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DEGRADATION OF PENTACHLOROPHENOL BY HIGH TEMPERATURE HYDROLYSIS

Abstract
The long-term use of plant protection products in agriculture, including pentachlorophenol (PCP), has contributed to their widespread distribution in the natural environment. So far, no cheap and effective techniques for removing chlorophenols by physicochemical or biological methods have been developed. Therefore, alternative methods of neutralizing them are currently being sought. The aim of the study was to investigate the possibility of pentachlorophenol decomposition by high temperature thermohydrolysis. The decomposition process was carried out at a constant pressure of 25 MPa, in the temperature range of 20°C to 500°C and at various volumetric flows of PCP through the reactor. Detailed analysis of the results showed that the process and degree of pentachlorophenol reduction depended on residence time in the reactor and the process temperature. The obtained results indicate that thermohydrolysis in supercritical water is not an effective method to neutralize pentachlorophenol. The high costs of conducting this process together with an average degree of PCP conversion (the conversion of pentachlorophenol at the lowest volumetric flow rate through the reactor reached about 45%) cause that thermohydrolysis at high temperature is not a cost-effective method of neutralizing pentachlorophenol.

Keywords
pentachlorophenol, thermohydrolysis, supercritical water, neutralization

Introduction

Civilization progress is inextricably linked to the increase in the amount of generated pollutants. The physicochemical and biological methods used so far in wastewater treatment cease to be effective against many new, biologically active and ecotoxic pollutants contained in wastewater [1-3]. Chlorophenols, especially pentachlorophenol (2,3,4,5,6-pentachlorophenol), are particularly toxic and dangerous to the environment.
PCP is a synthetic organic substance that does not occur naturally in the environment. Pure pentachlorophenol is in the form of colorless or white crystals, poorly soluble in water and very well in organic solvents. PCP is a stable compound and its stability is due to the presence of five chlorine atoms attached to the aromatic ring. Pentachlorophenol was first introduced in 1936 by the chemical companies Dow and Monsanto as a wood preservative. The long-term use of pentachlorophenol has contributed to its widespread distribution in the environment, which leads to a steady increase of PCP concentration in the ecosystem [4-5]. The main source of environmental pollution with pentachlorophenol was the use of preparations containing PCP, which as a result of various transformations got into the water, air and soil. Pentachlorophenol was commonly used as a wood preservative, herbicide, fungicide, bactericide, algaecide, molluscicide, insecticide, biocide and defoliant. Large amounts of pentachlorophenol got into the environment as a result of wood treatment with PCP-containing preparations and as a consequence of mass spraying of arable fields with biocides. As a result of surface runoffs, pentachlorophenol used in agriculture was transported together with other pollutants to surface and underground water. Additionally, PCP was used in soaps and detergents applied in medicine and as an additive to adhesives, latex paints and paper. Pentachlorophenol was used in sealing substances being in contact with food and in plastic reusable containers for storage of loose food products. Pentachlorophenol was also used in the photographic and tanning industry as well as in paper and cellulose plants [5-7].

Pentachlorophenol is highly toxic to both microorganisms and humans, and its toxicity increases with concentration. PCP is absorbed through the respiratory tract, digestive system and skin [8-9]. Pentachlorophenol can cause many different symptoms of poisoning in humans depending on how it enters the body and the time of exposure. PCP can cause fever, breathing problems, hyperhidrosis, tachycardia and metabolic acidosis, and can bring about liver damage and problems with the immune system. People exposed to prolonged contact with pentachlorophenol during the production of PCP, woodworking and impregnation may suffer from acute poisoning manifested by high fever, headaches, irritation of the mucous membranes,

skin redness, rash, vomiting, increased thirst, as well as accelerated heartbeat and breathing. Both in offices and in the home environment people are exposed to pentachlorophenol which is released into the environment from wooden elements impregnated with a PCP-containing agent. In chronically exposed workers (during PCP production, impregnation and woodworking) there may occur heavy poisoning with pentachlorophenol, which can result in high fever, headaches, irritation of the mucous membranes, redness of the skin, rash, vomiting, increased thirst, and accelerated heartbeat and breath. When relatively high doses of PCP are regularly introduced into the body, this compound is present throughout the body and accumulates in the liver, kidneys, brain, spleen and adipose tissue, which leads to enlargement and dysfunction of individual organs and weakens the immune system [10-12].

In 1999, the Environmental Protection Agency (EPA) classified pentachlorophenol as a moderately toxic xenobiotic and set standards for its maximum concentration in various environments. According to the standards, the maximum level of soil contamination with pentachlorophenol is 1 mg/kg, and the maximum permissible concentration of pentachlorophenol in drinking water is 0.022 mg/dm^3. Occupational Safety and Health Administration (OSHA) has introduced standards for the maximum concentration of pentachlorophenol that workers may be exposed to during a 40-hour working week. The highest permissible concentration of pentachlorophenol in the air at workplaces in production plants was set at 0.5 mg/m^3 [13-16].

Despite legal regulations regarding the restriction of the use of pentachlorophenol introduced at the beginning of the 21st century, its amount in the natural environment, due to its low biodegradability potential, has not significantly decreased [15]. The durability of PCP in the environment varies and ranges from several hours to many years. The rate of pentachlorophenol decomposition largely depends on PCP concentration, the presence of microorganisms capable of transforming pentachlorophenol, access of light radiation or the pH of the environment [17]. Due to its resistance to microbial degradation and high toxicity, numerous studies are carried out to develop a relatively cheap and efficient method of removing this xenobiotic from the environment [18-21].

Promising methods of neutralizing such toxic pollutants are the so-called hydrothermal technologies, in particular thermohydrolysis in supercritical water, occurring at high temperature and water pressure (above critical temperature T_{cr} = 374°C and critical pressure P_{cr}=22.1 MPa). Under supercritical water conditions, a reaction environment with very favorable application properties is obtained [22-26]. High diffusivity and heat capacity of water intensify heat and mass transfer processes. Features such as good miscibility with gases and the ability to manipulate thermodynamic properties such as polarity, solution, acid-base properties, etc. have made it possible to widely use thermohydrolysis to decompose various chemical compounds [27-29]. Despite numerous studies on this process, knowledge about the mechanisms governing it is still insufficient.

Aim of the work

The aim of the work was to investigate the possibility of decomposition of pentachlorophenol and to check the possibility of using the high-temperature thermohydrolysis process for its decomposition. The tests were carried out at a constant pressure of 25 MPa, in the temperature range from 20°C to 500°C and at four different volumetric flow rates of PCP through the reactor.

Experimental

The possibility of using a high-temperature thermohydrolysis process to decompose pentachlorophenol was investigated in the study. The experiments were carried out in a laboratory scale on a setup consisting of the following elements:

- HPLC high-pressure plug pump (Jasco, Japan) to supply solutions of the tested compounds at 25 MPa,
- electrically heated and 6.0 m long flow reactor made of SS216 stainless steel with external diameter of 6.0 mm and inner diameter of 2.5 mm,
- pressure and temperature meter,
- tube-in-tube heat exchanger serving as a cooler and allowing the reaction mixture leaving the reactor to cool down,
- temperature controller allowing a determined temperature to be kept in the system,
- Back Pressure Regulator (TESCOM, France) to maintain a set pressure in the system.

The setup for conducting thermohydrolysis in supercritical conditions is shown in Figure 1.

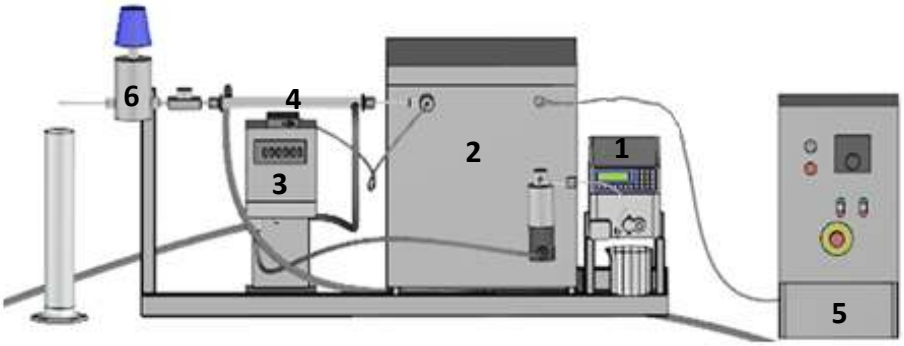

Fig. 1. Diagram of the installation for investigating the process of pentachlorophenol thermohydrolysis
1 – HPLC pump, 2 – electrically heated flow reactor, 3 – pressure and temperature measuring system, 4 – cooler, 5 – temperature regulator, 6 – pressure regulator
Source: Author's

Thermohydrolysis was carried out on model solutions of pentachlorophenol with initial concentration equal to 15 mg/dm^3, at temperature ranging from 20°C to 500°C, constant pressure 25.0 MPa and for four different volumetric flow rates through the reactor equal to 2.5 cm^3/min, 5 cm^3/min, 7.5 cm^3/min and 10 cm^3/min. After 30 minutes from the moment when the set temperature and pressure in the reactor were established, three 15 cm^3 samples of the reaction mixture were withdrawn at 20-minute intervals. The concentration of pentachlorophenol was determined by Reverse Phase High Performance Liquid Chromatography (RP HPLC). Before analysis, the samples were filtered through Whatman membrane filters of cellulose nitrate (porosity 0.2 µm). The measurement was carried out using a Perkin Elmer liquid chromatograph equipped with a Hypresil GOLD capillary column (250 × 4.6 mm) and a Hypresil GOLD pre-column, 5 µm 10 x 4 mm. The HPLC system used in the tests consisted of a pump and DAD type UV/VIS detector. The conditions for conducting analyses were selected in accordance with the principles of chromatographic separation of mixtures based on affinity to the substance for filling the column. The eluent was acetonitrile and acetate buffer, the proportions of which were 60 and 40%, respectively. The flow rate of the eluent through the column was 1 ml/min, while the retention time of pentachlorophenol was about 7.25 min. The injection volume of the sample per column was 2 µl. Detection was carried out at a wavelength of 252 nm, which roughly corresponded to the absorption maximum of pentachlorophenol. PCP concentration in the samples was determined using standard curves prepared using the Turbo Chrom program and developed for pentachlorophenol at concentrations ranging from 0 to 15 mg/l.

Results

The paper presents results of research on the process of pentachlorophenol thermohydrolysis under supercritical conditions. Figure 2 shows changes in the concentration of pentachlorophenol depending on the residence time in the reactor. In addition, the temperature corresponding to the critical point is marked with a dashed line in each chart of Fig. 2. From a chemical point of view, it is very important, because in its vicinity all water properties are changing rapidly.

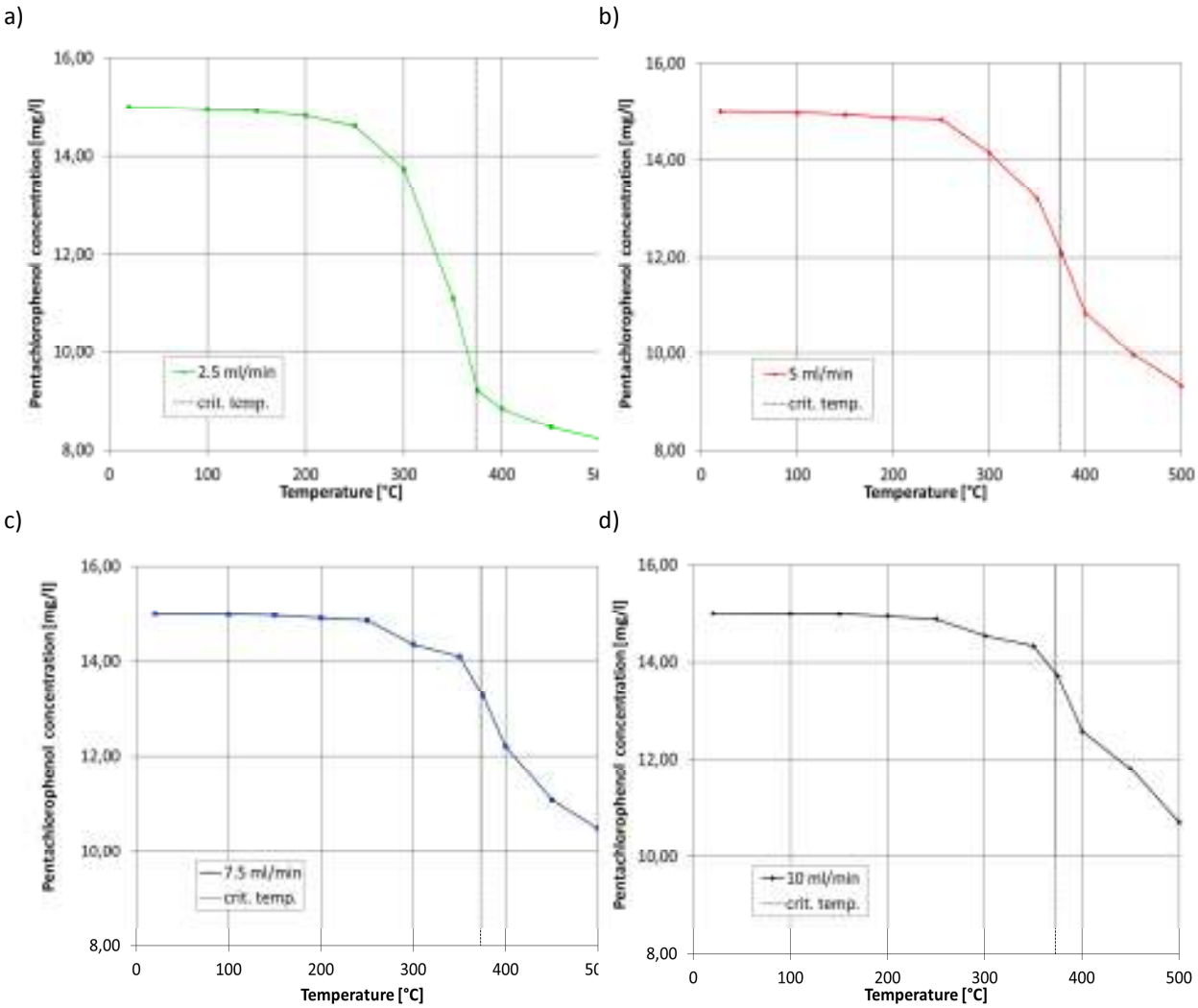

Fig. 2. Changes in the concentration of pentachlorophenol depending on the volumetric flow rate through the reactor: a) 2.5 cm^3/min, b) 5 cm^3/min, c) 7.5 cm^3/min, d) 10 cm^3/min
Source: Author's

When analyzing the curves that characterize the temperature dependence of initial concentration of pentachlorophenol fed to the reactor, it was observed that at low temperatures PCP concentration was virtually unchanged, and only above 300°C it dropped sharply. Based on the performed studies, it was found that the concentration of pentachlorophenol measured at the end of the process depended on temperature. For all analyzed flow rates of the solution through the reactor, a reduction in PCP concentration was observed with increasing temperature. In particular, these changes can be observed near the pseudocritical point. At the same time, it should be noted that as the volumetric flow rate through the final reactor increases, the PCP concentration grows. At the volumetric flow rate of the reaction mass equal to 2.5 cm^3/min and temperature 500°C, the decrease in PCP concentration was almost twice as high, falling from 15 mg/dm^3 to 8 mg/dm^3, while for the same conditions but at a volumetric flow through the reactor equal to 10 cm^3/min, the initial concentration was reduced by approximately 30%.

Figure 3 shows the dependence of the degree of conversion of the tested compound on the volumetric flow rate of PCP through the reactor for 2.5 cm^3/min, 5 cm^3/min, 7.5 cm^3/min and 10 cm^3/min at constant pressure of 25MPa.

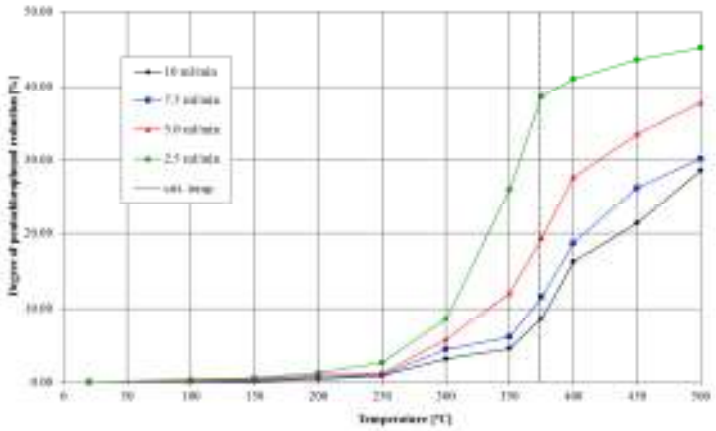

Fig. 3. Dependence of the degree of pentachlorophenol reduction as a function of temperature for different volumetric flow rates of liquid through the reactor equal to 2.5 cm^3/min, 5 cm^3/min, 7.5 cm^3/min and 10 cm^3/min at pressure 25 MPa.
Source: Author's

A detailed analysis of the temperature-dependent pentachlorophenol reduction curves allows us to conclude that the percentage of its conversion depends on the volumetric flow through the reactor. The longer the residence time of pentachlorophenol in the reactor, the greater the reduction of PCP. At low temperatures the degree of pentachlorophenol conversion is virtually zero. A gradual but slight increase in PCP conversion is observed only at 300°C. Approximately 45% PCP conversion was obtained for the lowest flow rate of 2.5 ml/min at 500°C. This level of conversion, considering the high costs of running the process, is not satisfactory and indicates that the high-temperature thermohydrolysis cannot be used as an effective method of pentachlorophenol decomposition.

In the literature there are many results of thermohydrolysis of organic compounds. However, there are no reports on this type of research in relation to pentachlorophenol. This is probably due to the fact that PCP dissolves very badly in water. The high-temperature hydrolysis process is tested for compounds with much better solubility. Nevertheless, the properties of this compound, its toxicity and use in many preparations cause that an effective method of PCP degradation is sought. Actually the best PCP degradation results are achieved by biological methods, which are characterized by low costs of the process.

Summary

Over fifty years of the use of chlorophenols, including PCP, has contributed to their widespread distribution in the natural environment and living organisms. People who come into contact with products containing PCP are particularly vulnerable to its toxic effects, which carry an increased risk of cancer, fetal defects, mutations, blood composition disorders and changes in the nervous system.

The paper presents the results of studies on high-temperature hydrolysis of pentachlorophenol. The tests were carried out at a constant pressure of 25 MPa in the temperature range of 20°C to 500°C and at four different volumetric flows of PCP through the reactor equal to 2.5 ml/min, 5 ml/min, 7.5 ml/min and 10 ml/min.

In studies on high-temperature thermohydrolysis of pentachlorophenol, an unsatisfactory degree of reduction of this compound was obtained. The PCP conversion increased with increasing process temperature. The highest degree of pentachlorophenol reduction amounting to about 45% was achieved for the lowest volumetric flow rate through the reactor equal to 2.5 ml/min at 500°C. This level indicates the average efficiency of the high-temperature hydrolysis process, which, combined with the high cost of the process, causes the process to be unprofitable for pentachlorophenol removal. This does not preclude the use of thermohydrolysis in supercritical water as an effective way to treat wastewater containing PCP. Therefore, it is necessary and justified to continue research on the process of high-temperature thermohydrolysis.

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