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An Overview of Coking Wastewater Characteristics and Treatment Technologies

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Abstract

Coke is a high-calorie carbon mass obtained by dry distillation of coal, and used in various processes, the most significant of which is production of iron and steel. Coke production is present worldwide, especially in recent years when due to economic growth the global demand for steel is growing, which consequently increases demand for coke. During coke production, enormous amounts of toxic wastewater of extremely complex composition are generated. Priority pollutants that coking wastewater contains are phenols, cyanides, and thiocyanates. For successful treatment of such wastewater and achieving safety discharge standards, the application of a single process is insufficient. Accordingly, a combination of different physicochemical and biological treatment procedures, of which biological treatment is the most important, should be applied. In this article, a literature review of coking wastewater characteristics and treatment technologies is presented. In addition, this review addresses the complexity and limitations associated with coking wastewater treatment, with special emphasis on biological treatment methods. The aim of this review was to summarise the current knowledge on coking wastewater treatment technologies, which could eventually help optimisation of existing solutions.

Keywords

Coke, wastewater, phenols, cyanides, thiocyanates, biological treatment

1 Introduction

More than 70 % of the global steel production is occurring in blast furnaces, which use coal to reduce iron oxides to ores. In order to achieve required quality of coal for steel production, it must be converted into coke. Coke has a higher calorific value in comparison with conventional fuels, such as wood or oil. Coke production is directly related to generation of considerable amounts of wastewater, known as coking wastewater.[1–5] The iron and steel industry is the largest consumer of fresh water compared to other industries.[6] Coking wastewater contains significant amounts of phenols, cyanides, thiocyanates, aluminium salts and chlorides, and therefore is considered toxic from the environmental point of view.[3] Discharge of coking wastewater into external environment, without adequate and sufficient treatment, directly affects the quality of surface water bodies, as well as groundwater, aquatic life, and even the food chain.[7] Therefore, special attention is being paid to the treatment of such wastewater in order to avoid serious environmental pollution.[8]

Given such a challenging composition and specificity of coking wastewater, efficient treatment involves a combination of physical, chemical, and biological processes, especially as environmental regulations become more stringent.[4]

1.1 Coke production

Coke is formed in complex technological plants – coke ovens, through carbonisation, by heating the coal at extremely high temperatures, in an oxygen-free atmosphere, for the purpose of evaporating volatile compounds.[4,7,9] In the process of melting iron ore, coke has a dual role: fuel and reducing agent.[6] There are more than 550 coke-oven plants worldwide at the moment, most of which are located in China.[4] Evidently, China is the largest coke producer in the world, and discharges more than 250 million tons of coking wastewater each year.[10,11] As reported by *Wang et al.*,[12] even 1.26 % of total industrial chemical oxygen demand (COD) discharge belongs to coking wastewater discharges.

1.2 Coking wastewater production

Coking wastewater is generated from coke washing and condensation of coke gas, as shown in Fig. 1.[13,14] It is considered one of the most challenging industrial effluents to treat.[9] For each ton of coke produced, approximately 4 m^3 of freshwater is used, of which 1 m^3 is discharged from the system as wastewater.[6,7]

1.3 Coking wastewater composition

Coking wastewater is characterised by extremely complex chemical composition, consisting of both organic and inorganic compounds.[2,3] The content can generally be divid-

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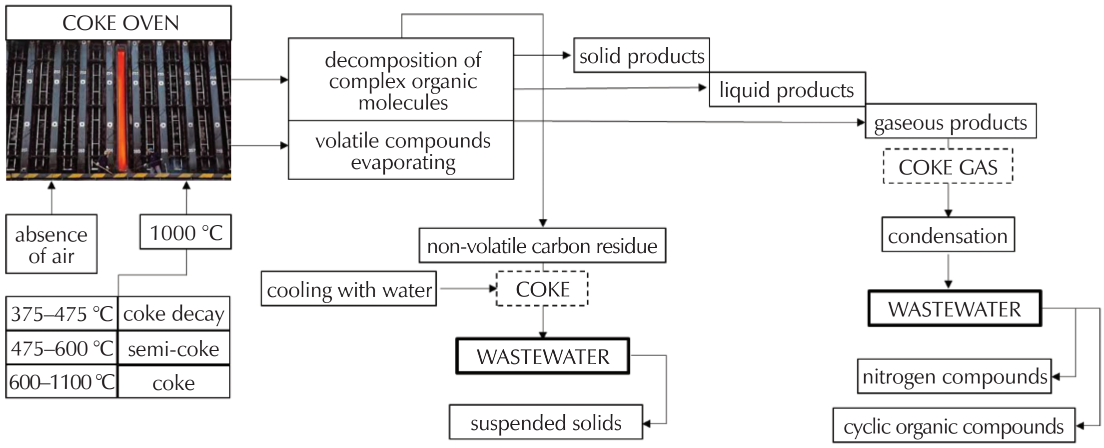


Fig. 1 – Coking wastewater production
Slika 1 – Nastajanje otpadne vode koksne industrije

ed into insoluble (suspended and colloidal) particles, and dissolved organic (hydrophobic and hydrophilic) matter.[15]

Coking wastewater contains high soluble COD amount, mainly composed of hardly biodegradable substances which causes difficulties in biological treatment, and slowly biodegradable organic compounds, such as phenols.[16] Major pollutants of coking wastewater are phenolic substances, formed by degradation of organic compounds during coke making, which normally account for half the total COD content, yet coking wastewater also consists of a number of other organic compounds, such as benzene and its derivatives (toluene, xylene, naphthalene, anthracene, phenanthrene, benzopyrene); monocyclic, polycyclic, and heterocyclic compounds; petroleum substances; fatty acids, *etc*.[2,3,17,18] During phenol degradation, a number of intensely coloured aromatic compounds are formed, which give the wastewater a dark brown colour.[18]

Concentration of polycyclic aromatic hydrocarbons (PAHs) is usually low compared to other organic contaminants, yet they are considered one of the most hazardous constituents of coking wastewater.[2,3,9] Predominant PAHs in coking wastewater consist of four to six aromatic rings.[11] Furthermore, nitrogen heterocyclic compounds (NHCs), such as pyridine, quinoline, isoquinoline, indole, and their derivatives make up 30–50 % of the total organic load.[3] However, *Fan et al*.[19] listed more than 300 organic compounds in coking wastewater, confirming the large presence of various organic constituents.

On the other hand, high concentration of inorganic salts, mainly sulphates, sulphides, chlorides, thiocyanates, cyanides, ferrocyanides, and ammonia nitrogen are also characteristic for coking wastewater.[2] The most significant inorganic compounds are cyanide-containing compounds, thiocyanate, ammonia, and sulphates.[3,20]

The main by-product of the coke production process is tar, which consequently is found in coking wastewater as emulsified coal tar. The share of tar is usually 2–5 %.[2,3]

Since the majority of those compounds is toxic, carcinogenic, teratogenic, and mutagenic, coking wastewater is considered one of the most toxic industrial effluents, which causes acute toxicity accompanied with genotoxicity if discharged into natural water bodies without adequate treatment.[2,21] Coking wastewater composition most certainly depends on the nature/quality of the coal and coke production process (technology level and people proficiency).[6,22–24] Therefore, concentrations of pollutants in coking wastewater vary significantly from different coking plants.[9] Table 1 shows physicochemical and ecotoxi-

Table 1 – Coking wastewater characteristics[4,6,7,9,13,14,16,21,25,26]
Tablica 1 – Sastav otpadne vode koksne industrije[4,6,7,9,13,14,16,21,25,26]

Physicochemical indicators	Unit	Range	Discharge requirements[27]
Tars	$mg\,l^{-1}$	5–150	–
Total suspended solids	$mg\,l^{-1}$	2–712	35
Conductivity	$\mu S\,cm^{-1}$	5000–12500	–
pH-value	–	6.5–11.5	6.5–9.0
Colour	–	black	–
COD	$mg\,O_2\,l^{-1}$	81–16000	125
BOD_5	$mg\,O_2\,l^{-1}$	60–5450	25
Phenols	$mg\,l^{-1}$	50–2000	0.1
Oil and grease	$mg\,l^{-1}$	4.7–1250	20
Cyanides	$mg\,l^{-1}$	0.1–210	0.1
Thiocyanates	$mg\,l^{-1}$	50–640	0.1
Ammonia	$mg\,l^{-1}$	49–790	10
Total nitrogen	$mg\,l^{-1}$	215–270	15
Chlorides	$mg\,l^{-1}$	2500–3500	–
Sulphates	$mg\,l^{-1}$	900–1200	250
Sulphides	$mg\,l^{-1}$	1.4–50	0.1
Ecotoxicological indicator			
EC_{50}	$mg\,l^{-1}$	34.4	–

cological indicators of coking wastewater. A huge range of various compounds in coking wastewater means a large number of possible interactions, different toxicity of each individual compound, as well as inhibition effect.[21] This is elaborated in more detail further herein.

1.3.1 Phenols

Phenols and phenolic compounds are toxic human carcinogens, the basic structure of which consists of hydroxyl group attached to a benzene ring. The phenol derivatives that are most common in coking wastewater are shown in Table 2. Phenolic compounds are soluble in water, which makes them resistant to biodegradation and thus their removal from wastewater much harder.[28] Serious amounts of 0.3 to 12 kg of phenols are generated *per* ton of coke produced.[6,29] Presence of phenols (≥ 200 mg l^{-1}) in wastewater interferes with the biodegradation of thiocyanates, seriously affects nitrification, and inhibits denitrification.[9,21] Apart from bacteria, most common of which are *Pseudomonas* (92 % phenol removal) and *Acinetobacter*, phenols can be biodegraded by yeast and fungi as well.[9,21,30] *Phalgune et al.*[30] investigated removal of phenol (2000 mg l^{-1}) by *Candida tropicalis,* and proved that biodegradation started after 8 h and was completed in 20 h. Furthermore, 2,6-dimethylphenol was removed by same mechanism, but with slower biodegradation rate.

The most common physicochemical phenol removal process is oxidation. Ozone is one of the strongest oxidants used, but Fenton process is also efficient, as well as alternative oxidants, such as potassium permanganate, chlorine dioxide, and chlorine.[29] *Tyagi et al.*[31] investigated combination of Fenton process and biological treatment for removal of phenol from synthetic coking wastewater. Initial phenol concentration was 1000 mg l^{-1}, while maximum removal efficiency after the Fenton process under optimal conditions was 74 %. Remaining 300 mg l^{-1} of phenol was reduced by 98.8 % after biological treatment. Synergy of Fenton's oxidation and biological degradation processes was found to be highly effective.

Furthermore, the same authors investigated inhibition of *Pseudomonas* and *Enterobacter* by presence of cyanide. In the absence of cyanide, phenol concentration was reduced from 300 to 74 mg l^{-1} by *Pseudomonas* strain within 48 h, while in contrast, phenol concentration remained the same in the presence of 50 mg l^{-1} cyanide. *Enterobacter* showed no significant degradation potential of phenol regardless of cyanide presence/absence.

1.3.2 Cyanides

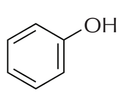
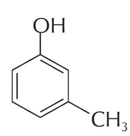
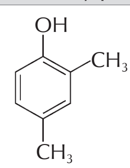
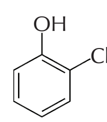
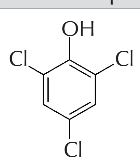
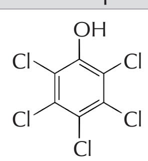
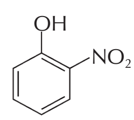
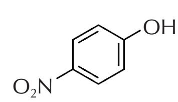
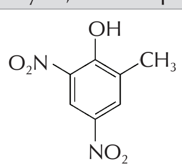
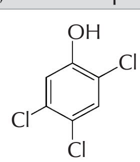
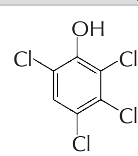
Raw materials (coke, ore, *etc.*) contain sodium and potassium oxides/silicates/carbonates that react with nitrogen from air blast and carbon from coke to form alkali cyanides due to high temperatures (> 1000 °C). Formed alkali cyanides dissolve in water.[18]

$$M_2SiO_3 + 3C \rightarrow 2M + Si + 3CO \quad (1)$$

$$M + 2C + N_2 \rightarrow 2MCN \quad (2)$$

Eqs. (1) and (2) show previously described reactions, where M stands for potassium/sodium, and MCN for formed alkali cyanides. Cyanide is a characteristic pollutant of coking wastewater, and can be found in two basic forms: less toxic *cyanide complex*, and extremely toxic *free cyanide* which blocks aerobic respiration and enzymatic activity of microorganisms in activated sludge.[3,4,7,15,20,32] Weak acid dissociable cyanides include cyanide complexes of silver, cadmium, copper, mercury, nickel, and zinc, while strong acid dissociable cyanides are complexes of cobalt and iron. However, the predominant form of cyanide pres-

Table 2 – Phenol derivatives present in coking wastewater[28]
Tablica 2 – Derivati fenola prisutni u otpadnoj vodi koksne industrije[28]

phenol	o-cresol	2,4-dimethylphenol	2-chlorophenol
			
2,4,6-trichlorophenol	pentachlorophenol	2-nitrophenol	4-nitrophenol
			
2-methyl-4,6-dinitrophenol	2,4,5-trichlorophenol	2,3,4,6-tetrachlorophenol	
			

ent in most natural waters is free cyanide, which includes hydrogen cyanide (HCN), and cyanide ions (CN^-). HCN is a weak acid with pK_a of 9.2.[33] Therefore, at pH > 9.5, most of the free cyanide is present in CN^- form, while at pH < 7.5, it is mostly present as HCN.[18,20]

Removal of cyanides from coking wastewater is the main objective of chemical pretreatment, and represents the major problem of wastewater detoxification, and of course, should include all three types of cyanides.[21,32] Most often, cyanides are removed by chemical precipitation with iron. Its removal is associated with reduction in COD, suspended solids, fats and oils if present, and simultaneous formation of ammonia subsequently oxidised to nitrate in aerobic conditions.[3,4,6,7,15,19,20,32] Concentrations of cyanides above 2 mg l^{-1} inhibit the nitrification and biodegradation of phenols and thiocyanates.[19,21,32]

Razanamahandry et al.[34] proved that 95 % of 80 mg l^{-1} of free cyanide can be oxidised by cyanide-degrading bacteria at optimal conditions within 25 h. Bacteria destroy C−N link, and use carbon or nitrogen for their metabolism. When the concentration of free cyanide was increased to 100 mg l^{-1}, bacterial growth was inhibited and so was the biodegradation of cyanide.

1.3.3 Thiocyanates

Thiocyanate (SCN^-) is a hazardous and chemically stable pollutant generated in the reaction of cyanide and sulphur in the coke production process, under high temperatures, as shown in Fig. 2.[25,35,36]

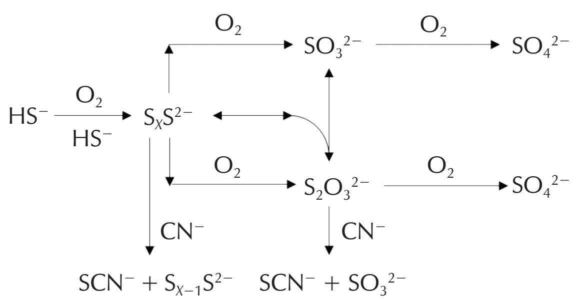


Fig. 2 – Possible reactions of thiocyanate formation in coking wastewater[37]
Slika 2 – Moguće reakcije nastajanja tiocijanata u otpadnoj vodi koksne industrije[37]

In coking wastewater, thiocyanate accounts for approximately 15 % of total COD.[38] Biological removal of thiocyanate is known to be the most sensitive process after nitrification, and may be achieved under both aerobic and anoxic conditions, and mesophilic temperature. Autotrophic bacteria use inorganic carbon from thiocyanate as carbon source, while heterotrophic microorganisms use nitrogen from thiocyanate and organic carbon as energy source. Unfortunately, biological degradation of thiocyanate increases ammonia and sulphate content in wastewater. For each mole of SCN^- degraded, 0.24–0.26 mol of NH_4^+-N are produced.[3,24,25,36,38] *Wu et al*.[10] proved that pH values from 6.12 ± 0.07 to 7.03 ± 0.12 are more favourable for the growth of thiocyanate-degrading bacteria than pH values from 7.00 ± 0.05 to 9.05 ± 0.11. The main thiocyanate-degrading bacteria is *Thiobacillus*.[8] Thiocyanate-degrading bacteria are less competitive for oxygen than heterotrophs.[10] Although thiocyanates are generally less toxic than cyanides, they may also inhibit the biodegradation process. On the other hand, ammonia, phenol, PAHs, and trace metals inhibit the thiocyanate removal.[3,25] Cyanides and thiocyanates contribute to inhibition of microorganisms within the activated sludge. Due to their toxicity, not only are these compounds resistant to microbiological degradation, but they also contribute to inhibiting biodegradation of other components of coking wastewater.

1.3.4 Ammonia

Raw coking wastewater is highly loaded with ammonia, and it is usually reduced by physicochemical pretreatment. In most coke industries, ammonia concentration is reduced through steam stripping or distillation, characterised by high operating costs.[39] Consequently, ammonia is recommended to be oxidised in the biological activated sludge process.[3,7] On the other hand, ammonia can be formed in biological process by ammonification or hydrolysis of thiocyanates. Another drawback in biological ammonia removal is inhibition of nitrification by phenols and thiocyanates.[6] Yet, possible solution to this problem is aerobic reactor before anoxic/oxic (A/O) biological treatment.[24] However, ammonia removal is a key process in coking wastewater treatment.[38] *Kim*,[14] discovered that *Nitrosomonas europaea* and *Nitrosomonas nitrosa* are the dominant ammonia oxidising bacteria. *Nitrospira* was also detected. Optimal conditions for ammonia oxidising bacteria are 25–30 °C and pH 8.0–8.5, yet they are resistant to changes of environmental conditions. Certain groups of bacteria are capable of aerobic conversion of ammonia into nitrogen by heterotrophic nitrification and aerobic denitrification.[10]

2 An overview of coking wastewater treatment methods

Although individual processes are effective, they cannot be used alone in the treatment of this type of wastewater with no shortcomings.[3,7,21] Difficulties in removing refractory organic compounds and the inhibitory effects of toxic compounds are the major limitations in successful wastewater treatment, making conventional technologies inefficient.[21] Coking wastewater is generally treated with the combination of physical, chemical, and biological processes, among which the biological process is indispensable and the most important.[3,7] Most of the wastewater treatment plants (WWTP) treat coking wastewater in the following order: 1. physicochemical pretreatment, 2. biological treatment, and 3. advanced treatment.[22] Despite complex wastewater treatment, discharge standard requirements are often not achieved.[4]

2.1 Physicochemical treatment

Considering high COD/total nitrogen (TN) ratio of coking wastewater, and majority of COD consisting of phenols and thiocyanate, which have an inhibiting effect on nitrification, it is necessary to reduce its concentrations by physicochemical processes prior to biology.[40] Physicochemical treatment is also applied to polish the composition of wastewater afterwards, to achieve discharge requirements.[3] Usually, physicochemical treatment of coking wastewater involves coagulation followed by sedimentation. Aluminium and iron salts are used as conventional coagulants.[6,41] In the study of *Chen et al.*,[17] polyferric sulphate showed better performances than polyaluminium chloride with COD removal of 24 and 2.5 %, respectively. Polyferric sulphate also has decolourisation effect due to adsorption and oxidation ability of Fe^{3+}. On the other hand, polyacrylamide showed no coagulation capability.

Treatment of coking wastewater with iron(II) sulphate is a two-step process. Iron(II) sulphide precipitation, cyanide complexation, and colloidal coagulation occur in the first step. The second step is immobilisation of soluble metal-cyanide complexes by Fe^{2+}.[32]

Today, adsorption of contaminants onto activated carbon, zeolites, natural polymers or cheap waste materials is becoming more popular.[6,41] The most important criteria for adsorbent to be suitable for application in wastewater treatment are specific surface area and price. Activated carbon can be substituted with activated coke, a material of specific surface area of 408 $m^2\,g^{-1}$, and the removal capacity of COD 92 %.[42]

Advanced oxidation processes (Fenton process, photo-Fenton process, ozone) are applied in order to destroy the molecular structure of hard-to-degrade/toxic organic substances, which results in an improvement in the biodegradability of wastewater.[5,6,20] *Verma and Chaudhari*[20] applied Fenton process for oxidation of phenols, cyanides, and COD from coking wastewater. Initial concentrations of these contaminants were 283, 19, and 2810 $mg\,l^{-1}$, respectively. The corresponding removal rates were 88, 79, and 85 %.[20] Sodium hypochlorite can be applied as an alternative to peroxide in Fenton process, with COD removal of 83 %.[43] Strong adsorption potential of iron(II) hydroxide formed during Fenton process should not be ignored. The Fe^{3+} formed under pH value 5 and Fe^{2+}:H_2O_2 ratio 1 : 1 served as an adsorbent with surface area of 23 $m^2\,g^{-1}$ and reduced COD concentration from 119–198 to 62–104 $mg\,l^{-1}$.[44] *Wang et al.*[24] applied coagulation with ozonation after the biological treatment, and achieved COD removal of 93 %. Coagulation was used to reduce the amount of suspended solids before ozonation. Ozone effectively oxidizes refractory/toxic organic compounds, *i.e.*, phenols, PAHs, and nitrogen heterocyclic compounds. The great advantage of ozone is that it creates no secondary pollution and, compared to the Fenton process, requires no pH adjustment.[17] *Chen et al.*[17] applied composite coagulant (20 $FeSO_4$:1 polyacrylamide) and catalytic ozone oxidation to treat coking wastewater with initial phenol concentration and COD of 1031 and 4881 $mg\,l^{-1}$, respectively. The removal efficiencies were 49 and 35 %.

2.2 Biological treatment

Since physicochemical treatment of coking wastewater is facing difficulties, biological treatment imposes itself as a solution, making it a billion-dollar industry.[6,29,38] The purpose of biological treatment is to reduce COD, followed by phenols, cyanides, thiocyanates, ammonia, and nitrates through aerobic or anaerobic biotransformation processes, *i.e.*, complete nitrification-denitrification cycles to gain stable end-products.[2,7,21,40] In general, biodegradability of coking wastewater is extremely low (BOD_5/COD < 0,1).[9,12,32] Therefore, coking wastewater must be adjusted for biological treatment. The least complicated way is to dilute wastewater with technical water, or to partially recirculate the effluent, but these methods are questionable in terms of water consumption and operating costs.[3]

Conventional activated sludge technology has become the most popular and widespread technology for the treatment of different types of wastewaters; however, conventional activated sludge alone usually cannot be applied to industrial wastewater treatment, due to the difference in the properties of both wastewater and activated sludge, compared to municipal wastewater.[16] *Chu et al.*[44] reported that coking wastewater could not be effectively treated in conventional sequencing batch reactors either. In general, biological treatment of coking wastewater cannot be carried out in a single bioreactor because individual steps of the biological process require different conditions and microorganisms.[3,16] Aerobic or anaerobic technologies alone are not capable of achieving discharge standards, yet the combination of these two processes significantly reduces the concentration of pollutants.[2] To overcome mentioned bottlenecks, new technologies and bioreactors have been developed in order to achieve efficient and sustainable wastewater treatment, some of which are given in Table 3.[10]

However, adoption of optimal biological treatment for industry-scale treatment is quite a challenge.[21] For example, anoxic/oxic (A/O), anoxic/anoxic/oxic (A/A/O), and anoxic/oxic/oxic (A/O/O) biological processes are dominant activated sludge processes for coking wastewater treatment in China.[19,41] *Wei et al.*[22] reported six different versions of biological treatment processes, divided according to high (A/A/O, O/A/O, oxic/hydrolytic/oxic (O/H/O)) or low organic load of coking wastewater (A/O, A/O/O, A/A/O, A/A/O/O), and which are applied in real systems in China, as follows: A/A/O process was applied at seventeen, O/A/O at eleven, O/H/O at three, A/O at seven, A/O/O at six and A/A/O/O at eight WWTPs.

A/A/O process is assessed to be the first option for biological treatment of coking wastewater and generally for wastewater containing high amounts of phenols and ammonia.[8,22,23,38] Beginning of biological treatment with anoxic phase is preferred due to reduction of toxicity/improvement of biodegradability.[21] However, *Zhu et al.*[38] found a deficiency in the anoxic phase performances, due to the inhibition of methanogenic bacteria by toxic organic molecules, determining only 2 and 3 % of COD and phenols removal, respectively. The same authors proved that the step feed A/O/A/O process had 80 % higher denitrification rate than traditional A/O/O process due to better distribution of organic carbon.[19]

Table 3 – Treatment methods of coking wastewater
Tablica 3 – Metode obrade otpadne vode koksne industrije

Influent characteristics	Applied treatment	Technical parameters	Effluent characteristics	Ref.
COD 7558 mg l^{-1} TN 4394 mg l^{-1} phenols 143 mg l^{-1} PAHs 82 µg l^{-1}	dephenolisation ammonia stripping A/O/A/O cyanide removal ($FeSO_4$) defluorination ($CaCl_2$) coagulation sedimentation oxidation (NaOCl)	HRT 120 h DO (A) 0–0.5 mg l^{-1} DO (O) 4.8–7.1 mg l^{-1}	98 % COD 99.5 % TN 99 % phenols 96 % PAHs	45
COD 401 mg l^{-1} TN 105 mg l^{-1} NH_4^+-N 95 mg l^{-1}	3 electrochemical reactors (ECR) 2 biological aerated filters (BAF) 3 biofilm electrode reactors (BER)	ECR HRT 1 h BAF HRT 15 h BER HRT 18–93 h	83 % COD 99 % TN 99 % NH_4^+-N	8
COD 2779 mg l^{-1} TN 324 mg l^{-1} NH_4^+-N 41 mg l^{-1} phenols 654 mg l^{-1} cyanide 41 mg l^{-1} PAHs 5034 µg l^{-1}	cyanide removal ($FeSO_4$) oil removal SP-A/O/A/O coagulation reverse osmosis	HRT 80 h DO (A) < 0.1 mg l^{-1} DO (O) 2.3–6.4 mg l^{-1} 70 % of influent to A1 30 % of influent to A2	89 % COD 86 % TN 95 % NH_4^+-N 99 % phenols 99 % cyanide 90 % PAHs	19
	cyanide removal ($FeSO_4$) oil removal A/O/O coagulation reverse osmosis	HRT 80 h DO (A) < 0.1 mg l^{-1} DO (O) 1.3–6.9 mg l^{-1} biofilm media 65 %	85 % COD 7 % TN 76 % NH_4^+-N 99 % phenols 99 % cyanide 90 % PAHs	
COD 4000 mg l^{-1} TN 500 mg l^{-1} NH_4^+-N 300 mg l^{-1}	ammonia stripping micro-electrolysis biological fluidised bed reactor	HRT 12 h	97 % COD 98 % NH_4^+-N	46
COD 2845 mg l^{-1} TN 385 mg l^{-1} NH_4^+-N 256 mg l^{-1} phenols 722 mg l^{-1} thiocyanate 371 mg l^{-1}	coagulation ($FeSO_4$) single microbial fuel cell biological reactor advanced oxidation	HRT 125 h, graphite electrodes, DO 8 mg l^{-1}, 30 °C	84 % COD 98 % TN 100 % phenols 99 % NH_4^+-N 100 % thiocyanate	10
COD 5451 mg l^{-1} TN 552 mg l^{-1} NH_4^+-N 107 mg l^{-1} phenols 1276 mg l^{-1} cyanide 51 mg l^{-1} thiocyanate 622 mg l^{-1} PAHs 414 mg l^{-1}	oil separator ammonia stripping pH equalisation O/H/O fluidised bed reactors coagulation sedimentation ozonation	HRT 98 ± 11 h DO (H) < 0.3–0.5 mg l^{-1} DO (O) 2.4–3.4 mg l^{-1} biofilm media 65 %	97 % COD 99 % phenols 97 % NH4+-N 97 % cyanide 100 % thiocyanate	38

Whereas coking wastewater is characterised as poor in nutrients, sometimes it may be required to add certain chemicals: carbonate as a carbon source to nitrifying autotrophic microorganisms, methanol as an electron donor for denitrification, inorganic phosphate as a source of phosphorus *etc.*[3,7] To overcome this drawback, especially in total nitrogen removal, anaerobic ammonia oxidation (ANAMMOX) offers itself as a solution, whereas ammonia is directly converted into nitrogen gas. Advantages of ANAMMOX process are less: energy required, external carbon source required, sludge produced, footprint, which make it adequate for real-scale applications. However, efficiency of ANAMMOX process is constrained due to inhibitory effect of phenols and thiocyanate.[21]

To improve effectiveness of biological treatment, activated sludge systems can be periodically inoculated with a particular microorganism, enhancing the ability of microbial consortium to biodegrade pollutants. Such bioaugmentation process could be easily applied and maintained.[6,21] For example, surfactants are frequently added to WWTPs in order to improve bioavailability of poorly soluble PAHs, but biosurfactants produced by bacteria (*i.e.*, *Pseudomonas aeruginosa, Bacillus subtilis*) are more attractive. The biodegradation of PAHs by augmentation with biosurfactant-producing bacteria, *P. aeruginosa*, increased from 26 to 45 %.[11] Biofilm processes, where biomass is attached to fixed or mobile media, are also one of the possibilities to conserve biomass from toxic and hydraulic shocks.[2,7,21] In view of the aforementioned, there is a need to apply a complicated biological process in order to achieve satisfactory results.[16] *Zhu et al.*[38] contend O/H/O process is preferable among others, due to shorter HRT, absence of sludge, reduced energy consumption, and better COD/TN removal, achieving TN concentration < 29 mg l^{-1}. Based on laboratory research and industrial applications, the combination of different biological processes is the main solution for the treatment of coking wastewater, and the anoxic part is considered the most important part of such combined process.[7] Anoxic microorganisms utilise phenol as carbon and energy source.[45] Advantages of anoxic biological processes over those aerobic are improved wastewater quality, less sludge production, and energy savings due to absence of aeration, yet anaerobic reactors require long start-up period, up to eight months. Also, it is often necessary to add a co-metabolite.[2] Combined aerobic-anoxic process favours overall biological treatment efficiency of coking wastewater, reducing operative costs at the same time.[23] Aerobic reactors serve oxidation of phenol and nitrification, while anoxic reactors allow denitrification.[10] Bacterial composition significantly differs from system to system, depending on the operating parameters within bioreactors and composition of wastewater.[19,38] The predominant phylum in bioreactors changes within change in C/N ration.[38] Table 4 shows most abundant bacterial phyla in biological WWTP treating coking wastewater with its roles. However, oftentimes up to 80 % of total sequences isolated from coking wastewater remains unknown at genus level.[38] Even though biological treatment is recommended for its cost-effectiveness and environmental acceptability, long start-up period and large time span for treatment may be an issue.[7]

3 Conclusion

This article intends to highlight an overview of coking wastewater treatment methods, with a detailed elaboration of its composition, mutual interactions of its compounds, and inhibitory effect on each other. Considering the complexity

Table 4 – Identified bacterial species in coking wastewater
Tablica 4 – Bakterijske vrste identificirane u otpadnoj vodi koksne industrije

Bacterial phylum	Bacterial genus	Target pollutants/performing	Abundance / %
Proteobacteria	*Acidovorax*	iron, nitrate	9[46]
Proteobacteria	*Acinetobacter*	alkane-based organic compounds	48[46]
Proteobacteria	*Afipia*	thiocyanate	2.37[10]
Proteobacteria	*Alcaligenes*	phenols	2.01[10]
Proteobacteria	*Azoarcus*	PAHs, denitrification, ethylbenzene	10.37[10]
Proteobacteria	*Bordetella*	chlorophenols and phenols	1.69[10]
Proteobacteria	*Bosea*	thiocyanate	0.81[10]
Proteobacteria	*Brevundimonas*	quinoline	0.02[46], 7.56[10]
Proteobacteria	*Comamonas*	phenols	10.81[10]
Proteobacteria	*Defluvibacter*	chlorophenols and phenols	2.96[10]
Proteobacteria	*Delftia*	amide contaminants	0.4[46]
Proteobacteria	*Denitratimonas*	aerobic denitrifier	2.64, 3.11[10]
Proteobacteria	*Halomonas*	thiocyanate	1.67[10]
Proteobacteria	*Hyphomicrobium*	PAHs, denitrification	1.58[10]
Proteobacteria	*Lysobacter*	phenols, sulphide, thiocyanate	1.95[38]
Proteobacteria	*Nitrobacter*	nitrification	2–5[46]
Proteobacteria	*Nitrosomonas*	nitrification	5.50[10]
Proteobacteria	*Ochrobactrum*	chlorophenols and phenols	1.97[10]
Proteobacteria	*Paracoccus*	aerobic denitrifier	5.78[10]
Proteobacteria	*Pseudomonas*	phenols, denitrification	3.11[10]
Proteobacteria	*Pusillimonas*	indole	3.50[10]
Proteobacteria	*Ralstonia*	chlorophenols and nitrophenols	2.08[10]
Proteobacteria	*Thaurea*	carbon compounds, denitrification	13.26[10]
Proteobacteria	*Thioalkalispira*	PAHs, autotrophic denitrifier	0.6[10]
Proteobacteria	*Thiobacillus*	sulphide, denitrification, thiocyanate, ammonia	7.53[38]
Actinobacteria	*Leucobacter*	phenols, sulphide, thiocyanate	1.21[38]
Chloroflexi	*Bellilinea*	denitrification, PAHs, quinoline	11.16[10]
Planctomycetota	*Planctomycetaceae*	ANNAMOX	1.10[38]
Thaumarchaeota	*Nitrosoarchaeum*	ammonia	1.47[10]

of the composition and extreme toxicity, it is not possible to treat coking wastewater successfully without integrated pretreatment, biological treatment, and post-treatment. Of course, conventional biological solutions are also inapplicable, and a combination of anoxic and oxic reactors is required. Physicochemical processes are used mainly for pretreatment, in order to decrease the toxicity of pollutants, to reduce the harmful impact on biology. Advanced oxidation processes are used most often for post-treatment to polish wastewater in order to achieve discharge parameters. This type of wastewater is considered one of the most challenging wastewaters to treat, and additional research in this area is necessary to optimise existing solutions for preserving nature and the environment, into which the wastewater is ultimately discharged.

List of abbreviations
Popis kratica

COD	– chemical oxygen demand – kemijska potrošnja kisika
PAHs	– polycyclic aromatic hydrocarbons – policiklički aromatski ugljikovodici
WWTP	– wastewater treatment plant – uređaj za pročišćavanje otpadnih voda
TN	– total nitrogen – ukupni dušik
HRT	– hydraulic retention time – hidrauličko vrijeme zadržavanja (retencije)
DO	– dissolved oxygen – otopljeni kisik
A/O	– anoxic/oxic – anoksično/aerobno
A/A/O	– anoxic/anoxic/oxic – anoksično/anoksično/aerobno
O/A/O	– oxic/anoxic/oxic – aerobno/anoksično/aerobno
A/O/O	– anoxic/oxic/oxic – anoksično/aerobno/aerobno
O/A/O	– oxic/anoxic/oxic – aerobno/anoksično/aerobno
O/H/O	– oxic/hydrolytic/oxic – aerobno/hidrolitičko/aerobno
A/A/O/O	– anoxic/anoxic/oxic/oxic – anoksično/anoksično/aerobno/aerobno
A/O/A/O	– anoxic/oxic/anoxic/oxic – anoksično/aerobno/anoksično/aerobno
ANAMMOX	– anaerobic ammonia oxidation – anaerobna oksidacija amonijaka

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SAŽETAK

Karakteristike i obrada otpadne vode koksne industrije

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Koks je visoko kalorično umjetno gorivo koje se upotrebljava u proizvodnji željeza i čelika, a dobiva se suhom destilacijom ugljena. Proizvodnja koksa zastupljena je širom svijeta, osobito posljednjih godina, kad zbog ekonomskog rasta raste i svjetska potražnja za čelikom, što kao posljedicu ima i povećanu potrebu za koksom. Tijekom proizvodnje koksa nastaju enormne količine toksične otpadne vode izrazito kompleksnog sastava, a prioritetne onečišćujuće tvari koje sadrži su fenoli, cijanidi i tiocijanati. Za uspješno pročišćavanje te vrste otpadne vode i postizanje izlaznih parametara primjena jednog procesa nije dovoljna. Shodno tome, primjenjuje se kombinacija različitih fizikalno-kemijskih i bioloških postupaka obrade, od kojih je biološka obrada najvažnija. U ovom radu dan je literaturni pregled karakteristika otpadne vode koksne industrije i načini njihova pročišćavanja. Osim toga, ovaj pregled osvrće se na složenost i ograničenja povezana s pročišćavanjem koksne otpadne vode, s posebnim naglaskom na metode biološke obrade. Cilj ovog rada je sažeti dosadašnja znanja o otpadnoj vodi koksne industrije, što bi u konačnici pomoglo u optimizaciji postojećih rješenja.

Ključne riječi
Koks, otpadna voda, fenoli, cijanidi, tiocijanati, biološki tretman

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