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The influence of modification of activated carbon on adsorption of Ni(II) and Cd(II)

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ABSTRACT

Adsorption of Cd(II) and Ni(II) ions on the modified activated carbon (WG-12) was measured. Two methods of activated carbon modification, i.e. a traditional method in a rotary furnace and a method developed by the author in a reactor that uses Joule's heat, were analysed. The effects of performed modification were evaluated based on the surface area, water vapour adsorption, volume of micro-, meso- and macropores, and a number of oxygen groupings measured with the Boehm method. The application of these two methods resulted in the increase in adsorption of Ni^{2+} and Cd^{2+}. The most favourable results for adsorption of both Ni^{2+} and Cd^{2+} were obtained for activated carbons modified in a rotary furnace at 800˚C and with atmospheric oxygen at 400˚C. Adsorption of Ni^{2+} and Cd^{2+} on activated carbons modified with Joule's heat was slightly higher than in the case of activated carbons modified in a rotary furnace with carbon dioxide and water vapour at the same temperature (400˚C). The presented method developed by the author is far more energy efficient. Less mass reduction and changes in a porous structure are observed which is favourable during adsorption of organic compounds.

Keywords: Activated carbon; Modification; Cadmium; Nickel

1. Introduction

Heavy metals are contaminants present in wastewater generated by various industries. Toxic metals that are often present in wastewater include: copper, cadmium, chromium, zinc, nickel and lead—the latter being toxic even in trace amounts [1,2]. Therefore, removal of heavy metals from wastewater is an important issue. Removal of heavy metals can be performed through: coagulation and flocculation, chemical precipitation, ion exchange, cementation, complexation, adsorption, biosorption and membrane processes.

Adsorption is one of the most thoroughly investigated methods of removal of contaminants from wastewater in order to recover valuable heavy metals. Adsorption of chromium, lead, cadmium, copper, mercury, iron, zinc, manganese, cobalt and arsenic is the subject of many investigations [3–6]. Different types of adsorbents are used for adsorption from

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unary and multicomponent solutions, on oxidized and non-oxidized activated carbons and modified activated carbons [7–9]. These investigations aim at:

- determining the potentials of adsorption of heavy metals on commercially available activated carbons,
- searching for new affordable adsorbents, e.g. for waste materials and
- modifying activated carbons in order to increase their adsorption capacity towards ions of heavy metals.

Adsorption of heavy metal ions depends on the size of specific surface, porous structure but first and foremost on chemical structure of the activated carbon surface [10]. According to Giraldo-Gutierrez and Moreno-Pirajan, the highest adsorption of heavy metals occurs on activated carbons with a significant number of functional groups capable of ion exchange [1]. Also, the kind of anion subjected to sorption—in particular the Cartledge ionic potential—plays an important role in adsorption.

The overall goal of the presented research was to investigate the effect of high-temperature modification of activated carbon on adsorption of Cd(II) and Ni(II) ions. Two methods of modification, i.e. a traditional method in a rotary furnace at temperatures of 400 and 800˚C with atmospheric oxygen, carbon dioxide and water vapour and a method developed by the author that uses Joule's heat to modify activated carbons were compared. In the presented method of modification, the activated carbon was heated up to 400˚C and the air or carbon dioxide was purged during both heating and cooling or cooling of activated carbons.

2. Materials and methods

2.1. Modification activated carbon

Before the modification, WG-12 carbon was rinsed a few times with distilled water. Then, it was dried at the temperature of 400˚C. The first part of carbon samples was modified in a rotary furnace. The modification was conducted within 1 h at the temperature of 400˚C and 800˚C under the constant flow of water vapour, carbon dioxide or air. They were initially heated up to the temperatures at which carbon oxidation was conducted. Initial carbon was further denoted as WG0 and modified carbons, respectively: 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 as oxidizing gases (carbon dioxide, water vapour and air, respectively).

The second part of carbon samples was modified in an electrical stand for carbon heating (SEOW). In this stand, carbon samples were heated up to 400 ± 20˚C. The first part of carbon samples was modified in a rotary furnace. Its diagram was presented in the author's work [11]. The carbons were modified using the cycles of heating up followed by cooling down. The carbons modified in this stand were denoted according to the following pattern: WG/400EI+80/80 AIR, where WG means carbon, WG-12, 400E—heating in SEOW stand up to the temperature of 400˚C, I—number of heating–cooling cycles, +80—flow of gas through reactor during heating up in dm^3/h, 80 AIR —volume of gas that flows during cooling the bed in L/h, d—location of carbon sampling: d—lower part of reactor, ś—medium part of reactor, g–upper part of reactor.

2.2. Measurement of sorption of Ni and Cd

The adsorption of heavy metals was conducted in static conditions with solutions of concentrations of: 0.02, 0.05, 0.07, 0.9 and 0.1 mmol/L. The results of the study were presented as arithmetic means of three measurements. The adsorption was conducted for the solution with a volume of 0.25 L, to which 1 g of the proper activated carbon was added. For the first two hours, carbon was shaken with the solution of metal and then it was put away for 22 h. After this period of time, the final concentration was measured. The solutions of heavy metals were obtained from the following chemical compounds: cadmium—$3CdSO_4 \times 8H_2O$ and nickel—$NiSO_4$.

The measurements of concentrations were made on the atomic emission spectrometer with inductively coupled plasma.

The Ni(II) and Cd(II) sorption data correlate with the theoretical models of Langmuir and Freundlich:
Langmuir equation

$$Q = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{1}$$

Freundlich equation

$$Q = K_F C_e^{\frac{1}{n}} \tag{2}$$

where Q is the amount of metal ions adsorbed per unit mass of adsorbent (mg/g), C_e—equilibrium concentration of solute in bulk solution (mg/L), Q_0—solid phase concentration corresponding to the complete monolayer coverage of adsorption sites,

K_L—the constant related to free energy of adsorption. The constants K_F and n in the Freundlich model can be related to the strength of the adsorptive bond and bond distribution [12].

2.3. The measurements of chemical character of the surface

The surface acidic and basic functional groups were estimated using the method developed by Boehm [13].

FTIR spectra of the carbon samples were obtained with a Perkin-Elmer FTIR Spectrum 2000 spectrometer [14].

Measurements of sorption isotherms for water vapour under static conditions were also carried out for these carbons at different pressures of H_2O over sulfuric acid and different concentrations at the temperature of 20˚C. Sorption isotherms for water vapour at lower concentrations were represented by the isotherm proposed by Dubinin and Sierpiński [15,16]. Isotherms of water vapour adsorption are also described by other equations. However, Dubinin–Sierpiński equation is still considered to be fundamental:

$$a = a_0 \cdot c \frac{\frac{p}{p_0}}{1 - c\frac{p}{p_0}} \tag{3}$$

With linear form, of which the constants a_0 (the number of primary adsorption centres) and c ($c = k_2/k_1$, where k_1 and k_2 are the constants of adsorption and desorption rate) can be derived by the equation is given by:

$$\frac{\frac{p}{p_0}}{a} = \frac{1}{a_0 \cdot c} - \frac{\frac{p}{p_0}}{a_0} \tag{4}$$

where a is the volume of adsorbed water vapour with relative pressure p/p_0.c

3. Results and discussion

The measurements of specific surface area and macro-, meso- and micropore volumes were measured for initial carbon WG-12 and the carbon after modification (Table 1).

Evaluation of changes in the surface as a result of modification was carried out by means of nitrogen adsorption at the temperature 77 K and was computed based on BET model. This model is typically used for the evaluation of specific surface area [17–19]. It

Table 1

Changes in pore structure of WG0 carbon after modification and the number of surface functional groups in initial WG0 and modified activated carbon determined by means of the Boehm method

Parameter	WG0	WG/ 400/ $1CO_2$	WG/ 800/ $1CO_2$	WG/ 400/ $1H_2O$	WG/ 800/ $1H_2O$	WG/ 400/ 1AIR	WG/ 400EI/ 40AIRdś	WG/ 400EI/ 80AIRdś	WG/400EI/ $40CO_2$dś	WG/ 400EI+40/ $40CO_2$d	WG/ 400EI/ $80CO_2$d	WG/ 400EI+80/ $80CO_2$d
Changes in pore structure of WG0 carbon after modification												
$S_{BET,}$ 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
The number of surface functional groups in initial WG0 and modified activated carbon determined by means of the Boehm method												
$\sum A$, mmol/g	0.582	0.629	0.569	0.585	0.549	0.858	0.626	0.595	0.617	0.597	0.579	0.546
$\sum B$, Mmol/g	0.467	0.535	0.546	0.521	0.534	0.525	0.524	0.522	0.515	0.505	0.518	0.502

Notes: S_{BET}—surface area; $\sum A$—acid groups/sites; $\sum B$—basic groups/sites.

should also be stressed that particularly for highly microporous carbons, the evaluation of specific surface area is susceptible to errors [10,20].

For different methods of oxidation, the surface of activated carbon might increase or decrease. This depends primarily on the modification method and also on the material the carbon was obtained from and the production method. The results contained in Table 1 confirm some insignificant changes that occurred in a specific surface area. Most of the oxidized carbons (except for WG/400/H_2O) were characterized by the same or slightly increased specific surface area. These differences were not significant and reached the maximum of 6% at the temperature 800°C for H_2O vapour. Slightly different changes were observed in the distribution of pore volume. An increase in micropore volume, reaching the maximum of 4.3% was observed in almost all carbons. A decline in meso- and macropores was found for the most of the carbons.

In the present study, the evaluation of the chemical character of the surface was based on the neutralization of functional groups with bases and FTIR spectra (Table 1, Fig. 1).

Evaluation of chemical character of the surface of activated carbons was carried out by means of the Boehm titration method to determine the number of millimoles of surface oxides (see Table 1). The highest number of acidic groups (with particular focus on carboxylic and phenolic) was found in WG/400/1AIR. The total number of oxygen groups in the initial WG0 amounted to 0.586 and 0.858 mmol/g in WG/400/1AIR. Initial carbon was characterized by a relatively high number of carbonyl groups (14%) which dissociate at very high pH and are not involved in the processes of ion exchange. These formations were not found (or found with much lower contents) in oxidized activated carbons. Other carbons had a bit higher number of acidic groups, which ranges from 0.546 mmol/g for WG/400EI+80/80CO$_2$d to 0.629 mmol/g for WG/400/1CO$_2$. However, in the case of the oxidized activated carbons, their surface did not exhibit carbonyl groups which have only marginal effect on ion exchange connected with a high content of pK. However, these groups might increase acid dissociation constant in other groups. Adsorption capacity of the oxidized carbons might be also affected by an increased number of basic groups observed in all oxidized sorbents. The increase in their number was not high (ranging from below 8% for WG/400/1H$_2$O to over 15% for WG/400/1CO$_2$ and WG/800/1H$_2$O).

FTIR examinations were also carried out. They are often used for chemical determination of the surface character [21,22]. The shape of these curves reveals that there were some differences between the oxidized carbons, but they were not high. This correlates with

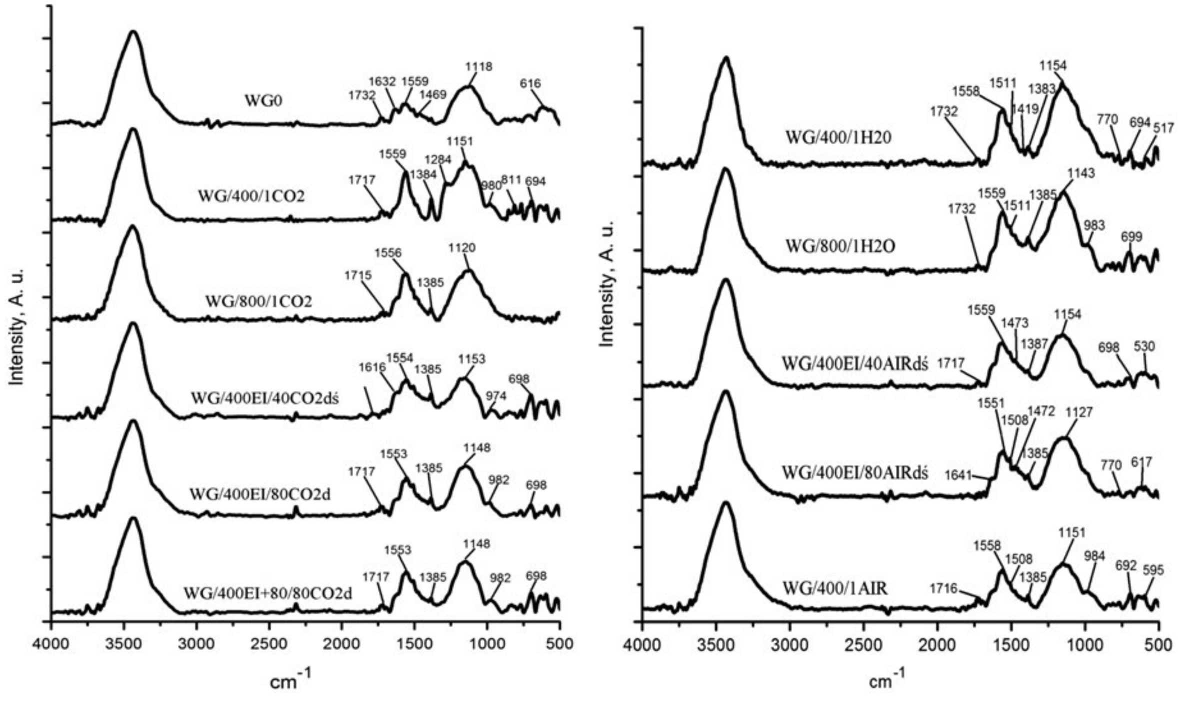

Fig. 1. FTIR spectra for carbon WG0 modified with carbon dioxide, air and water vapour.

Table 2
Coefficients equations of Freundlich, Langmuir, Dubinin and Sierpiński

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/40AIRdś	WG/400EI/80AIRdś	WG/400EI/40CO$_2$dś	WG/400EI+40/40CO$_2$d	WG/400EI/80CO$_2$d	WG/400EI+80/80CO$_2$d
Isotherms of Ni(II)													
Freundlich isotherms	$1/n$	0.8	0.81	0.85	0.82	0.87	0.85	0.82	0.83	0.81	0.81	0.80	0.8
	$K_F^{(1)}$	0.39	0.47	0.60	0.51	0.61	0.56	0.56	0.56	0.54	0.52	0.52	0.52
	R^2	0.98	0.996	0.999	0.89	0.998	0.998	0.983	0.975	0.978	0.978	0.968	0.974
Langmuir isotherms	$Q_m^{(2)}$	32.8	35.7	48.3	45.7	62.5	48.8	50.3	65.8	49.3	48.5	47.9	45.1
	$K_L^{(3)}$	7.6×10^{-3}	9.1×10^{-3}	9.7×10^{-3}	7.8×10^{-3}	7.8×10^{-3}	8.8×10^{-3}	7.7×10^{-3}	5.9×10^{-3}	7.4×10^{-3}	7.2×10^{-3}	7.2×10^{-3}	7.4×10^{-3}
	R^2	0.997	0.999	0.998	0.997	0.996	0.984	0.994	0.990	0.953	0.993	0.988	0.992
Isotherms of Cd(II)													
Freundlich isotherms	$1/n$	0.78	0.83	0.82	0.8	0.8	0.88	0.8	0.78	0.78	0.79	0.79	0.78
	$K_F^{(1)}$	0.3	0.3	0.45	0.43	0.46	0.49	0.44	0.44	0.45	0.44	0.44	0.42
	R^2	0.984	0.983	0.992	0.983	0.981	0.984	0.98	0.973	0.968	0.971	0.97	0.978
Langmuir isotherms	$Q_m^{(2)}$	21.8	37.5	39.7	35.7	38.8	95.2	36.1	33.4	36.6	35.2	36.4	30.5
	$K_L^{(3)}$	8.3×10^{-3}	5.5×10^{-3}	7.9×10^{-3}	7.8×10^{-3}	7.5×10^{-3}	3.9×10^{-3}	7.9×10^{-3}	8.0×10^{-3}	7.5×10^{-3}	7.8×10^{-3}	7.5×10^{-3}	8.4×10^{-3}
	R^2	0.998	0.997	0.994	0.996	0.998	0.994	0.995	0.994	0.991	0.993	0.990	0.995
Isotherms of water vapour													
Dubinin and Sierpiński equation	C	0.906	0.535	0.956	0.814	0.985	0.603	0.556	0.541	0.596	0.570	0.672	0.705
	$a_0^{(4)}$	49.5	116.3	22.8	71.4	20.6	131.6	111.1	108.7	98.0	103.4	82.6	74.6
	R^2	0.999	0.993	0.998	0.996	0.985	0.979	0.989	0.998	0.998	0.965	0.999	0.975

Notes: $K_F^{(1)}$—mmol/kg, $Q_m^{(2)}$—mmol/kg, $K_L^{(3)}$—m^3/mmol, $a_0^{(4)}$—mg/g, R^2—correlation coefficient.

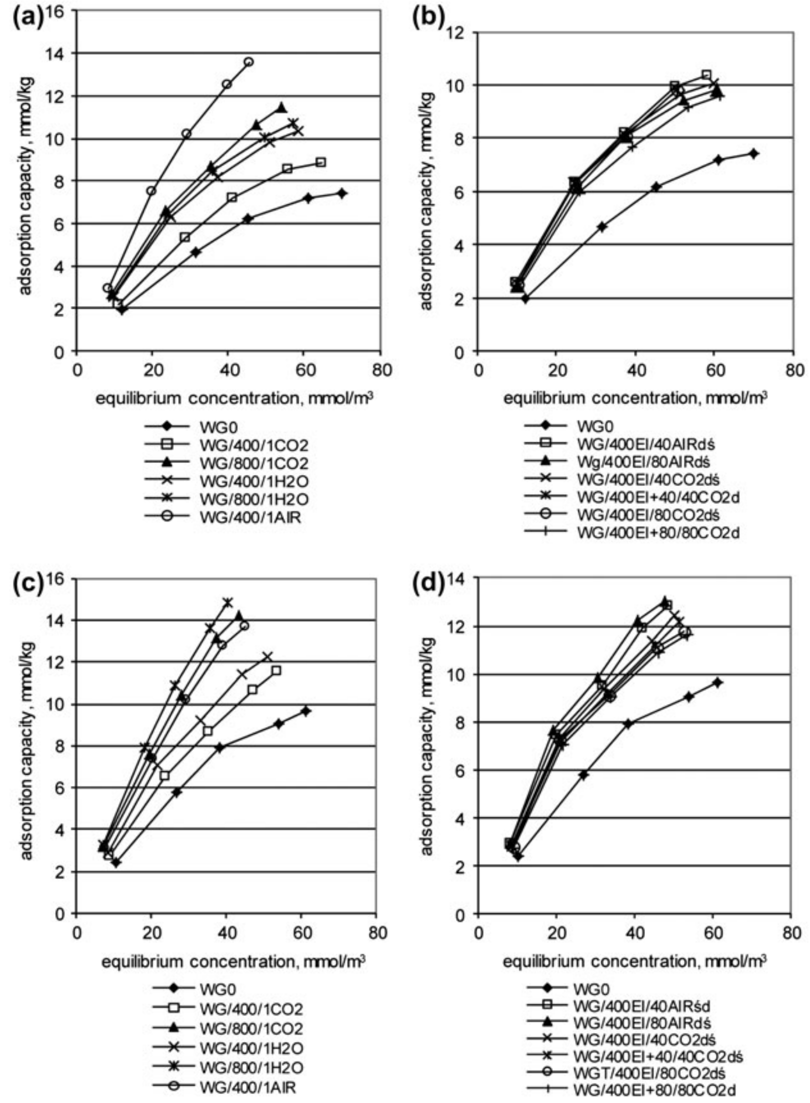

Fig. 2. Isotherms of Cd(II) and Ni(II) in modified activated carbons from WG0 group (a) isotherms of Cd(II) in carbons modified in a rotary furnace, (b) isotherms of Cd(II) in carbons modified in the SEOW, (c) isotherms of Ni(II) in carbons modified in a rotary furnace and (d) isotherms of Ni(II) in carbons modified in the SEOW.

the results obtained for the evaluation of oxygen groups by means of Boehm method.

Much more serious problems arise during the analysis of chemical character of the surface of activated carbons. A variety of physical, chemical and physical methods are used in order to identify and determine surface groups quantitatively. These include desorption of functional groups, alkaline neutralization, potentiometric titration, spectroscopy, adsorption of polar pairs, etc. None of them describes entirely and reliably the chemical properties of the surface and therefore researchers usually use only a few of them [22,23]. There are a lot of difficulties in interpretation of the results obtained when using these methods with respect to adsorption of heavy metals ions. Therefore, some researchers restrict their efforts to practical assessment of adsorption capacity with respect to metal/metals and evaluation of chemical character of the surface by means of other methods [24–26]. In the present study, the evaluation of the chemical character of the surface was based on neutralization of functional groups with bases and adsorption of water vapour.

Another parameter that indirectly determined the chemical character of the surface in activated carbons is adsorption of water vapour. Adsorption isotherms for water vapour at lower concentrations can be represented by the isotherm proposed by Dubinin and Sierpiński (Table 2). The pattern of adsorption isotherms of water vapour on activated carbons differs from those observed for the initial carbons, particularly at lower values of p/p_0. Thus, it can be expected that the chemical character of the carbon surface was changed. Higher adsorption of water vapour on the oxidized carbons points to higher effect of water molecules on carbon surface and, consequently, higher concentration of acidic oxygen groups. The highest values of adsorption were obtained for the concentration of $p/p_0 < 0.5$ (which determines chemical character of the surface) on the carbon oxidized in a rotary furnace at the temperatures of 400˚C in the air. Slightly lower values of adsorption capacity (but higher than those for initial WG0) were obtained for the carbons modified at the same temperature, both in a rotary furnace and in the SEOW stand. The carbons modified at the temperature of 800˚C were characterized by reduced adsorption capacity compared to the initial carbon for the relative pressures used in the study.

Ion adsorption of Ni(II) and Cd(II) was also examined in selected modified active carbons. Adsorption isotherms are presented in Fig. 2, whereas Langmuir and Freundlich isotherm constants are presented in Table 2. It was demonstrated that the better sorption among the heavy metals studied occurs for Ni(II), and the poorer one was found for Cd(II). The modified carbons sorbed more effectively the heavy metal ions compared to the initial WG0. For initial WG0 for Ni (II) cations, adsorption capacity values reached 10 mmol/kg, whereas for Cd(II) ions these values were over 7 mmol/kg. Ions of both Ni(II) and Cd(II) were sorbed much better in most of the cases on the oxidized active carbons. The highest values of adsorption for Ni(II) were obtained for carbons WG/800/1CO_2, WG/400/1AIR and WG/800/1H_2O (adsorption ranged from 13.7 to 14.8 mmol/kg). Adsorption on carbons modified in the SEOW was more efficient for the carbons modified in the air compared to carbon dioxide, but these differences were not high (maximum adsorption for these carbons ranged from 11.6 to 13.1 mmol/kg). The carbons modified in the SEOW adsorbed more Ni(II) ions compared to those modified in a rotary furnace at the analogous temperature (400˚C) in water vapour and carbon dioxide.

Cd(II) ions were adsorbed more efficiently on carbon WG/400/1AIR where maximum adsorption capacity was obtained. Adsorption with respect to Cd(II) ions for this carbon under the conditions of the experiment reached almost 14 mmol/kg whereas for the carbons modified at the temperature 800˚C, ca. 11 mmol/kg. For the carbons modified in the SEOW stand, the obtained adsorption capacities ranged from 9.5 to 10.5 mmol/kg (for WG0 for 7.4 mmol/kg).

4. Conclusions

Modification of activated carbon WG0 both in a rotary furnace and the SEOW made it possible to obtain sorbents with increased adsorption abilities compared to individual cations. The highest efficiency of removal of the ions of these metals was observed on the carbons modified in a conventional manner at the temperature of 800˚C and on the carbons oxidized with the air at the temperature of 400˚C (Ni(II) to 64.4% on WG/800/1H_2O and Cd(II) to 58,7% on WG/400/1AIR). The carbons modified in the SEOW stand adsorbed more Ni (II) and Cd(II) compared to the initial WG0 and modified in a rotary furnace at the temperature of 400˚C in the atmosphere of water vapour and carbon dioxide (e.g. Ni(II) 60.4% on WG/400EI/80AIRdś and Cd(II) 51.0% on WG/400EI/40AIRdś). Adsorption of Ni(II) on carbons modified in a rotary furnace and the SEOW differed by 4% whereas adsorption of Cd(II) exhibited the difference of 7.7%.

Modification of active carbon in a rotary furnace and the SEOW stand allows one to achieve similar results for adsorption of the investigated ions. The benefit of oxidation in the SEOW stand is an insignificant decrease in mass (e.g. compared to carbons oxidized at the temperature of 800 or 400˚C in air atmosphere) and very low electricity consumption that typically determines the cost-effectiveness of the process of oxidation in a gaseous phase. The lack of noticeable changes in the size of the specific surface area and pore structure of carbons as a result of modification also represents a benefit of the presented author's method since besides the ions of e.g. a heavy metal, some non-dissociated organic compounds are present in the solutions.

Adsorption of heavy metals is connected with chemical character of the carbon surface and pore structure. Unequivocal evaluation of both pore structure and chemical composition of the surface is still impossible taking into account the current state of technology. The situation seems much complex if one considers the system of adsorbent/adsorbed ion of a heavy metal which is characterized by specific properties, e.g. during the change in solution pH.

The study presented the use of electrical carbon heating based on Joule heating in new areas of application. One advantage of carbon heating in the SEOW is that the process requires much less energy compared with the conventional method (from several to several 10 times).

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