



Decomposition of Carcinogenic Hydrocarbons in an Integrated Oxidation – Sorption System

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1. Introduction

At present no law sets limits for concentration of organic micropollutants, such as polycyclic aromatic hydrocarbons (PAHs). Simultaneously these compounds are listed among the pollutants which should be removed from wastewater because of their carcinogenic and mutagenic effect on water organisms (Regulation... 2014). These compounds are included in the list of the priority substances for water environment, which should be monitored in surface water (Regulation... 2016). Up to now, the research studies have shown that despite of the high rate of COD (or BOD₅) degradation, effectiveness of organic micropollutants removal in wastewater treatment plants is unsatisfactory (Włodarczyk-Makuła 2011, Litter & Quici 20103). This applies to both municipal and industrial wastewater. In the case of industrial wastewater, part of micropollutants load is removed in company sludgeworks. Efficiency of micropollutants removal does not meet rising requirements for the quality of environment. This brings us to the necessity of using advanced methods of pollutants removal and degradation. It concerns mainly the pollutants which are resistant to degradation, such as PAHs, organochlorine derivatives or dyes (Zhang et al. 2012, Dąbek et al. 2013). Some of these pollutants show carcinogenic, mutagenic or/ and teratogenic effect to organisms and are relatively persistent in the environment (Abdel-Shafy & Mansour 2016). Both literature data and our own research indicate that effective removal of PAHs from wastewater is possible by sorption or by using advanced oxidation processes (AOPs)

(Włodarczyk-Makuła 2011, Brandli et al. 2008, Smol et al. 2014, Trapido et al. 1995, Beltrán et al. 1999). Use of these processes meets the requirements of IED Directive (Industrial Emissions Directive 2010/75/EU). This directive aims in integrated prevention and reducing emissions of pollutants from the industry by using the Best Available Techniques (BAT) (Directive 2010/75/EU). Among commonly used sorbents the activated carbons are the ones most carefully examined. Many researchers is now also focusing on using of some waste materials as sorbents (Brandli et al. 2008, Smol et al. 2014, Pan & Baoshan 2008). Few studies exist on sorption of PAHs from wastewater on activated carbons. In earlier own studies it was confirmed that PAHs can be removed from sewage by sorption (Smol et al. 2014). Use of granular activated carbon allowed for 97% removal of carcinogenic hydrocarbons whereas on mineral sorbents removal efficiency of these compounds did not exceed 84%. Literature review has show that also powdered activated carbons can be successfully used for removal of organic micropollutants from aqueous solutions. However it should be noted that in real life situations various organic and inorganic pollutants are present in wastewater, both in form of sediments, colloids and dissolved. Taking into consideration competitive sorption on suspended solids, effectiveness of adsorption of organic compounds on activated carbons can be limited. Because of this in the case of wastewater treatment other methods are recommended, including AOPs. Advanced oxidation processes allow for degradation of the organic pollutants instead of removal them (Trapido et al. 1995, Beltrán et al. 1999, Nkansah et al. 2012, Rubio-Clemente et al. 2014). High efficiency of AOPs in degradation of organic substances is widely discussed in research literature. These methods are based on generation of hydroxyl radicals – OH^{*}, which nonselectively oxidize most organic compounds. The most frequently used oxidant is hydrogen peroxide, both alone, or as a component of Fenton's reagent (Neyens & Baeyens 2003, Pouran et al. 2014). Effectiveness of PAHs degradation depends on initial concentration of the compounds, kind and dose of reagents, pH of the environment, presence of the other pollutants and temperature (Rubio-Clemente et al. 2014). Presence of the catalysts is the factor which supports degradation of organic pollutants via free radical reactions. Also UV radiation increases the effectiveness of degradation processes. Titanium dioxide is frequently used as a catalyst, but also oth-

er chemicals are used for these purpose, including cobalt or wolfram compounds (Rubio-Clemente et al. 2014, Turek et al. 2016). In Fenton's process Fe^{2+} is used as catalyst. Information on two stage (oxidation plus sorption) removal of pollutants are also available in scientific literature. In this case sorption allows for preliminary removal of organic compounds, whereas oxidation is used as main degradation process. Sorption and oxidation can also be conducted simultaneously by using activated carbon as adsorbent and catalyst for generation of hydroxyl radicals. Under these conditions both soluble and adsorbed compounds can be oxidized (Ayranci & Duman 2010, Huang et al. 2003, Yuan et al. 2010). In the studies on advanced oxidation of PAHs conducted to date mainly symulant solutions were used. The solutions contained individual compounds or a mixture of several compounds. In wastewater PAHs are, however, mainly present as a mixture of various compounds. The composition of the mixture is affected by the kind of production processes. High concentrations of PAHs are reported in coke plant wastewater, also this pretreated in company sludgeworks. Despite of high efficiency of COD removal concentration of PAHs in treated wastewater is still high. Previous coauthored research works on this topic involved:

- oxidation of PAHs by hydrogen peroxide, also in the presence of catalysts, in water solutions (Turek et al. 2016),
- photooxidation of PAHs with hydrogen peroxide in municipal and coke plant effluents (Włodarczyk-Makuła 2011, Włodarczyk-Makuła et al. 2016),
- oxidation of selected PAHs by Fenton's reagent using CaO_2 as a source of hydroxyl radicals (Kozak & Włodarczyk-Makuła 2018),
- oxidation of selected PAHs in the presence of activated carbon (Włodarczyk-Makuła & Popenda 2018).

Because the results of PAHs removal/degradation using the processes mentioned above were satisfactory, research on carcinogenic hydrocarbons removal by integrated oxidation/ sorption have been undertaken. The aim of the study was to evaluate the effectiveness of carcinogenic PAHs removal during simultaneous oxidation-sorption process.

2. Research methods

2.1. Technological studies

Technological studies were performed with coke plan wastewater. Wastewater were taken from the secondary settlement tank of company sludgeworks. Biological processes (organic compounds removal plus nitrification) are used for sewage treatment in this plant. Wastewater was analyzed for total organic compound content (COD) and for initial PAHs concentration. 30% solution of hydrogen peroxide (H_2O_2) at dose equal to 2.5 g/L was used. The dose was selected taking into consideration the results of the previous research works (Litter & Quici 2010, Yuan et al. 2010). Powdered activated carbon C2186 (Merck) was used as a sorbent. Also catalyst (titanium dioxide – TiO_2) was added to support oxidation of PAHs. The doses of active carbon and catalyst were equal to 0.5 g/L and 1.0 g/L, respectively. The following samples were prepared:

- with H_2O_2 (control sample) (H),
- with H_2O_2 and TiO_2 (catalyst and sorbent) (H+T),
- with H_2O_2 , TiO_2 catalyst and powdered activated carbon (H+T+C).

Simultaneous oxidation and adsorption in all samples were performed for 24 hours. Analysis of COD and selected PAHs were done after 2 and 24 hours. The initial concentration of PAHs was equal to 6615 $\mu\text{g/L}$.

2.2. Qualification and quantification of PAHs

In order to determine concentration of PAHs in wastewater (both before and after simultaneous oxidation-sorption process) the samples were treated as follows. At the beginning extraction of organic matrix from wastewater was performed using liquid-liquid extraction. To extract organic matrix from wastewater cyclohexane: dichloromethane mixture (v/v – 5:1) was spiked into wastewater. After this, the extract was separated from wastewater in glass separator. In order to drain the separated extract anhydrous sodium sulphate was added followed by purification on silica gel (liquid-solid extraction). Cleaned extracts were concentrated under nitrogen stream to 2 mL. Such prepared extracts were qualified and quantified by GC-MS chromatograph Fisons. It was calibrated with AccuStandard mixture. Analysis of PAHs was performer for 50 min. Sample flow rate was equal to 1.5 mL/min. Recovery rates for individual

PAHs were evaluated using standard solution and based on this average concentration of the compounds was calculated. Concentration of the following PAHs was determined: benzo(a)anthracene (BaA), chrysene (Ch), benzo(b,k)fluoranthene (BbF, BkF), benzo(a)pyren (BaP), dibenzo(ah)anthracene (DahA), benzo(ghi)perylene (BghiP) and indeno (123cd)pirene (IP). These compounds contain 18, 20 or 22 carbon atoms in the particle, as well as 12 or 14 atoms of hydrogen in 4-6 ring system. BbF, BkF and IP have not only benzene, but also cyclopentane ring in their structure. All analyzed compounds are considered as carcinogenic or potentially carcinogenic.

3. The results

COD of coke plant effluents was at average equal to 689 mg/L. Table 1 presents COD changes after simultaneous oxidation – sorption in the presence of catalyst (titanium dioxide).

Table 1. Changes in the COD of wastewater

Tabela 1. Zmiany wartości ChZT w ściekach

Sample	After 2 h		After 24 h	
	COD, mg/L	Effectiveness %	COD, mg/L	Effectiveness %
H	426	38	192	71
H+T	358	48	146	79
H+T+C	273	60	94	86

Removal efficiency of COD after 24 h simultaneous sorption-oxidation process reached 86%. Use of hydrogen peroxide alone (H) or catalyzed oxidation without sorption (H+T) allowed to obtain efficiencies by several percent lower, compared to integrated oxidation-sorption system. This is an indication of the effect of sorption on activated carbon and of presence of catalyst, accordingly. Effectiveness of degradation and/or sorption of COD was comparable with the results obtained by other authors given in research paper by Rubio et al. (Rubio-Clemente et al. 2014).

3.1. Effectiveness of 4-ring PAHs degradation

Initial concentration of 4-ring PAHs was equal to 2359 $\mu\text{g/L}$. In the sample treated with hydrogen peroxide in the presence of catalyst, PAHs removal was about 31% after 2 h and 53% after 24 h. Removal rate of these compounds in catalyzed system increased as the time of reaction increased. Additive of activated carbon allowed for 84% removal of PAHs. Catalyst increased 4-ring PAHs removal rate by 16-18%, whereas sorbent by 6 to 13%, compared to control sample. Fig. 1 presents the changes in benzo(a)anthracene and chrysene concentration during oxidation or simultaneous oxidation-sorption.

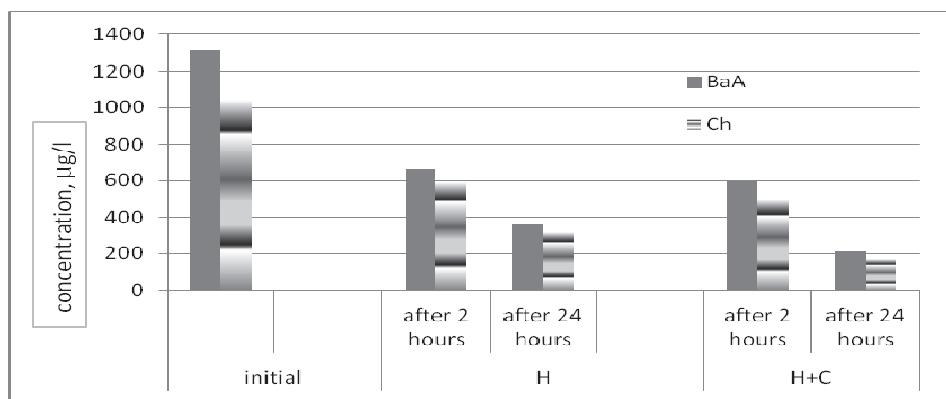


Fig. 1. Changes in the concentrations of benzo(a)anthracene and chrysene during integrated processes

Rys. 1. Zmiany stężenia benzo(a)antracenu i chryzenu w procesie zintegrowanym

3.2. Effectiveness of 5-ring PAHs degradation

In Fig. 2 and 3 changes in concentration of benzofluoranthenes, benzo(a)pirene and dibenzo(ah)anthracene are presented. Initial total concentration of 5-ring compounds was equal to 3235 $\mu\text{g/L}$. Benzo(a)pirene represented about 30% of total 5-ring compounds concentration. This compound is considered as the most carcinogenic PAH. Trend in concentration changes of 5-ring compounds was similar to the 4-ring ones. PAHs were progressively oxidized. Addition of activated carbon allowed to remove part of PAHs by sorption process. PAHs removal effectiveness did not exceed 43% in the case of (H) sample and 57% in the case of (H+T) sample. It increased to 80% when activated

carbon was present in the sample. Degradation of 5-ring PAHs was slower than 4-ring ones which would seem to indicate higher resistance of benzo(b)fluoranthenes, benzo(a)pyrene and dibenzo(ah)anthracene to the degradation. Hydrocarbons which contain cyclopentane ring (it means benzo(b)fluoranthenes) were better adsorbable on activated carbon, but less vulnerable to oxidation than other 5-ring compounds.

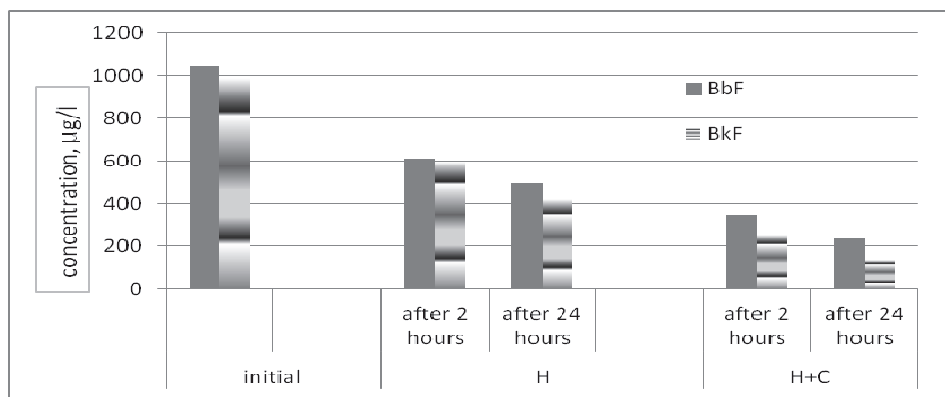


Fig. 2. Changes in the concentrations of benzo(b)fluoranthene and benzo(k)fluoranthene during integrated processes

Rys. 2. Zmiany stężenia benzo(b)fluorantenu i benzo(k)fluorantenu w procesie zintegrowanym

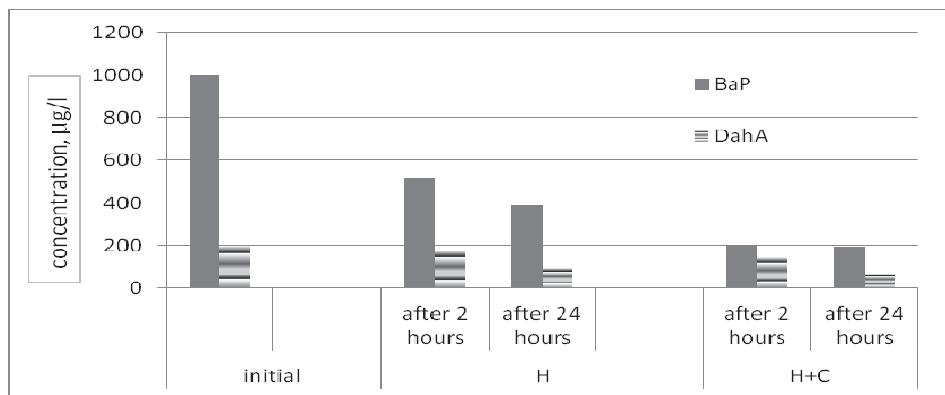


Fig. 3. Changes in the concentrations of benzo(a)pyrene and dibenzo(ah)anthracene during integrated processes

Rys. 3. Zmiany stężenia benzo(a)pirenu i dibenzo(ah)antracenu w procesie zintegrowanym

3.3. Effectiveness of 6-ring PAHs degradation

In Fig. 4 changes in concentration of indeno(123cd)pyrene and benzo(ghi)perylene during oxidation and simultaneous oxidation-sorption are presented. Initial total concentration of analyzed 6-ring PAHs was 1021 $\mu\text{g/L}$. After 24 h of hydrogen peroxide oxidation it decreased by 27%. Addition of catalyst increased the effectiveness of 6-ring PAH removal by 15%, use of activated carbon by another 26%.

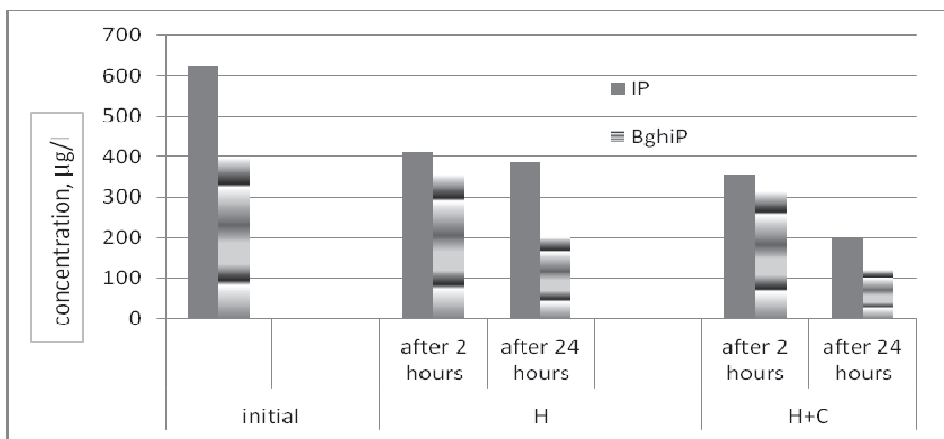


Fig. 4. Changes in the concentrations of indeno(123cd)pyrene and benzo(ghi)perylene during integrated processes

Rys. 4. Zmiany stężenia indeno(123cd)piranu i benzo(ghi)perylenu w procesie zintegrowanym

In so doing, the highest degradation efficiency of 6-ring PAHs was achieved under simultaneous catalytic oxidation-sorption. It was characteristic for all carcinogenic compounds. Effectiveness of PAHs removal decreased as the number of rings in PAH congeners increased.

4. Summary and conclusions

The results of research work indicate that the most preferable conditions for removal of carcinogenic hydrocarbons from coke plant wastewater are ensured in integrated catalyzed oxidation-sorption system. It can be emphasized that under conditions of the experiment significant removal of 4 and 5-ring was achieved, which was a result of oxidation of these compounds. In the case of 6-ring PAH removal sorption

played more important role. It can be explained by higher octanol/water values of 6-ring PAHs. Higher removal efficiency was achieved for the PAH compounds which contain cyclopentane ring in molecule structure. It can be assumed that they contain in the molecule larger number of persistent bounds than other. Based on the obtained results the following points can be made:

- Removal rate of individual hydrocarbons depended on their structure, as well as on the presence of catalyst and activated carbon in the sample.
- Effectiveness of the oxidation of carcinogenic hydrocarbons were in the range of 27 to 55%, addition of catalyst (TiO_2) increased it to 38-72%.
- Integrated catalytic oxidation – sorption ensured the efficiency of removal in the range 67-86%.

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Rozkład rakotwórczych węglowodorów w zintegrowanym układzie: utlenianie-sorpcja

Streszczenie

Celem badań było określenie efektywności degradacji rakotwórczych WWA w zintegrowanym procesie utleniania i sorpcji. Badania technologiczne prowadzono z wykorzystaniem biologicznie oczyszczonych ścieków koksowniczych. Utlenianie prowadzono z wykorzystaniem ditlenku diwodoru. Proces adsorpcji polegał na wprowadzeniu pylistego węgla aktywnego. Katalizatorem reakcji utleniania był ditlenek tytanu. Badania prowadzono przez 24 godz. Stężenia WWA oznaczano przed procesem oraz po 2 godz. i 24 godz. trwania procesu utleniania. Efektywność degradacji WWA wyliczono na podstawie zmian stężenia WWA przed i po procesie. Analizę jakościowo-ilościową WWA prowadzono z wykorzystaniem układu chromatografu gazowego i spektrometru masowego. Badania prowadzono przy stałym odczynie środowiska i stałej temperaturze. Efektywność degradacji analizowanych węglowodorów w warunkach utleniania była w zakresie od 27 do 55%. Obecność katalizatora tytanowego wspomagała utlenianie, co powodowało, że efektywność degradacji węglowodorów była w zakresie od 38 do 72%. W procesie zintegrowanym (utlenianie katalityczne w warunkach sorpcji) efektywność degradacji WWA była w granicach od 67 do 86%. Wyniki badań potwierdzają że proces utleniania i sorpcji może być skuteczny w doczyszczaniu ścieków przemysłowych i zapewniać ograniczenie ładunku WWA wprowadzanego do środowiska.

Abstract

The aim of the study was to evaluate the removal of carcinogenic PAHs during integrated processes: catalytic oxidation and sorption. Technological research was conducted using biologically treated industrial wastewater (coke plant wastewater). Oxidation was carried out with dihydrogen peroxide. The adsorption process was carried out onto powdered activated carbon. TiO_2 was added to the wastewater as a catalyst of oxidation reaction. The experiment was carried out for 24 hours. The concentration of PAHs at the beginning, after 2 and after 24 hours of integrated processes was analyzed. The effectiveness of PAHs degradation was evaluated based on the the individual compounds concentration changes before and after process. Quantitative and qualitative determination of

polycyclic aromatic hydrocarbons was conducted using gas chromatograph - mass spectrometer system. The experiments were conducted under constant pH as well as under constant temperature. The efficiency of oxidation of the analyzed hydrocarbons under oxidation conditions ranged from 27 to 55%. In the presence of the titanium catalyst the efficiency of PAHs degradation was enhanced to 38-72%. During the integrated process (catalytic oxidation and adsorption on activated carbon) the PAHs removal was in the range 67-86%. The results lead to the conclusion that simultaneous oxidation and adsorption can be successfully apply in the final treatment of industrial wastewater and results in the minimizing PAHs load discharged to the environment.

Słowa kluczowe:

WWA, ścieki koksownicze, utlenianie, sorpcja, TiO_2

Keywords:

PAHs, coke wastewater, oxidation, sorption, TiO_2