

Contemporary methods for treatment of phenolic coke wastewater

Czesław OLCZAK – Environmental Engineering CARBOCHEM, Czarnowąsy near Opole, Grzegorz LIGUS – Opole University of Technology, Faculty of Mechanical Engineering, Department of Environmental Engineering, Opole, Jan M. MIODOŃSKI – Institute of Environmental Protection, branch in Wrocław, Wrocław, Poland

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Introduction

The phenolic coke wastewater is produced from the processes of coal carbonization and receiving carbon derivatives. Their chemical composition is very complex. The major substances present in the coke wastewater are oils and tars, phenols, ammonia, thiocyanates, cyanides and sulphides [1]. Due to their high concentrations and toxicity, there is a need for multistage treatment before they can be discharged to the collection system. The treatment of coke wastewater involves many processes: removal of inhibitors and composition adjustment, biochemical treatment of wastewater and refractory compounds removal [2]. The used methods for the biochemical treatment of coke wastewater are efficient and highly developed in terms of technology. [5, 7]. After the multistage treatment is completed, the coke wastewater contains: COD compounds up to 200 g O₂/m³, phenols up to 0.1 g/m³, thiocyanates up to 2 g/m³, sulphides up to 0.2 g/m³ and cyanides up to 0.2 g/m³. The European Union issued the legal regulations on the requirements and standards of concentration of substances in the coke wastewater discharged to the collection system for the years 2014–2020 [9, 10]. The aim of this work is to analyse the contemporary methods for coke wastewater treatment and to evaluate their compliance with environmental regulations on discharge of wastewater to the collection system.

Sources of phenolic coke wastewater

The post-process coke waters are produced from the process of coal carbonization and receiving carbon derivatives. They contain the ammoniacal liquor and waters from carbon derivatives [1].

The ammonia liquor is the product of condensation of steam from the cooled coke gas. The steam present in this gas comes from the humidity, decomposition of coal charge and technological steam introduced directly into the gas. The ammonia liquor is generated from the water-tar condensates arising in battery receivers, degas coolers, dehydrators and hydraulic seals of gas pipelines. Their amount and chemical composition depend on the coal quality and technology of coal carbonisation.

The post-process waters from carbon derivatives contain separator waters, post-process waters from desulfurization and deamination and waters from the catalytic ammonia decomposition. The significant contribution to the amount and composition of post-process waters from carbon derivatives is made by water condensates of the coke gas deriving from technological steam directly introduced into a gas unit and devices for carbon derivatives. The post-process coke waters contain high concentrations of oil-tar compounds, ammonia, hydrogen sulphide and hydrogen cyanide [1]. Figure 1 presents the scheme of the post-process coke water pretreatment.



Fig. 1. Post-process coke water pretreatment scheme

The post-process coke waters contain up to 300 g/m³ of oil and tar substances. To reduce the concentration of oil and tar substances in the post-process coke waters, they are pretreated by filtration and coagulation processes. Water filtration is conducted in the sand filters, together with coagulation with aluminium and ferric salts. The efficiency of tar removal from water amounts to 85%.

After the tar removal process is completed, the post-process coke waters are under the processes of deamination, desulfurization and decyaniding. These processes are conducted by distillation with steam and water alkalization with sodium hydroxide. After the stage of post-process coke waters pretreatment, the following concentrations are reached: ammonium up to 160 g/m³, sulphides up to 20 g/m³ and cyanides up to 20 g/m³ of waters [2].

After the pretreatment, the post-process coke waters are the phenolic coke wastewaters which are discharged from the coke installation to a sewage plant.

According to the contemporary technological solutions of coal carbonization and receiving carbon derivatives, the concentration of coke in the wastewater ranges from 0.25 to 0.35 m³/Mg. Table I present the composition and load of pollutants in the coke wastewater discharged from the coke installation to a sewage plant.

Table I
Composition and loads of pollutants in phenolic coke wastewater [2]

No.	Substance name	Substance concentration g/m ³	Substance load g/Mg of coke
1	Oils and tars	150	45
2	COD	4200	1260
3	Volatile phenols	1200	360
4	Ammonium nitrate	150	45
5	Thiocyanates	330	99
6	Cyanides	20	6
7	Sulphides	20	6

Methods for treatment of phenolic coke wastewater

The coke wastewaters discharged from the coke installation undergo a multistage treatment before they are introduced to the collection system. Figure 2 presents the scheme of the multistage coke wastewater treatment.



Fig. 2. Diagram of multistage coke wastewater treatment

In the biological processes of wastewater treatment, some of the substances contained in the coke wastewater are the inhibitors: sulphides, cyanides, oils, tars and compounds which are the product of polyhydroxy phenols oxidation.

Coagulation with ferric salts, supported by the coke dust, is commonly used for removal of inhibitors from the coke wastewaters [3]. Compensation tanks with more than 8 hours of wastewater retention are used for the temperature and composition adjustments. After this stage of treatment, the coke wastewaters contain oils and tars in the concentration below 60 g/m^3 , sulphides up to 10 g/m^3 and cyanides up to 10 g/m^3 and the temperature of wastewater should not exceed 35°C [3].

In the majority of installations, two methods are used for the biological treatment of coke wastewaters: denitrification, biodegradation and nitrification (DBN) or the biological treatment of coke wastewaters in combination with sewage waste treatment [4, 5].

DBN method for biological coke wastewater treatment is used in two variations: with and without the addition of an external source of organic carbon [6].

Figure 3 presents the scheme of biological coke wastewater treatment without the addition from an external source of organic carbon.

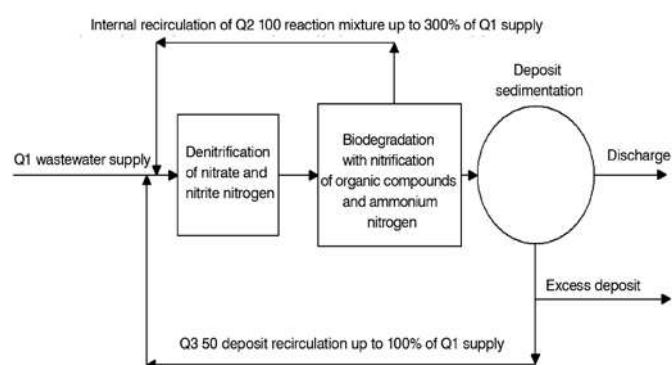


Fig. 3. Diagram of biological coke wastewater treatment without the addition of an external source of organic carbon

Discharged wastewater treated in this way has the following composition: COD compounds up to 300 g/m^3 ; volatile phenols up to 0.5 g/m^3 ; ammonium nitrogen up to 10 g/m^3 ; total cyanides up to 0.5 g/m^3 ; sulphides up to 0.6 g/m^3 . This method for coke wastewater treatment requires the recirculation of the recirculative mixture from the nitrification reactor through a denitrification reactor, in the extreme case, reaching 300% of wastewater arriving to a sewage treatment plant.

Figure 4 presents the scheme of biological coke wastewater treatment with the addition of coke from an external source of organic carbon.

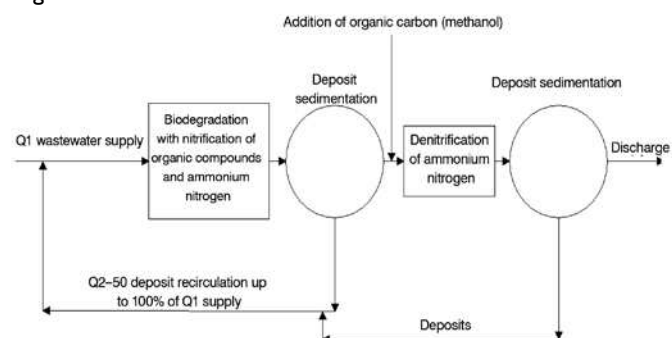


Fig. 4. Diagram of biological treatment with the addition of coke from an external source of organic carbon

Discharged wastewater treated by the biological method with the addition from an external source of organic carbon has the following composition: COD compounds up to 250 g/m^3 ; volatile phenols up to 0.5 g/m^3 ; ammonium nitrogen up to 5 g/m^3 ; total cyanides up to 0.5 g/m^3 ; sulphides up to 0.4 g/m^3 . This method provides a significant reduction of pollutants concentrations in the wastewater

discharged from a sewage plant: ammonium nitrogen by 50%, total cyanides by 44% and sulphides by 33%. However, the cost of the coke wastewater treatment increases due to the extra raw material consumption. The biological treatment of the coke wastewater with the addition of organic carbon from an external source reduces the sensitivity of installation to the ammonium nitrogen concentrations in the wastewater discharged to a sewage plant.

In the industrial practises of the coke wastewater treatment, the combination of both methods is often used, mainly due to the need to compensate high concentrations of pollutants arriving to the installation together with the wastewater.

In the last decade, the biological method for coke wastewater treatment in combination with biological treatment of sewage waste was implemented and popularised. This method is based on supporting the nitrification with activators generated in the process of biological treatment of sewage waste, the process of coke wastewater treatment [7, 8]. Figure 5 presents the scheme of the biological coke wastewater treatment in combination with biological treatment of sewage waste [8].

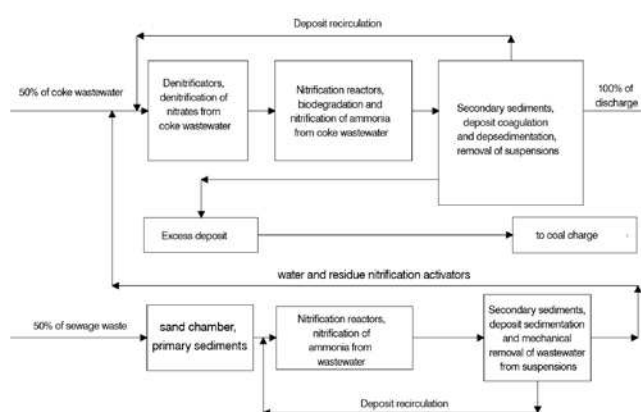


Fig. 5. Diagram of biological coke wastewater treatment in combination with biological treatment of sewage waste

The process of coke wastewater treatment in combination with treatment of sewage waste is conducted at few stages. The first stage is based on the biological treatment of sewage waste by prolonged aeration with the waste retention time longer than 12 hours, generating activators of the nitrification of ammonium nitrogen for the coke wastewater treatment. At the second stage, water and residue nitrification activators are mixed with the coke wastewater and the recirculated biological residue from an industrial sewage plant. At the third stage, the reaction mixture of coke wastewater, nitrification activators and biological residues flows through a cascade of reactors of denitrification, biodegradation and nitrification, whereas, at the fourth stage, biological residues are separated from the wastewater of the reaction mixture by sedimentation. After this stage, biological residues are recirculated to the second stage of the coke wastewater treatment, and the coke wastewater is discharged to the collection system.

Discharged coke wastewater treated in combination with biological treatment of sewage waste contains: COD compounds up to $200 \text{ g O}_2/\text{m}^3$; volatile phenols up to 0.1 g/m^3 ; ammonium nitrogen up to 3 g/m^3 ; general cyanides up to 0.3 g/m^3 and sulphides up to 0.2 g/m^3 . The method for biological treatment of coke wastewater in combination with biological treatment of sewage waste reduces the treatment costs by 60% in relation to the methods described above.

After a multistage treatment of the coke wastewater, they still contain refractory compounds which are almost not biologically degradable. These compounds introduced with the wastewaters to the collection system inhibit the process of biodegradation and nitrification, i.e. selftreatment of waters in the collection system. Refractory compounds in the coke wastewaters are polycyclic organic compounds, generated mainly from the oxidation and

condensation of polyhydroxyl phenols, which are characterised by the rich brown colour, cyanides and sulphides. The COD index value and concentrations of cyanides and sulphides are an indicator of concentration of refractory compounds in the wastewaters.

There is no efficient method for the final treatment of coke wastewaters from refractory compounds; the previous solutions were mainly based on adsorption on active coal and coagulation. They require a huge amount of raw materials and sorbents, are little effective and require high investment and operational costs for installations.

State of compliance with environmental requirements for coke wastes discharged to the collection system

The environmental requirements for the years 2013–2020 for coke oven plants and provided in the Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions [9], and Commission Implementing Decision of 28 February 2012 establishing the best available techniques (BAT) on industrial emissions for iron and steel production [10]. New coke manufacturing plants must comply with the environmental requirements as of 7 January 2013, while the compliance date for the existing plants is 2016 [9].

The environmental requirements for wastes discharged from the coke installations are as follows:

- usage of the coke wastewater treatment with integrated denitrification/nitrification
- after treatment, the coke wastes should not exceed the following emission levels: COD < 220g O₂/m³; phenols < 0.5g/m³; thiocyanates < 4g/m³; sulphides < 0.1 g/m³; cyanides < 0.1 g/m³ and total nitrogen < 15 do 50 g/m³.

Table 2 presents the state of compliance with environmental requirements for the coke wastes discharged from a sewage plant to the collection system [11].

Table 2

State of compliance with environmental requirements for phenolic coke wastes [11]

Index	Values g/m ³		Mark
	Permissible	Reached	
COD	< 220	200	compliant
Volatile phenols	<0.5	0.1	compliant
Total nitrogen	<15-50	50	compliant
Thiocyanates	<4	2	compliant
Cyanides	0.1	0.3	exceeded
Sulphides	0.1	0.2	exceeded

Summary

The concentration of phenolic coke wastewater generated in the process of coal carbonization and receiving carbon derivatives ranges from 0.25 to 0.35 m³/Mg. These wastewaters contain high concentrations of: phenols, ammonia, thiocyanates, sulphides and cyanides. The coke wastewaters undergo a multistage treatment by removal of inhibitors of biological processes, biochemical treatment and refractory compounds removal before they are introduced to the collection system. Nowadays, two methods are used for the biological treatment of wastewaters: denitrification, biodegradation and nitrification (DBN method) or the biological treatment of coke wastewaters in combination with sewage waste treatment. The multistage treatment enables the compliance with emission standards, except for sulphides and cyanides.

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Czesław OLCZAK – Ph.D., graduated from the Faculty of Chemistry of the University of Wrocław in 1967. In 1974, he obtained his doctoral degree in chemical sciences at the University of Silesia in Katowice. Scientific and technical interests: environmental engineering, coke technology and engineering, design and operation of installations for environmental protection. Author of more than 80 science and technical articles. Author and co-author of more than 60 inventions, including more than 45 implemented industrially.

Grzegorz LIGUS – Ph.D. (Eng.), graduated from the Faculty of Mechanical Engineering of Opole University of Technology (2004). He obtained his doctoral degree at Opole University of Technology (2008), his doctoral thesis concerning the field of machine construction and operation. Until 2010 he was working as the Head of the Environmental Engineering Unit at the Institute of Ceramics and Building Materials in the Building Materials Engineering Division in Opole. Currently, he works as Assistant Professor in the Department of Environmental Engineering of the Faculty of Mechanical Engineering of Opole University of Technology. Scientific interests: environmental management, waste management, thermal engineering, hydrodynamics in multiphase systems. He is the author and co-author of 8 chapters in monographs, over 30 scientific and technical papers, and numerous posters and lectures on conferences in Poland and abroad.

Jan Maciej MIODOŃSKI – M.Sc. (Eng.) graduated from the Faculty of Environmental Engineering at Wrocław University of Technology, speciality: water and wastewater technologies. Since 1980, he has been working in the Institute of Creation of Environment in the branch in Wrocław (actual name: the Institute of Environmental Protection, PIB). From the second half of the 80's, he is a director of the Institute of Wastewater Technology and Water Protection. Expert in the Polish Association of Sanitary Engineers and Technicians (PZiTS). In 1991-93, he was assigned to the Water Management Authority (RZWG) in the upper and middle Odra basin. Achievements in the field of water management include participation in realisation of numerous planistic regional and national works, such as the National Programme for Municipal Waste Water Treatment for the years 2005-15. Achievements in the field of wastewater technology and processing of wastewater deposits include: numerous research and development, implementation and construction works, opinions, expertises and publications.