# A NOVEL ADVANCED TECHNOLOGY FOR REMOVAL OF PHENOL FROM WASTEWATERS IN A VENTURY REACTOR

## by

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Phenol is a major pollutant in the waste waters coming from coal processing. Hydrodynamic cavitation presents a novel technology for phenol removal from waste waters. Hydrodynamic cavitation device with a cavitator of Ventury type for waste water purification was constructed. The hydraulic characteristic of the device were determined: the dependences of flow and cavitation number on inlet pressure. The effects of cavitation number, phenol concentration, pH, temperature, time, and quantity of added  $H_20_2$  on the degree of phenol reduction in the waste water was investigated. The optimal technological parameters of the investigated cavitation purification process of waste waters from phenol were determined.

Key words: hydrodynamic cavitation, phenol, removal, wastewaters, Ventury

## Introduction

Phenol is one of the most common pollutant in industrial wastewaters, such as wastewater from refineries (6-500 mgL<sup>-1</sup>), petrochemical industry (from 2.8-1200 mgL<sup>-1</sup>), coal processing (9-6800 mgL<sup>-1</sup>), coke production (28-3900 mgL<sup>-1</sup>), pharmaceutical industry, the paint industry, processing of leather, plastic, production of phenolic resins, disinfectants [1]. Improper handling and improper disposal of organic pollutants can lead to long-term consequences for the environmental impacts of water [2].

The US Environmental Protection Agency requires the reduction of phenol content in wastewater to a concentration of less than 1 mg/L [3]. Different methods and treatment used for the removal and degradation of phenol are biodegradation [4-6], photocatalytic degradation [7-9], gas or vapor deposition, phase transfer catalysis [10], chemical coagulation [11], chemical oxidation [7, 12], membranes separation [9,13], adsorption by porous inorganic materials [11, 14-17] and synthetic polymeric adsorbents [12, 19, 20], ultrasound cavitation [21, 28], *etc.* 

Hydrodynamic cavitation (HC) is a new, low cost and energy efficient technology for wastewater treatment. The removal of organic pollutions from waste waters by HC technology is based on the ability of cavitation bubbles and cavities to induce water sonolyses and to generate reactive radicals when implode violently. The formed OH radicals oxidize the pollutants molecules and by means of that they are removed. There are literature data about application of HC for degradation Rhodamine B [23], Acid Red color 88 [24], diclofenac sodium [25], orange-G color [26]. Berkani *et al.*, [26] examined photocatalytic decolorization of textile azo dye Basic Red 46. Jaia *et al.* [27] showed in their paper application of the ozonization method in combination with HC for degradation phenol from wastewater.

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Since there are no available data for phenol degradation from wastewaters by using HC with a cavitator of Ventury type, in this work the effects of basic process parameters (cavitation number,  $C_N$ , concentration of phenol,  $C_0$ , concentration of hydrogen peroxide,  $C_{H_2O_2}$ , pH, temperature, T, number of passes of solution through the cavitator, n, on the degree of reduction of phenol content in wastewaters were investigated.

## Experimental

## Materials

Reagent grade phenol (99.5% from Sigma Aldrich, Germany) was used to prepare aqueous solution of phenol. Hydrogen peroxide (30% w/v from Merck, Germany) and sulfuric acid (96% w/v from Sigma Aldrich, Germany) were analytically pure. The solutions were prepared using distilled water, which was also freshly prepared in the laboratory.

## Experimental set-up and methodology

Table 1. The structural

Figure 1 shows the schematic representation of HC device (HDCD). The HDCD including a holding tank where the phenol solution is taken of 5 L volume, a positive displacement pump of power rating 5 kW, for the recirculation of the solution through the main line and bypass line where control valves (V1, V2, and V3) are also provided to control the pressure at the desired values, flow meter (F1) and the recovered pressure have been performed based on the use of pressure gauges (P1 and P2) and Ventury type cavitator.

The structural characteristic (size and shape) of Ventury cavitator are given in tab.1.

characteristic of ventury cavitator		
Ventury length	8.5 mm	
Diameter throat	1 mm	
Length of convergent section	15 mm	
Length of divergent section	65 mm	
Half angle of convergent section	23.2°	
Half angle of divergent section	6.4°	



## Analytical method for

determination concentration of phenol

Concentration of phenol in water solution was determined by the spectrophotometric method ASTM D 1783-01 [28]. The VIS spectra of water solution of phenol were recorded at UV-VIS spectrophotometer Shimadzu UV mini 1240, Japan. Phenol concentration in solution was determined by measuring the absorbance of phenol at wave number (510 nm).

## Calculation of the cavitation number

The cavitation number,  $C_N$ , represents the degree of development of the cavitation process, and is calculated by the following equation [29, 30]:

$$C_{N} = \frac{P_{2} - P_{v}}{\frac{1}{2}\rho V_{0}^{2}}$$
(1)

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where  $P_2$  is the measured downstream pressure,  $P_v$  – the vapor pressure of the solution,  $\rho$  – the density of the solution, and  $V_{q}$ , is the measured linear fluid velocity.

#### The number of passes

The number of passes, *n*, of the solution through the Ventury cavitator can be calculated by following expression:

$$n = \frac{Q}{V}t \tag{2}$$

where Q is volumetric flow rate, V – total volume of solution in the holding tank, and t – duration of cavitation treatment.

## Determination the reaction order

Determination of the reaction order of phenol reduction by HC technology was performed by using the method of initial rates [31]. In accordance with that method, the initial rate,  $r_i$ , is proportional to the  $n^{\text{*th}}$  degree of the initial concentration  $C_0^*$  of the reactant:

$$r_{i} = k(C_{0}^{*})n^{*}$$
(3)

By the logarithmic of the above expression we get:

$$\ln r_{i} = \ln k + n^{*} \ln C_{0}^{*}$$
(4)

The dependence of  $\ln r_i$  on  $\ln C_0^*$  should give straight line whose slope corresponds to the reaction order with respect to the reactant.

# Cavitation yield of hydrodynamic cavitation reduction

Energy efficiency of HC can be determined by calculation the cavitation yield, *Y*, of the process. Cavitation yield (mol/J) can be defined as number of moles (mol) of reduced phenol per unit energy supplied to the system (J), according to following expression:

$$Y = \frac{n_m}{P_j t} \tag{5}$$

where  $n_m$  [mol] is the number of moles of reduced phenol,  $P_t$  [Js<sup>-1</sup>] – the power input to the system, the t [s] – duration of cavitation.

## Degree of phenol reduction

Calculation of the degree of reduction of phenol,  $\alpha$ , was performed using the expression:

$$\alpha = \frac{(C_0 - C)}{C_0} [\%]$$
(6)

where  $C_o$  is the initial concentration of phenol solution.

#### **Results and discussion**

With the aim to determine the conditions for stable operation of the HDCD its hydraulic characteristics, were determined: the dependence of the water flow rate and cavitation number on the inlet pressure. Figure 2 shows the dependence of the flow rate on the inlet pressure.

As can be seen from the results presented in fig. 2, the flow rate linearly increases with increase in the inlet pressure. The linear increase of the flow rate with the inlet pressure indicate that HDCD can work as much as to the inlet pressure  $P_1 = 18$  atm. The dependence of  $C_N$  on inlet pressure was calculated by using known dependence of flow rate on inlet pressure fig. 2 and the structural characteristic of the cavitator. Figure 3 shows the dependence of  $C_N$  on inlet pressure.



Figure 2. The dependence of flow rate on the inlet Fig pressure cav

Figure 3. The effect of the inlet pressure on the cavitation number

The cavitation number complexly decreases with the increase in inlet pressure. A decrease in cavitation number indicates that the number of cavities generated and collapsing event per unit volume increases, as well as the intensity of cavitation process and concentration of OH radicals.

In order to preliminary determine the possibility of removal of phenol from waste water by using HC technology without using any additional chemicals, the effect of duration of cavitation treatment on the degree of reduction of phenol was investigated. The duration of cavitation treatment was varied from 1-10 min keeping constant all other reaction parameters:  $C_0 = 50 \text{ mg/L}, T = 293 \text{ K}, \text{pH} = 3, C_N = 0.3$ . The dependence of the degree of reduction of phenol on time is shown in fig. 4.

As can be seen from the results presented in fig. 4 the HC technology without using additional chemicals does not enable complete reduction of phenol. The limited degree of phenol reduction (12%) indicates that the quantity of OH radicals formed under the investigated conditions is not sufficient for complete oxidation of phenol [32].

Since the amount of generated radicals OH depends primarily on the cavitation number of the used device, the effect of  $C_N$  on the degree of phenol reduction has been investigated. The



Figure 4. The dependence of the degree of reduction of phenol *vs.* cavitation time

values of  $C_N$  were varied ranging from 0 to 1, keeping constant all other parameters:  $C_0 = 50$  mg/L, T = 293 K, pH = 6, n = 10. Table 2 shows the effect of the  $C_N$  value on the degree of phenol reduction.

In the case when  $C_N \ge 1$ , reduction of phenol in solution does not since under that conditions cavitation does not lead to formation of OH radicals. The decrease in the value of  $C_N$ , in the range  $0.7 \ge C_N > 0.1$ , leads to an increase in the degree of phenol reduction due to an increase in the concentration of cavitation bubbles and OH radicals. Bearing in mind that the reduction degree of phenol during ultrasonic degradation is influenced by the pH value of the solution [33], the effect of pH value of phenol solution was investigated. The pH values were varied from 3 to 11, under the constant reaction parameters:  $C_0 = 50 \text{ mg/L}$ , T = 293 K, n = 10,  $C_N = 0.3$ . The effect of pH value of phenol solution on the degree of reduction is shown in tab. 3.

As can be seen from the results shown in tab. 3. the degree of reduction of phenol is significantly influen-ced with a change in the pH value. At the pH values of  $pH \ge 10$ , HC does not lead to the reduction of phenol content. On the contrary, within the pH values range between 9 > pH > 3, the degree of phenol reduction increases with a decrease in the pH value.

Based on these results, with a high degree of confidence can be stated that the dominant form of the phenol (phenolate ions or molecular form) in solution directly effects on the effects of HC. In the case where the dominant ionic species of phenol are phenolate ions (pH > 9.78), which cannot be concentrated at the boundary phase of water bubble, due to its hydrophobicity, cavitation effects cannot lead to the degradation of phenol [34]. On the contrary, when  $pH \le 9.78$  in the solution is dominant molecular phenol form, which easily

concentrated at the boundary phase and evaporates into the cavitation bubble, the cavitation effects increase.

The obtained results imply that HC technology without any additional chemicals does not enable to achieve complete reduction of phenol since the quantity of generated OH radicals are not sufficient for phenol oxidation. With the aim to increase the degree of phenol reduction H<sub>2</sub>O<sub>2</sub> was introduced in the solution. The effect of  $C_{\text{H-O}}$  in solution on the degree of phenol reduction, was investigated. The  $C_{\text{H-O}}$  was varied from 50 mg/L to 300 mg/L, keeping constant all other reaction parameters:  $C_{\theta} = 50$  mg/L, T = 293 K, pH = 3,  $C_N = 0.3$ . Figure 5 shows the effect of  $C_{\text{H-O}}$  in solution on the degree of phenol reduction.

Table 2. The effect of  $C_N$  onthe degree of phenol reduction

$C_n$	Degree of phenol reduction [%]
1	0
0.7	5
0.5	10
0.3	13
0.1	25

Table 3. The effect of pH value of solution on the degree of phenol reduction

pН	Degree of phenol reduction [%]
3	48
6	13
9	5
10	0
11	0



Figure 5. The effect of  $C_{\text{H.O.}}$  on the degree of phenol reduction

The increase in  $C_{\text{H-O}}$  the for all of the investigated cavitation treatment times, leads to the increase in the degree of phenol reduction. When  $C_{\text{H-O}} = 200 \text{ mg/L}$  complete degradation of phenol from the reaction system is after 10 minutes with n = 15, whereas at  $C_{\text{H-O}} = 300 \text{ mg/L}$  the time for completely degradation of phenol is shortened to 5 minutes with n = 7. Therefore, HC leads to the H<sub>2</sub>O<sub>2</sub> degradation and formation of additional radical which enables total reduction of phenol content in solution. According to the above presented results it may be concluded that the degradation oxidation of phenol in the presence of H<sub>2</sub>O<sub>2</sub> occurs in accordance with the stoichiometric equation:

$$C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O$$
 (7)

To investigate the effect of initial concentration of phenol on the degree of phenol reduction and to find out the kinetics of phenol oxidation, experiments were conducted with different initial concentration of  $H_2O_2$  from 50 to 300 mg/L, keeping constant al other reaction parameters  $C_0 = 50$  mg/L, T = 293 K, pH = 3,  $C_N = 0.3$ . Figure 6 shows the dependence of lnr<sub>i</sub> on ln  $C_{\text{H-O}}$ . Based on the conversion curves (the dependence of the degree of reduction on time), the initial rates are calculated,  $r_i$ .

The dependence of  $\ln r_i$  on  $\ln C_{Hot}$  gives the straight line from whose slope according to the initial rate method [31] can be used to calculate the order of reaction. The calculated values of the reaction order n = 1 indicates, that the kinetics of the 261

phenol removal in conditions of HC can be described with the model of the first-order chemical reaction.

As in the case of HC without using chemicals, the effects of pH and temperature of the solution on the degree of phenol reduction were examined. In fig. 7, the effect of the pH of the solution on the degree of phenol reduction is shown, for the f ollowing constant parameters:  $C_0 = 50 \text{ mg/L}, C_{\text{H-O}} = 300 \text{ mg/L}, T = 293 \text{ K}, t = 10 \text{ min}, C_N = 0.3.$ 



Figure 6. The dependence of  $lnr_i$  on  $ln C_{H:0:}$ 

The results shown in fig. 7 clearly reveals that the pH values of phenol solution significantly

effects on the degree of phenol reduction as in the case of phenol reduction without chemicals. At  $pH \ge 6$ , HC does not lead to degradation of phenol. In the range of  $2 \ge pH \ge 6$  the degree of phenol reduction increases with the decrease in the pH value of the solution. The effect of pH value on the degree of phenol reduction is related with molecular form of phenol present in the solution and its ability to interact with cavitation bubbles.



The effect of temperature on the degree of phenol reduction was investigated. The temperature was varied in the range from 278 to 298 K, keeping constant all other reaction parameter:  $C_0 = 15 \text{ mg/L}$ ,

As can be seen from fig. 8, the increase in temperature leads to the increase in the degree of phenol reduction which indicates that cavitation degradation of phenol is a thermally activated reaction.

#### Conclusion

The HC technology without additional chemicals enables to achieve limited degree of phenol reduction. The maximum achieved cavitation degree of phenol reduction is 48% for the initial phenol concentration of 50 mg/L. Hydrodynamic cavitation in the presence of hydrogen peroxide is a simple, highly efficient technology for the complete reduction of phenol content from wastewater. The increase in temperature and in the  $C_{\text{H-O}}$  as well as the decrease in the values of the  $C_{\text{N}}$  and in the pH values of the solution leads to the increase in the degree of phenol reduction. The values of the optimal reaction parameters of cavitation removal of phenol from wastewater are determined. The complete reduction of the phenol from solution is achieved in a very short time interval, from 3 to 5 minutes, for the stoichiometric ratio of H<sub>2</sub>O<sub>2</sub> to phenol in the reaction solution. The archived cavitation yield is  $1.7^*10^{-9}$  mol/J, which is significantly higher than the cavitation yield for acoustic cavitation.

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