

Removal of chlorophenols from aqueous solutions by UV photodegradation

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Abstract— The main aim of the paper was to carry out the degradation of 3,5 - dichlorophenol using progressive oxidation method - photochemical degradation and monitor the progress of the process using gas chromatography with mass detector. To achieve the objectives were chosen two photochemical reactors (125W and 400W UV lamp). Degradation of 3,5 - dichlorophenol we tried to accelerate with the use of adsorption layer SAERTEX. We found that the sample concentration of 3,5 - DCP degradation with increasing time decreased, but even the longest UV irradiation did not caused full degradation of 3,5 - DCP. We have confirmed that the adsorption layer of the fiber SAERTEX did not affect the acceleration of the degradation of 3,5 - dichlorophenol, the cause of which may be preferential sorption of the fiber surface, which reduced the effectiveness of UV degradation.

Keywords—component; chlorophenols, GCMS, UV photodegradation

I. INTRODUCTION

Chlorophenols (CPs) are a group of chemicals that have an interest in living and working environment. Chlorophenols compounds have an aromatic ring to which a reactive hydroxyl group is attached and the remaining positions are substituted by chlorine atoms. They consist of nineteen different isomers, including five basic types of chlorophenols, mono-, di-, tri-, tetra- and pentachlorophenol. CPs toxicity depends on pH of the medium, the position and the number of chlorine atoms and on the hydroxyl group. After release into the environment, CPs subject to physical, chemical and biological change. [1]

The pH value of the water, soil and sediment is a major factor affecting the fate of a movement of the chlorophenols, since the rate of ionization of a compound increases with increasing pH. Except physical - chemical properties the transport process influences environmental parameters as well, such as the content of organic matter and clay in the soil, sediment and water. Chlorophenols are subject to abiotic and biotic degradation and transformation

processes. In general, the number of chlorine molecules can be increased by reducing the vapor pressure of chlorine, increasing the boiling point and decreasing the solubility in water. Thus the higher toxicity of the more chlorinated CPs is generally attributed to the increasing lipophilicity, leading to more potential for absorption in the human body. [2]

Wide incidence of CPs in the living and working environment has a negative impact on living organisms. Chlorophenols are among the common pollutants of soils, water resources and their origin is usually mixed. Main source of them is their production and the use of pesticides. [3] Large quantities of chlorophenols occur as intermediates during the degradation of pesticides (Linden, hexachlorobenzene, pentachlorobenzene and dichlorophenylacetic acid) and aromatics. They are highly bioaccumulative and therefore their presence in relatively-small concentrations in water, soil, sediments and human tissues is toxic. The primary source of pollution is the use of pesticides that are made directly from CPs. The proportion of incidence of CPs in the countryside comes to a large extent and nature of activities. [4]

The main source of CPS in water is the leaching of industrial waste from landfills. The compounds that are harmful to the environment and discharged into surface waters, especially dichlorophenol, 2,4 - dichlorophenol (2,4 - DCP) and 2,4,6 - trichlorophenol (2,4 - TCP). 2,4 - DCP and 2,4,6 - TCP appeared in the effluents from industries that produce iron and steel, electrical components, photographic equipment, pharmaceuticals and organic chemicals. [1] Another source discharges chlorophenol in aqueous systems are wastewater treatment plants and drinking water treatment. 2,4,6 - TCP has been detected in leachate from municipal landfills, while 2,4 - DCP was found in the leachate from industrial landfill. Permitted concentration of CPs in drinking water is limiting to 10 mg l⁻¹. [5]

Chlorophenols are ubiquitous in the environment and the bulk of pollution comes from anthropogenic

activities. Chlorophenols as chemical compounds due to their excellent properties permanently are used for various purposes in many sectors of industry, agriculture and households for over 50 years. As they have antimicrobial properties are of particular importance as wood preservatives, colors and the skin material, deodorants, disinfectants, and because of the solubility of the all-round use in organic solvents, and the solutions of sodium salts. Moreover, they are widely used in many industrial processes as synthetic intermediates or as raw material for the manufacture of plant protection products used. In the chemical industry it is used as an antiseptic and selective solvent for mineral oils. [6]

Chlorophenols are crystalline solid with a characteristic odour, capable of using the heat converted from the solid state to the gas on the other hand refrigeration from the vapor state to the solid. In terms of the dissociation chlorophenol we include a weak acid, with the number of chlorine atoms increases the dissociation constant K_a , but decreases their solubility in water. pK_a of CPs compared to phenol is 9.9. With decreasing pK_a on the surface of non-polar compounds increases the ability of adsorption. The solubility of CPs depends on the amount of chlorine atoms bonded to the aromatic ring, and chlorophenols with fewer chlorine atoms are more soluble. [7]

Due to the high pollution chlorophenolate we know many methods that can degrade chlorophenols products more acceptable to the environment or the most efficient remedy. Contamination of environment contributes to improper removal of mono- and di polychlorophenols in landfills and in low - temperature incineration, so it is important to select effective methods and processes for the removal and degradation of CPs. The main goal of the methods of removing the CPs is to achieve complete mineralization to CO_2 and H_2O , and the reduction of certain ions such as chloride ion. The methods for removal of CPs include biological, thermal and chemical methods. Use of biodegradation is impractical due to the slow decomposition of contaminants. Thermal decomposition CPs are significantly present in the emissions of other dangerous substances, such as processes comprising flocculation, precipitation, adsorption on granular activated carbon and reverse osmosis, which require a subsequent treatment to remove the contaminants from the newly contaminated environment. Alternative methods to such well-established techniques include the oxidation of CPs with agents, air and oxygen in a wet oxidation, electrons in an electrochemical oxidation and potassium permanganate, chlorine, hydrogen peroxide and ozone. The oxidation takes place to the destruction of chlorophenols in waste water, and a primary particle reaction is highly reactive hydroxyl radical (OH) because of the high standard of the reduction potential in an acid medium. These radicals are able to oxidize nearly all organic compounds to CO_2 and H_2O . Reactive hydroxyl radicals should be extremely volatile and continuously

generated by chemical, photochemical and electrochemical reactions. Depending on the nature of the organic material are two types of initial reaction, the first reaction is to separate the hydrogen from the binding, as is particularly the case of alkanes and alcohols, or another option of the reaction may, alone hydrogen atom attached to the molecule, this reaction is preferably carried out in aromatic compounds such as chlorophenols. In economic terms, it is sometimes preferable to use a combination of pre-treatment by means of AOPs and subsequent use of cheap biological processes Combination of methods AOPs are effective in completely removing CPs and their by-products and is therefore regarded as an expanded method used. [8]

II. EXPERIMENTAL

The solution of 3,5 - dichlorophenol in methanol with the concentration of 20 mg L^{-1} was prepared. The photochemical reactor with 125 W and 400 W UV lamps was used for 3,5 - dichlorophenol degradation. The concentration of 3,5 - dichlorophenol was monitored after 10, 20, 30, 40, 50, 60, 90 and 120 minutes of UV degradation with the use of GCMS.

III. RESULTS AND DISCUSSION

Monitoring of the photochemical degradation of 3,5 - dichlorophenol has identified the chromatograms of several chromatographic peaks that are appropriate oxidizing degradation products of 3,5 - DCP. Sample concentration of 3.5 - DCP with increasing degradation time decreased, but at the maximum irradiation has not reached zero. We can conclude that that the photodegradation process was more effective if adsorbent fibers SAERTEX were not used. The cause of it is due to preferential sorption on the fiber surface, which has reduced the effectiveness of UV degradation.

The results of the degradation we can see in table 1. The order of efficiency degradation of 3,5-dichlorophenol for the longest time of UV exposure was UV 400 W > UV 125 W > UV 400 W + fiber SAERTEX. > UV 125 W + fiber SAERTEX, which in percentage terms was 75.57% > 73.52% > 67.38% > 58.35%.

The photochemical degradation of 3,5 - dichlorophenol in the photoreactor with 125 W UV lamp we have found to be less effective than 400 W UV lamp, but more effective than the treatment with SAERTEX layer (Fig. 1-2).

Table 1: Degradation efficiency of 3,5 dichlorophenol

Time [min.]	Degradation efficiency [%]			
	UV 125 W	UV 125 W SAERTEX	UV 400 W	UV 400 W SAERTEX
0	0	0	0	0
10	17,31	3,84	57,04	19,22
20	19,94	21,08	58,07	26,87
30	23,34	25,34	63,91	36,56
40	68,91	26,29	66,34	47,94
50	72,65	48,97	68,46	50,39
60	72,91	-	72,65	64,41
90	73,17	52,27	74,82	67,18
120	73,52	58,35	75,57	67,38

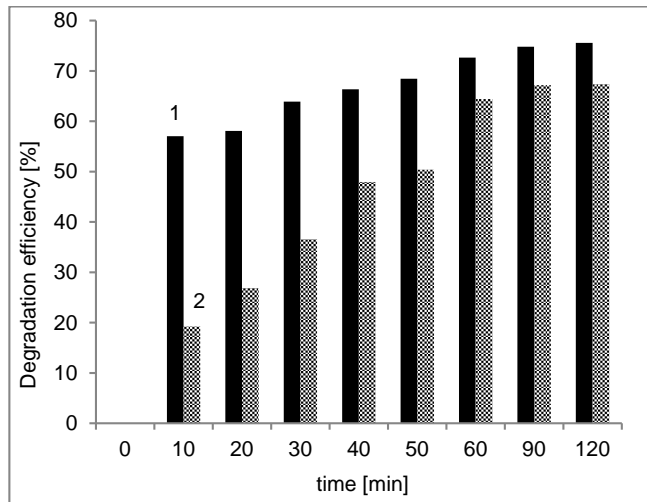


Fig. 1 Degradation efficiency of 3,5 – DCP with (1) and without (2) SAERTEX layer, UV 125 W

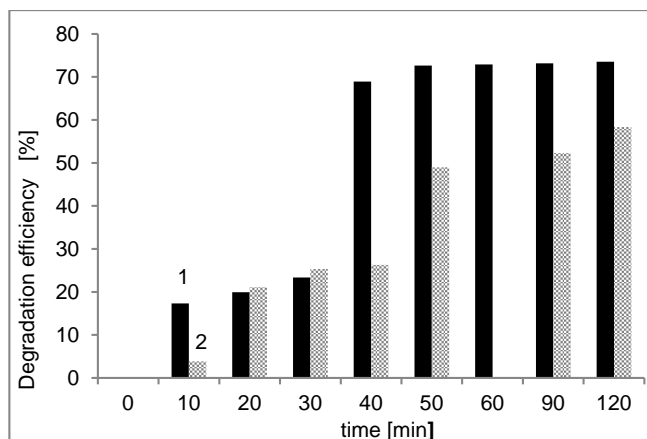


Fig. 2 Degradation efficiency of 3,5 – DCP with (1) and without (2) SAERTEX layer, UV 400 W

IV. CONCLUSIONS

We have found out that the process of 3,5 - dichlorophenol degradation was more effective

without the use of adsorption layers of SAERTEX. The highest degradation efficiency was 75.57 % after 120 min. of irradiation with 400 W UV lamp.

V. ACKNOWLEDGEMENTS

This contribution was created with the support of the Operational Programme Research and Development for project: „Hybrid power source for technical and consulting laboratory use and promotion of renewable energy sources” (ITMS 26220220056), financed from resources of the European Regional Development Fund.

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