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Piotr Bargieł* Magdalena Zabochnicka-Świątek*

Technologies of coke wastewater treatment in the frame of legislation in force

* Institute of Environmental Engineering, Czestochowa University of Technology;
e-mail: mzabochnicka@is.pcz.czest.pl

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Abstract
The paper focuses on the present legal requirements regarding the quality of coke wastewater resulting from coal coking and coke-oven gas treatment before discharge to water, ground or sewage of an external entity. Characteristics of coke wastewater were carried out and the methods of coke wastewater treatment currently used in installation in Poland were presented.

1. INTRODUCTION

Increasing demand for energy carriers, including coke, increases the production of this fuel, which in turn leads to an increase in the amount of industrial wastewater that is very burdensome for the environment. Current coke wastewater treatment technologies require action to meet the above mentioned needs of the increasing amount of such waste water and the growing market demand for new or improved environmentally friendly technologies.
Due to the fact that the legal regulations in the field of industrial waste water treatment are more and more restrictive, it is necessary to develop innovative technological solutions ensuring the highest efficiency of process water treatment installations. It is recommended to use integrated systems, combining classical unit processes used in wastewater technology (biological, chemical and physical) [Decyzja …2012; Sobolewski et al. 2014].
The diverse composition of coke wastewater is a major problem while selecting the treatment method. The main task of the plant's process water treatment installations is to reduce the pollution load to the values specified in the Regulation of the Minister of the Environment [Rozporządzenie…2014] as well as in the Regulation of the Minister of Construction [Rozporządzenie…2006]. At present, the coking plants carry out investments related to the construction of new coke oven gas and process water treatment facilities, where the requirements of the Best Available Techniques 'BAT' have been applied so far [Decyzja…2012; Sobolewski et al. 2014].
The aim of the study was to discuss the current state of coke wastewater treatment methods in the coking plants in Poland in the frame of legislation in force.
Scope of the study comprised: (i) the characteristics of coke wastewater; (ii) presenting the most important regulations concerning the quality of coke wastewater generated from the coal coking process and the treatment of coking gas before discharging it into water, ground or external entity's sewage system; and (iii) the discussion of coke wastewater treatment methods presently used in the installations operating in Poland.

2. CHARACTERISTICS OF COKE WASTEWATER

Phenolic coke wastewater is formed in the process of coal coking and obtaining coal derivatives. It is a very complex chemical composition. The basic substances found in coke wastewater are: oils and tars, phenols, ammonia, rhodium, cyanides and sulphides [Olczak 2000]. Very high concentration of contaminants and their toxicity cause the necessity of multi-stage treatment before discharging into water, soil and sewage system of an external entity. Coal caking and separation of coal-derivative products cause the formation of process coking waters. They consist of coal water and water from facilities for coke gas purification [Olczak 2000]. Gaseous water is formed as a result of condensation of water vapour from coal gas in the process of its process of cooling down. The steam contained in the gas is derived from the moisture and decomposition of coal and process steam directly introduced into the gas.
Coal water is released from the condensation of water and tar that are formed in gas receivers on coking battery, gas coolers, steam traps and closures of hydraulic gas

pipelines. The amount of this water as well as it chemical composition, depends mainly on the quality of coal and coking technology. Process water from the treatment of coal gas consists of separator waters, process water from desulphurisation plants, ammonia plants and water from the catalytic decomposition of ammonia. The water condensates of coal gas produced from process steam directly introduced into the gas system and the equipment of the treatment plant have a significant share in the quantity and composition of this water. Process coking water contains high concentration of oil-tar, ammonia, hydrogen sulphide and hydrogen cyanide compounds [Olczak 2000].

In Table 1 shows the basic values of parameters characterizing coke wastewater that were collected during the study.

The Table 1 shows that coke wastewater contains very high concentration of pollutants that are harmful to the soil and water environment, which require the search for increasingly advanced technologies of wastewater treatment.

3. LEGISLATION IN FORCE

Until 4th September 2018, the coking plant installations were obliged to adapt their sewage treatment facilities to the new pollutant limits set out in the best available techniques, known as BAT 56 [Decyzja …2012]. It means that, in accordance with the BAT conclusions 56, the coking plant must achieve concentrations in treated wastewater after biological sub-treatment of coking wastewater before discharge to waters or land at new levels:

COD <220 mg/dm^3;
BOD5 <20 mg/dm^3;
Free sulphides <0.1 mg/dm^3;
Thiocyanates <4 mg/dm^3;
Free cyanides <0.1 mg/dm^3;
Polycyclic aromatic hydrocarbons (PAHs) <0.05 mg/dm^3;
Phenols <0.5 mg/dm^3;

Total nitrogen (sum of ammonium nitrogen, nitric nitrogen and nitrite nitrogen) <15–50 mg/dm^3.

In addition to the requirements of BAT 56, coke wastewater treatment plants shall meet the requirements for treated wastewater set out in: (1) the Minister's for the Construction Regulation dated 14th July 2006 on how the obligations of industrial wastewater suppliers and the conditions under which wastewater is discharged into sewer systems are to be met [Rozporządzenie…2006] as well as (2) the Minister's for the Environment Regulation dated 18th November 2014 on the conditions to be met for the discharge of wastewater into water or soil and on substances particularly harmful to the aquatic environment [Rozporządzenie…2014]. The permissible range of values for the selected sewage parameters are shown in Table 2.

Table 1. Raw coke wastewater [Miodoński et al. 2010].

Parameter	Concentration mg/dm^3
Ammonium nitrogen	600
Total nitrogen	900
Chemical oxygen demand	4500
Phenols	2000
Thiocyanates	30
Free cyanides	5
Hydrogen sulphide	50

4. METHODS OF COKE WASTEWATER TREATMENT

Conventional wastewater treatment methods with nitrogen compounds removal involve the use of nitrification, denitrification and assimilation processes by living organisms. In addition to the conventional methods, in recent years, the attention has been paid to the nitrogen removal processes [Sadecka 2010] such as: the Sharon process, the Anammox process, the Oland process, the Canon process, simultaneous nitrification and denitrification, oxygen deammonification and the BABE process.

Dynamically developing coke production in Poland requires effective methods of sewage treatment. Due to the content of many chemical compounds, coke wastewater treatment poses a number of problems, and therefore, is usually carried out in many stages [Zabochnicka-Świątek 2017]. A coagulation process is used for wastewater treatment. Modern wastewater treatment methods are being implemented in order to obtain treated wastewater, which will meet the requirements of the legislation and be environmentally friendly at the same time. The methods currently used for the treatment of coke wastewater are described in detail below.

Pop-process coking water contains up to 300 g/m^3 of oil and tar substances. In order to reduce the concentration of oil and tar substances in process coking water, they are cleaned by filtration and coagulation. Water filtration is carried out in gravel filters with coagulation of aluminium and iron salts. The desulphurisation process efficiency is 85%. A diagram of the process treatment of coke wastewater is shown in Figure 1 [Olczak 2000].

Advantage:

– Relatively low costs of conducting the process

Table 2. Quality parameters of the wastewater discharged.

Type of substance	Dz.U. 2006 nr 136 poz. 964 mg/dm³ mgO_2/dm^3	Dz.U. 2014 poz. 1800 mg/dm³ mgO_2/dm^3	Requirements of BAT 56** mg/dm³
Ammonium nitrogen	100–200	10	-
Nitrite nitrogen	10	1	-
Total nitrogen	-	30	<15–50
Chlorides	1000	1000	-
COD	*	250*	<220*
BOD_5	*	25*	<20*
Free cyanides	0.5	0.1	<0.1
Combined cyanides	5	5	-
Thiocyanides	-	-	<4.0
Free sulphides	-	0.2	<0.1
Thiocyanates	30	10	-
Volatile phenols	15	0.1	<0.5
PAHs	15	15	<0.05

* The values of the indicators shall be determined on the basis of the permissible load of the treatment plant.
** Decyzja …2012.

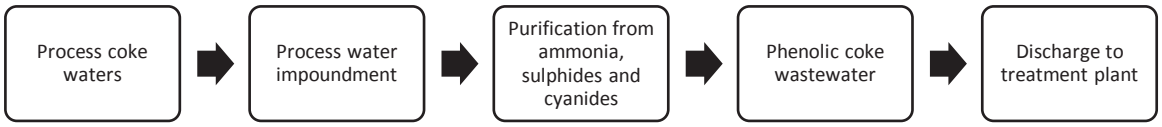

Figure 1. Diagram of the process treatment of coke wastewater.

Disadvantage:
– No degradation of pollutants

After desalination, the process water is purified from ammonia, desulphides and decocyanated. These processes shall be carried out by the vapour distillation method with alkaline water using sodium lye. After this stage of process treatment of coke wastewater, the ammonia concentration reaches up to 160 g/m³, sulphides up to 20 g/m³, and cyanides up to 20 g/m³ of waters. Such a purified process coking waters constitutes phenolic wastewaters, which are discharged from the coking plant installation to the wastewater treatment plant [Burmistrz et al. 2003]. In the process of coking coal and recovering coal derivatives, 0.25 to 0.35 m³ of phenolic coke wastewater per ton of coke is produced.

Coke wastewater discharged from the coke production plant but before being introduced into the receiver, are treated in several stages. Figure 2 [Olczak 2000] shows the multi-stage treatment of coke wastewater.

4.1. Biological methods of coke wastewater treatment

In domestic coking plants, the wastewater treatment process is carried out by integrated biochemical sewage treatment plants.
They are used in:
– biochemical coking sewage treatment plants comprising: a chemical reactor, averaging tank, bioreactor I level (denitrification of nitrogen

Figure 2. Diagram of the multi-stage treatment of coke wastewater.

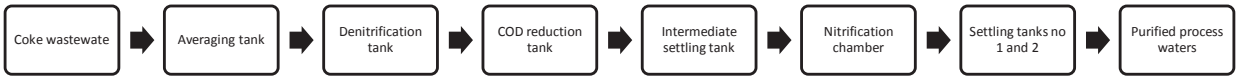

Figure 3. Biological treatment scheme for process waters.

compounds under anaerobic conditions), bioreactor II level (biodegradation with nitrification under aerobic conditions), final settling tanks, averaging and storage tanks for purified wastewater, gravitational sludge thickener and sludge filter presses [Sobolewski et al. 2014]
- biological treatment of wastewater using nitrification and denitrification processes [Sobolewski et al. 2014]

The purpose of the biological process water treatment plant is to treat coking wastewater (excess ammonia water and other highly polluted wastewater from the coke production plant, including certain process steam condensates, water from hydraulic seal overflows and from tray, tank and grid dewatering), from impurities such as phenol, ammonium nitrogen and free cyanides, up to the levels required by the Best Available Techniques. Diagram of biological treatment of process waters is presented in Figure 3.

The biological coking wastewater treatment plant consists of [Pozwolenie Zintegrowane 2016]:
- steel averaging tank (input) with capacity 1600 m^3
- concrete denitrification tank with capacity 589 m^3
- concrete tank for COD reduction with capacity 831 m^3
- concrete intermediate settling tank with a suction sweeper with working surface of 174 m^2 and capacity 694 m^3
- concrete sediment chamber with capacity 7 m^3
- nitrification chamber with filling and aeration system with capacity 713 m^3
- degassing tank
- flocculant dispensing tanks (coagulation)
- settling tanks no. 1 and no. 2
- sediment compaction system (I level – gravitational, with chemical support for the sedimentation process, II level – centrifuge)
- dispensers, pumps, accessories, fittings, control systems, and so on
- Treatment efficiency:
- 25 – 30 m^3/h (600 m^3/day)

Continuous work – 365 days per year.

In biological wastewater treatment processes, some of the substances contained in coke wastewater are inhibited, for example, sulphides, cyanides, oils and tars and compounds derived from oxidation of polyfunctional phenols. Coagulation with iron salts supported by coke dust is commonly used to remove inhibitors from coke wastewater [Burmistrz et al. 2003].

Compensatory tanks with a retention time of more than 8 hours are used to compensate for wastewater composition and temperature. After this stage, the coke wastewater contains less than 60 g/m3 of oils and tar, sulphides up to 10 g/m^3 and cyanide up to 10 g/m^3. Wastewater temperature after this stage shall not exceed 35 ˚C [Burmistrz et al. 2003]. Two methods are used for biological treatment of coke wastewater in most installations: DBN – denitrification, biodegradation and nitrification and/or biological treatment of coke wastewater in combination with urban wastewater treatment.

Advantages:
- high treatment effects
- marginal production of excessive sludge
- automated process
- capacity to expand

Disadvantages:
- high demand for construction land
- high costs of construction and operation

5. SUMMARY

In the process of coal pyrolysis and coil gas purification, large quantities of process water are produced, which contain substances harmful to the groundwater environment, that is, ammonium nitrogen, cyanides, thiocyanates, phenols, and so on. In order to meet the legal requirements, coke wastewater must be subject to purification processes.

Legislation, which is to be modified in the near future, will introduce increasingly stringent requirements for

the quality of wastewater from coking plants. At present, the sewage treatment process is being carried out in the national coking plants using:

- the biochemical coking sewage treatment plants comprising chemical reactor, averaging tank, I level bioreactor (denitrification of nitrogen compounds under anaerobic conditions), II level bioreactor (biodegradation with nitrification under aerobic conditions), final settling tanks, averaging and storage tanks for purified wastewater, gravitational sludge thickener and sludge filter presses.
- the biological wastewater treatment plants using nitrification and denitrification processes.

Multi-stage treatment of coke wastewater ensures that the parameters specified in the legal requirements are met, in addition to PAHs, free cyanides and sulphides. In order to meet the new requirements, the coking plants will be forced to modernize their existing wastewater treatment plants in the near future or to implement new solutions.

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