Study of the process of phenanthrene degradation in a cavitated liquid environment

Joanna SZULŻYK-CIEPLAK – Institute of the Fundamentals of Technology, Faculty of the Fundamentals of Technology, Lublin University of Technology, Janusz OZONEK – Institute of Environmental Protection Engineering, Faculty of Environmental Engineering, Lublin University of Technology, Poland

Introduction

The development of industry as well as the increasing production of chemical compounds critical for the manufacture of daily use commodities have contributed to high levels of hazardous substances in the natural environment and, by the same token, to greater exposure to their negative impact of living organisms. Polycyclic aromatic hydrocarbons (PAHs) [11, 21] are among the most widespread xenobiotics in the natural environment. Due to their polycyclic structure, the said contaminants show poor degradability and negative effects on living organisms [13, 24]. Surface water pollution with PAHs often derives from uncontrolled industrial and domestic wastewater discharge as well as leachates from municipal landfills. In addition, as shown in studies, also treated wastewater and sludge accumulated in receiving surface bodies contain a significant content of PAHs [3, 4].

In view of the above, it is vital to streamline the efforts to launch more effective sewage treatment methods. Multi-step technologies offer a promising solution for the treatment of wastewater containing durable and poorly biodegradable compounds [6, 9]. The first step consists in purification by physicochemical means of the streams found to be the most contaminated, whilst the final step involves biological treatment of wastewater.

Among physicochemical methods, advanced oxidation processes (AOPs) prove to be the most effective. The said methods rely on the reactions with highly reactive hydroxyl radicals and typically ensure a high rate of contaminant disintegration as well as good effectiveness in the degratation of poorly biodegradable compounds [14, 16]. In spite of numerous advantages, methods based on advanced oxidation processes applied in wastewater treatment have been implemented in Poland to a very limited extent. This is associated with the significant costs of the deployment of the said processes, on the one hand, and lack of economic justification for their introduction, on the other. Technologies developed on the basis of hydrodynamic cavitation must be assessed against this background [15, 22, 23]. By virtue of lower process costs and a less complex structure of reactors, hydrodynamic cavitation comes to the fore as the prospective method for the degradation of organic contaminants found in wastewater [2, 10].

The mechanism behind the phenomenon of hydrodynamic cavitation is the formation, growth and subsequent collapse of cavitation bubbles in the flowing liquid. Cavitation bubble implosion is accompanied by a host of physicochemical phenomena (Fig. 1).
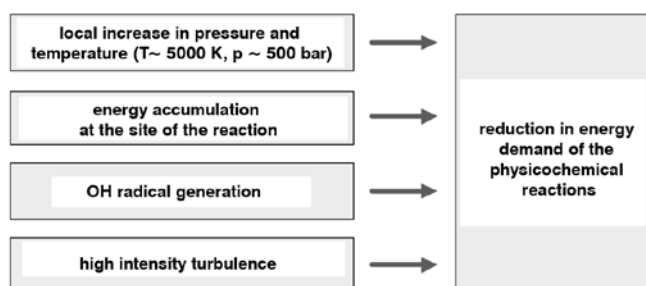
Research dedicated to the phenomenon of cavitation, both acoustic (ultrasonic) and hydrodynamic in the processes of advanced oxidation, has been the subject of growing attention over the past years [15]. The findings of the studies performed point to its high effectiveness in the treatment and disinfection of water [1, 7], sewage [5, 19, 20] and sludge treatment [8].

Method and laboratory station

Subjected to laboratory examinations was a tricyclic compound of the group of polycyclic aromatic hydrocarbons – phenanthrene. Phenanthrene has the lowest molecular weight among PAHs that have the so-called bay-area and its structure evinces a cancerogenic effect (e.g., benzo(a)pyrene). Hence, it serves as a standard compound in the research concerning the metabolism of polycyclic aromatic hydrocarbons with a more complex structure [18]. Investigated in our study were standard phenanthrene solutions in distilled water of the reference substance (97%, *Fluka Analytical*). Three initial concentrations were set at, respectively, 5.50 and 500 $\mu g/dm^3$.
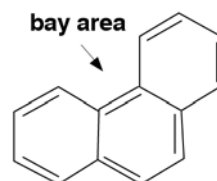

Fig. 2. Phenanthrene chemical structure

A static hydrodynamic cavitation reactor has been used (Photo. 1). In this type of reactor, cavitation is induced by means of positioning a dedicated element in the flow path, namely, the so-called cavitation inductor.
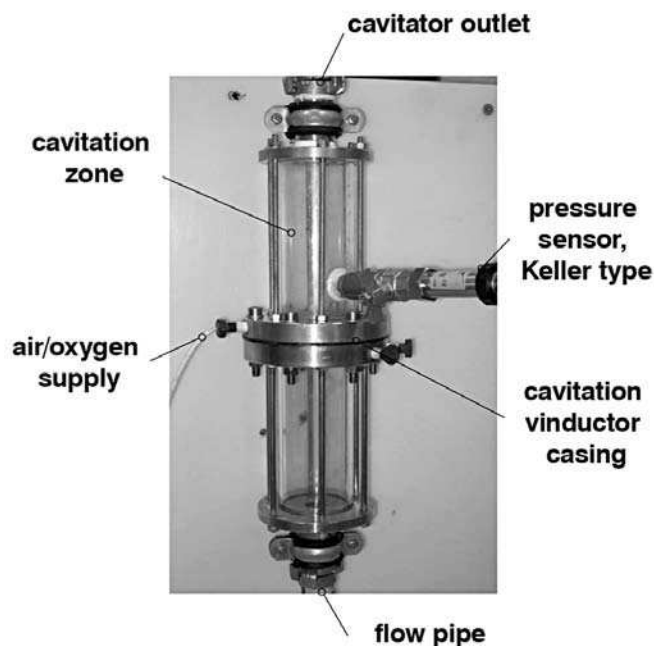

Fig. 1. Physicochemical effects within cavitation zone

Photo 1. Hydrodynamic cavitation reactor

5 cavitation inductors differing in terms of the number, size and spatial distribution of the orifices have been alternately used (Tab. 1).

Geometrical characteristics of the inductors applied in the study

Number	Orifice dimensions, mm	Orifice number	Flow area, mm²	Total orifice perimeter, mm	α mm⁻¹	β
inductors with orifices characterized by a circular cross-section						
1	ϕ 1	5	3.925	15.7	4	0.0013
2	ϕ 1	9	7.065	28.26	4	0.0023
3	ϕ 2	9	28.26	56.52	2	0.0094
inductors with orifices characterized by a rectangular cross-section						
4	1.5 x 5	4	30	52	1.73	0.0099
5	1 x 5	5	25	60	2.4	0.0083

The aim of the study was to assess the impact of both the course and intensity of the hydrodynamic cavitation process on the phenanthrene degradation rate. The cavitation number K has been assumed as the parameter defining the intensity of the phenomenon investigated:

$$K = \frac{p - p_n}{\frac{1}{2} \cdot \rho \cdot w^2} \qquad (1)$$

where: p – static pressure in the conditions of undisturbed flow, Pa; p_n – vapour pressure, Pa; ρ – liquid density, kg/m³; w – the velocity of the liquid flowing through the cavitation inductor, m/s.

As may be inferred from the bibliography [12, 19, 20], the course of cavitation depends on such factors as the geometry of the inductor, i.e., the flow area of the liquid passing through a cavitation inductor as well as the total perimeter of orifices in the shield. For the purpose of the assessment of the effect of geometrical dimensions of the respective inductors on cavitation rate, geometrical parameters α and β that determine the hydrodynamic flow conditions have been applied. They are derived from the following ratios (2) and (3).

$$\alpha = \frac{total\ perimeter\ of\ orifices\ in\ the\ shield,\ sum}{total\ cross\text{-}sectional\ area\ of\ the\ orifices\ in\ the\ shield} \qquad (2)$$

$$\beta = \frac{total\ cross\text{-}sectional\ area\ of\ the\ orifices\ in\ the\ shield}{cross\text{-}sectional\ area\ of\ the\ pipeline} \qquad (3)$$

The efficiency of the hydrodynamic process of phenanthrene degradation has been evaluated relative to the variation in the compound level as opposed to the initial level, defined by the following formula:

$$\zeta = \frac{C_0 - C_\tau}{C_0} \qquad (4)$$

where: C_0 – initial concentration of phenanthrene solution, µg/dm³; C_τ – initial concentration of phenanthrene solution, after the period τ of cavitation duration, µg/dm³.

Compound degradation in a hydrodynamic cavitation system develops relative to circulation rate L_c (5). The required effect of the compound disintegration is usually achieved through an iterative passage of the investigated solution through the cavitation zone. An increased circulation rate leads to greater energy demand, which is why it is essential to adopt such parameters of the system operation as to ensure the lowest rate possible.

$$L_c = \tau \cdot \frac{\dot{V}}{V_u} \qquad (5)$$

where: τ – cavitation process duration, s; $\dot{V}$ – volumetric flow rate, [m³/s]; V_u – test system volume, m³.

Study outcome analysis

Prior to the scheduled examinations, subject to analysis was the cavitation process in the test system. The findings confirmed that both the course and the development of cavitation process are determined by the hydrodynamic characteristics of the liquid flow as well as the structural properties of the device. In the hydrodynamic cavitation system applied in the study, cavitation occurred at the initial pressure equal to approximately $p_0 = 3$ bar (cavitation number was set at $K < 1$ for all inductors). Cavitation number (K) drops as pressure grows, showing that the process evolves towards greater intensity [22].

The test results of phenanthrene degradation in a variable cavitation system point to the interdependence of the degradation rate of the compound under study and the course of the process of cavitation (Figs. 3, 4). Hydrodynamic cavitation method has been proved to be highly effective in terms of phenanthrene level reduction. A single passage of the solution through the cavitation zone was sufficient to achieve a high rate of phenanthrene degradation, ranging from 70–87% for respective cavitation inductors.
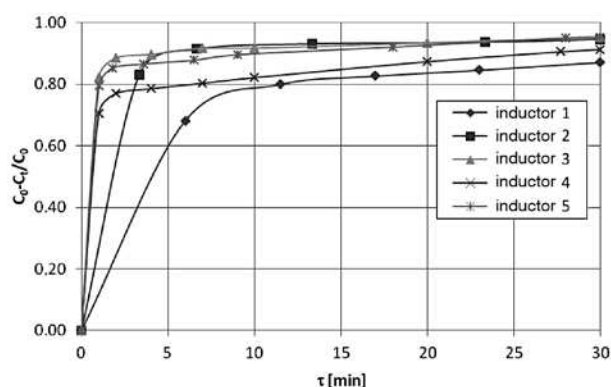

Fig. 3. Impact of the structure of the cavitation inductor on the variation in phenanthrene degradation rate, $p_0 = 7$ bar, $t = 30 \pm 2°C$, $C_0 = 50$ µg/dm³
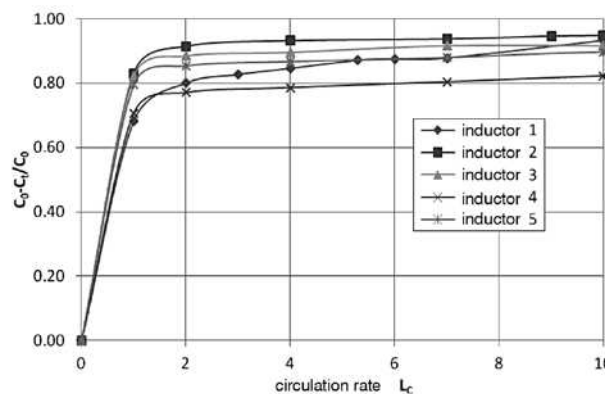

Fig. 4. Impact of the circulation rate L_c and inductor type on the phenanthrene degradation rate, $p_0 = 7$ bar, $t = 30 \pm 2°C$, $C_0 = 50$ µg/dm³
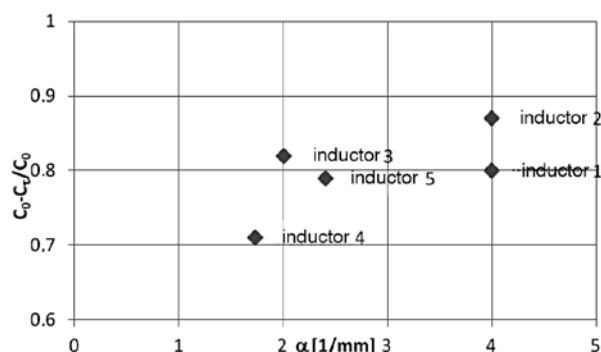

Fig. 5. Impact of the parameter α on phenanthrene degradation rate, $L_c = 1$, $p_0 = 7$ bar, $t = 30 \pm 2°C$, $C_0 = 50$ µg/dm³

The structural properties of the reactor significantly affect the efficiency of the degradation of the compound under study. Consequently, the impact of geometrical characteristics α and β on phenanthrene degradation rate (Figs. 5 and 6) was assessed.
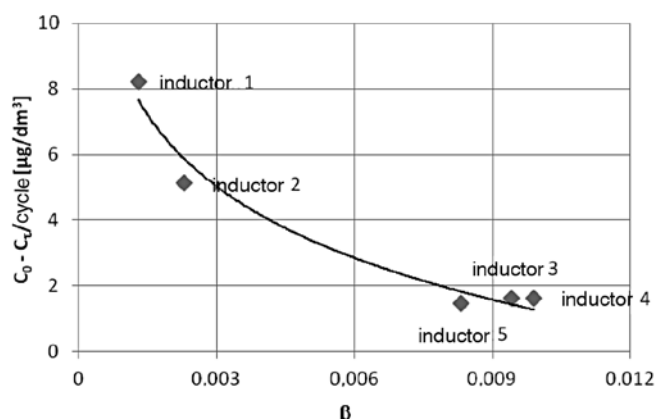
Fig. 6. Impact of the parameter β on phenanthrene level per a single recirculation cycle, p_0=7 bar, t=30±2°C, C_0=50μg/dm³

The results obtained indicate that higher levels of the parameter α correlate with a greater phenanthrene degradation rate. For inductors that damp the flow of the liquid to a comparable extent -the parameter β shows to be similar (inductors 3, 4 and 5 as well as inductors 1 and 2) the degradation rate is higher for inductors with more orifices in the shield, i.e., greater total perimeter of cavitation orifices. As the damping rate of the solution passing through the cavitation inductor solution gets higher (lower β values), the phenanthrene degradation rate per a single recirculation cycle (Fig. 6) becomes higher accordingly. After τ=30 min of cavitation, the mean drop in phenanthrene level per one working cycle reached the following levels: for the inductor with the highest damping rate (inductor 1) – 8.22 μg/dm³, whereas for inductors 3, 4, 5 (comparable values of parameter β) – within the range of 1.45–1.63 μg/dm³. Higher damping rate leads to decreased intensity of the flow of the liquid passing through the system. As a result, the solution remains within the cavitation zone for an extended period. The upshot of this is that the amount of the degraded compound per a single cycle relative to a given time unit is greater for inductors with lower values of parameter β. As regards inductors with comparable flow area of 28.26 mm² (inductor 3) versus 30 mm² (inductor 4), the inductor to ensure a higher degradation rate is the inductor with more cavitation orifices, i.e., inductor no. 3.
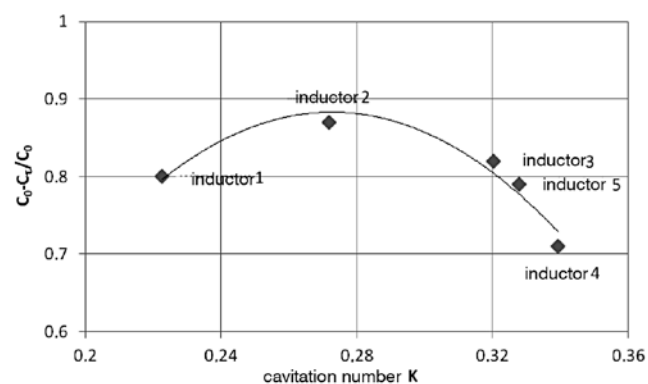
Fig. 7. Impact of cavitation number and inductor type on phenanthrene degradation rate, L_c=1, p_0=7 bar, t=30±2 C, C_0=50 μg/dm³

Plotted in the chart (Fig. 7) is the effect of cavitation intensity (K) on phenanthrene degradation rate relative to the structure of the inductor, under the assumption of a constant initial pressure p_0. Phenanthrene degradation rate rises as cavitation number

increases. Once it reaches the maximum level, it gradually abates. Therefore, an optimal value of the number K may be defined that corresponds to the highest phenanthrene degradation rate under study conditions.

At a subsequent stage of examinations, the test system has been fitted with inductor 3, characteristic for its high phenanthrene degradation rate in relation to both circulation rate and process timeframe. The subject of the analysis was the impact of inlet pressure (p_0) on phenanthrene degradation (Fig. 8).
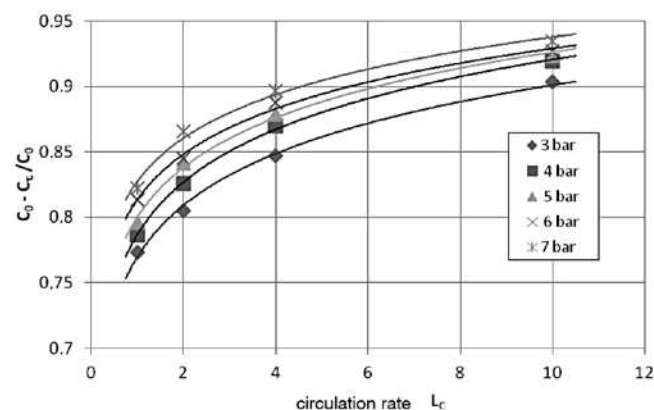
Fig. 8. Variation in phenanthrene degradation rate relative to circulation rate L_c for variable inlet pressure (p_0) values, inductor 3, t=30±2°C, C_0=50 μg/dm³

The tests have been conducted at inlet pressure (p_0) varying from 1 to 7 bar. No variation in the concentration level of the compound under study has been observed for pressure below $p_0 \leq 2$ bar. This is due to the fact that the phenomenon of cavitation does not occur for such values of pressure ($K>1$) [22]. Whereas, within the range of pressure spanning 3–7 bar phenanthrene degradation rate has been seen to increase as has a rise in inlet pressure (Fig. 9). The growth in pressure causes flow rate through the active cavitation zone to intensify by several or more times, eventually leading to higher phenanthrene degradation rate.

As may be inferred from the bibliography items [17, 26], the value of the solution initial concentration affects the compound degradation rate. A hydrodynamic cavitation system with constant structural properties has been subjected to tests (inductor 3) in the conditions of inlet pressure at p_0=7 bar, analysed against three respective values of phenanthrene solution initial concentration, namely, C_0=5.50 and 500 μg/dm³. The results (Fig. 9) indicate that the solution initial concentration affects phenanthrene degradation rate. At a circulation rate of L_c=1 and the initial solution concentration of C_0=5 μg/dm³, phenanthrene degradation rate amounts to 83%, and for a solution concentration of C_0=500 μg/dm³, only 13%.
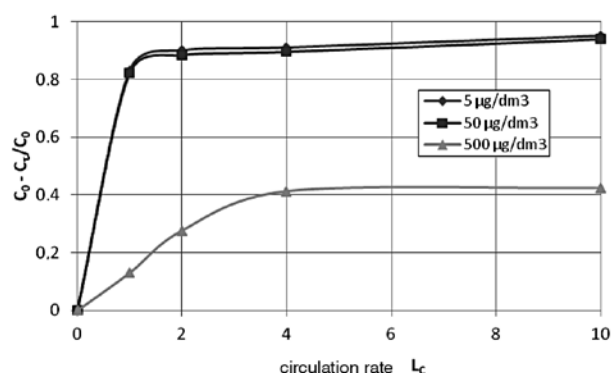
Fig. 9. Impact of initial level and circulation rate on the variation in phenanthrene degradation rate, inductor 3, p_0=7 bar, t=30±2°C

Conclusions

The test results obtained have confirmed the occurrence of the physicochemical effects of cavitation. Both the structural properties of the reactor and the parameters of the overseen process significantly affect the course and efficiency of phenanthrene degradation. What can be used for the optimisation of hydrodynamic cavitation systems as measures for the purpose of disintegration of poorly biodegradable organic compounds are the parameters attributable to cavitation inductor, i.e., the geometrical parameters α and β as well as the cavitation number K.

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Joanna SZULŻYK-CIEPLAK – PhD., (Eng.), graduated from the Faculty of civil and Sanitary Engineering, Lublin University of Technology (1994). Her professional career has evolved within the structures of the university since her graduation. She has defended her doctoral thesis at the Faculty of Environmental Engineering, Lublin University of Technology (2012). Scientific interests: advanced oxidation processes in wastewater treatment, the phenomenon of hydrodynamic cavitation as facilitating the degradation of organic compounds in an aqueous environment.

e-mail: j.szulzyk-cieplak@pollub.pl

Janusz OZONEK – Professor (Ph.D., Eng.), has graduated from the Faculty of Chemistry, Silesian University of Technology in Gliwice. He is employed at the Faculty of Environmental Engineering, Lublin University of Technology. Specialisation – chemical engineering, environment protection and engineering, chemistry of low-temperature plasma.

j.ozonek@wis.pol.lublin.pl