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The effect of modification of activated carbon WG-12 on lead adsorption from water

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ABSTRACT

The presented work aimed at comparing two types of gaseous modification: the conventional method using an external source of energy (heat) and an originally developed method utilizing Joule heat generated during the flow of electric current through a carbon bed. The conventional modification of the WG-12 activated carbon was conducted in a rotary furnace at a temperature of 400°C and 800°C, respectively. Modification of activated carbon in an experimental electric heating system (referred to as the SEOW) occurred in a process whereby activated carbon was heated up to 400°C during the flow of electric current through the carbon bed, followed by cooling down with air or carbon dioxide. Both activated carbon modification methods enhanced the adsorption capacity toward Pb(II) ions. The monolayer capacity, as calculated from the Langmuir isotherm for the initial carbon, was q_m = 44.05 mmol/kg, while for carbon modified in the rotary furnace, q_m = 112.36 mmol/kg, and for carbon modified on the SEOW stand, q_m = 76.92 mmol/kg. The modification resulted in an increase in the specific surface area of activated carbon and the number of acid (mainly hydroxyl) functional groups. The advantage of activated carbon heating using the SEOW required much (up to several times) less energy, compared with the conventional method.

Keywords: Adsorption; Activated carbon; Lead; Modification

1. Introduction

Activated carbons are broadly used to remove organic compounds from water and wastewater. In some cases, they are also effective in removing organic and inorganic compounds, that is, heavy metals [1–3]. Apart from ion exchange, other processes that occur during adsorption include complexation, reduction, oxidation, and precipitation. The efficacy of Pb(II) adsorption depends on the number and type of functional groups [4–7]. Therefore, a lot of scientific research has been devoted to increasing the oxygen content on the surface of activated carbon [8,9]. This oxidation process can be achieved by the use of oxidizing gases and liquids [4,10]. The oxidation in a liquid-phase medium (especially when using nitric acid) results in the highest increase in oxygen quantities. When oxidizing carbon in a gaseous-phase medium, the oxygen content may rise even up to 15%, whereas in a liquid phase this value can reach 25% [11]. Nevertheless, in the case of modification with liquids, it is necessary to carefully flush out the oxidizing liquid, which is fairly difficult and time-consuming.

The high consumption of energy required for oxidizing in a gaseous phase is considered one of the biggest disadvantages of this method. The modification method presented in this article is much less energy-consuming than conventional methods.

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This study focuses on the high-temperature gas modification of activated carbon WG-12 and the evaluation of its effect on the adsorption of Pb(II) ion. The study compares two methods of gas modification: the conventional one that uses an external source of energy and the authors' method that uses Joule energy released during the passage of electric current through an activated carbon bed. The designed test stand (SEOW) and the method of conducting modification is a new solution proposed by the authors of the publication.

2. Research methodology

2.1. Activated carbons used in the study

Tests were carried out on activated carbon WG-12 produced from brown coal supplied by the Dry Distillation Plant at Hajnówka, Poland. The technical specification of this carbon is presented by Chen [12].

2.2. Modification of the WG-12 carbon

Before modification, activated carbon WG-12 was rinsed several times with distilled water. The rinsed WG-12 activated carbon is denoted as WG0. Then, it was dried at a temperature of 400°C. The first part of the carbon samples were modified in a rotary furnace. The modification was conducted for 1 h at a temperature of 400°C and 800°C, respectively, and at a constant flow of water vapor, carbon dioxide, or air. The carbon was initially heated up to temperatures at which carbon oxidation was conducted. The initial carbon is hereinafter denoted as the WG0, while modified carbons, as WG/400/1CO_2, where the number 400 denotes the modification temperature in °C, 1 denotes modification time, and CO_2, H_2O, or AIR are oxidizing gases (carbon dioxide, water vapor, and air, respectively) (Fig. 1).

The second part of the carbon samples were modified in an electric carbon heating test stand (SEOW). In this test stand, carbon samples were heated up to 400°C ± 20°C (Fig. 2). With reference to the results of previous investigations into the adsorption of Cr(III), it was observed that the activated carbon sampled from various heights of the reactor differed in adsorption properties. Therefore, for the investigation of Pb(II) adsorption, activated carbon was sampled only from that part of the reactor, which showed the highest adsorption capacity toward Cr(III) cations [9]. The carbons were modified by exposing them to cyclic heating up, followed by cooling down. The carbons modified on this stand are denoted with the formula WG/400E*I* + 80/80AIR*dśg*, where WG means carbon (WG0); 400E, heating on the SEOW stand up to a temperature of 400°C; *I*, the number of heating–cooling cycles; +80, the rate of gas flow through the reactor during heating up, in L/h; 80 AIR, volume of gas that flows during cooling the bed, in L/h; *dśg*, the location of carbon sampling: *d*, the lower part of the reactor; *ś*, the medium part of the reactor; *g*, the upper part of the reactor. If "*dś*" is used in carbon denotation, this means that carbons from the upper and middle parts of the SEOW reactor have been mixed with one another.

Electric power consumption during the modification of 1 L activated carbon at the test stand shown in Fig. 1 is as follows:

- For modification at a temperature 400°C for a duration of 1 h
  Preparation for working: 3.2 kW
  Operation for 1 h: 5.0 kW
- For modification at a temperature 800°C for a duration of 1 h
  Preparation for working: 9.3 kW
  Operation for 1 h: 7.9 kW

Modification of activated carbon on the SEOW (Fig. 2) is much more energy intensive. A carbon batch of 0.382 dm^3 was punt in the SEOW reactor. After modification, the bed was divided into three equal parts (upper, *g*; middle, *ś*;

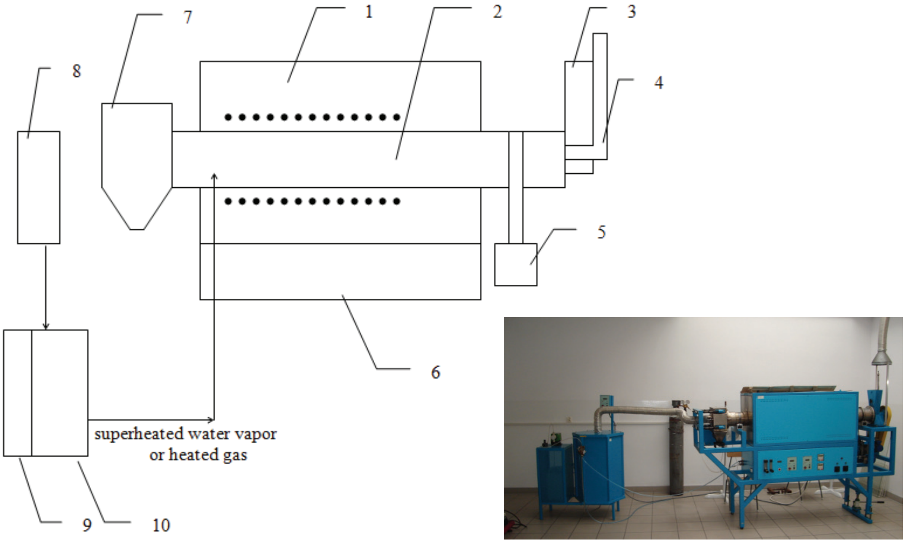


Fig.1. Testing stand for the high-temperature modification of activated carbon: (1) insulating casing, (2) rotary reactor, (3) activated coal feeder, (4) gas discharge, (5) reactor drive, (6) power and control cabinet, (7) activated carbon receiving chamber, (8) gas cylinder, (9) water tank, (10) superheater steam or gas heater.

and lower, *d*), each 0.127 L of activated carbon. Considering the longest time of heating up to 400°C, which was 24 min, one-off carbon modification in the reactor consumed 0.2 kWh. Power consumption in the most advantageous situation, when carbon to be modified was drawn only from one reactor height (e.g., from the bottom), was 1.6 kWh/L per L dm^3 of carbon, and when carbon was mixed from the lower and the middle reactor parts, it was only 0.8 kWh/L (a single heating–cooling cycle).

2.3. Measurement of Pb adsorption

The adsorption of heavy metals was conducted under static conditions from solutions with the following concentrations: 0.02, 0.05, 0.07, 0.09, 0.1, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, and 0.45 mmol/L. The test results are presented as the arithmetic means of three measurements. The adsorption was conducted from a solution of a volume of 0.25 L. A total of 1 g of selected activated carbon was added to that solution. In order to determine the time required for reaching the adsorption equilibrium, the experiments were conducted in two combinations (Fig. 1). In the first combination (the A adsorption curve), the solution with the activated carbon was stirred for 4 h. The concentrations were determined every 30 min. In the second combination (the B adsorption curve), the solution with the activated carbon was stirred for 2 h and then left for 2, 4, 6, 22, 46, and 70 h, respectively.

The isotherms of lead adsorption on activated carbon, depending on the solution pH (pH = 2, 4, 6) and solution temperature (20°C, 30°C, 40°C), were determined.

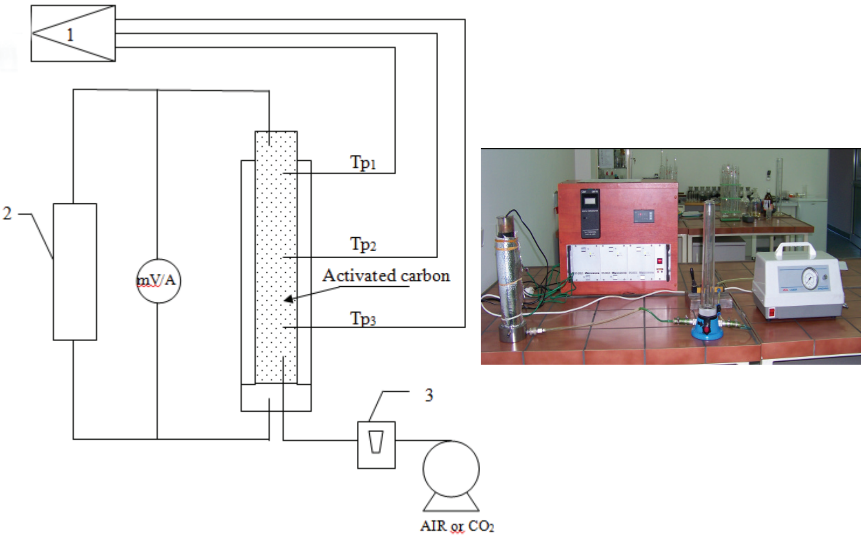


Fig. 2. Testing stand for activated carbon modification using Joule heat (SEOW): (1) measuring position change-over switch, (2) power supply, (3) rotameter, and Tp_1, Tp_2 and Tp_3 are thermocouples.

Table 1
Isotherms and their linear forms

Isotherm		Linear form	Plot	Eq. No.
Langmuir-I	$q=\frac{q_m K_L C_e}{1+K_L C_e}$	$\frac{1}{q}=\left(\frac{1}{K_L\cdot q_m}\right)\frac{1}{C_e}+\frac{1}{q_m}$	$1/q$ vs. $1/C_e$	(1)
Langmuir-II		$\frac{C_e}{q}=\frac{1}{q_m}C_e+\frac{1}{q_m K_L}$	C_e/q vs. C_e	(2)
Langmuir-III		$q=\left(-\frac{1}{K_L}\right)\frac{q}{C_e}+q_m$	Q vs. q/C_e	(3)
Langmuir-IV		$\frac{q}{C_e}=\left(-K_L\right)q+K_L\cdot q_m$	q/C_e vs. q	(4)
Freundlich	$q=K_F C_e^{\frac{1}{n}}$	$\ln Q=\frac{1}{n}\ln C_e+\ln K_F$	$\log q$ vs. $\log C_e$	(5)
Dubinin–Radushkevich	$q=q_s\exp(-K_D\varepsilon^2)$	$\ln q=\ln q_s-K_D\varepsilon^2$	$\ln q$ vs. ε^2	(6)
Temkin	$q=B\ln A_T C$	$q=B\ln A_T+B\ln C$	q vs. $\ln C_e$	(7)

The concentrations were determined using an inductively coupled plasma atomic emission spectrometer.

2.4. Adsorption kinetics and isotherm models

The Pb(II) adsorption data correlated with the Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin theoretical models (Table 1) [12–14].

Where q is the amount of metal ions adsorbed per unit mass of adsorbent (mg/g); C_e, equilibrium concentration of the solute in bulk solution (mg/L); q_m, solid phase concentration corresponding to the complete monolayer coverage of adsorption sites; K_L, the constant related to the free energy of adsorption; K_F, the Freundlich isotherm constant; n, adsorption intensity; q_s, a constant in the Dubinin–Radushkevich isotherm model, which are related to adsorption capacity; K_D, a constant related to the mean free energy of adsorption; ε, the Dubinin–Radushkevich isotherm constant $\varepsilon = RT\ln(1+\frac{1}{C_e})$; R, the gas constant; T, the absolute temperature; A_T, the Temkin isotherm equilibrium binding constant; B,a constant related to heat of sorption $B = \frac{RT}{b_T}$; and b_T, the Temkin isotherm constant [14].

Various models have been suggested to express the kinetics of adsorption of solute molecules onto a sorbent. The Pb adsorption kinetic data were correlated with the adsorption kinetic models [15,16]:

- The pseudo-first-order kinetic model:

$$\log(q_e - q_t) = \log q_1 - \frac{k_1}{2.303}t \tag{8}$$

- The pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1_1}{k_2 q_2^2} + \frac{1}{q_2}t \tag{9}$$

In these models, k_1 is the rate constant for the pseudo-first-order kinetic model, k_2 is the rate constant for the pseudo-second-order kinetic model, q_e is the amount of solute adsorbed at equilibrium, and q_t is the amount of solvent adsorbed at time t.

2.5. Examination of active carbons

The surface acidic and basic functional groups were determined by the method developed by Boehm [17].

Fourier-transform infrared (FTIR) spectroscopy of the carbon samples were obtained with a Perkin-Elmer FTIR Spectrum 2000 spectrometer [4].

Pore texture parameters were determined from nitrogen adsorption–desorption isotherms measured at 77 K with a Micromeritics sorptometer, model ASPA 2010. Surface area measurements were taken from the adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation [18]. The activated carbon pore volume was measured using the Horvath–Kawazoe method [19].

3. Results and discussion

The dependence of the degree of adsorption on the time of activated coal contact with the Pb(II) solution was examined in two variants (agitation, Curve A in Fig. 1; or agitation followed by static contact, Curve B in Fig. 1). Fig. 1 does not show the concentrations obtained after 48 and 72 h, because the differences in concentration after 24 and 72 h were less than 1% (C_0 0.45 mmol/L, pH 6). The equilibrium of adsorption was reached after 3 h of stirring, and the same effect was observed after 2 h of stirring and 22 h of static contact. For the tests, we used the second combination (i.e., 2 h of stirring and 22 h of static contact). After this period of time, the final concentration was measured.

For the analysis of Pb(II) adsorption (Fig. 3, Curve A, Table 2) on WG0 activated carbon, the pseudo-first-order and pseudo-second-order models were employed. These are the models that are the most frequently used for the description of the kinetics of heavy metal adsorption from water solutions, and which describe the results with high correlation coefficients, R^2 [20–22]. Better results of adsorption kinetics description (a higher R^2) were obtained when using the second-order kinetic model, compared with the pseudo-first-order kinetic model (Table 2). Similar results were obtained by other researchers [23,24].

The effect of initial pH on the adsorption process is presented in Fig. 4. The tests were conducted in the pH range of 2–6, because in solutions with higher pH values, the precipitation of insoluble lead compounds would be likely [25,26]. In those solutions, lead occurred in the form of divalent cation,

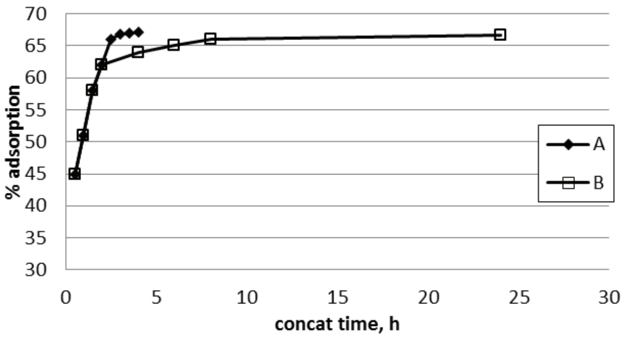


Fig. 3. Effect of the time of WG0 activated carbon contact with the solution on the adsorption of Pb(II): (A) stirred, (B) stirred 2 h agitation followed by static contact 2, 4, 6, or 22 h.

Table 2
Adsorption kinetics parameters of the pseudo-first-order and pseudo-second-order models

Activated carbon	q_e(exp) mmol/kg	First-order kinetic model		Second-order kinetic model	
		k_1 m^3/min	R^2	k_2 mmol/(kg min)	R^2
WG0	16.8	0.0313	0.9509	0.0022	0.9977

Pb^{2+} [27]. The lead adsorption was the greatest from solutions with pH = 6, and very little from solutions with pH = 2. Other researchers also obtained the highest values of lead adsorption under similar conditions [28,29]. Such results might be due to a poor dissociation of functional groups that are able to exchange lead cations in a strongly acid medium. The low adsorption of lead from the solution of pH = 2 is due to the little dissociation of carboxyl and hydroxyl groups on the activated carbon surface. The remaining functional groups are undissociated in an acid medium. Moreover, a large quantity of H^+ hydrogen ions in the acid medium imparts a positive charge to the carbon surface. So, an acid medium is not advantageous to the adsorption of Pb^{2+}. The higher the pH, the greater the dissociation of function groups, the smaller the concentration of H^+ cations and the higher the adsorption of lead ions.

The temperature of an adsorption medium could be important for energy-dependent mechanisms in metal adsorption by activated carbon (Fig. 5). An increase in temperature from 20°C to 40°C leads to an increase in adsorption capacity from 2.57 to 3.93 mmol/kg at a concentration of 0.45 mmol/m³. After the equilibrium has been attained, the uptake increases with increasing temperature, this effect may be explained by the availability of more active sites on the adsorbent at higher temperatures. The enhancement of adsorption capacity at higher temperature may be attributed to the enlargement of pore size and/or activation of adsorbent surface [30,31].

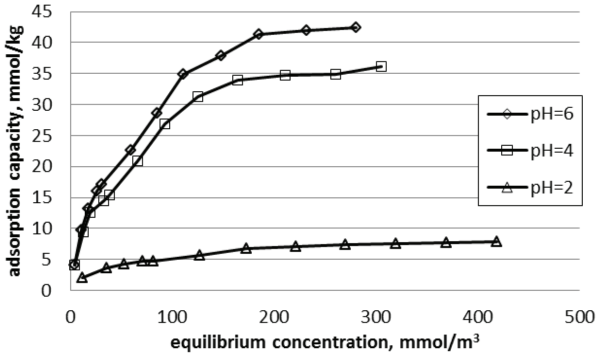


Fig. 4. Effect of initial pH on Pb(II) adsorption on activated carbon WG0.

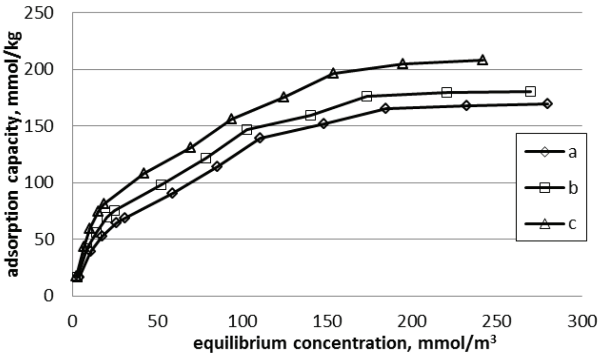


Fig. 5. Effect of temperature on Pb(II) adsorption on activated carbon WG0: (a) 20°C, (b) 30°C, (c) 40°C.

The obtained effect might also result from the increase in the dissociation of functional groups on the activated carbon surface with the increase in temperature. Another cause might also be increased leaching of ash at higher temperatures and unlocking the access to part of pores.

The isotherms of lead adsorption from solutions varying in pH and at different temperatures were described with the Freundlich, Langmuir (forms I, II, III, and IV), Temkin and Dubinin–Radushkevich equations (Table 3). The poorest fitting of the obtained results to the model was obtained for the Dubinin–Radushkevich isotherm case (R^2 from 0.624 to 0.689). In the remaining cases, the obtained values of R^2 were higher. In one Temkin isotherm case, R^2 amounted to 0.73, but in the other cases it was above 0.9. When analyzing different forms of the Langmuir isotherm, a better fitting to the results for forms I and II compared with forms III and IV were found. In spite of the high R^2 values for forms I and II, distinct differences between the determined parameters of this isotherm were found. The often compared parameter q_m, defining the capacity of the monolayer, assumes the lowest values when calculated from Form I, and the highest values, when calculated from Form II of the Langmuir isotherm. These differences are considerable, and, for example, for adsorption from a solution with pH = 4 at 20°C, the q_m, as calculated according to Form I of the Langmuir isotherm, amounts to 32.5 mmol/kg, while according to Form II, 42.6 mmol/kg. For the description of subsequent tests, two Freundlich and Langmuir isotherms of Form I were selected, which were characterized by high values of the correlation coefficient R^2, and which are the most often used by other authors [31,32].

The adsorption of Pb(II) ions was also examined in selected modified activated carbons. The adsorption isotherms are presented in Fig. 6, whereas the Langmuir and Freundlich isotherm constants are given in Table 4.

The modified carbons adsorbed heavy metal ions more effectively compared with the initial WG0. In the case of Pb(II) adsorption, the best results were obtained for carbons modified at the temperature of 800°C in the CO_2 and water vapor (H_2O) atmosphere and at the temperature of 400°C in air in the rotary furnace (q_m from about 73 to 81 mmol/kg, and, for WG0, 32 mmol/kg for the equilibrium concentration of 100 mmol/m³). The carbons modified in the SEOW sorbed more Pb(II) (up to 68 mmol/kg), compared with the initial WG0 (32 mmol/kg), and more than carbons modified in the rotary furnace in the water vapor and carbon dioxide atmosphere did (the maximum adsorption amounted to 46 mmol/kg). Among the modified carbons, the best adsorption properties were obtained for the carbons modified in the air atmosphere. The affinity series in the oxidized activated carbons vs. lead is as follows:

WG/800/1CO_2 > WG/400/1AIR > WG/800/1H_2O
> WG/400E*I*/80AIR*dś* > WG/400E*I*/40AIR*dś* >
WG/400E*I* + 40/40CO_2*d* > WG/400E*I*/40CO_2*d* >
WG/400E*I*/80CO_2*d* > WG/400E*I* + 80/80CO_2*d* >
WG/400/1CO_2 > WG/400/1H_2O > WG0

The modification of activated carbon WG0, both in the rotary furnace and in the SEOW, allowed sorbents with increased adsorption capacity for individual cations to be obtained. The adsorption isotherms are presented in Fig. 4,

Table 3
Values of Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich constants for the adsorption of Pb(II)

Isotherm	Constants	pH = 2	pH = 4	pH = 6		
		20°C	20°C	20°C	30°C	40°C
Freundlich	K_F, mol/kg	0.91	2.52	2,57	3.25	3.93
	$1/n$, –	0.3738	0.4961	0.5319	0.5052	0.5017
	R^2	0.969	0.971	0.973	0.960	0.956
Langmuir 1	q_m, mmol/kg	7.68	32.47	41.49	46.30	53.76
	K_L, m^3/mmol	0.0283	0.0355	0.0282	0.0313	0.0342
	R^2	0.978	0.987	0.996	0.998	0.997
Langmuir 2	q_m, mmol/kg	8.91	42.55	51.54	52.63	59.52
	K_L, m^3/mol	0.0173	0.0191	0.0179	0.0230	0.0257
	R^2	0.996	0.990	0.990	0.992	0.9872
Langmuir 3	q_m, mmol/kg	8.17	37.85	46.90	48.65	53.8
	K_L, m^3/mmol	0.0238	0.0265	0.0227	0.0286	0.0343
	R^2	0.903	0.863	0.918	0.938	0.9294
Langmuir 4	q_m, mg/g	8.42	40.30	48.82	50.10	55.55
	K_L, m^3/mmol	0.0215	0.0228	0.0208	0.0268	0.0319
	R^2	0.903	0.8626	0.918	0.938	0.929
Temkin	A, m^3/mmol	0.2259	0.2571	0.2425	0.3162	0.3820
	B, –	1.76	8.33	10.07	10.19	11.20
	R^2	0.985	0.955	0.962	0.73	0.973
Dubinin–Radushkevich	q_s, mmol/kg	6.14	23.35	26.41	28.45	31.42
	K_{ad}, mol^2/kJ	3×10^{-5}	6×10^{-6}	6×10^{-6}	5×10^{-6}	3×10^{-6}
	R^2	0.689	0.624	0.636	0.664	0.671

whereas the Langmuir and Freundlich isotherm constants are given in Table 4. The highest efficacy in Pb(II) ion removal was observed for the carbons modified in the conventional manner at the temperature of 800°C and for the carbons oxidized with air at the temperature of 400°C (35.9%–92.5% of Pb(II) were removed on WG/800/1CO$_2$, while 35.9%–79.5% on WG0). The carbons modified in the SEOW stand adsorbed more Pb(II), compared with the initial WG0 and the carbon modified in the rotary furnace at the temperature of 400°C in the water vapor and carbon dioxide atmosphere (e.g., 65.4%–88% of Pb(II) on WG/400E*I*/80AIR*dś*). Differences between carbons oxidized conventionally in the rotary furnace and by means of Joule heating were not significant (by several percent).

The modification of activated carbon in the rotary furnace and in the SEOW stand yields similar adsorption results for the ions under investigations. A benefit of oxidation in the SEOW stand is a negligible mass reduction (e.g., compared with carbons oxidized at 800°C or 400°C in the air atmosphere) and very low electricity consumption that typically determines the cost-effectiveness of the gaseous phase oxidation process.

The Freundlich and Langmuir adsorption isotherms describe the obtained test results (Table 4) with a high correlation coefficient ($R^2 > 0.955$). In the majority of instances, higher R^2 values were obtained for the Langmuir model. The obtained q_m value, which characterizes the rate of adsorption, is for all modified carbons higher than for the initial activated carbon. The obtained q_m values are contained in the range from 44.05 mmol/kg (9.1 mg/g) to 112.36 mmol/kg (23.3 mg/g). These are medium values, compared with those obtained by other authors ($q_m = 4.7 \div 26.5$ mg/g [33], $q_m = 53.8$ mg/g [34], $q_m = 17.2 \div 40.2$ mg/g [35], $q_m = 12$ mg/g [36]).

The adsorption of heavy metals is associated with the chemistry of carbon surface and pore structure. With currently available technologies, it is not feasible to fully evaluate both the pore structure and the chemical composition. The situation seems much more complex, if one considers the system of an adsorbent—an adsorbed heavy metal ion that is characterized by specific properties, for example, during change in solution pH.

The evaluation of surface changes due to modification was carried out by means of nitrogen adsorption at a

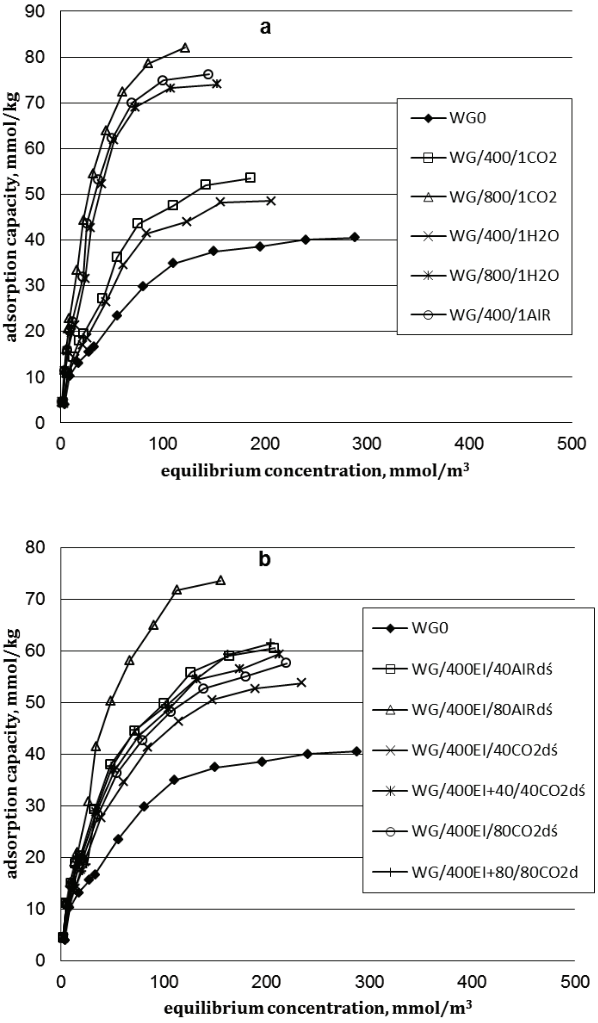


Fig. 6. Adsorption isotherms for Pb(II) adsorption on modified activated groups of WG0: (a) carbons modified in the rotary furnace, (b) carbons modified in the SEOW.

temperature of 77 K and was computed based on the BET model (Table 5). This model is typically used for the evaluation of the specific surface area [18,37,38]. As a result of activated carbon modification in the manner presented herein, adsorbents of a specific surface area greater than that of the initial WG0 carbon were obtained. A slight increase in the volume of micropores was also observed.

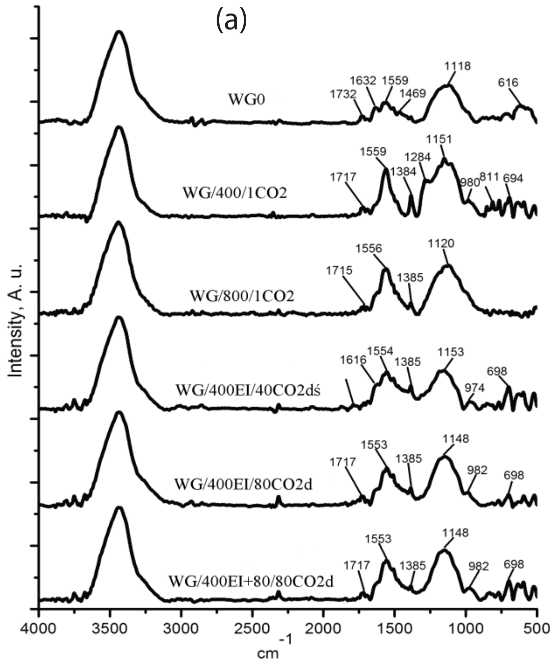
The analysis of the chemical properties of the surface of activated carbons poses many difficulties. There is a variety of physical and physicochemical methods that are used for the identification and quantitative determination of the surface groups. They include desorption of functional groups, alkaline neutralization, potentiometric titration, spectroscopy, adsorption of polar pairs, etc. None of them describes completely and reliably the chemical properties of surface, and therefore researchers usually use some of them [37,39]. There are many difficulties in the interpretation of results obtained using these methods, as regards the adsorption of heavy metal ions. Therefore, some researchers restrict their efforts to the practical assessment of adsorption capacity with respect to metal/metals and the evaluation of the chemical nature of the surface by other methods [9,35,40]. In this study, the evaluation of the chemical properties of surface was based on the neutralization of functional groups with bases and FTIR spectra (Table 5, Fig. 7). The examinations of the oxygen group contents by the Boehm method were considered as elementary examinations that allowed the direct evaluation of their number and quality. The total number of groups of an acidic character, neutralizable with sodium base (carboxyl, lactone, and phenol), was greater for all oxidized carbons, though these differences were not significant and ranged from 9% to 26%. Only for the carbon oxidized in air at 400°C did the quantity of acidic groups increase by 70%. From among the examined acid oxygen groupings, hydroxyl groups most probably had an overriding importance. As a result of modification, their number increased by a factor of 1.87 ÷ 3.46 compared with the initial carbon. These groupings are most likely responsible for the enhanced adsorption on modified carbons. A considerable importance of these groupings in the adsorption of iodine was also highlighted by the

Table 4
Coefficients of the Freundlich and Langmuir isotherms for Pb(II) ion adsorption on carbon WG0 modified in air, CO_2, or water vapor

Carbon	Coefficients of Freundlich isotherms			Coefficients of Langmuir isotherms		
	1/n	K_F, mmol/kg	R^2	q_m, mmol/kg	K_L, m^3/mmol	R^2
WG0	0.53	2.57	0.955	44.05	0.0252	0.977
WG/400/1CO$_2$	0.59	3.06	0.976	53.19	0.0328	0.994
WG/800/1CO$_2$	0.63	4.88	0.964	112.36	0.0287	0.999
WG/400/1H$_2$O	0.57	2.87	0.968	50.51	0.0298	0.990
WG/800/1H$_2$O	0.65	4.02	0.964	81.97	0.0327	0.995
WG/400/1AIR	0.64	4.34	0.963	92.59	0.0306	0.998
WG/400E*I*/40AIR*dś*	0.56	3.73	0.964	66.67	0.0291	0.986
WG/400E*I*/80AIR*dś*	0.67	3.24	0.973	76.92	0.0257	0.989
WG/400E*I*/40CO$_2$*dś*	0.56	3.06	0.963	60.24	0.0243	0.982
WG/400E*I* + 40/40CO$_2$*d*	0.56	3.57	0.967	62.5	0.0296	0.988
WG/400E*I*/80CO$_2$*dś*	0.56	3.36	0.968	61.73	0.0274	0.989
WG/400E + 80/40CO$_2$*d*	0.64	2.55	0.972	63.69	0.0228	0.993

Table 5
Changes in the pore structure and surface functional groups of carbon WG0 after modification

Parameter	WG0	WG/400/ 1CO$_2$	WG/800/ 1CO$_2$	WG/400/ 1H$_2$O	WG/800/ 1H$_2$O	WG/400/ 1AIR	WG/400EI/ 40AIR*dś*	WG/400EI/ 80AIR*dś*	WG/400EI/ 40CO$_2$*dś*	WG/400EI + 40/40CO$_2$*d*	WG/400EI/ 80CO$_2$*d*	WG/400EI + 80/80CO$_2$*d*
Porous structure												
S_{BET}, m^2/g	1,098	1,181	1,239	1,163	1,199	1,208	1,161	1,184	1,114	1,109	1,142	1,166
V_{micro}, cm^3/g	0.530	0.551	0.553	0.541	0.548	0.538	0.541	0.539	0.541	0.529	0.538	0.537
V_{meso}, cm^3/g	0.048	0.040	0.051	0.045	0.046	0.044	0.046	0.043	0.048	0.047	0.049	0.048
V_{macro}, cm^3/g	0.417	0.343	0.370	0.413	0.321	0.412	0.419	0.420	0.418	0.419	0.417	0.406
Surface functional groups, mmol/g												
Carboxylic groups	0.182	0.133	0.109	0.146	0.103	0.307	0.149	0.136	0.157	0.142	0.162	0.173
Lactonic groups	0.209	0.205	0.151	0.252	0.100	0.193	0.151	0.184	0.147	0.163	0.155	0.168
Phenolic groups	0.110	0.291	0.302	0.187	0.346	0.358	0.326	0.275	0.313	0.309	0.268	0.205
Carbonyl groups	0.085	0.000	0.000	0.019	0.000	0.011	0.000	0.004	0.000	0.002	0.006	0.000
Basic groups/sites	0.467	0.535	0.546	0.521	0.534	0.525	0.524	0.522	0.515	0.520	0.518	0.502



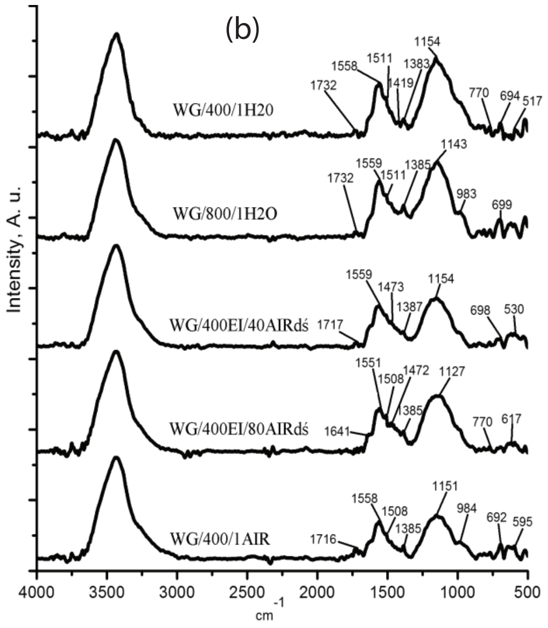


Fig. 7. FTIR spectra for carbon WG0 as modified: (a) with carbon dioxide and (b) with air and water vapor.

authors of other studies [41,42]. At the same time, the number of groups with basic character increased (from 7 to 17).

FTIR examinations were also carried out in this work. This method is often used for the chemical determination of the surface structure [43,44]. The shape of these curves reveals that there were some differences among the oxidized carbons, but they were not significant. The procedures used for activation allowed the mild oxidation of the carbon surface, resulting in a relative increase in the zonal intensity of carbonyl

>C= (1,740 ÷ 1,500 cm^{-1}) and ester C–O–C (1,300 ÷ 1,000 cm^{-1}) groups in comparison with hydroxyl groups (ca. 3,450 cm^{-1}). The modification with CO_2 (and to a lesser extent with H_2O) resulted in the occurrence of an additional zone of acetyl-aldehyde groups, –O–CH=O (1,385 cm^{-1}). Oxidation with air results in an increase in the intensity of the small peak of carboxyl groups –COOH (ca. 1,720 cm^{-1}). This correlates well with the results obtained from the evaluation of oxygen groups by the Boehm method.

The investigation of the chemical properties of surface, presented herein, can be considered as a preliminary study done for the purpose of further investigations into the adsorption of heavy metal cations. Świątkowski et al. [5] investigated the sorption of lead on alkaline and acidic activated carbons, and they suggested the following mechanisms for sorption (Eqs. (10)–(16)).

- On amphoteric and alkaline activated carbons:

$$\ni C:+Pb^{2+} \rightarrow \ \ni C\ :\ Pb^{2+}\ (C\pi - \text{cation interactions}) \tag{10}$$

- Additionally on alkaline activated carbons:

$$>C-OH + Pb^{2+} + 3H_2O \rightarrow\ >COPbOH + 2H_3O^{+} \tag{11}$$

$$>C-O^{-*} + Pb^{2+} + 2H_2O \rightarrow\ >C-O-PbOH\ +\ H_3O^{+} \tag{12}$$

$$>N:+Pb^{2+} + 2H_2O \rightarrow\ >N-Pb\left(OH\right)^{+} + H_3O^{+} \tag{13}$$

- On oxidized "acidic" activated carbon:

$$>C-COOH + Pb^{2+} + H_2O \rightarrow\ >C-O-COOPb^{+} + H_3O^{+} \tag{14}$$

$$\left(>C-COOH\right)_2 + Pb^{2+} + 2H_2O \rightarrow \left(>C-COO\right)_2 Pb + 2H_3O^{+} \tag{15}$$

$$>C-OH + Pb^{2+} + H_2O \rightarrow\ >C-OPb^{+} + H_3O^{+} \tag{16}$$

Apart from the ion-exchange and complexation reactions presented herein, lead can be removed on activated carbons through the sedimentation of oxides and hydroxides. Because the adsorption of the Pb(II) cation occurred not only in the presence of acidic functional groups, the role of basic functional groups should also be assessed. One of the proposed methods is the neutralization of functional groups. However, despite the ion-exchange that occurs during the adsorption of heavy metal ions, other phenomena, such as complexation, microprecipitation, the creation of dipolar bonds, and electrostatic interaction between the Cπ–electrons of the graphene carbon layer and physical adsorption, may occur [5]. Although the presence of functional groups plays an important role, the arrangement of functional groups and their mutual interactions (i.e., reinforcing or weakening) in the pores of activated carbon are also of crucial importance. With a view to this, further investigations into the adsorption of selected cations should be undertaken.

4. Conclusions

It has been found that both the temperature and pH of solution have an influence on the adsorption of Pb(II) on activated carbon WG0. The best adsorption results were obtained in adsorption from a solution with pH = 6 and at a temperature of 40°C. The adsorption kinetics has been analyzed, and it has been found that a better fitting of the obtained results is provided by the pseudo-second-order kinetic model, compared with the pseudo-first-order and pseudo-second-order models.

For the description of the results, the Freundlich, Langmuir (forms I, II, III, and IV), Temkin, and Dubinin–Radushkevich isotherms were used. The obtained results are most poorly described by the Dubinin–Radushkevich isotherm model. The other isotherms describe the results with a high correlation coefficient; nevertheless, the best fitting of the results to the model was achieved for the Langmuir (forms I and II) and Freundlich isotherms.

The examinations have confirmed that the modification of activated carbons can have an effect on the adsorption of Pb(II). Both carbon modification methods described in this study (i.e., the conventional rotary furnace method and the SEOW method proposed by the authors) increase the adsorption of Pb(II). The modification resulted in a slight increase in specific surface area and an increase in the total quantity of acid groupings on the activated carbon surface, among which the increase in hydroxyl groups was the most significant (even by several times).

The study has presented the use of Joule-heat electric heating of carbon in new areas of application. The biggest advantage of carbon modification in the SEOW is that this method requires (up to tenfold) less energy than the conventional method. What is more, the proposed SEOW stand is very easy to build and operate. The obtained results of Pb adsorption on activated carbons modified on the SEOW stand were better compared with unmodified activated carbons. The carbons modified on the SEOW stand showed slight changes in pore structure and a small reduction in bulk density.

The adsorption of heavy metal ions on the carbons modified on the SEOW was in many cases higher than those obtained for carbons modified conventionally at the temperature of 400°C. This was due to different modification process parameters. In this case, the electricity was converted directly into heat in the activated carbon. When the carbon was heated on the SEOW, the thermal decomposition of oxygen groups predominated on the carbon surface. The proper modification was observed when the carbon was cooled down and the oxidizing media were sucked in to pores due to a reduction in the temperature of gases present in those pores. Therefore, the modification of this surface occurred only in bigger pores because of the short carbon cooling time, and it was very intensive because the desorption of the groups caused an increase in the reactivity of the carbon surface. The main advantage of the modified carbons was the identification of functional groups in locations that are relatively well available to large hydrated ions of heavy metals.

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