Research Article

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The role of a chemical loop in removal of hazardous contaminants from coke oven wastewater during its treatment

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Abstract: Coke oven liquor is one of the most contaminated liquid streams generated by the coal processing industry, thus its proper treatment and utilization is crucial for sustainable and environmentally neutral plant operation. The conventional wastewater treatment process comprises of chemical and biological processes. Within the current research the detailed role of chemical treatment is described. Commercially available iron-based coagulants (PIX100, PIX100COP, PIX113, PIX116) were tested to understand their removal efficiency and impact on the stream parameters. The influence of iron dose in the range of 300–500 mgFe/L on the process performance was also examined.

It was found that the main role of chemical treatment was to bind toxicants harmful to activated sludge microorganisms, i.e. free and complex cyanides and sulphides. Among the tested iron-based conventional coagulants ferrous salts were more efficient than ferric salts. It was also observed that efficiency of the process strongly depended on wastewater properties (especially in regard to pH, which should be in the range of 9–10) and the coagulant selection needed to be done individually for a given wastewater type. The removal rates of particular contaminants were diversified and for free cyanides, complex cyanides and sulphides they were in the range of 23–91%, 156–77% and 357–98%, respectively. The expected, simultaneous removal of chemical oxygen demand (COD) during the treatment was not observed and even the parameter value increased after the process due to probable formation of compounds less vulnerable to oxidation.

Keywords: coke oven wastewater; coagulation; cyanides; sulphides; treatment.

1 Introduction

Coke is produced during pyrolysis of coal carried out in coke oven batteries comprised of special chambers called coke ovens operated at temperatures reaching up to 1,200°C. During the process, volatile compounds are released from coal forming coke oven gas, whereas the remaining mass, i.e. coke, contains mainly carbon and non-volatile minerals [1]. The scheme of coke production at a typical coke oven plant is shown in Figure 1.

The coke is mainly used in the iron and steel industry and its worldwide annual production in the last decade varied from 650 to 700 Mt [2]. The second product of coal pyrolysis, i.e. coke oven gas, after the treatment and recovery of so called coal derivatives, i.e. tars and benzol, is used for heating of coke ovens and for other energy generation purposes, usually inside the plant. The processing of coke oven gas starts with cooling, during which condensation of organic compounds and water vapor, which washes out some inorganic gas components like ammonia, hydrogen cyanide and hydrogen sulphide from the gas, occurs [3,4]. The condensate, known also as coal liquor, is firstly introduced to the tars separation department, in which water insoluble organic compounds are separated and directed to further processing. The remaining aqueous phase, from this stage called ammoniacal liquor, is used for flushing cooling of coke oven gas and, in case of plants operated with ammoniacal method of gas desulphurization, is involved in further washing of hydrogen sulphide from the gas [5–7]. However, the amount of ammoniacal liquor is always higher than the amount required for technological purposes. This excess liquor is directed to ammonia stripping carried out at alkaline conditions, and the stripping column downstream is the influent of coke oven wastewater

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Figure 1: The scheme of coke production at a coke oven plant.

Figure 2: The scheme of formation of coke oven wastewater.

treatment plant [8-10]. The scheme of formation of coke oven wastewater is presented in Figure 2.

It is assumed that at a typical plant for every 1 ton of coke produced 1-1.5 m³ of coke oven wastewater is generated [11-13]. The qualitative composition of coke

oven wastewater is well recognized whereas ranges of concentrations of particular compounds present in the stream vary depending on many factors, among which the coal quality and coke oven gas processing methods are the most important. In Table 1 the typical composition of

Table 1: Typical composition of raw coke oven wastewater.

Parameter	Unit	Concentration range
pH	-	7-9.5
Specific conductivity	μS/cm	5,000-12,500
COD	mgO ₂ /L	2,000-6,500
BOD ₅	mgO ₂ /L	800-3,000
PAHs	mg/L	5-150
Sulphides	mg/L	10-50
Cyanides	mg/L	5-20
Thiocyanates	mg/L	50-420
Phenols	mg/L	500-1,500
Ammonia	mg/L	50-200
Chlorides	mg/L	2,500-3,500
Sulphates	mg/L	900-1,200

a raw coke oven wastewater (i.e. ammoniacal liquor after stripping) is presented.

A coke oven wastewater treatment plant is usually arranged in a conventional way, i.e. firstly the physico-chemical treatment of the stream is performed and it is followed by biological removal of ammonia (by nitrification/denitrification) and organic compounds (phenols) [14-17]. The chemical treatment is based on a coagulation process in which iron containing coagulants (ferrous/ferric chloride/sulphate) are used which results in the occurrence of following reactions [7-8, 11-12]:

The biological treatment usually comprises of nitrification and denitrification processes which enable the efficient removal of ammonia and phenols. For better performance

of the treatment, preliminary ammonification dedicated to decomposition of nitrogen-containing organic compounds and thiocyanates may be used, while for the improvement of COD decrease separate biological reactors for organic compounds decomposition may be installed. The exemplary schemes of different coke oven wastewater treatment plant arrangements are shown in Figure 3.

Within the current research the role and the efficiency of chemical treatment carried out with the use of commercially available iron-based coagulants was examined. The impact of the coagulant type and dose on cyanides, sulphides, COD, pH and salinity of coke oven wastewater compared to the raw stream parameters was investigated.

2 Methods

2.1 Feedstock characteristics

Four types of commercially available coagulants based on different iron salts were used to treat raw coke oven wastewaters of different parameters sampled at three coke oven plants of diversified production profile. In Table 2, the characteristic of the coagulants is given and the parameters of raw coke oven wastewaters (COW) used in the experiments are presented in Table 3.

2.2 Experimental procedure

1 L of coke oven wastewater was introduced to the laboratory coagulation reactor of total volume of 1.3 L and mixed for 1 minute at 50 rpm using a magnetic stirrer. Next, the proper dose of coagulant corresponding to the desired amount of iron was introduced and the system was vigorously mixed for 1 minute at 200 rpm. All coagulants were tested at three different doses, recalculated to the amount of iron introduced to the system, i.e. 300, 400, 500 mgFe/L. Next, the mixing was slowed down to 50 rpm and the system was mixed at such conditions for 5 minutes. Finally, the mixture was left for 30 minutes for flocculation and settling and after this time the portion of supernatant was collected for analysis.

2.3 Analytical procedures

The content of free cyanides (CN free) and sulphides was determined using ion chromatography with pulsed

Figure 3: Different arrangements of coke oven wastewater treatment plants.

Table 2: The characteristics of coagulants used in the research.

Coagulant	Trade name	Fe ²⁺ content	Fe _{tot} content	pH	Free acid
FeCl ₂	PIX100	10.3±0.7%	10.3±0.7%	<1	2÷4%
FeSO ₄	PIX100COP	6.0±1.0%	6.0±1.0%	~1	1.5÷2.5%
Fe ₂ (SO ₄) ₃	PIX113	0.4±0.3%	11.8±0.4%	<1	-0.5÷0.0%
FeCl ₃	PIX116	max. 0.5%	11.5±0.5%	<1	0.5÷3.0%

Table 3: Characteristics of coke oven wastewater used in the research.

Parameter	Unit	COW1	COW2	COW3
pH	-	9.84	9.37	12.25
Conductivity	µS/cm	10,423	8,729	14,738
Redox potential	mV	-135.2	-107.5	-263.1
Free cyanides	mg/L	7.79	6.17	9.29
Complex cyanides	mg/L	7.97	1.20	7.10
Sulphides	mg/L	9.39	2.20	9.97
COD	mgO ₂ /L	3,649	4,125	5,370
Chlorides	mg/L	2,700	1,794	2,698
Sulphates	mg/L	135	255	293

amperometric detection (IC-PAD). The standard procedure included isocratic separation of both anions in 15 minutes using Thermo-Scientific IonPac AS7 (250mm×2mm) analytical column and guard (50mm×2mm) column set with 600 mM degassed sodium hydroxide at a flow rate of 0.250 cm³/min and column temperature of 30°C. Analytes were detected by PAD using a silver working electrode, combined with pH-Ag/AgCl reference electrode in AgCl mode. The PAD waveform used for these experiments was a three-potential waveform optimized for silver electrodes and cyanide, sulphide, iodide, and thiosulphate anions in a hydroxide eluent. The method was suitable for cyanides and sulphides concentrations in the range 0.05 to 5 mg/L. Due to the complexity of the coke oven wastewater matrix, the analytical samples were firstly diluted with eluate solution in order to assure complete dissociation of cyanide and sulphide salts and allowed analysis in the desired detection range. Determination of total cyanide concentration comprised of thermal distillation in acidic conditions with a copper catalyst, during which evolved hydrogen cyanide was collected in alkaline solution placed in gas washers. The obtained analytical samples were then introduced to IC-PAD analysis and the procedure used for free cyanides detection was followed. The content

of complex cyanide (CN complex) was calculated as the difference between total and free cyanides concentration. The amounts of chlorides and sulphates were analyzed using ion chromatography with conductometric detection (IC-CD) and the chemical oxygen demand (COD) was determined by a spectrophotometric method preceded with sample mineralization with potassium dichromate according to HACH procedure. pH and conductivity of process streams were measured with the use of dedicated measuring probes.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Free cyanides

In Figures 4-6 the impact of coagulant type and dose on the final concentration of free cyanides measured in particular coke oven wastewater is shown. The desired free cyanide concentration permitted for biological loop influent was established at 0.5 mg/L (standard).

Figure 4: Final concentration of free cyanides in coke oven wastewater 1 (COW1).

Figure 5: Final concentration of free cyanides in coke oven wastewater 2 (COW2).

Figure 6: Final concentration of free cyanides in coke oven wastewater 3 (COW3).

Figure 7: Final concentration of complex cyanides in COW1.

Figure 8: Final concentration of complex cyanides in COW2.

It was found that coagulation efficiency strongly depended on all considered process parameters, i.e. coagulant type, dose and coke oven wastewater properties and any relevant relationship between these parameters could not be found. It is a very important conclusion which suggests that coagulation/chemical treatment loop of every coke oven wastewater treatment plant should be recognized individually and coagulation process parameters should be selected on the basis of preliminary research. Among tested coagulants, PIX100COP most efficiently decreased free cyanides concentration in COW1 (Figure 4), when it was dosed in the amount of 400 and 500 mgFe/L, while in case of COW2 PIX116 at dose of 500 mgFe/L was the most sufficient (Figure 5). The best treatment effect in COW3 was obtained for PIX100 coagulant (Figure 6).

3.2 Complex cyanides removal

In Figures 7-9 the impact of coagulant type and dose on the final concentration of complex cyanides in all treated coke oven wastewaters is shown. The standard, i.e. maximum complex cyanides concentration equal to 5.0 mg/L permitted for biological loop influent was established. Additionally, as complex cyanides appeared in the stream as a result of free cyanides complexation, the results were referred to initial concentration of the contaminant in the raw stream.

The best removal of complex cyanides was observed for COW2 for which the standard concentration (5 mg/L) was always obtained regardless of coagulant type or dose (Figure 8). It resulted from the relatively low concentration of the contaminant in raw stream (1.2 mg/L) and the effect

Figure 9: Final concentration of complex cyanides in COW3.

Figure 10: Final concentration of sulphides in COW1.

of pH discussed in chapter 3.4. On the other hand, the decrease in contaminant concentration in COW3 was very poor which was most probably related to the pH effect, as even after coagulant addition the wastewater remained highly alkaline (Figure 9). In the case of COW1, only the PIX100COP coagulant did not assure the required elimination of complex cyanides (Figure 7). Nevertheless, the conclusion from free cyanides removal efficiency was confirmed, i.e. the affinity of a wastewater to chemical treatment should be checked individually for a given wastewater.

3.3 Sulphides removal

In Figures 10-12 the impact of coagulant type and dose on the final concentration of sulphides in the tested coke

oven wastewaters is shown. The same standard as for free cyanides, i.e. maximum sulphides concentration equal to 0.5 mg/L permitted for biological loop influent was established.

In the case of sulphide removal, better performance of ferrous coagulants was observed for COW1 and COW2, for which the permissible concentration or level close to it was obtained for both PIX100 and PIX100COP coagulants. On the other hand, the addition of ferric coagulants to COW2 resulted in the increase of sulphide concentration, even above their initial concentration in raw coke oven wastewater (Figure 11). Probably, ferric ions caused the decomposition of some sulphuric compounds present in the wastewater and free sulphides were revealed. In the case of COW3 the doses of all coagulants equal to 400 and 500 mgFe/L allowed for efficient sulphides concentration decrease with the exception of PIX100COP coagulant

Figure 11: Final concentration of sulphides in COW2.

Figure 12: Final concentration of sulphides in COW3.

where the performance was not sufficient enough to effectively eliminate the contaminant from this wastewater (Figure 12).

3.4 Effect on COD, pH and salinity

Coagulation, except for cyanides and sulphides removal, is also regarded as a process suitable for elimination of some organic compounds, which is accompanied by decrease of COD. Thus, in Figures 13-15 the effect of coagulant type and dose on COD removal rate is shown.

Surprisingly, it was observed that coagulation not only did not improve COD of coke oven wastewater but also, in many cases increased the parameter value and negative removal rates were observed. It was probably caused

by reactions of ferric and ferrous ions with a number of compounds present in coke oven wastewater, which led to formation of compounds less vulnerable to oxidation.

Despite its treatment effect, coagulation is also known to cause both, pH decrease and salinity increase. Thus, in Figures 16-18 the impact of coagulant dose on wastewater pH is shown, while in Table 4 the increase of chlorides and sulphates concentration in regard to the respective coagulant dose is presented.

It was observed, that in general pH decreased with coagulant dose, however the final effect depended on coagulant type and the buffering capacity of wastewater. Hence, in COW1 and COW2 the pH decreased most significantly with ferric coagulant addition. On the other hand, the effect of dose was more noticeable for the ferrous coagulant PIX100 in case of COW2, while in case of COW1,

Figure 13: COD removal rate in COW1.

Figure 14: COD removal rate in COW2.

Figure 15: COD removal rate in COW3.

Figure 16: Effect of coagulant type and dose on pH of COW1.

Figure 17: Effect of coagulant type and dose on pH of COW2.

Figure 18: Effect of coagulant type and dose on pH of COW3.

Table 4: Effect of coagulant addition on wastewater salinity.

	Concentration in raw wastewater, mg/L		mg of Cl ⁻ /100 mg of Fe		mg of SO ₄ ²⁻ /100 mg of Fe	
	Cl ⁻	SO ₄ ²⁻	PIX100	PIX116	PIX100COP	PIX113
COW1	2,700	135	187	110	36	207
COW2	1,794	255	174	181	52	209
COW3	2,696	293	164	160	44	210
Average	2,397	228	175	151	44	208

increase in ferric coagulants dose more significantly influenced on the pH change. COW3, the most alkaline among all investigated wastewaters, was less susceptible to pH decrease. Finally, it was observed that PIX100COP coagulant affected coke oven wastewater pH to the lowest extent regardless of the stream type.

In the case of salinity it was found that chloride based coagulants affected the wastewater salinity in a comparable way and the amount of chlorides in wastewater increased by 175 mg Cl⁻/100 mg of Fe in the case of PIX100 and by 151 mg Cl⁻/100 mg of Fe for PIX116. On the other hand, significant differences in salinity change were found for sulphate based coagulants. For PIX100COP, amount of sulphates introduced with coagulant was 44 mg SO₄²⁻/100 mg of Fe, while for PIX113 it was 208 mg SO₄²⁻/100 mg of Fe. In refer to raw coke oven wastewater, introduction of chlorides with coagulants resulted in 6-7% increase in their concentration per 100 mg of Fe added, while in case of sulphate based coagulants, the anion concentration increased from 20 to 91% per 100 mg of Fe added.

4 Conclusions

The research on the conventional coagulation process application to coke oven wastewater treatment resulted in very interesting conclusions. First of all, affinity of wastewater to treatment by means of coagulation should be checked for each wastewater type as removal of the process target contaminants, i.e. cyanides and sulphides, strongly depends on raw wastewater parameters. Therefore the coagulant type and dose has to be specifically selected. However, considering the valence of iron in applied coagulants, it may be concluded that ferrous based coagulants are more efficient in eliminating target contaminants than ferric ones. The desired effect of COD decrease is quite poor and in some cases a negative removal rate can be obtained. Coagulation always results in pH decrease, however the parameter affection depends

on wastewater type and coagulant type, but this decrease is always greater with coagulant dose increase. Ferrous coagulants decrease the solution pH to a lesser extent than ferric ones. Finally, the overall salinity affection is less significant if chloride based coagulants are used, as the amount of chlorides in raw coke oven wastewater is much higher than the amount of sulphates. Thus, chloride based coagulants cause the increase in chlorides content below 10% per every 100 mg of Fe added in refer to their initial concentration in the stream, while the addition of sulphate based coagulants changes sulphates content in the stream from 20 to 91% per every 100 mg of Fe added.

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