

Post-treatment of coke wastewater on activated carbons

Anna Kwarciak-Kozłowska^{1,*}, Magdalena Madela¹, Magdalena Wrońska¹

¹Czestochowa University of Technology, Institute of Environmental Engineering, Dabrowskiego 69, 42-200 Czestochowa, Poland

Abstract. The aim of this research was to determine the effect the ozonation and sonification processes for post-treatment of coke wastewaters using activated carbons. The tests were carried out in three systems ie. I- AC (activated carbon), II- O₃+AC (ozonation + activated carbon) and III- US+AC (ultrasound + activated carbon). In the experiment were used a three types of activated carbons: WG-12, ROW 08 Supra and Picabiol. The sorption process was carried out in static conditions at contact for 24h time of the wastewater with activated carbons. Coke wastewater was oxidized through ozonation at a constant ozone dose of 10 mg/dm³. Sonication of coke wastewater was conducted at vibration amplitude was 61.5 μm, with sonication time of 8 min. Results of removing of COD were estimated on the base of sorption capacity and COD removal efficiency. The second system was the most effective (O₃+AC) for carbons WG-12 and ROW 08 Supra, whereas in the case of carbon Picabiol, the best efficiency was found for system I (AC). The lowest efficiency of removal of COD from coke wastewater was the systems III (US+AC) for all three activated carbons.

1 Introduction

Coking wastewater refers usually to the wastewater which is produced during high-temperature carbonation, coal gas purification and chemical products refining in coke plant [1, 2]. Coke plants have a negative impact on natural environment due to e.g. generation of industrial coke wastewaters which are difficult to be degraded with a substantial load of toxic substances. They include, among other things, polycyclic aromatic hydrocarbons, heterocyclic compounds, phenols, oils, tar, inorganic substances (e.g. cyanides, sulphides, sulphates, thiosulphates, ammonia and heavy metals) [1–4].

Because of the different processing technologies and multiple managerial systems of semi-coke production, the composition of the discharged wastewater is quite complex, and the wastewater from different coke plants have different pollutant removal requirements [5]. Due to the difficulty in removing refractory organic matter, treated wastewater released from conventional processes can not effectively meet current effluent standards [6]. In the last years, much attention has been paid to processes of oxidation of organic compounds using the methods of advanced oxidation process (AOP). The characteristic feature of AOP

* Corresponding author: akwarciak@is.pcz.czest.pl

is generation of reactions of hydroxyl radicals numbered among the strongest oxidants (with oxidative potential of 2.7 mV). Free hydroxyl radicals are generated e.g. during ozonation, oxidation with hydrogen peroxide, Fenton's reaction or during the exposure to the ultrasound field. While reacting with molecules of various organic substances (either solved or suspended), the generated hydroxyl radicals lead to their chemical decomposition (oxidation or destabilization) or formation of new compounds [4, 7, 8]. Although oxidation of organic compounds under conditions of advanced oxidation represents an extremely efficient method to remove them, increasingly high requirements for treated wastewater discharged to waters or to the ground force continuous improvement in the process of treatment. Due to the important amount of organic compounds with varied physicochemical properties to remove them from wastewater, it is necessary to use so-called integrated systems which combine several methods such as biodegradation, coagulation, filtration, sorption, chemical oxidation or ozonation.

In the present study, the coke wastewater initially treated using the ozonation process and sonication process were combined with the next treatment step which consisted in adsorption of contaminants on activated carbon [7, 8].

2 Materials and methods

2.1 Substrate

The post-industrial wastewater produced in the coking plant, located in the province of Silesia, Poland, was used for the examination. The wastewater was initially mechanically treated to remove e.g. solid contaminants, oils and tar substances. The analysed wastewater was characterized by the smell of phenol, brown colour and alkaline reaction (pH 8.7–9.0). COD in the raw wastewater generated during production processes was on average 4600 mg/dm³, whereas BOD/COD ratio was 0.29. High TOC contents (840 mg/dm³) and ammonium nitrogen (550 mg/dm³) were also very high in the coke wastewater.

2.2. Carbon adsorbents used

The analysis was based on three activated carbons with symbols: WG-12, ROW 08 Supra and PICABIOL. Due to various raw materials used for their production, the activated carbons differed substantially between each other in their physical and chemical properties (Fig.1). WG-12 was obtained from the hard coal by the Polish manufacturer GRYFSKAND. ROW 08 Supra was obtained from peat by the Dutch company NORIT. Picabiol was obtained from charcoal. Characterization of the activated carbons is presented in Table 1. Ash content was initially partially removed from activated carbons used in the study. Due to their pH, the carbons were washed by the NaOH solution (Picabiol) and HCl solution (WG-12 and ROW 08 Supra) and next all of them were washed with distilled water until reaching pH=7. All the carbons from which ash content was removed were dried at the temperature of 145°C [9].

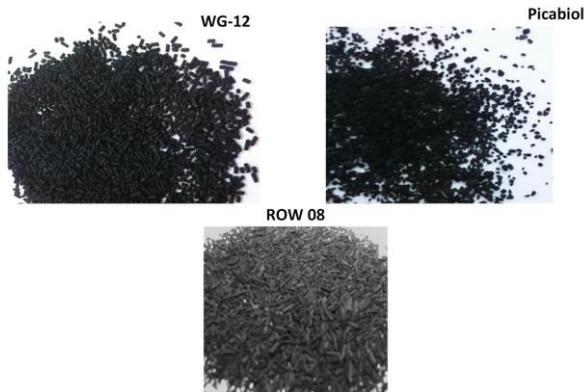


Fig. 1. Photos of active carbons used.

Table 1. Characteristic of used activated carbons (PN-90/C-97555) [10].

Parameters	WG-12	ROW 08 Supra	PICABIOL
Specific surface, m ² /g	1005	796	1344
Bulk mass, g/dm ³	420	381	234
The water absorbability, cm ³ /g	0,90	0,97	2,17
The iod number, mg/g	1050	1090	1071
Resistance mechanical, %	98	98	85
The ash content, %	11,0	5,94	2,8

2.3. Apparatus

Ozonation of raw coke wastewater was performed in a cylindrical glass reactor with volume of 4000 cm³. Raw wastewater was supplied to the reactor through its upper part, whereas treated wastewater was supplied using the drain valve located in its lower part. Fine-bubble aeration with air-ozone mixture was performed using the diffuser located centrally at the reactor bottom. Ozone was obtained from oxygen using the OZOMATIC LAB 802 ozonizer. Rate of production of air and ozone mixture ranged from 0.1 to 1 dm³/min. Flow rate was controlled by means of RO6 RP T96193 rotameter (max. 45 dm³/h). The measurement of the ozone content at the outlet from the reaction chamber was conducted using the Dreschel washing bottle with the absorption solution connected with the valve located at its top [11]. Sonication of the coke wastewater was performed using the Sonics vibro cell ultrasonic disintegrator which generated the ultrasonic wave with vibration frequency 40 kHz. Power adjustment in the device was possible through digital adjustment of the percentage of maximal amplitude of the sonotrode, with its maximal value of 123 μm. The amount of energy supplied to the sample was monitored during the examination. Knowledge of this value allowed for the evaluation of the magnitude of the intensity of the ultrasound wave [12].

2.4. Research methodology

The process of final treatment of coke wastewater on activated carbons was realized using three technological systems. In the first system, an independent process of contaminant sorption from the examined wastewater was performed for three types of activated carbons (system 1: AC). In order to determine sorption capacity of the carbons with respect to coke wastewater, we used 4 doses of carbons. The examined carbons with the doses of 0.75 g, 0.9 g, 1.2 g and 1.5 g were covered with coke wastewater with volume of 150 cm³ (5, 6, 8,

10 g/dm³). These carbon samples were shaken for 2 h and next they were left for 22 h of static contact. Before the analysis of the treated wastewater, the samples were centrifuged (15 min) with the speed of 1120 rpm and next filtered through a soft filter.

In the second arrangement (system 2: O₃+AC), sorption of carbons from coke wastewater on activated carbons was preceded by their oxidation using the ozonation process. This stage was performed at a constant ozone dose of 10 mg/dm³. Ozonation time was 60 min and next initially treated wastewater was directed to the activated carbons for final treatment. The third system (system 3: US +AC) was sonication of coke wastewater followed by sorption on the activated carbons. Sonication of coke wastewater was conducted in a container with diameter of 8 cm (volume: 500 cm³). The vibration amplitude was 61.5 μm, with sonication time of 8 min. After sonication the wastewater was subjected to sorption on the activated carbons. The efficiency of the unit processes used in the study was controlled based on the changes in the levels of COD, TOC, pH, BOD and ammonium nitrogen, whereas in the sorption process only the reduction of COD was investigated. The study design and methodology of determinations is presented in Fig. 2.

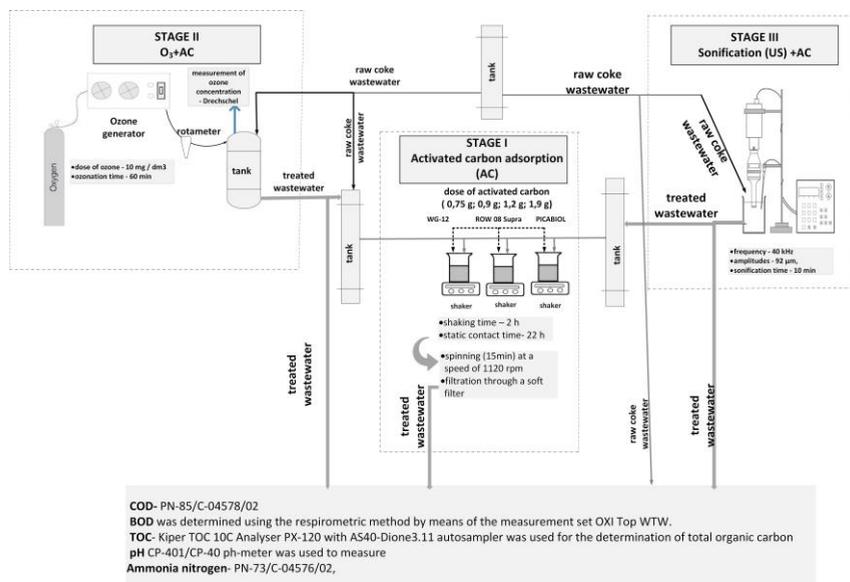


Fig. 2. The scheme of post-treatment of coke wastewater on activated carbons.

3 Results and discussion

3.1. Wastewater treatment using activated carbons

In the first arrangement (I - AC), adsorption of contaminants was evaluated for activated carbons WG-12, ROW 08 Supra and Picabiol for raw coke wastewater in order to determine adsorption isotherms. Fig. 3 presents isotherms for COD adsorption on the activated carbons and the degree of removal of contaminants on activated carbons depending on the dose.

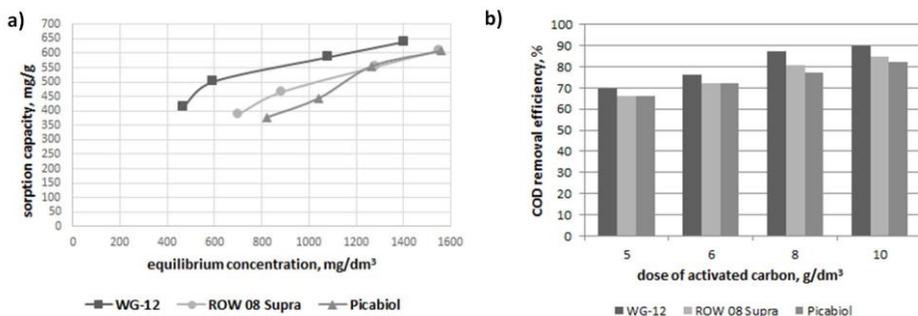


Fig. 3. Isotherms of adsorption of COD from coke wastewater on activated carbons and removal rate depending on the carbon dose.

The isotherms of COD adsorption from coke wastewater point to a varied sorptive capacity of the activated carbons with regard to the removed contaminants. The best carbon was WG-12, with its maximal sorptive capacity of 639.4 mg/g, whereas sorptive capacity of the two other activated carbons was slightly lower: 609.68 mg/g for ROW 08 Supra and 607.93mg/g for Picabiol. The Freundlich equation was used to describe the pattern of sorption isotherms. Using the logarithmic form of this equation, the K_F and $1/n$ constants were determined for the activated carbons studied, with their values presented in Table 2.

Table 2. The Freundlich isotherm constants from COD.

Carbons	$K_F, \text{mg/g}$	$1/n$	R^2
WG-12	46.15	0.3642	0.949
ROW 08 Supra	10.98	0.5478	0.988
Picabiol	2.08	0.7754	0.975

As can be seen in Table 2, values of coefficient of correlation R^2 for the Freundlich equation are high, which may reflect good fit of the model to COD adsorption from coke wastewater. Isotherm constants $1/n$ and K_F are very important to determination of sorptive capacity of contaminants from wastewater and reduction of COD contents by activated carbons. Devi et al. demonstrated that the slope $1/n$ depends on the order of changes in reduction in COD contents with the adsorbent dose, whereas K_F depends on the degree of removal of COD by adsorbents [13]. Degree of removal of COD from wastewater in the activated carbons ranges from 66.08 to 89.87% (Fig. 3b). It increases for all three activated carbons with the increase in carbon dose. The highest COD removal rate was obtained for WG-12 (89.87%) with the carbon dose of 10g/dm³. Slightly less adsorbable were two other carbons with removal rates of 84.74% for ROW 08 Supra and 82.16% for Picabiol.

3.2. Treatment of coke wastewater in the system that combines ozone with adsorption

In the second system (O_3+AC), coke wastewater was oxidized through ozonation at a constant ozone dose of 10 mg/dm³. After this process, COD content decreased substantially and was 2898 mg/dm³, whereas BOD was 910 mg/dm³. Wastewater remained to show alkaline reaction of pH 8.77. The TOC content in the wastewater was 571 mg/dm³ whereas for ammonium nitrogen, this value was 480 mg/dm³.

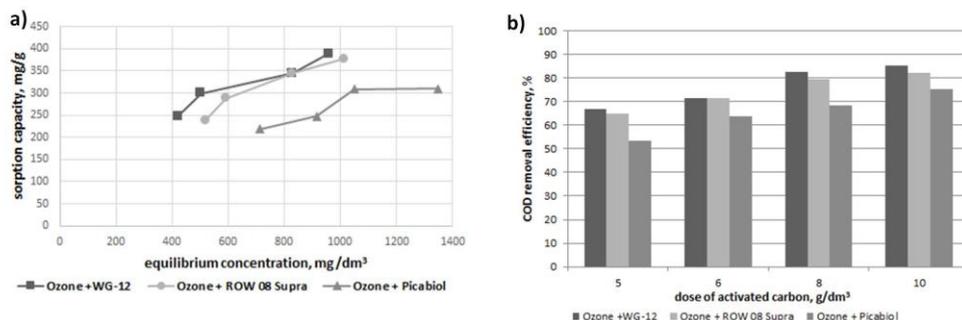


Fig. 4. Isotherms of COD sorption from coke wastewater on activated carbons after the ozonation process.

Initially oxidized wastewater was subjected to contact with selected activated carbons. Fig. 4a presented isotherms of COD adsorption on activated carbons. Isotherms of the carbons studied showed similar tendencies as in the first system (AC). Activated carbon WG-12 had better adsorption capacity compared to COD in the system studied (387.81 mg/g). Slightly lower values were obtained using the ROW 08 Supra carbon (376.4 mg/g) and Picabiol (310.08 mg/g). The Freundlich isotherm constants $1/n$ and K_F are presented in Table 3.

Table 3. Freundlich isotherm constants for COD in the second system (O_3+AC).

Carbons	$K_F, \text{mg/g}$	$1/n$	R^2
WG-12	14.57	0.4757	0.934
ROW 08 Supra	4.39	0.6465	0.945
Picabiol	4.42	0.5957	0.849

The coefficient of correlation R^2 for the Freundlich equation presented in Table 3 is high in the case of WG-12 carbon and ROW 08 Supra carbon and slightly lower for Picabiol. With regard to K_F , COD sorption from coke wastewater initially oxidized was the most efficient for WG-12 carbon, whereas it was substantially lower for ROW 08 Supra and Picabiol. The study showed that the degree of COD removal from wastewater using WG-12 and ROW 08 Supra is similar (over 80%) whereas in the case of Picabiol, it was reduced to 74.4% (Fig. 4b).

3.3. Treatment of coke wastewater in the system that combines sonication with adsorption

The aim of the third stage of the experiment was to establish how ultrasound waves impact on the quality of coke wastewater and their sorption on activated carbons. The examinations performed previously by the authors demonstrated that the most effective sonication of this type of industrial wastewater occurs at the vibration amplitude of 61.5 μm and reaction time of 8 minutes. The value of the acoustic energy which was supplied to the wastewater sample for such parameters of ultrasound field was ca. 29885 J [12]. The exposure to the ultrasound field leads to cavitation, which is responsible for destabilization and oxidation of contaminants contained in wastewater using the hydroxyl radicals. It is generally accepted that in order to start cavitation in a liquid medium, ultrasound wave intensity should be at least 1.0 W/cm^2 . It was found that with these parameters of the ultrasonic field, intensity of the ultrasound wave was higher than the theoretical threshold of cavitation and was 1.28 W/cm^2 [12]. After sonification process, COD content decreased substantially and was 3542 mg/dm^3 , whereas BOD was 1730 mg/dm^3 . The TOC content in the wastewater was 940 mg/dm^3 whereas for ammonium nitrogen, this value was

520 mg/dm³. Wastewater remained to show alkaline reaction of pH 8.4. The coke wastewater prepared using this method was supplied to activated carbons for final treatment.

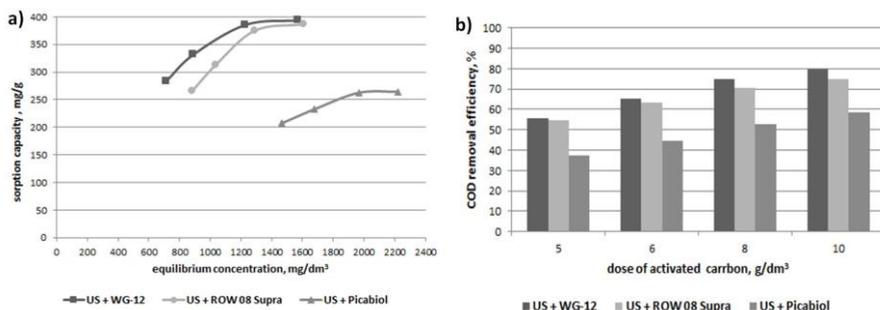


Fig. 5. Isotherms of COD sorption from coke wastewater on activated carbons after the sonification process.

Examinations of sorption on activated carbons in the third system (US + AC) were used to determine sorption isotherms. As shown in Fig. 5a, sorption isotherms reveal that COD sorption from initially sonicated wastewater was the most efficient for two carbons: WG-12 and ROW 08 Supra, with 393.87 and 386.79 mg/g, respectively. A substantially lower sorption was obtained for Picabiol (264.37mg/g). Over 30% lower sorption capacity was obtained for this carbon. Isotherms of COD sorption from wastewater on selected activated carbons were described using the Freundlich equation. The results are presented in Table 4.

Table 4. Freundlich isotherm constants for COD in the third system (US+AC).

Carbons	K _F ,mg/g	1/n	R ²
WG-12	18.34	0.4219	0.922
ROW 08 Supra	3.71	0.6356	0.910
Picabiol	2.49	0.6096	0.927

The Freundlich equation describes, with high accuracy, sorption isotherms determined during examinations for activated carbons. All the correlation coefficients R² (Tab. 4) are higher than 0.9. Fig. 5b presents the efficiency of COD sorption from initially sonicated wastewater which was next subjected to sorption on carbons. It can be noted that Picabiol carbon was characterized by substantially weaker sorption, with efficiency below 59%. This difference in sorption efficiency is likely to result from the effect of ultrasounds on the structure of organic compounds. With smaller particles, microporous carbons such as WG-12 or ROW 08 Supra are more sorptive. Devi et al. [14] explained this phenomenon by diffusion and smaller surface compared to bigger particles.

Support for the process through initial sonication of coke wastewater for all three carbons demonstrated the lowest efficiency of removal of COD from the systems examined (Fig. 6).

4 Conclusions

The results of our investigations indicated that GAC can be used in the removal of COD from coke wastewater. Sorption performances were evaluated using Freundlich isotherm model. The model were good fitted. The higher reduction of COD (89.8%) was obtained for carbon WG-12 with adsorbent dose of 10 g/l. Based on the examinations of coke wastewater treatment in three arrangements: (1) AC, (2) O₃+AC and (3) US +AC (are

shown Fig. 3b, 4b, 5b), it was found that the second system was the most effective (O₃+AC) for carbons WG-12 and ROW 08 Supra. In the case of Picabiol, the best efficiency was found for system 1 (AC).

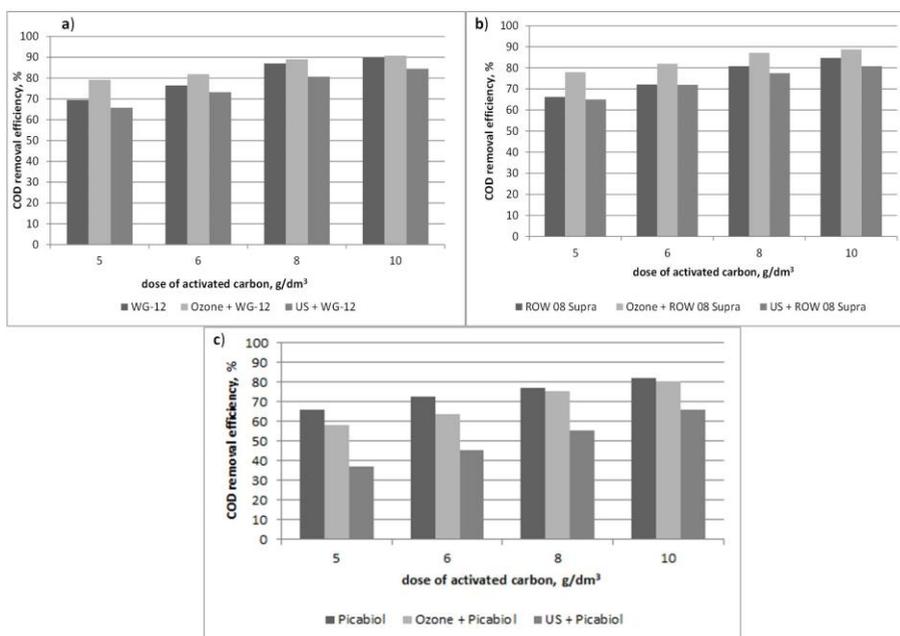


Fig. 6. Effect of the dose and type of activated carbon WG-12 (a), ROW 08 Supra (b) and Picabiol (c) on the degree of COD removal in the studied systems.

The study has been funded by BS/PB-401-301/1

References

1. W.T. Zhao, X. Huang, D.J. Lee, *Sep. Purif. Technol.* **66**, 279–286, (2009)
2. S. Zhang, J. Zheng, Z. Chen, *Sep. Purif. Technol.* **132**, 610–615, (2014)
3. K. Mielczarek, J. Bohdziewicz, A. Kwarciak-Kozłowska, *Rocz. Ochr. Środ.* **3**, 1965–1984, (2011)
4. A. Krzywicka, A. Kwarciak-Kozłowska, *Wat. Sci. Tech.* **69**, 1875–1878, (2014)
5. Y. Liu, J. Liu, A. Zhang, Z. Liu, *Envir. Pollu.* **220A**, 13–19, (2017)
6. E.E. Changa, H-J. Hsingb, P-Ch. Chiangc, M-Y. Chenc, J-Y. Shyngd, *Jour. of Hazar. Mater.* **156(1-3)**, 560–567, (2008)
7. L. Dąbek, E. Ozimina, *OSiZN*, **41**, 427–436, (2009)
8. L. Dąbek, E. Ozimina, A. Picheta-Oleś, *Ecolo. Chemist. and Enginn. A*, 17(11), 1421–1433, (2010)
9. Z. Debowski, M. Madela, *EPE*, **(4)**, 91–96, (2004)
10. M. Madela, D. Krzemińska, E. Neczaj, *Techn. Wody*, **5(37)**, 46–50, (2014)
11. A. Kwarciak-Kozłowska, A. Krzywicka A, M. Gałwa-Widera, *Rocz. Ochr. Środ.* **18**, 61–73, (2016)
12. A. Kwarciak-Kozłowska, A. Krzywicka, A. AGOiOŚ, **17(3)**, 133–142, (2015)
13. R. Devi, V. Dahiya, *Bioresour. Technol.* **99**, 344–349, (2008)
14. R. Devi, V. Singh, A. Kumar. *Bioresour. Technol.* **99**, 1853–1860, (2008)