# Treatment of the spent caustic wastewater by hydrodynamic cavitation and its combination with $H_2O_2$ and Air

Kolivand Zahra[a], Nabi Bidhendi Gholam Reza[b*], Mehrdadi Naser[c]

[a] PhD Candidate, Faculty of Environment, College of Engineering, University of Tehran, Tehran, Iran

[b] Prof., Faculty of Environment, University of Tehran, Tehran, Iran

[c] Prof., Faculty of Environment, University of Tehran, Tehran, Iran

**Abstract:** One of the issues in the world is the spent caustic wastewater with high TDS, which can cause many problems in the environment. This study investigates the treatment of spent caustic wastewater with high total dissolved solids (TDS) using hydrodynamic cavitation (HC), both independently and in combination with air and hydrogen peroxide ($H_2O_2$). The investigation focused on the influence of various operational parameters, including inlet pressure, temperature, initial concentration, recirculation time, TDS concentration, $H_2O_2$ concentration, and air volume, to optimize the chemical oxygen demand (COD) degradation. The results indicated that HC alone, utilizing an orifice-based cavitation device with a 4 mm orifice diameter under optimal conditions specifically, an inlet pressure of 4 bar, temperature of 30 °C, pH of 7.5, and a residence time of 120 minutes achieved COD, phenol, and sulfide degradation rates of 39%, 100%, and 7.15%, respectively. The integration of HC with $H_2O_2$ at an optimal COD to $H_2O_2$ molar ratio of 1:1 enhanced COD removal efficiency to 78.75%, whereas the combination of HC and air adversely affected the treatment of the effluent. The results further indicated that the decomposition of spent caustic wastewater followed a second-order kinetics. The energy efficiency and operational costs of the various combined processes were compared based on cavitation efficiency and electricity cost, revealing that the combined HC and $H_2O_2$ process was the most economical due to its superior cavitation efficiency and reduced electricity consumption.

**Keywords:** Hydrodynamic Cavitation (HC), Spent Caustic Wastewater, Advanced oxidation processes (AOP), Kinetics, Cavitation Yield

## 1. Introduction

Recent advancements in various sectors and their industrial applications have resulted in the proliferation of pollutants and hazardous substances that exhibit resistance to biodegradation [1]. Industries such as oil, gas, petrochemical, and chemical refineries are notable for generating diverse forms of hazardous waste. These facilities typically employ sodium hydroxide (NaOH), commonly referred to as caustic soda, as a chemical cleaning agent to eliminate sulfur compounds, including hydrogen sulfide, cresylic acids, mercaptans, and naphthenic acids. The resultant wastewater from this process is termed waste caustic [2]. In petrochemical industries, waste caustic is predominantly produced during the extraction of aromatic compounds or the production of BTXs, characterized by relatively high concentrations of sulfide and phenolic compounds. This wastewater poses challenges such as offensive odors, pH fluctuations, foaming, or inadequate settling of biological solids in biological treatment processes. Consequently, due to its low biodegradability, achieving effluent standards for this wastewater can be challenging. Typically, this type of wastewater undergoes biological treatment with significant dilution [3].

As previously noted, spent caustic is a hazardous wastewater, and its release into the environment causes contamination of resources such as water and soil, thereby posing a threat to living organisms. For instance, sulfide compounds in discarded caustic not only produce unpleasant odors but also constitute hazardous substances that must be partially treated in compliance with regulations before environmental discharge. Additionally, phenol in discarded caustic, a cyclic aromatic hydrocarbon, exhibits high solubility in water and environmental stability. Furthermore, phenol was identified as one of the 129 priority pollutants for removal in 1982, according to the USEPA [4] classification, due to its toxicity, impact on water taste and odor, and detrimental effects on humans and living organisms. From another perspective, one of the main components of spent caustic wastewater is salt, the salinity of which varies from 1,000 to 150,000 mg/L. Moreover, COD in this wastewater typically varies from 5,000 to 240,000 mg/L. Therefore, treating the COD in this type of wastewater to achieve environmental discharge standards, despite the high salinity concentration, presents numerous challenges. High salinity induces toxicity in bacteria, rendering biological methods without pretreatment unfeasible. High salt concentrations adversely affect biological systems, thereby reducing the efficiency of organic matter removal [2,5,6].

Recent studies have been explored various methodologies for the treatment of spent caustic wastewater, including wet, classic, and advanced air oxidation, Fenton chemical oxidation, liquid-liquid extraction, neutralization, membrane distillation, polymer and ceramic nanofiltration membranes, biochar, photocatalysis, electrocoagulation, and biological methods such as fluidized bed reactors, gas lift reactors, and sequencing batch reactors (SBR), among others. A significant observation in these studies is the implementation of a dilution step before treatment with some of the aforementioned processes, including biological treatment [2,7–16].

Conversely, advanced oxidation methods have been identified as a promising approach for treating such wastewaters. These processes are predicated on the generation of highly reactive hydroxyl radicals (●OH), which react non-selectively with most organic materials and are capable of degrading highly resistant compounds [17]. In recent years, cavitation has emerged as a promising technique for the oxidation of various pollutants in wastewater. Typically, cavitation involves three phases: the formation, growth, and eventual collapse of the bubbles, which over time release significant energy on a microscale. This process leads to the production of free radicals, local hot spots, and intense turbulence, all of which are conducive to the oxidation of pollutants [18].

Cavitation induced by ultrasound waves (frequency range of 16 kHz to 2 MHz) is predominantly used for wastewater treatment; however, the use of ultrasonic reactors for large-scale operations presents significant challenges, including energy inefficiency and high operational costs. To address these limitations, hydrodynamic cavitation (HC), which involves inducing pressure changes through alterations in flow geometry, has been proposed as an efficient alternative with considerable potential [19]. Among the various cavitation generation techniques, HC offers the greatest active areas and energy efficiency [20].

HC offers a cost-effective alternative by using expensive chemicals, such as hydrogen peroxide and Fenton reagents, while reducing the formation of undesirable by-products, such as acetic acid, which can lead to corrosion in the wet air oxidation process. This technique can be conducted at neutral pH levels, unlike the Fenton method and other advanced oxidation processes, thereby eliminating the need for costly chemical adjustments to lower the pH of wastewater. Furthermore, this method is recognized as a green chemistry approach due to its minimal environmental impact.

Numerous studies have been conducted on the utilization of HC and its combination with other processes, primarily focusing on removing specific pollutants from water or wastewater. For instance, Wang et al. [21] examined the removal of tetracycline at a concentration of 30 mg/L using HC, reporting a degradation rate of 12% for the pollutant. By combining HC with $TiO_2$, they achieved a removal efficiency of 78.2% for a concentration of 100 mg/L. In another study, Rajoriya et al. [22] investigated the use of HC for the removal of Rhodamine 6G (Rh6G) at a concentration of 10 mg/L, achieving a 32% degradation of the pollutant during 120 minutes. Additionally, Saxena et al. [23] used coagulation and cavitation as a pretreatment method in tannery wastewater to reduce COD, TOC, and TSS and enhance the biodegradability of the wastewater, making it suitable for anaerobic digestion. Rajoriya et al. [24] investigated the treatment of wastewater from the textile dyeing industry using HC in combination with advanced oxidation reagents, including air, oxygen, ozone, and Fenton reagent. The study investigated the influence of various process parameters, such as inlet pressure, cavitation number, wastewater concentration, ozone and oxygen flow rate, $H_2O_2$ loading, and Fenton reagent, on the reduction of TOC, COD, and color. The highest removal efficiency was observed in the combined mode of HC and Fenton reagent, achieving a 48% reduction in TOC and a 38% reduction in COD within 15 and 120 minutes, respectively, along with nearly complete decolorization (98%) of the effluent. Boczkaj et al. [25] indicated the application of HC aided by external oxidants ($O_3$/$H_2O_2$/Peroxone) to reduce the total pollutant load in bitumen production effluent. They determined that the most effective treatment process involved HC with ozonation, resulting in a 40% reduction in COD and a 50% reduction in BOD. The study also indicated that most volatile organic compounds

(VOCs) were effectively degraded during these processes. Innocenzi et al. [26] investigated the degradation of tetramethylammonium hydroxide (TMAH) from synthetic liquid wastes in the electronics industry by using an HC process. They achieved a removal efficiency of 44% for synthetic solutions with an initial concentration of 2 g/L, utilizing a venturi tube at 4 bar pressure, pH=3, for 20 minutes. Thanekar et al. [27] examined the degradation of various pollutants, including pharmaceuticals, pesticides, phenolic derivatives, and dyes, as well as the treatment of actual industrial wastewater using combined HC-based methods (HC/$H_2O_2$, HC/$O_3$, HC/Fenton, HC/UV, and HC). Their findings indicated that combining HC with other AOPs enhanced degradation due to the increased production of hydroxyl radicals. They also noted that while acidic conditions favor cavitation-based treatment, the benefits must be balanced against the operational costs, as pH adjustment incurs additional chemical expenses. Arbab et al. [28] investigated the removal of Reactive Black 5 (RB5) from textile wastewater using HC (employing an orifice plate with an inlet pressure of 4 bar) in combination with photocatalysts. The findings indicated that the combined process was the most effective, achieving a decolorization efficiency of 83%. Thanekar et al. [29] examined the degradation of benzene-contaminated wastewater through HC and compared the results with a combination of HC and air. The study reported a maximum energy efficiency of 53.4% at an inlet pressure of 3.9 bar. It was also observed that the combined techniques performed significantly better than cavitation alone in the degradation of phenolic derivatives. Wang et al. [30] used pefloxacin (PEF) in a study to degrade HC using ozone and $H_2O_2$ oxidants. The results exhibit that the highest PEF removal efficiency of 91.5% was achieved through the combination of HC with $O_3$ within 20 minutes. In another study, Mohod et al. [31] indicated the impact of various parameters on the pollutant degradation rate, alongside strategies for optimizing operating conditions, concluding that HC holds significant promise for industrial wastewater treatment. Merdoud et al. [17] investigated the removal of Methyl Orange (MO) from synthetic wastewater using HC alone and in combination with $H_2O_2$ and a Photocatalyst (PC), employing a catalyst coated on Glass Fiber Tissue (GFT). The data indicated that using HC with vortex cavitation at a pressure drop of 1.5 bar and a residence time of 230 minutes caused a degradation of over 9%. The addition of $H_2O_2$ reduced the degradation time from 230 to 36 minutes. Ultimately, the degradation time was further reduced to 21 minutes by combining HC with PC using glass fibers coated with $TiO_2$ and $H_2O_2$. Chaudhuri et al. [32] simulated a numerical method to provide a comprehensive depiction of radical production and its locations, guiding the design of a novel and efficient cavitation reactor. Xue et al. [33] showed that a reverse-rotation HC reactor has a significant efficacy in the disinfection of seawater. In another study, Liu et al. [34] explored the application of a rotating HC reactor for the degradation of organic pollutants. They achieved an 84.3% destruction rate of simulated colored wastewater in 18 minutes. Marques et al. [35] investigated the treatment of textile wastewater, finding that cavitation and ozone alone resulted in removal efficiencies of 45% and 56% for apparent color and COD, respectively. Also, in another scenario, when employing a combination of coagulation-flocculation followed by HC and ozone, the study achieved removal efficiencies of 94%, 97%, and 84% for color, turbidity, and COD, respectively.

Review of previous research indicates that the use of HC in the treatment of spent caustic wastewater has not been investigated yet. Vice versa, HC has been effective in the treatment of various pollutants, including Reactive Red 180, Reactive Black 5, Rhodamine 6G, benzene, chlorophenol, 4-chloro 2-aminophenol, dimethylhydrazine, trimethylammonium hydroxyl, tetracycline, diclofenac sodium, and carbamazepine, as well as in the treatment of wastewaters from textile, tanning, distillery wastewater, and other industrial sources. These studies have assessed the use of HC alone or in combination with other AOPs such as ozone, air, oxygen, Fenton reagents, photocatalysts, acoustic cavitation, coagulation, UV, ZnO, $TiO_2$, among others.

Considering these factors and the benefits of the HC method, it seems that using this method for spent caustic wastewater treatment is a suitable field for research.

This study aims to reduce COD, phenol, and sulfide concentrations in spent caustic wastewater, which is characterized by high concentrations of TDS, without diluting the wastewater with water or other effluents. This reduction is achieved through the use of HC, both independently and in combination with air and $H_2O_2$. Additionally, the study aims to clarify the kinetics of COD removal.

In this study, we investigate the use of the HC method to remove COD from the spent caustic wastewater of a petrochemical facility located in Assaluyeh, southern Iran, to enable the discharge of treated wastewater into the sea. Given the high salinity of the spent caustic wastewater under investigation, and considering the ultimate goal of marine discharge, salinity reduction was not a focus of this study. Instead, the emphasis is placed on identifying a method capable of effectively reducing COD in high salinity. Furthermore, even if salinity removal systems are deemed necessary, it is imperative first to reduce the COD of the wastewater to achieve the standard levels required for such systems. Thus, the reduction of COD is of paramount importance. It should be noted that following COD reduction, the wastewater can be directed to the reverse osmosis (RO) section for reuse, or it can be combined with other treated wastewater within the facility and subsequently processed by desalination units.

## 2. Materials and Methods

As mentioned in section 1, in this study, the spent caustic wastewater of a petrochemical facility located in Assaluyeh was used. The concentration of pollutants present in this wastewater is shown in Table 1.

**Table 1. Properties of spent caustic wastewater from a petrochemical facility in southern Iran**

| Parameter | Value (Output of Neutralization) |
|---|---|
| BOD | 200-2500 mg/L |
| COD | 1000-5000 mg/L |
| TSS | 200-500 mg/L |
| TDS | 10000-50000 mg/L |
| Phenol | 0-20 mg/L |

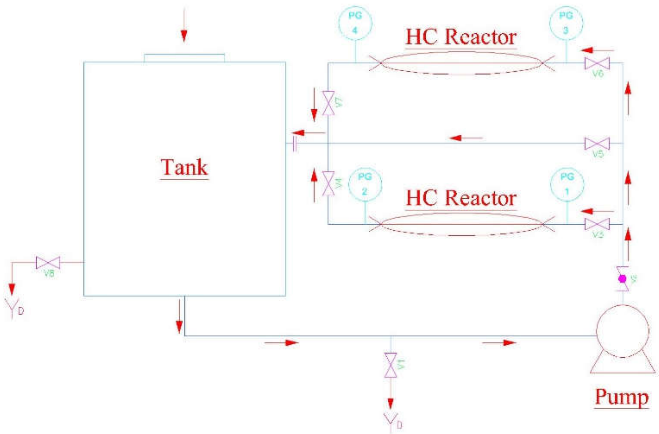
| | |
|---|---|
| $Na_2S$ | 0-20 mg/L |
| pH | 6-8 |
| Temp. | 40°C |

The data presented in Table 1 shows that the BOD/COD ratio ranges from 0.2 to 0.5. According to the literature, the optimal range for this ratio in biological treatment is reported to be between 0.3 and 0.8. Therefore, using a pretreatment stage appears necessary to enhance the biodegradability of the wastewater, for which advanced oxidation methods are usually used. Furthermore, based on information from various sources, it is evident that the application of aerobic biological systems for treating COD levels higher than 1500 mg/l is not economically possible; therefore, the existence of a pretreatment stage in such scenarios seems necessary. This pretreatment may include various anaerobic biological methods or oxidation methods. To solve the mentioned challenges, the present study considers the use of an HC reactor and its combination with $H_2O_2$ and air as a pretreatment. This approach is also anticipated to be effective in the removal of phenol and sulfide, thereby reducing the impact of toxic shock caused by these pollutants on the biological system.

To execute this project, actual wastewater and a semi-industrial scale pilot (Fig. 1) were used. It is important to note that to ensure precise analysis and establish stable conditions in the subsequent stages of the experiment, synthetic wastewater was used.

The pilot system includes the following components: a 80 liter water tank constructed from triple-walled polyethylene; a one-way valve located at the outlet of the cavitation reactor to prevent backflow into the pump; an inlet water pump ($Q_{max}$=50l/min, $H_{max}$=180m) with a power rating of 2.2 kW; an air pump with a power rating of 0.02 kW, a connecting pipe between the pump and the tank, with a diameter of 25 mm; a cavitation generating device, specifically an orifice plate with a hole diameter of 4 mm; and pressure gauges positioned before and after the orifice plate to monitor the upstream and downstream pressures.

The preparation of synthetic wastewater includes the use of several chemicals, each offering a specific purpose: Glucose ($C_6H_{12}O_6$) is utilized as a carbon source; Urea ($CH_4N_2O$) provides nitrogen; Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) supplies phosphorus; Sodium chloride (NaCl) or Sodium Sulphate ($Na_2SO_4$) contributes to salinity; Sodium hydroxide (NaOH) and Hydrochloric acid (HCl) are used to adjust pH levels; Sodium sulfide ($Na_2S$) used as a sulfide source; Phenol ($C_6H_6O$), and hydrogen peroxide ($H_2O_2$, purity = 35%) are included in the mixture. All chemicals referenced in this study were procured from Merck, Germany, as well as from Dr. Mojallaly and Dr. Baghdadi, Iran. It should be noted that a synthetic wastewater solution was prepared using potable water for different known concentrations.




PG1~PG4: Pressure gauge
V1~V8: Control valve
HC Reactor: Orifice plate type hydrodynamic cavitation reactor

**Fig. 1. Schematic of the Hydrodynamic Cavitation Pilot**

Methodology for Experimentation, Sampling, and Measurement of Samples for each experimental phase, the desired COD was achieved by dissolving the specified materials, as outlined in the preceding section, in 1 liter of potable water. Subsequently, the prepared solution was introduced into the reactor. To ensure uniform distribution within the tank, the pump was activated, directing the flow to the tank via the bypass for a duration of 15 minutes. After that, the inlet pressure was regulated using the valve in the main path and the bypass valve, and the flow was subjected to cavitation for two hours. During this period, samples were collected from the reactor's lower valve at intervals of 15 to 30 minutes. The removal rate of COD, phenol, and sulfide ($\eta$) was then calculated using the following equation:

$$\eta = \frac{C_i - C_t}{C_i} \times 100 \tag{1}$$

In this context, the removal efficiency is expressed as a percentage, with $C_i$ and $C_t$ representing the initial concentration of the target pollutant at the initial moment and any given moment, respectively. All experiments were conducted using a single factorial method, wherein one variable parameter was altered while the others remained constant, and were repeated two or three times until the minimum error rate (less than 5 percent) was achieved.

To assess the inlet and outlet COD of samples, 2.5 mL of each sample was introduced into specialized vials designed for this test, which contained a digestion solution comprising potassium dichromate, sulfuric acid, and mercuric sulfate, as well as a sulfuric acid reagent consisting of sulfuric acid and silver sulfate. Additionally, 2.5 mL of distilled water was added to a separate vial to serve as a control sample. Subsequently, the vials were heated for 2 hours at 150°C within a digestion reactor. Following the cooling process, the absorbance of the samples was measured at a wavelength of 620 nm using a spectrophotometer. The concentrations of sulfide and phenol were determined using spectrophotometry at wavelengths of 460 and 610 nm, respectively [36]. In this study, a Shimadzu spectrophotometer from Japan (model UV mini-1240), a pH meter from ATC, China, an EC meter from Ogawa Seiki, Japan (model OSK 14821), and a thermometer from Zeal, England, were employed.

It is noteworthy that before each stage, the apparatus was thoroughly cleansed with potable water to eliminate any residual chemicals.

Upon determining the optimal reactor conditions in terms of residence time, inlet pressure, and temperature, the optimal quantities of air and $H_2O_2$ were established. Additionally, the COD and TDS values were assessed from minimum to maximum, and the system's efficiency under various conditions was evaluated. In a separate scenario, the percentage removal of sulfide and phenol under optimal conditions was investigated. Subsequently, the removal efficiency, energy consumption, and cost were compared in the final states, and the different processes were ranked accordingly.

This study investigated the impact of parameters such as inlet pressure, initial temperature, initial pollutant concentration, time, and salinity, as detailed in Table 2.

**Table 2. Different Cavitation Experiment Conditions and Investigated Parameters**

| Inlet Pressure (Bar) | Temp. (°C) | Inlet COD (mg/L) | Inlet TDS (mg/L) | Phenol (mg/L) | Sulfide (mg/L) | Air Flow Rate (L/min) | $H_2O_2$ (mg/L) |
|---|---|---|---|---|---|---|---|
| 3<br>4<br>5 | 20<br>30<br>40 | 1000<br>2000<br>3000<br>4000<br>5000 | 138<br>2000<br>5000<br>10000<br>30000<br>50000 | 20 | 20 | 15<br>30<br>45 | 1000<br>1500<br>2000 |

## 3. Results and discussion

### 3.1. Effect of Inlet Pressure and Circulation Times in the reactor

Determining the optimal pressure of the system is essential to achieve maximum efficiency. Therefore, the system's efficiency in COD removal was evaluated at pressures of 3, 4, and 5 bar over 2 hours, under conditions of temperature, pH, and initial COD concentration, specifically 30 °C, 7.5, and 1000 mg/L, respectively. For the specified inlet pressures, the downstream pressure was maintained at 1 bar. As shown in Figure 2, an increase in initial pressure is associated with enhanced COD decomposition rates. Increasing the inlet pressure from 3 to 4 bar, the COD degradation rate increased from 19.95% to 39%, and the maximum degradation rate was observed at 4 bar and a residence time of 120 minutes. This acceleration in pollutant degradation with increased inlet pressure can be attributed to the increase in the production of hydroxyl radicals, which is achieved as a result of the intensification of pore activity at higher pressures. However, with an increase in the inlet pressure to 5 bar, the degradation rate decreased by 11% (from 39% to 28%), potentially indicating the onset of super cavitation conditions. Under super cavitation, the pores fail to collapse, and as they increase downstream, they merge and form larger pores, creating a super cavitation-like state. These pores either collapse earlier or return to the tank with the flow. In this scenario, the absence of pore collapse and subsequent hydroxyl radical formation results in reduced pollutant degradation and decreased removal efficiency compared to lower pressures. Higher degradation with increasing inlet pressure, and its decrease with passing the optimal point, has been supported by previous studies [37–42].

It is important to note that cavitation intensity is also influenced by the recovered pressure. However, in the reactor under investigation, the variation in recovered pressure downstream, or other words, the change in cavitation length, was minimal compared to the change in inlet pressure. However, cavitation intensity is primarily affected by changes in inlet pressure. This observation aligns with previous studies [43]. It should be noted that most prior research has concentrated on the effect of inlet pressure, with limited reports on the impact of outlet pressure. This may be attributed to the constant outlet pressure when the outlet is connected to the atmosphere. When the discharge is not to the atmosphere, downstream pressure increases with rising inlet pressure [44]. In this study, the effect of downstream pressure was examined by altering the position of the downstream orifice valve.

Another significant observation from these scenarios is the increase in cavitation efficiency with extended residence time. Over time, the number of circulations within the system increases, leading to more frequent encounters between the pollutant and hydroxyl radicals, thereby enhancing removal efficiency. As observed, up to 60 minutes from the reaction's onset, the graph exhibits a steeper slope, attributable to the higher concentration of pollutants in the reactor and, consequently, more encounters with hydroxyl radicals as oxidants. Over time, this slope diminishes and stabilizes. The increase in removal efficiency with prolonged residence time is consistent with other studies [45].

Another parameter evaluated in cavitation systems is the dimensionless cavitation number ($C_v$), defined by equation 2 [46,47]:

$$C_v = \frac{P_2 - P_v}{\frac{1}{2} p {v_0}^2} \tag{2}$$

Where $\rho$ is the density of wastewater, $P_2$ is the total pressure recovered downstream, $P_v$ is the saturated vapor pressure of the liquid, and $v_0$ is the liquid velocity at the contraction position. Accordingly, by altering the downstream pressure from 1 to 1.2 bar at an inlet pressure of 4 bar, the cavitation number increases from 0.68 to 0.82, indicating a decrease in cavitation efficiency. In a practical experiment, this change resulted in a reduction in COD removal efficiency from 39% to 17.4% (see Fig. 3). As noted in other researchers' reports, an increase in the cavitation number signifies an increase in the number of bubbles created, collapse events per unit volume, as well as the intensity of the cavitation process and the concentration of OH radicals [48].

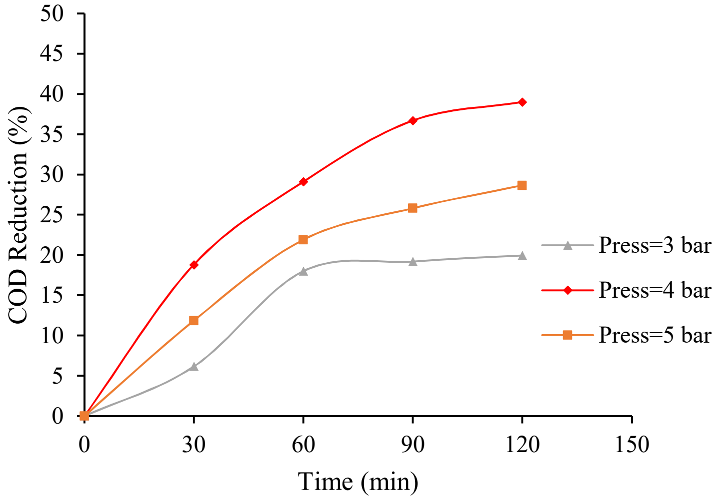



**Fig. 2. Effect of inlet pressure on COD reduction**

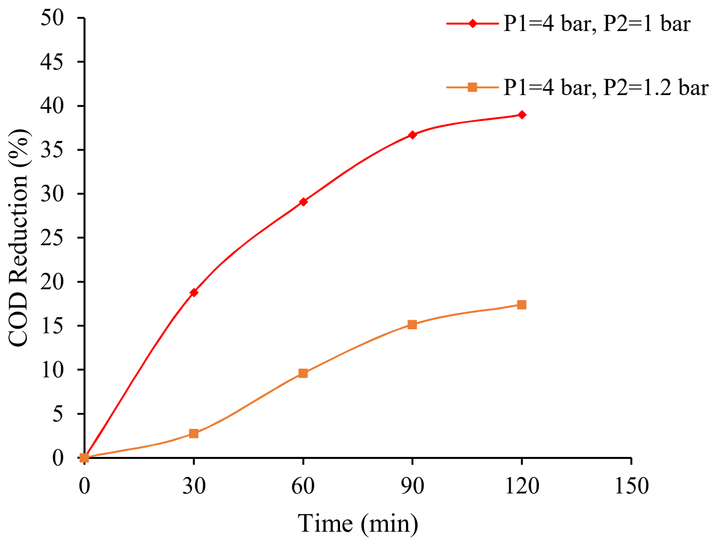



**Fig. 3. Effect of changing the downstream recovered pressure on COD reduction**

### 3.2. Effect of Inlet Temperature

Operating temperature is a critical parameter because it can influence the intensity of HC. In this study, degradation of COD has been studied at three temperatures: 20, 30, and 40°C. These experiments were conducted for 2 hours, with conditions of pressure, pH, and initial COD set at 4 bar, 7.5, and 1000 mg/L, respectively. The results, as shown in Figure 4, indicate that the degradation rate of COD increased about 12% (from 39% to 27%) with the increase in temperature from 20 to 30°C. However, degradation decreased further with an increase in temperature from 30 to 40°C (from 27% to about 19.95%). This phenomenon can be explained by the fact that the rate of destruction enhances with increasing operating temperatures due to kinetic effects and an increase in reaction rate, characterized by more frequent collisions between the pollutant and hydroxyl radicals, and the formation of nuclei, which collectively intensify cavitation. However, increasing the temperature above a certain temperature leads to the formation of large cavities and collapse of the cushion, which reduces the intensity of cavitation and, consequently, the removal efficiency [49]. This conclusion aligns with previous studies [50,51].

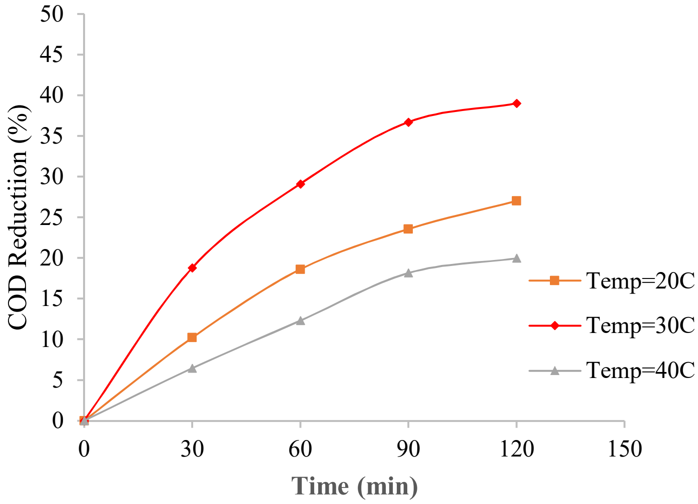



**Fig. 4. Effect of initial temperature on COD reduction**

### 3.3. Effect of Initial Pollutant Concentration

To investigate the impact of initial COD concentration on the reactor's efficiency, the concentration was varied from 1000 to 5000 mg/L, and the removal process was assessed for 120 minutes under conditions of 4 bar pressure, pH 7.5, and an initial temperature of 30 °C. It was observed that the graph exhibited a steeper slope up to 60 minutes from the reaction's start, attributed to the higher pollutant concentration in the reactor, which increased the frequency of collisions with hydroxyl radicals as oxidants (see Fig. 5). Over time, this slope diminished, reaching a near-constant trend. Generally, an increase in initial pollutant concentration enhances the probability of hydroxyl radical attacks, leading to greater purification. However, further increases in pollutant concentration result in a decreased rate of degradation. This is because the increased pollutant load cannot be effectively oxidized by the constant quantum of hydroxyl radicals produced. The observed reduction in pollutant degradation is attributed to the saturation of the cavitation surface area at higher COD concentrations and the insufficiency of radicals generated by HC to oxidize all pollutants. Overall, it can be concluded that the concentration should be determined based on the process requirements and the properties of the degraded materials [44]. Similar findings have been reported in numerous studies [44,52,53].

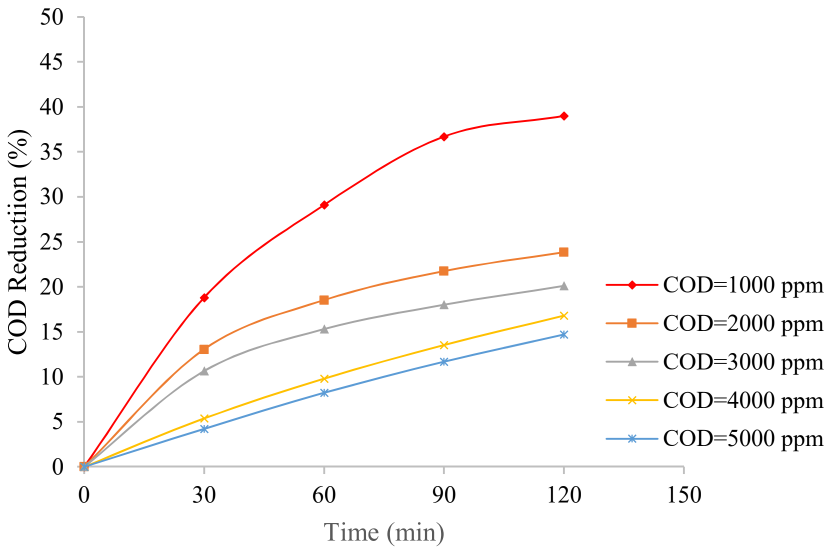



**Fig. 5. Effect of initial concentration on COD reduction**

### 3.4. Effect of initial TDS concentration

HC is expected to be influenced by the concentration of dissolved solids because it depends on the implosion of cavities. However, no comprehensive study has been reported in this context.

To examine the impact of TDS, experiments were conducted by varying the TDS concentration from 138 to 50,000 mg/L (achieved through the addition of NaCl) for 2 hours, under conditions of pressure, temperature, pH, and initial COD of 4 bar, 30°C, 7.5, and 1000 mg/L, respectively.

The results showed that with an increase in TDS concentration, the COD removal efficiency diminished, decreasing from 26% to less than 8% (see Fig. 6). In another study, the removal of aminophenol was examined by varying the TDS from 0 to 2000 mg/L, which demonstrated that a rise in TDS concentration led to a 10% reduction in the removal efficiency of the substance [54].

In another scenario, the effect of the TDS source was investigated. In this context, $Na_2SO_4$ was introduced as a TDS source instead of NaCl. It was observed that altering the TDS source had minimal impact on cavitation, with the only effect being a 2% decrease in COD removal efficiency.

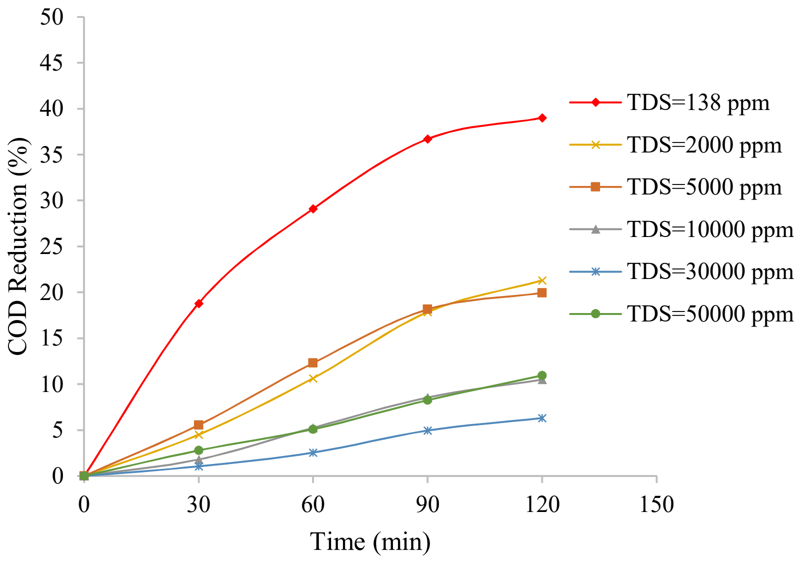



**Fig. 6. Effect of initial TDS (with addition of NaCl) on COD reduction**

### 3.5. Effect of $H_2O_2$ Addition

The combined effect of HC and hydrogen peroxide (purity = 35%) at varying molar ratios of $H_2O_2$:COD equal to 1, 1.5, and 2 was investigated to evaluate the rate and efficiency of COD degradation. The experiments were conducted for 2 hours under conditions of pressure, temperature, pH, and initial COD, set at 4 bar, 30 °C, 7.5, and 1000 mg/L. As shown in Figure 7, the efficiency of cavitation markedly increased at the specified ratios. A detailed analysis shows that at a concentration of $H_2O_2$ equal to 1000 mg/L or ratio of $H_2O_2$:COD equal to 1:1, the system's efficiency surpasses that of the other two conditions (1.5:1 and 2:1). This phenomenon can be referred to the synergistic effect of HC and $H_2O_2$, where the high-temperature conditions promote the generation of hydroxyl radicals, and finally enhancing degradation. This process continues until an optimal point is reached, beyond which excess $H_2O_2$ reacts with hydroxyl radicals, forming water and hydroperoxyl radicals. As a result, the efficiency of removal improves with the addition of $H_2O_2$ until it reaches an optimal level, beyond which no further enhancement in degradation is noted. The study of the combined use of $H_2O_2$ and HC for pesticide degradation revealed a 16% increase in TOC removal efficiency compared to using cavitation alone. However, increasing the concentration of $H_2O_2$ beyond this point leads to a reduction in the degradation rate, which is due to the recombination and scavenging of OH radicals [55]. These recombination reactions are represented by the following equations [17]:

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{3}$$

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{4}$$

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{5}$$

Many other studies have supported these findings [17,27,56–58].

Another scenario investigated was the impact of increasing TDS on the removal efficiency of the combined $H_2O_2$+HC process. The results indicated that, unlike previous observations where TDS addition reduced HC efficiency, increasing TDS to 50,000 mg/L resulted in a 3 to 5 percent improvement in COD removal efficiency.

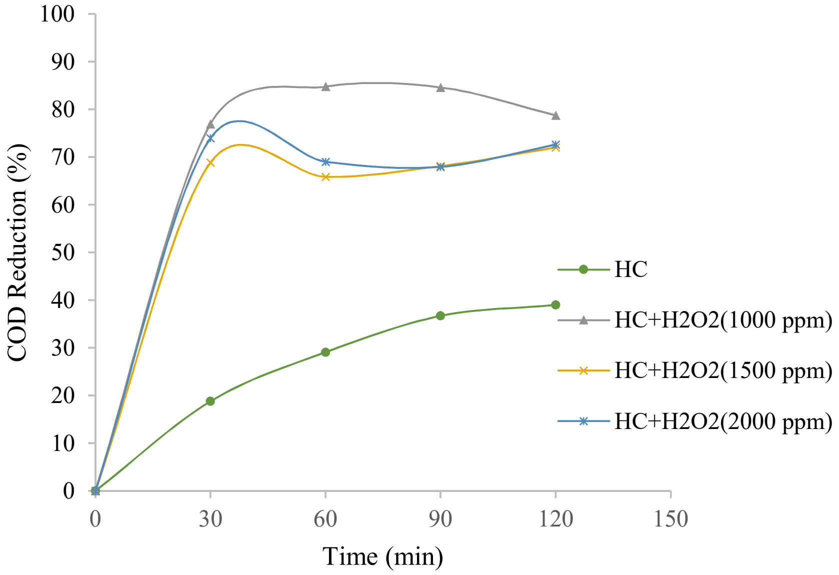



**Fig. 7. Effect of the addition of $H_2O_2$ on HC**

### 3.6. Effect of Air Addition

The effects of HC treatment with air at flow rates of 15, 30, and 45 l/min for 2 hours, under conditions of pressure, temperature, pH, and initial COD, 4 bar, 30°C, 7.5, and 1000 mg/l, respectively. As shown in Figure 8, the removal efficiency improved with an increase in air flow; however, the positive impact of air injection on HC was observed only up to approximately 60 minutes from the commencement of the reaction, after which a decline in system efficiency was noted. Literature indicates that dissolved gas is a critical parameter influencing the intensity of HC. The presence of dissolved gases enhances the number of cavities that contribute to the initiation of cavitation. It is evident that an excess of gas adversely affects cavitation, aligning with findings from previous studies [29,59]. Conversely, some studies have reported varying outcomes when combining air with HC. For example, one study showed that the HC+Air process resulted in a 4 to 10-fold increase in ammonia nitrogen [54]. Thus, it can be inferred that the influence of dissolved gases on cavitation efficiency is contingent upon the specific pollutant being investigated.

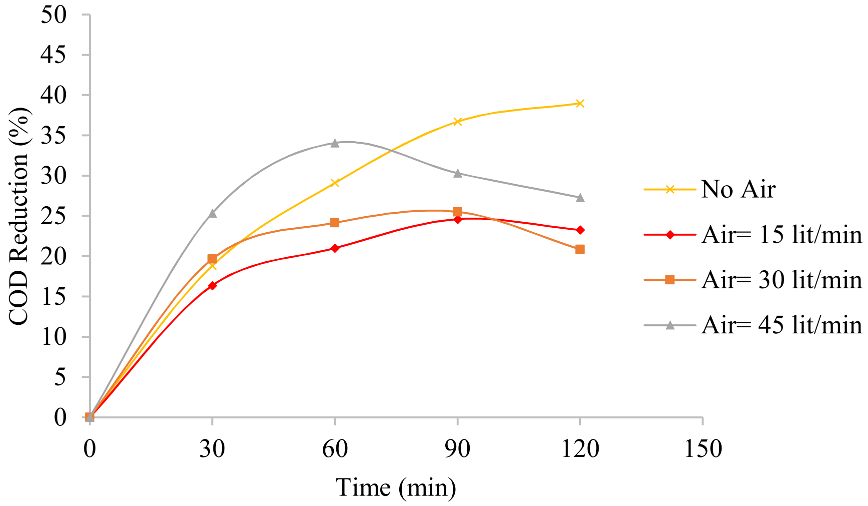



**Fig. 8. Effect of the addition of Air on HC**

### 3.7. Investigation of Sulfide and Phenol Removal Percentage

As previously discussed, the highest removal efficiency was achieved through the combined process of cavitation and $H_2O_2$. Consequently, this mode was selected as the optimal method to investigate its effect on the removal of sulfide and phenol. The experiments were conducted for 2 hours under conditions of pressure, temperature, pH, COD, and initial TDS set at 4 bar, 30°C, 7.5, 1000 mg/L, and 50000 mg/L, respectively. It is evident that HC alone is more effective in removing sulfide and phenol (see Fig. 9). This can be attributed to the higher concentration of $H_2O_2$ added relative to the amount of sulfide and phenol in the wastewater, indicating that the added $H_2O_2$ acted as a radical scavenger and reduced the treatment efficiency. The results indicate that within 60 minutes of initiating the reaction, a removal efficiency of over 95% for sulfide was achieved. However, the conditions for phenol were different. After 120 minutes from the start of the reaction, the removal efficiency remained low, which could be attributed to phenol's high resistance to purification.

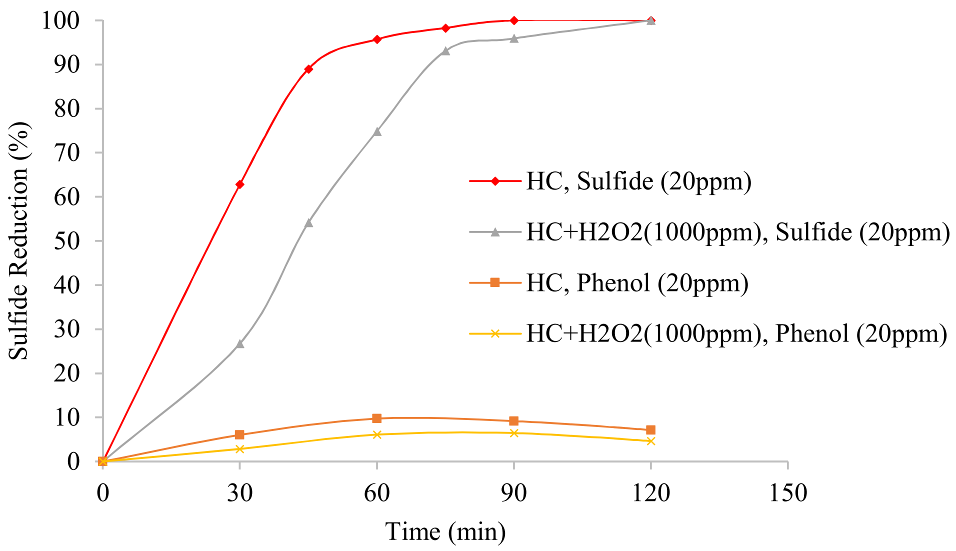



**Fig. 9. Sulfide and phenol reduction**

### 3.8. Investigation of Reaction Kinetics

To investigate the kinetics of removal, zero-order, pseudo-first-order, and second-order kinetics were examined. The constant rate was calculated using the following equations [60]:

$$C = C_0 - k_0 t \tag{6}$$

$$C = C_0 e^{-k_1 t} \tag{7}$$

$$\frac{1}{C} = \frac{1}{C_0} + k_2 t \tag{8}$$

In these equations, $C_0$ and C represent the concentrations of COD before and after treatment (mg/l), respectively, t denotes time in minutes, and $k_0$, $k_1$, and $k_2$ are the apparent rate constants of the reaction.

Given that the removal predominantly occurs within the initial 60 minutes (in inlet pressure 4 bar and initial temperature 30°C), the data were accordingly fitted, and the coefficient of determination ($R^2$) was calculated. The rate constant values are presented in Table 3. It is established that the degradation in both the only HC and the combined processes of HC+$H_2O_2$ and HC+Air is more closely related to the second-order model. The kinetic rate constant *k* for the HC alone mode, with CODs of 1000, 2000, 3000, 4000, and 5000 mg/L, is 0.000007, 0.000002, 0.000001, 0.0000005, and 0.0000003, respectively. In the combined HC+$H_2O_2$ and HC+Air processes, for a COD of 1000 mg/L, the rate constants are 0.00009 and 0.000009, respectively.

**Table 3. Summary of Kinetic Model Coefficients in Spent Caustic Wastewater Treatment**

| Scheme | $COD_{in}$ (ppm) | Zero-Order Kinetics | | Pseudo-First-Order Kinetics | | Second-Order Kinetics | |
|---|---|---|---|---|---|---|---|
| | | $k_0$ | $R^2$ | $K_1$ | $R^2$ | $K_2$ | $R^2$ |
| HC | 1000 | 4.8500 | 0.9723 | 0.0057 | 0.9854 | 0.000007 | 0.9946 |
| | 2000 | 6.1750 | 0.9472 | 0.0034 | 0.9575 | 0.000002 | 0.9670 |
| | 3000 | 7.6500 | 0.9512 | 0.0028 | 0.9594 | 0.000001 | 0.9671 |
| | 4000 | 6.5333 | 0.9969 | 0.0014 | 0.9999 | 0.0000005 | 0.9993 |
| | 5000 | 6.5333 | 0.9998 | 0.0317 | 0.9983 | 0.0000003 | 0.9999 |
| HC + $H_2O_2$ | 1000 | 6.8500 | 0.8184 | 0.0313 | 0.9052 | 0.00009 | 0.9867 |
| HC + Air | 1000 | 5.675 | 0.9262 | 0.0069 | 0.9482 | 0.000009 | 0.9679 |

### 3.9. Comparison of Cavitation Yield and Energy Consumption

Cavitation yield is defined as the quantity of chemical transformation achieved per unit of energy expended and is calculated as Eq. (9). In HC reactors, the centrifugal pump serves as the primary source of energy consumption and is calculated as Eq. (10) [38]. The energy consumption in the HC reactor was determined based on a flow rate of 0.00021 $m^3/s$ at maximum removal efficiency and a residence time of 120 minutes for three operational modes: HC alone, HC+$H_2O_2$, and HC+Air (in initial concentration 1000 mg/l, inlet pressure 4 bar, and initial temperature 30°C).

The results are presented in Table 4 (Considering 1 kWh = 19,964 Rials (data from Iran Ministry of Industry, Mine and Trade). Evidently, the highest removal efficiency was associated with the HC+ $H_2O_2$ combined process, which also exhibited superior cavitation efficiency. Regarding treatment cost, due to the low electricity costs in Iran, the expense associated with treatment using the HC reactor is significantly lower than that of the other two combined processes. Conversely, other studies conducted in different countries indicate that a substantial portion of the operational costs associated with cavitation-based processes are attributed to the electrical energy supply of the system. This is because the expense of reactants, such as $H_2O_2$, is minimal compared to the cost of electrical energy [55]. Consequently, when considering the global criterion, the energy efficiency of a single HC is significantly enhanced by its combination with $H_2O_2$.

$$Y = \frac{V(C_0 - C)}{\Delta PQt} \tag{9}$$

$$E = \frac{C_0}{Y} \times 2.78 \times 10^{-7} \tag{10}$$

In these equations, Y is the Cavitation yield (mg/j), V is liquid volume (lit), $C_0$ and C are the concentrations of COD before and after treatment (mg/l) respectively, t denotes time in minutes, $\Delta P$ and Q are pressure drop ($N/m^2$) and flow rate ($m^3/s$), E denotes energy required for degradation of COD in kWh $L^{-1}$.

**Table 4. Comparison of Cavitation Yield and Treatment Cost of Different Processes in Spent Caustic Wastewater Treatment**

| Scheme | COD reduction (%) | Cavitation yield (mg/J) | Energy required (kWh) | Cost related to power (Rials/L) | Additive cost (Rials/L) | Total treatment cost (Rials/L) |
|---|---|---|---|---|---|---|
| HC | 39.00 | 2.57E-02 | 0.011 | 216.19 | - | 216.19 |
| HC+$H_2O_2$ | 78.75 | 5.18E-02 | 0.005 | 107.07 | 4424.78 | 4531.85 |
| HC+Air | 27.30 | 1.80E-02 | 0.015 | 308.85 | - | 308.85 |

## 4. Conclusion

In this study, we examined the degradation of COD, sulfide, and phenol utilizing the AOP method at a laboratory scale. A cavitation device based on an orifice plate was employed for HC. The results were obtained using HC alone and in conjunction with $H_2O_2$ and air. The principal findings of this study are as follows:

- The maximum degradation of COD was achieved at an inlet pressure of 4 bar and a downstream pressure of 1 bar; further increases led to entry into the super cavitation zone, resulting in decreased removal efficiency.
- The rate of COD degradation increased with a temperature rise from 20 to 30°C, but decreased at 40°C, which can be attributed to the formation of large pores and the collapse of the cushion.
- The combined use of air and cavitation adversely affected pollutant removal, whereas the combined process of HC and $H_2O_2$ resulted in an approximately twofold increase in removal efficiency. This combination also demonstrated efficacy in mitigating the adverse effects associated with elevated levels of TDS.
- The HC process successfully removed sulfide within 90 minutes; however, it only achieved approximately 10% removal of phenol in the same timeframe.
- The reaction kinetics study established that the reactions in all three cases, HC alone, HC+$H_2O_2$, and HC+Air, fitted the second-order kinetics model.
- The cavitation performance of the optimal treatment method, HC+$H_2O_2$, was significantly better than that of HC alone. Additionally, the electrical energy cost for the combined HC+$H_2O_2$ process was significantly lower than that of the HC process alone. Overall, the findings suggest that the use of HC alone may not achieve satisfactory results in terms of the target pollutant destruction rate; thus, it is recommended to use HC in conjunction with other suitable AOPs.

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## Using artificial intelligence chatbots

During the preparation of this work, the authors used AI-assisted technologies, such as language models like ChatGPT, to enhance grammar, style, and language clarity. After using these tools/services, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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