficiency. The effect of pressure difference was less direct, although $\cdot\text{OH}$ formation increased with Δp and was highest at 900 kPa, maximum RR120 decolorization occurred at 700 kPa, showing that stronger chemical effects do not necessarily translate into greater decolorization. Sample volume had the strongest and most unexpected effect. An eightfold increase in treated volume resulted in a 32-fold and 12-fold increase in dye removal at 100 and 25 mg/L RR120, respectively, suggesting that larger volumes at the same number of cavitation passes improve the process effectiveness. Salicylic acid dosimetry confirmed that the micro-Venturi exhibited chemical activity comparable to previously studied micro-reactors, while outperforming macro-scale reactors. Machine learning further identified sample volume and initial dye concentration as the most important predictors of dye removal.

From a practical perspective, the strong volume effect suggests promising scale-up potential through multiple micro-reactors operated in parallel or in series rather than by conventional reactor enlargement. However, since the presented results were obtained in a simple water matrix, their applicability to real textile wastewater needs to be

Table 4
The best algorithms and their prediction performances.

	Best algorithm	Mean absolute error (mg in 250 mL)	Root mean square error (mg in 250 mL)	R^2 (/)
Model 1	SVR RBF	1.90	3.97	0.84
Model 2	Random Forest	4.92	9.39	0.09

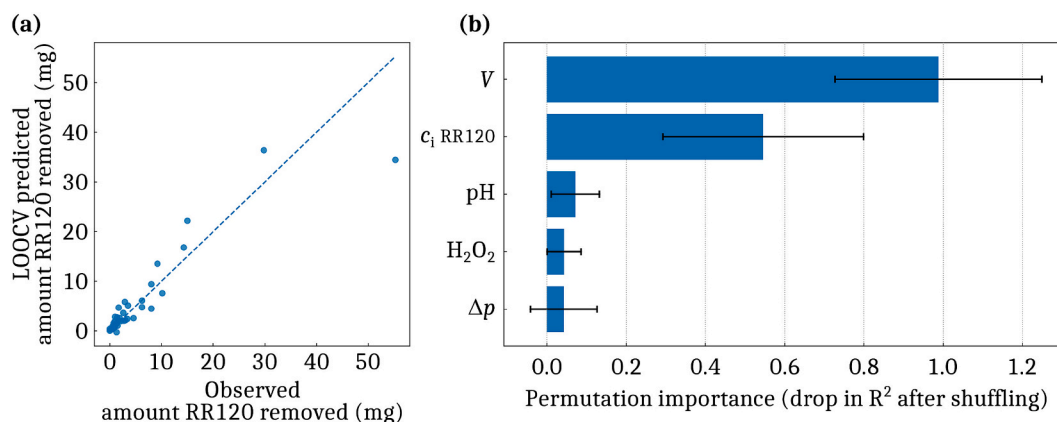


Fig. 8. a) Predicted vs. actual values of the removed amount of RR120 (Model 1, SVR RBF algorithm); b) feature importance analysis result for Model 1.

validated because as both cavitation behaviour and radical based reactions may be affected in more complex water matrices. Future studies should also assess mineralization, identify degradation products, and evaluate the toxicity of treated solutions to establish the environmental relevance and safety of the process. Furthermore, in-depth research is needed to confirm these results under optimized operating conditions using real textile wastewater, where salts, organic matter, and other coexisting constituents may influence cavitation behaviour and treatment efficiency.

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CRediT authorship contribution statement

Martin Petkovšek: Writing – original draft, Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Validation. **Alberto Benato:** Writing – review & editing, Supervision, Resources. **Matevž Dular:** Conceptualization, Writing – review & editing, Visualization, Methodology. **Dominik Kozjek:** Writing – original draft, Visualization, Investigation. **Edoardo Sech:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology. **Alenka Šmid:** Writing – original draft, Methodology, Formal analysis, Data curation. **Mojca Zupanc:** Funding acquisition, Writing – original draft, Conceptualization, Methodology, Investigation, Formal analysis, Validation, Supervision, Writing – review & editing, Resources, Project administration.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT only to improve language and readability. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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.

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Data availability

Data are available at Zenodo link: <https://doi.org/10.5281/zenodo.20137153>.

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