

Removal of mercury from contaminated water by activated carbon produced from waste coal and biomass materials

I. G. Stoycheva^{1*}, B.N. Petrova¹, B.G. Tsyntsarski¹, T.K. Budinova¹, N.V. Petrov¹, B. Nagel², U. Szeluga², S. Pusz², S. Chajkowska², B. Trzebicka²

¹Lab. Chemistry of Solid Fuels, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad.G.Bonchev Str., Block 9, 1113 Sofia Bulgaria

²Center of Polymer and Carbon Materials, Polish Academy of Sciences, M. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland

Received December 12, 2014; Revised February 26, 2016

Adsorption of mercury ions on activated carbons - oxidized and non-oxidized - prepared by hydro-carbonization from mixture of coal tar pitch and furfural, was investigated. The structure and surface properties of the samples were characterized by N₂ adsorption, IR spectroscopy and surface oxygen groups determination. The activated carbon, obtained from a mixture of furfural and coal tar pitch, and oxidized carbon demonstrate high adsorption ability towards mercury ions (149 and 136 mg/g, respectively). The relative part of the surface occupied by mercury ions is higher for the oxidized carbon. It was found that Hg (II) uptake increases with increasing pH.

Key words: activated carbon, coal tar pitch, furfural, mercury, adsorption

INTRODUCTION

The rapid urbanization and the extensive development of agriculture and tourism during the last decades have intensified the use of underground and surface waters. So there appears the issue of water contamination. The strive for alignment to standard legislation norms requires development of efficient methods for purification of waste and potable waters. Water pollution is a big problem for the modern world and it inflicted a lot of investigations, dedicated to protection of environment and living organisms. Metals such as Hg, Cd, Ni, As, Pb, etc. are highly toxic and carcinogenic, they have irreversible harmful, even lethal effect on human physiology and other biological systems. In order to ensure consistent protection of surface waters, the European Parliament and the Council of the European Union have announced Directives on the Environmental Quality Standards in the field of water policy. The European Environmental Agency (EEA) has included different heavy metal ions in the List of Priority Pollutants to be monitored in industrial effluents [1].

Mercury is generally considered to be one of the most toxic metals found in the environment. The major sources of mercury pollution in the aquatic environment are industries such as chloralkali, pulp

paper, paint industry, rubber processing, oil refining, electrical power and fertilizer productions [2,3]. Numerous methods are available for removal of mercury, including membrane separation [4,5], chemical precipitation [6,7], coagulation [8], photodegradation [9], reverse osmosis [10], biodegradation [11-13]. These methods are associated, however, with high operational costs and incomplete removal, and they require large amounts of energy and chemicals.

Adsorption is a suitable purification process, but the high price of commercial activated carbon decreases the economical efficiency of pollutant removal. Therefore it is very important to find new effective adsorbents. Nowadays the researchers are focused on the preparation of low-cost activated carbons from different waste materials for the treatment of drinking and waste waters. Activated carbons can be produced from a large variety of precursors - bituminous coal, wood, peat, petroleum pitch, polymer and biomass [14-16]. Preparation of activated carbons from waste materials and industrial by-products, like coal tar pitch and furfural (contained in waste products from treatment of biomass), reveals a possibility for their appropriate utilization.

This work presents the results from the investigation of the adsorption activity of activated carbon, obtained from coal by-product (coal tar pitch) and furfural (waste material from pyrolysis of biomass), towards Hg (II) ions.

* To whom all correspondence should be sent:
E-mail: racheva89@abv.bg

EXPERIMENTAL

A mixture of coal tar pitch and furfural (45:55 wt.%) was treated with concentrated H₂SO₄ added dropwise under continuous stirring at 120 °C until solidification. The obtained solid product was heated at 600 °C in a covered silica crucible at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. The carbonized solid product was further submitted to steam activation at 800°C for 1 h (carbon A).

The synthesized material was oxidized in order to incorporate more oxygen functionalities. For this purpose, carbon A sample was oxidized with HNO₃. The oxidation treatment with HNO₃ was performed according to the following procedure: about 10 g of the sample was treated with 100 cm³ 10% HNO₃ and boiled for 1 h. After that the sample was washed with distilled water, dried at 105°C and kept in a desiccator until use. The oxidized carbon was labeled as carbon B.

The nanotexture of the synthesized carbon materials was characterized by N₂ adsorption at -196°C, carried out in an automatic volumetric apparatus (ASAP 2010 from Micromeritics). Before the experiments, the samples were outgassed under vacuum at 300°C for overnight. The isotherms were used to calculate specific surface area S_{BET}, total pore volume V_T, micropore volume W_o. The samples were further characterized by elemental analysis and Boehm titration to determine the amount of oxygen, incorporated after oxidation treatment, and the nature of the appeared surface functionalities. FTIR experiments were performed on a spectrometer IFS 113V using KBr pellets.

The pH of the carbons was measured according to the following procedure: 4.0 g of carbon was weighed into a 250 cm³ beaker, and 100 cm³ of

water was added. The beaker was covered with a watch glass, and the mixture was boiled for 5 min. The suspension was set aside, and the supernatant liquid was poured off at 60 °C. The decanted portion was cooled down to ambient temperature and pH was measured to the nearest 0.1 pH unit.

Batch adsorption studies were carried out with 10 mg of adsorbent and 50 cm³ of Hg (II) solution with the desired concentration at pH 5.5 in 100 cm³ conical flasks. The amount of Hg (II) in the final volume of 25 cm³ was determined spectrophotometrically on a Pfar0 300 UV-Vis spectrometer. Rhodamine 6G and potassium iodide were used to obtain a pink-colored solution in the presence of Hg (II). The reaction occurs immediately in the pH range 1-7, when the system is stabilized with gelatin. The absorbance at 575 nm remains unchanged for at least 24 h. The pH values are adjusted with dilute solutions of hydrochloric acid.

RESULTS AND DISCUSSION

Characterization of carbon adsorbents from coal tar pitch and furfural

Furfural resin is a suitable oxygen-containing raw material for the production of carbon adsorbents with insignificant ash and sulphur content. There are many sources of furfural, because most agricultural wastes contain sufficient quantities of pentosans allowing industrial exploration by a well-established technique. The elemental analysis of coal tar pitch shows that the amount of oxygen containing structures is not high, whereas the high C/H ratio indicates the presence of a considerable amount of aromatic species in the pitch (Table 1).

Table 1. Chemical composition of the samples (wt.%).

	Ash	C	H	N	S	O	C/H
Coal tar pitch	-	90.90	4.95	0.90	0.50	2.75	1.53
Carbon A	0.8	90.81	0.82	0.75	0.51	7.11	9.23
Carbon B	1.5	86.77	1.02	1.30	0.56	10.35	7.09

Table 2. Quantification and identification of the oxygen surface groups [meq g⁻¹].

	Carboxylic	Lactonic	Phenolic	Carbonyl	Basic groups	pH
Carbon A	BDL	BDL	0.210	1.356	0.78	8.1
Carbon B	0.109	0.239	0.456	1.767	0.330	3.7

BDL – below detection limits

The content of surface oxygen-containing functional groups in carbon has a significant effect on metal ion adsorption on carbon. The results from Boehm titration of surface groups (Table 2) show that carbon A and carbon B are characterized with the presence of different oxygen-containing surface functionalities. The presence of surface oxygen groups is also confirmed by IR spectroscopy (Fig. 1). The band at 1704 cm⁻¹ could be related to the stretching of C=O in aliphatic aldehydes, ketones and carboxyls. The bands around 1600 cm⁻¹ cannot be unequivocally interpreted. They could be due to: i) aromatic ring stretching couples to highly conjugated carbonyl groups (C=O); ii) stretch vibrations of C=C bonds in aromatic structures; iii) OH groups. The bands in the region of 1360-1150 cm⁻¹ are due to C=O in complex ethers and ring structures. [17-19].

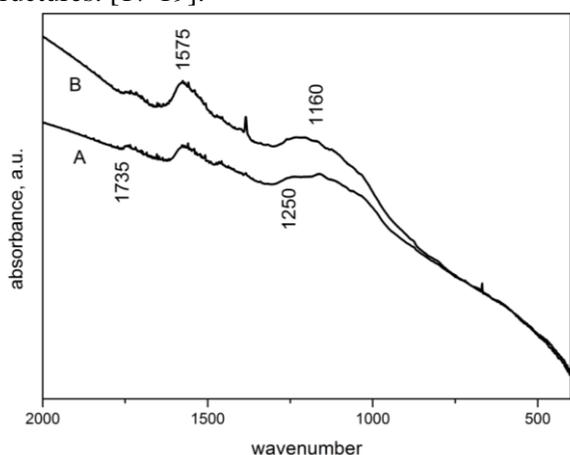


Fig. 1. IR spectra of the samples (A – Carbon A; B – Carbon B).

We have observed that the furfural content has a strong effect on the porosity of the resulting carbons. Lower proportions of furfural leads to synthesis of activated carbons with a narrow microporosity. With rising the furfural content this microporosity is gradually opened in favor of appearance of large micropores and mesopores. Carbon A was prepared with a moderate proportion of furfural in the precursor mixture (45 wt.%), and as a result it is characterized by a moderate BET surface area and well developed microporosity (Table 3 and Figure 2).

Table 3. Surface characteristics of the samples.

Sample	S _{BET} m ² /g	V _{tot} * cm ³ /g	V _{micro} ** cm ³ /g	V _{meso} ** cm ³ /g
Carbon A	678	0.316	0.216	0.030
Carbon B	487	0.217	0.113	0.010

* evaluated at p/p₀~0.99

** evaluated from DFT applied to N₂ adsorption data

The nitrogen adsorption/desorption isotherms of the carbon samples are shown in Fig.2. It can be seen that the adsorption isotherms are of type I, indicating a microporous material. These porous features should be ideally adapted for the removal of aromatics from aqueous phase. Oxidation brought about a slight decrease in the porous features of the carbon (likely due to the boiling step during oxidation), although the fall in the micropore volume accounts for only 16 %.

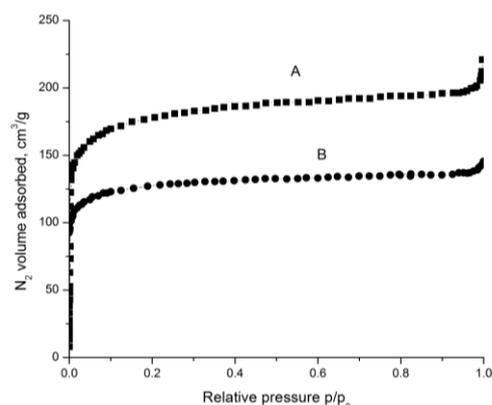


Fig. 2. N₂ adsorption isotherms at -196 °C of the samples (A-Carbon A; B-Carbon B).

Adsorption measurements

The equilibrium adsorption isotherms of Hg (II) on activated carbons are presented on Fig. 3. The adsorption isotherms belong to the L(2)-type according to the Giles classification [20, 21] showing a steep initial rise and a concave curvature at low equilibrium concentrations, followed by a plateau, i.e. saturation limit. L-type isotherms reflect adsorption at higher contaminant concentrations, corresponding to the completion of a monolayer in the experimental range.

The adsorption capacity, Q₀, was calculated from the linearized Langmuir plot [22]:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (1),$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount of Hg (II) adsorbed at equilibrium (mg/g) and Q₀ and b are the characteristic Langmuir parameters related to the maximum adsorption capacity and intensity of adsorption, respectively. The model is frequently used for adsorption from dilute solutions. The value Q₀ gives the saturation limit for adsorption from solution and b can be considered as a measure of the adsorption energy [22]. The Q₀ values determined for synthetic (carbon A) and oxidized activated carbon (carbon B) are 149 and 136 mg/g, respectively (Table 4).

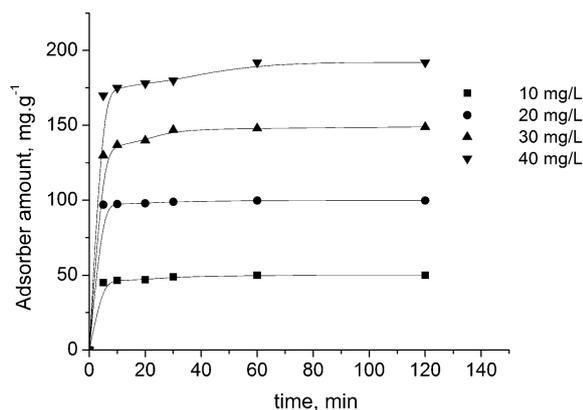


Fig. 3. Adsorption isotherms of Hg (II) ions on the different activated carbons. Conditions: C_0 10-40 mg/dm³; pH =5.5; τ 60 min; carbon amount, 10 mg/50 cm³.

Table 4. Data for mercury ion adsorption obtained from the Langmuir plot.

Sample	Q_0 mg/g	B L/mg	S_m^{2-} m ² /g	S_m^{2-}/S_{tot} %
Carbon A	149	1.17	20.64	3.04
Carbon B	136	1.39	20.64	4.24

Some theoretical parameters in the Langmuir equation were calculated from the experimental data and are presented in Table 4. The surface area S_m covered by Hg (II) ions was calculated on the basis of the Goldschmidt ionic radius, which is 0.112 nm [23]. Metal ions with amphoteric character are adsorbed to a considerably greater degree by activated carbons *via* alkaline reaction. The increased porosity and specific surface area after activation with water vapor leads to increased uptake of mercury ions. The water steam-activated carbon adsorbs Hg ions to a lower extent than the oxidized carbon, due to the fact that part of the surface of the former is inaccessible to mercury ions.

The investigation of the effect of pH on the adsorption activity of different carbons is very important. In the case of mercury (II) solutions, most of the mercury exists in the form of complexes, which can be positive, neutral or negative, depending on the composition and pH. Appropriate amounts of hydrochloric acid and sodium hydroxide were added in order to obtain solutions with different pH values. The adsorption capacities of the carbon were studied at different pH values and a maximum was established near pH 6.0 for all samples. The metal uptake increases in the range of pH values from 2 to 5.5, and stays constant above pH 6 for all carbons. The effect of the pH on mercury ion adsorption for the studied samples is illustrated in Fig. 4 (for initial concentration of 40 mg/dm³).

Bearing in mind that activated carbon A has

higher pore volume and total surface area than carbon B, it is evident that the removal efficiency is not directly related to these values. Most probably removal efficiency could be related to differences in the pore size distribution and the surface chemistry of the carbons.

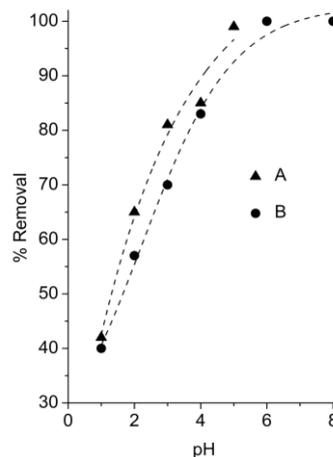
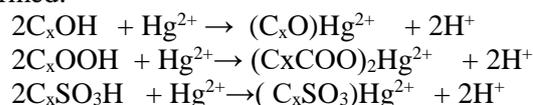


Fig. 4. Influence of pH on the adsorption equilibrium of mercury (II) ions on carbon A and carbon B. Conditions: τ , 60 min, carbon concentration, 10 mg/dm³.

It can be shown by stability constant calculations that, in the presence of Cl⁻, the predominant form at pH > 4.0 is Hg(OH)₂, and at pH < 4, the predominant form is HgCl₂ [24]. The dominant form in the range of highest sorption efficiency is Hg(OH)₂. When the pH drops, various chloride species, especially HgCl₂(aq), appear, however they are poorly adsorbed. It was assumed that, in addition to the different oxygen-containing groups, C_xSO₃H groups are present on the carbon surface as a result of effect of H₂SO₄ in the process of activated carbon preparation.

We suggest that following complexes could be formed:



CONCLUSIONS

Activated carbons with good adsorptive properties were synthesized from biomass and coal waste materials, and were applied for removal of mercury ions from aqueous solutions. The obtained activated carbons exhibited very good ability to adsorb mercury ions from aqueous solution, oxidized carbon (136 mg/g) having lower adsorption capacity than the non-oxidized sample (149 mg/g). The relative part of the surface occupied by mercury ions is greater for the oxidized activated carbon. Stable chemical bonds (chemisorption) are formed between Hg (II) ions and oxygen-containing groups present on the carbon surface.

REFERENCES

1. Directive 2008/105/EC Environmental quality standards for priority substances and certain other pollutants, 16 December 2008.
2. O. Rodriguez, I. Padilla, H. Tayibi, A. Lopez-Delgado, *Journal of Environmental Management*, **101**, 197 (2012).
3. F. Di Natale, A. Lancia, A. Molino, M. Di Natale, D. Karatza, D. Musmarra, *Journal of Hazardous Materials*, **132**, 220 (2006).
4. H. Bessbousse, T. Rhilalou, J.F. Verchere, L. Lebrun, *Chem. Eng. J.*, **164**, 37 (2010).
5. K. Chakrabarty, P. Saha, A.K. Ghoshal, *J.Membr. Sci.*, **346**, 37 (2010).
6. J. Esalah, M.M. Husein, *Sep. Sci. Technol.*, **43**, 3461 (2008).
7. A. Essa, L. Macaskie, N. Brown, *Biotechnol. Lett.* **27**, 1649 (2005).
8. C.P. Nansu-Njiki, S.R. Tchamango, P.C. Ngom, A. Darchen, E. Ngameni, *J. Hazard. Mater.*, **168**, 1430 (2009).
9. L.R. Skubal, N.K. Meshkov, *J. Photochem. Photobiol., A*, **148**, 211 (2002).
10. M. Mullett, L. Mohamed, Removal of mercury from solution using reverse osmosis filtration, in: Proc. 37th Chemeca 2009 - Engineering Our Future: Are We up to the Challenge, 27 - 30 September 2009, Burswood Entertainment Complex, Perth W.A., Barton, ACT: Engineers Australia, 2009, p. 2207.
11. H.R. Dash, S. Das, *International Biodeterioration and Biodegradation*, **75**, 207 (2012) 3
12. D. Jaysankar, N. Ramaiah and L. Vardanyan, Detoxification of toxic heavy metals by marine bacteria highly resistant to mercury, *Marine Biotechnology*, **10**, 471 (2008).
13. L. Svecova, M. Spanelova, M. Kubal, E. Guibal, Cadmium, lead and mercury biosorption on waste fungal biomass issued from fermentation industry. I. Equilibrium studies, *Separation and Purification Technology*, **52**, 142 (2006).
14. T.J. Bandosz, Activated carbon surface in environmental remediation, In: T.J.Bandosz (Editor) Interface Science and Technology Series, Elsevier, New York, 2006.
15. D. Savova, E. Apak, E. Ekinci, F. Yardim, N. Petrov, T. Budinova, M. Razvigorova, V. Minkova, Biomass conversion to carbon adsorbents and gas. *Biomass and Bioenergy* **21**, 133 (2001).
16. N. Petrov, T. Budinova, M. Razvigorova, J.B. Parra, P. Galiatsatou, Conversion of olive wastes to volatiles and carbon adsorbents. *Biomass Bioenergy*, **32**, 1303 (2008).
17. G. Socrates, Infrared and Raman Characteristic Group Frequencies – Tables and Charts, 3rd ed., John Wiley & Sons Ltd., England, 2001.
18. J. Zawadzki, B. Azambre, O. Heintz, A. Krzton, J. Weber, IR study of the adsorption and decomposition of methanol on carbon surfaces and carbon-supported catalysts, *Carbon*, **38**, 509 (2000).
19. J. Zawadzki, M. Wisniewski, J. Weber, O. Heintz, B. Azambre, IR study of adsorption and decomposition of propan-2-ol on carbon and carbon-supported catalysts, *Carbon*, **39**, 187 (2001).
20. F. Rouquerol, J. Rouquerol, K. Sing, In: Adsorption by powders and porous solids. Principles, methodology and applications, Academic Press: London, 1999.
21. C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of solutions adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.*, 3973 (1960).
22. I. Langmuir, The constitution and fundamental properties of solids and liquids, Part I Solids. *J. Am. Chem. Soc.*, **38**, 2221 (1916).
23. A.F. Holleman, E. Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, 1995.
24. W.R. Knocke, L.H. Hemphill, *Water Res.*, **15**, 275 (1981).

ПРЕЧИСТВАНЕ НА ОТПАДНИ ВОДИ ОТ ЖИВАК ПОСРЕДСТВОМ АКТИВЕН ВЪГЛЕН, ПОЛУЧЕН ОТ ОТПАДНИ СУРОВИНИ ОТ ВЪГЛИЩА И БИОМАСА

И. Г. Стойчева^{1*}, Б. Н. Петрова¹, Б. Г. Цинцарски¹, Т. К. Будинова¹, Н. В. Петров¹, Б. Нагел², У.
Шелуга², С. Пуш², С. Чайковска², Б. Тржебицка²

¹Лаб. Химия на твърдите горива, Институт по органична химия с Център по фитохимия, Българска Академия
на Науките, ул. Акад. Г. Бончев, бл.9,1113 София, България

²Център за полимерни и въглеродни материали към Полската Академия на Науките, ул. Мария Склодовска-
Кюри 34,41-819 Забже, Полша

Постъпила на 12 декември, 2014 г., коригирана на .26 февруари, 2016 г.

(Резюме)

Изследвана бе адсорбцията на живачни йони върху окислени и неокислени проби активен въглен, получени чрез хидро-пиролиз от смес от каменовъглен пек и фурфурол. Структурата и повърхностните свойства на пробите бяха характеризирани чрез азотна физисорбция, ИЧ спектроскопия и бе определена концентрацията на повърхностните кислородни групи. Активният въглен, получени от смес от каменовъглен пек и фурфурол, и окисленият въглен демонстрират висока адсорбционна способност спрямо живачните йони (съответно 149 и 136 мг/г). Частта от повърхността, заета от живачни йони е по-висока за окисления въглен, в сравнение с неокисления. Бе установено, че отстраняването на Hg (II) се увеличава с увеличаване на рН на разтвора.