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Removal of phenol from contaminated water by activated carbon, produced from waste coal material

B. G. Tsyntsarski [1], B. N. Petrova [1], T. K. Budinova [1], N. V. Petrov[1], D. K. Teodosiev[2]*

[1] Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia
[2] Space Research and Technology Institute, Bulgarian Academy of Sciences, Sofia

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The adsorption behavior towards phenol of different modifications of activation carbon, prepared from mixtures of coal tar pitch and furfural, was investigated. The structure and surface properties were characterized using N_2 adsorption, IR spectroscopy and surface oxygen groups. The activated carbon, obtained by pyrolysis in the presence of water vapor, has higher adsorption ability (150 mg g^{-1}) than the other investigated samples - the oxidized carbon sample (126 mg g^{-1}) and the carbon sample thermally treated (117 mg g^{-1}) up to 1300^{o}C. The adsorption capacity towards phenol of carbon after thermal treatment is similar to the oxidized carbon, in spite of reduced surface area and pore volume of the former. This is probably due to the formation of water molecular clusters. The effect of the micropore structure was discussed, which reveals that the adsorption towards phenol of activated carbon from mixture of furfural and coal tar pitch correlates with its surface area and micropore volume.

Keywords: activated carbon, coal tar-pitch, furfural, adsorption, phenol

1. INTRODUCTION

In the last years a lot of countries, especially these from Central and Eastern Europe (CER), continue their efforts to resolve water management problems in the very unique conditions of a transition from the centrally planned to market economies. These processes were accompanied with expansion of heavy industries often using coal as the main source of energy. The pollution effects were intensified by the underpricing and overuse of energy, water and other raw material inputs. Limited steps have been implemented to improve control and safety equipment as well as operating procedures but not much more. As a result, water pollution is one of the most important problems for CER countries, inherited from the past.

In order to ensure consistent protection of surface waters, the European Parliament and the Council of the European Union has announced a number of Directives on the Environmental Quality Standards in the field of water policy. The European Environmental Agency has included different aromatic pollutants in the List of Priority Pollutants to be monitored in industrial effluents (Directive 2008/105/EC Environmental quality standards for priority substances and certain other pollutants, 16 December 2008).

Both the environment and human beings are exposed to the hazards of different pollutants (organic, metal ions, etc.) from waste and potable water.

Chemical pollution of surface waters is a serious threat for the aquatic environment, with undesired effects, such as acute and chronic toxicity for aquatic organisms, accumulation in ecosystems and loss of habitats and biodiversity, as well as a threat to human health.

The aromatic organic compounds are frequently present as polluting agents in continental waters, especially phenolic substances, used in production of pesticides, insecticides, surfactants, etc. As a pure substance, phenol is used as a disinfectant, as appetizing agent, as an extracting solvent, for producing phenolic resins, etc. Phenols are also the main organic constituents present in condensate streams in coal gasification and liquefaction processes. Other sources of waste stream waters containing phenols are pharmaceutical, plastic, wood products and pulp and paper industries. Phenol-containing waste waters may not be launched into open water without treatment because of the toxicity of phenol [1]. Well known characteristics of the phenolic chemicals are their resistance towards biodegradation. Phenol compounds rated as No 11 in the list of 126 chemicals issued as priority pollutants by the Environmental Protection Agency of USA. There

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* To whom all correspondence should be sent:
E-mail: goriva@orgchm.bas.bg

are many methods such as chlorination [1], catalytic and photocatalytic oxidation [2,3], ozonation [4], nanofiltration [5], adsorption [6]. Thus, chlorination of phenol containing water leads to formation of chlorophenolic substances, which are well known as poisonous and carcinogenic; ozonation and catalytic oxidation are related with use of high doses of the active substance; phenol removal by adsorption is suitable purification process, but the high price of commercial activated carbon decrease the economical efficiency of removal of phenol by adsorption.

Therefore seeking novel effective adsorption materials is still of recent interest. In this sense in the last years a special emphasis on the preparation of activated carbons from different waste materials was made, because of the growing interest in low-cost activated carbons, especially for applications concerning treatment of drinking and waste waters. Activated carbons can be produced from a large variety of precursors. Usually used precursors include bituminous coal, wood, peat, petroleum pitch, polymer and biomass [7-12].

It is well known that coal tar pitches are excellent raw materials in the carbon manufacturing industry, because of their high carbon content, low price and ability to produce carbon with different structure and properties. Chemical composition and physical properties of pitches, which in turn influence their transformation to carbons, are of great importance for controlling the properties of the final product. On the other hand, recent interest in the substances of biomass origin has renewed the attention in furan compounds. Earlier studies have shown that furfural resin is a suitable oxygen-containing raw material for the production of carbon adsorbents with insignificant ash and sulphur content – it should be noted that such activated carbons are characterized with a large number of oxygen-containing groups on the surface. Indeed, carbon adsorbents with different structure and properties have been prepared from mixtures of furfural and biomass-derived tars, while optimizing the operating conditions (including the composition of the mixtures, activation reagents, pre-treatment of the precursors, etc.) [13]. There are many sources for the production of furfural because most agricultural wastes contain sufficient quantities of pentosans to justifiy industrial explotation by well-established and relatively simple techniques [14].

In this paper, the application for the phenol removal of new synthesized carbon adsorbents, obtained from coal by-product (coal tar pitch) and furfural (waste material from pyrolysis of biomass), was studied.

2. EXPERIMENTAL

2.1. Materials and methods

2.1.1. Synthesis procedure for preparation of activated carbon from coal tar pitch and furfural

A mixture of coal tar pitch and furfural (45:55 wt. %) was treated with concentrated H_2SO_4 (drops of H_2SO_4 were added under continuous stirring) at 120 ºC until solidification. The obtained solid product was heated at 600 ºC in a covered silica crucible with a heating rate of

10 ^{o}C min^{-1} under nitrogen atmosphere. The carbonized solid was further submitted to steam activation at 800 ^{o}C for 1 h (carbon A).

2.1.2. Oxidation treatment with HNO_3

The synthesized material was oxidized in order to incorporate of oxygen functionalities. For this purpose, the sample Carbon A was oxidized with HNO_3. The oxidation treatment with HNO_3 was performed according to the following procedure: about 10 g of the sample was treated with 100 mL 10% HNO_3 and boiled for 1 h. After that the sample was washed with distilled water and dried at 105^{o}C and kept in dessicator until use. The oxidized carbon was labeled as carbon B.

2.1.3. Thermal treatment

The activate carbon B was heated at 1300^{o}C at nitrogen atmosphere for 1 h in order to eliminate the oxygen containing groups. This carbon was labeled as carbon D.

2.2. Adsorbent characterization

2.2.1. Pore structure analysis

Nanotexture of the synthesized carbon materials was characterized by N_2 adsorption at -196ºC, carried out in an automatic volumetric apparatus (ASAP 2020 from Micromeritics). Before the experiments, the samples were outgassed under vacuum at 120°C for overnight. The isotherms were used to calculate specific surface area S_{BET}, total pore volume V_T, micropore volume W_o [15].

2.2.2. Chemical structure and composition

The samples were further characterized by elemental analysis and Boehm’s titration to determine the amount of oxygen incorporated after oxidation treatment and the nature of the formed surface functionalities [16]. Details of the experimental procedure for Boehm’s titration have been described elsewhere [17].

The carbon samples were analyzed using FTIR spectroscopy using Bruker IFS 113V. The samples were mixed with potassium bromide and the mixture was pressed into pellets to be used in the analysis.

2.2.3. pH determination

The pH of the carbons was measured according to the following procedure: 4.0 g of carbon was weighed into a 250 mL beaker, and 100 mL 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 ºC. The decanted portion was cooled down to ambient temperature and its pH was measured to the nearest 0.1 pH unit.

2.3. Adsorption measurements

Phenol substance was obtained from Merck (99% purity). The phenolic solutions were prepared in unbuffered distilled water in the concentration range of 100-250 mg L^{-1}. About 100 mg of activated carbons were mixed with 50 mL of phenolic solution of the desired concentration, and the suspensions were shaken for 2 h. The samples were filtered and the equilibrium concentrations of the phenolic compounds remaining in solution were determined spectrophotometrically (at wavelength 269 cm^{-1}) by Pfaro 300 UV spectrometer. Each determination is performed in triplicate.

3. RESULTS AND DISCUSSION

3.1. Characterization of carbon adsorbent from coal tar pitch and furfural.

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 considerable amount of aromatic species in the pitch (Table 1). After carbonization and activation of the mixture, a carbonaceous solid is obtained with a final yield of 58 wt%. Analysis of the chemical composition of carbon A shows that, along with the prevailing content of aromatic structures in the pitch, the resulting material has relatively large oxygen content. This confirms the fact that inserting oxygen in the carbon precursor (i.e. furfural) leads to the formation of oxygen containing structures on the surface of the final product.

Table 1. Chemical composition and pH value of the coal tar pitch and the synthesized activated carbons (wt.%)

Sample	Ash	Volatiles (daf)	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	1.9	90.81	0.82	0.75	0.51	7.11	9.23
Carbon B	1.5	7.7	86.77	1.02	1.30	0.56	10.35	7.09
Carbon D	0.1	-	98	0.6	0.6	0.4	0.4	13.61

3.2. Chemical character of the surface by Boehm's titration of surface groups

The surface functionalities were further characterized by the Boehm's titration (Table 2). Data shows that the surface chemistry of carbon A is comprised of carbonyl and phenolic functionalities, which render a basic character to the adsorbent. Despite the large amount of oxygen, the synthesized carbon also displays strong alkaline character, as inferred from the pH value.

Table 2. Data corresponding to Boehm's titration for the quantification and identification of the oxygen surface groups on the activated carbons [meq g-1].

Sample	Carboxylic	Lactonic	Phenolic	Carbonyl	Basic groups	pH
Carbon A	BDL	BDL	0.210	1.356	0.778	8.1
Carbon B	0.109	0.239	0.456	1.767	0.330	3.7
Carbon D	BDL	BDL*	BDL	BDL	0.440**	9.7

*BDL – below detection limits
**basic centers

After oxidation with nitric acid, as expected, there is a slight enhancement in the overall oxygen content, accompanied by a fall of the pH value, confirming the different nature of the surface functionalities, appearing upon oxidation. In contrast, even if the groups of the parent carbon are well preserved, oxidation with nitric acid leads to the formation of acidic groups (carboxyl and lactonic structures), which are responsible for the decrease in the pH of the carbon (ca. 4 pH units fall). Along with the incorporation of acidic surface groups, a twofold decrease in the content of basic groups was also observed after oxidation of carbon A. This could be attributed to the incorporation of the surface groups appearing at the edges of the basal planes in the graphene layers, thereby reducing the capacity of these sites to accept H^+ ions (acting as Lewis base). Thermally treated activated carbon (Carbon B) possess basic centers and basic character of the surface (pH 9.7).

3.3. Pore structure

In a previous work [14], we have observed that the furfural content has a strong effect on the porosity of the resulting carbons. Lower proportions of furfural give rise to activated carbons with a narrow microporosity, which with rising furfural content is gradually opened in favor of large micropores and mesopores. That's why 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 with an well developed microporosity (Table 3 and Figure 1).

The nitrogen adsorption/desorption isotherms of the carbon samples are shown in Fig.1. 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 %. Thermal treatment at 1300 °C leads to decrease in the surface area and micropore volume. Summarizing, we have prepared three carbon materials with various surface chemistry (oxygen-enriched materials) and different basicity, which are investigated towards adsorption of phenol and to investigate the influence of oxygen containing groups on the adsorption of phenol from water solution.

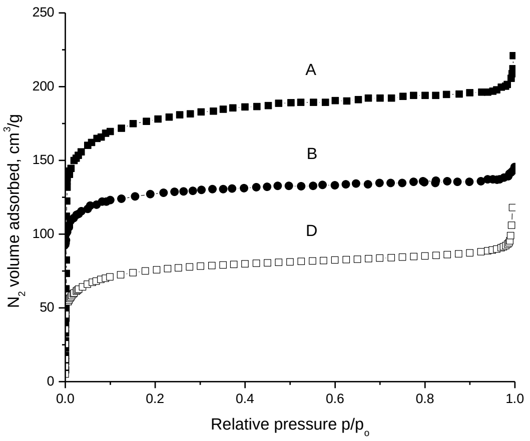

Fig. 1. N_2 adsorption isotherms at -196 °C of the studied carbons (A – Carbon A; B – Carbon B; Carbon D)

3.4. Adsorption isotherm of phenol

Fig. 2 shows the influence of the time of treatment on the adsorption capacity of the carbons. The initial adsorption rate is rapid and a plateau is reached after 15 min for carbon A and 20 min for Carbon B. Moreover, the amounts adsorbed with time show smooth continuous curves in both cases, with a well-defined saturation plateau. This behavior is attributed to the decrease in the number of available adsorption sites on the carbon surface as the adsorption proceeds and only part of the molecules of adsorbate retain. Comparatively, the uptake is slightly faster in the most hydrophobic sample (carbon A). The faster uptake on the hydrophobic carbon A, compared to carbon B, suggests that besides the enhanced water adsorption of the carbon after oxidation, kinetic restrictions for the accessibility of the aromatic compound to the adsorption sites arise, probably due to the fact that the water also competing for these sites

Table 3. Surface characteristics of the samples

Sample	S_{BET}	V_{tot}*	V_{micro}**	V_{meso}**
Carbon A	678	0.316	0.216	0.030
Carbon B	487	0.217	0.113	0.010
Carbon D	287	0.151	0.080	0.028

* evaluated at p/p_0~0.99

** evaluated from DFT applied to N_2 adsorption data

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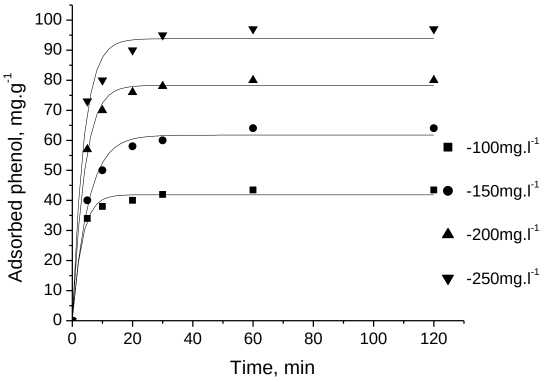

Fig. 2. Effect of contact time on adsorption of phenol on Carbon A.

Equilibrium studies on adsorption provide information about the capacity of the sorbent or the amount required to remove a unit of mass of pollutant. The most widely used isotherm equation for modeling the adsorption equilibrium is the Langmuir equation, which is valid for monolayer sorption on to a surface with a finite number of identical sites, and is given by the equation [18]:

$$Q_{eq} = Q_o\, bC_{eq}/(1+b\, C_{eq}) \qquad (1)$$

where C_{eq} is the equilibrium pollutant concentration remaining in solution after adsorption (mg L^{-1}), Q_{eq} is the amount of pollutant bound to the adsorbent (mg g^{-1}), Q_o is the maximal amount of the pollutant per unit weight of adsorbent (mg g^{-1}), and b is a constant related to the affinity of binding sites (L mg^{-1}).

The adsorption capacity of phenol on activated carbon A is higher than its oxidized form (Carbon B) and than the thermally treated sample (Carbon D). Moreover, the Langmuir linear fitting of experimental data is very good (Fig. 3). The parameters of fitting the experimental adsorption equilibrium data are given in Table 4. The data calculated from the Langmuir equation reveal a pronounced increase of the maximal adsorption capacity (Q_o) for the activated carbon A.

Thermally treated activated carbon (Carbon D) has adsorption properties similar to this of oxidized activated carbon (Carbon B), nevertheless that the micropore volume and specific surface area porosity of the first sample are lower (Table 4). This indicates that the oxygen-containing groups of Carbon B hinder the phenol adsorption.

Figure 4 shows the equilibrium adsorption isotherms of phenol on all three activated carbons. They belong to type L of Giles classification, indicating that adsorption proceeds by the formation of a monolayer in the range of concentrations used [19].

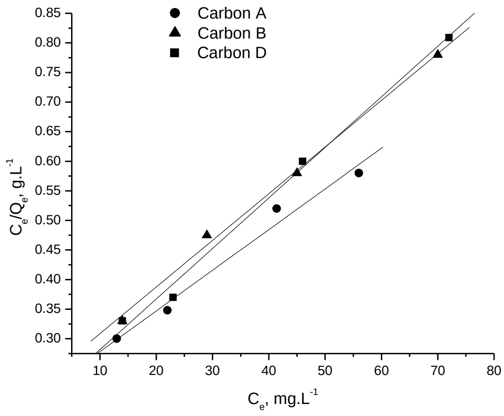

Fig. 3. Langmuir plot for adsorption of phenol. Conditions: Phenol concentration, 100-250 mg. L-1, time of treatment 1 h, carbon concentration, 100mg/50 mL.

Table 4. Results obtained from Langmuir equation applied to the adsorption isotherms of phenol compound on the studied activated carbons.

Sample	Q_o, mg g^{-1}	b, g L^{-1}	R^2
Carbon A	150	0.00670	0.99074
Carbon B	126	0.03436	0.99813
Carbon D	117	0.00855	0.99717

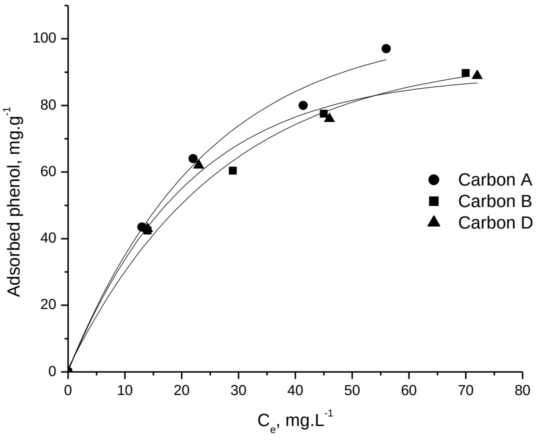

Fig. 4. Equilibrium adsorption isotherms of phenol studied activated carbons, expressed in terms of the amount adsorbed per gram of adsorbent [mg. g-1] and per equilibrium concentrations [mg. L-1]

3.5. Effect of pore structure

Carbon A (with higher BET surface area and micropore volume) shows higher adsorption ability in comparison with carbon B and carbon D. Obviously in this case the maximal phenol adsorption capacity (Q_o) of the activated carbons increases with the surface area and micropore volume.The adsorption capacity depends generally on the accessibility of the organic molecules to inner surface of carbon adsorbent. It is well known that, to some extent, the adsorption of phenol is mainly due to micropore filling especially in the case of microporous carbons. In phenol solutions, water molecules are preferentially adsorbed by the oxygen groups and then the remainder of the surface and/or micropore volume is available to the phenol molecules – this was proven by our investigations on the adsorption of phenol on thermally treated activated carbon (carbon D), which have similar adsorption ability with the oxidized activated carbon (carbon B). The maximal adsorption capacity towards phenol of activated carbon from mixture of furfural and coal tar pitch correlates with its surface area and micropore volume.

3.6. Effect of surface chemistry

Chemical nature of the surface of the activated carbon is the most important factor - apart from the porous structure - that determines its adsorption properties. Table 2 shows the distributions of different oxygen groups on the carbon surface. Carbon B possesses acidic oxygen groups and twice lower content of basic groups, compared to the initial activated carbon A. The data for Boehm titratation were confirmed by the results for IR spectra (Fig. 5), which show, that the bands at 1730 cm^{-1} and 1570 cm^{-1}, assigned according to [20-22] oxygen containing groups - mainly carbonyl and carboxylic - increase in intensity after oxidation, and decrease significantly after thermal treatment.

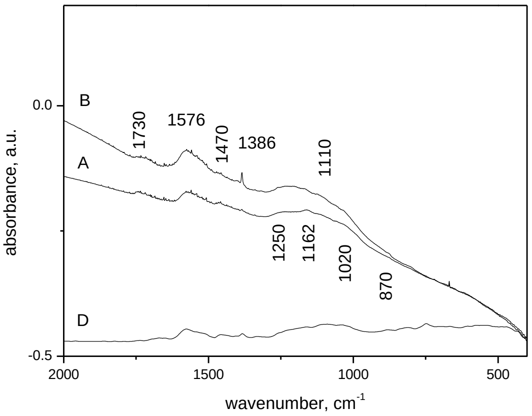

Fig.5. IR spectra of the samples

Predominant impact of oxidation and reduction of activated carbon surface on phenol adsorption was pointed out by some authors. An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemical modified activated carbons was discussed in [23-25].

According to their results, the carboxyl and hydroxyl groups inhibit the adsorption of phenol and increase the affinity of carbon towards adsorption of water molecules, and therefore, the solvent molecules could effectively block some micropores. This effect is explained by phenol adsorption that is governed by π-π dispersion interaction between the basal plane of carbon and the aromatic ring of the adsorbate. Oxygen atoms bound to the graphite edges can localize electrons and, thereby, remove them from π-electron system of the basal plane - consequently, the π-π interaction is weakened. Contrary to these effects of surface carboxyl and hydroxyl groups, the surface of quinone (or carbonyl) groups promote the adsorption of phenols, involving formation of an electron donor-acceptor complex of aromatic ring of adsorbate with the surface carbonyl groups, as proposed by [26, 27]. The data in Table 2 show that the formation of carboxylic groups and the increase of the content of hydroxyl groups leads to the decrease of the adsorption activity of Carbon B towards phenol. However the higher uptake of phenol on activated carbon A (150 mg g^{-1}) is to be expected in the view of the above mentioned. Thus adsorption of phenol on activated carbon is enhanced on hydrophobic carbon A, in comparison with its oxidation modification carbon B (126 mg g^{-1}).

It has been noted that during thermal treatment (after which it is converted to Carbon D) of.Carbon A losses approximately half of its specific surface area . Carbon D shows adsorption ability towards phenol very close to carbon B - this is indication that when a porous carbon comes into contact , water will first adsorb on the hydrophilic polar oxygen groups, including those located at the micropore entrances, because water molecules can form H-bonding with surface oxygen molecules and water molecules are more competitive than phenol towards adsorptive sites.

The adsorbed water molecules will be further associated with each other to form water clusters, which remarkably stabilized in micropores, causing partial blockage of the micropores, reducing the accessible surface area, and impeding or even preventing phenol adsorption. As demonstrated by the data shown in Table 2 thermal treatment can substantially remove oxygen-containing groups, thus lessening the possibility of the formation of water clusters, and enhancing the accessibility of the pores for phenol molecules, as well as improving interaction. That's why activated Carbon D shows adsorption ability close to Carbon B, independently that Carbon B posses more developed texture and higher micropore volume.

3.7. Effect of pH

In this study the influence of pH on phenol adsorption was investigated and interpreted. It was established that the amount adsorbed decreases at high pH values as well as at low pH values. The pKa value for phenol is 9.89, so the adsorbed species above this pH are mostly anionic. The The repulsion interactions between the surface layer and the anionic phenolates leads to reduced adsorption. The low pH value was obtained by using an acidic solution. Obviously additional protons were introduced in the solution in this way, and these protons are competing for the carbonyl sites, and thus 'blocking' them - therefore the adsorption was reduced at low pH. The influence of the pH on the adsorption of phenol on both activated carbons can be seen in Fig. 6.

At acidic pH the amount of phenol adsorbed, Q_o, remains constant or increases slightly with increasing pH, and at a certain value of pH, the value of Q_o begins to decrease, which continues while pH increases. The decrease in phenol adsorption from pH = 6.3 to pH = 3.07 is due to the increased H^+ adsorption on carbonyl sites, which suppresses phenol adsorption on these sites.

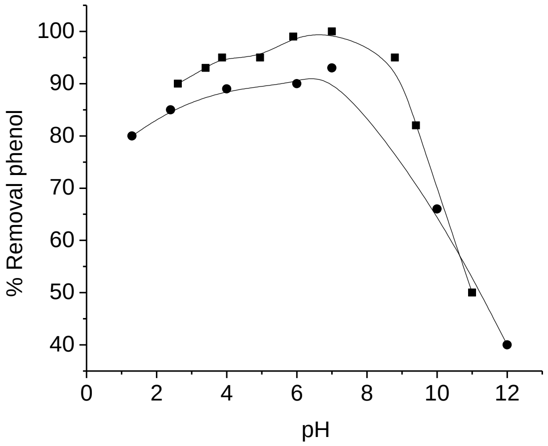

Fig. 6. Effect of pH on the retention of phenol (■ - Carbon A; ● -Carbon B).

On the other hand, the decrease in the phenol amount adsorbed from more alkaline solution is attributed to the greater solubility of dissociated phenol at pH> pKa as well as to the increased repulsion forces between the dissociated form of the adsorbate and the carbon surface.

CONCLUSIONS

The results reported in this work show that mixtures of coal waste (coal tar pitch) and furfural (material contained in biomass wastes) is appropriate raw materials for the synthesis of nanoporous carbons with negligible ash content and well-developed porosity. The synthetic activated carbon shows higher adsorption activity towards phenol, comparable and higher in comparison with other activated carbons reported in the literature.

The adsorption capacity of the activated carbon and its oxidized modification towards phenol depends on the porous parameters and surface chemistry, the latter governing the retention mechanism – this is confirmed by the investigation of phenol adsorption of thermally treated activated carbon. Thermally treated sample, independently of its lower surface area and micropore volume, has adsorption capacity similar to the oxidized sample. Non-specific interactions are dominant for phenol adsorption on carbon A, whereas for the oxidized adsorbent electrostatic interactions (repulsive and/or attractive) may appear during adsorption process, depending on the pH of the solution.

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ИЗВЛИЧАНЕ НА ФЕНОЛ ОТ ЗАМЪРСЕНИ ВОДИ ЧРЕЗ АКТИВЕН ВЪГЛЕН, ПОЛУЧЕН ОТ ОТПАДНИ ПРОДУКТИ ОТ ПРЕРАБОТКАТА ВЪГЛИЩА

Б. Г. Цинцарски [1], Б. Н. Петрова [1], Т. К. Будинова [1]*, Н. В. Петров [1], Д. К. Теодосиев[2]

[1] Институт по органична химия, Българска академия на науките, ул. „Акад. Г. Бончев”, бл. 9, София 1113
[2] Институт по космически изследвания и технологии, Българска академия на науките, ул. „Акад. Г. Бончев”, бл. 1, София 1113

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(Резюме)

Беше изследвана адсорбцията на фенол върху различни модификации от активен въглен, получен от смес от каменовъглен пек и фурфурол. Текстурата, порьозната структура и химическият характер на повърхността бяха изследвани посредством адсорбция на азот, ИЧ спектроскопия и кислородни функционални групи. Активният въглен, получен чрез пиролиз в присъствие на водна пара, има по-висока адсорбционна способност (150 mg g^{-1}) спрямо другите изследвани активни въглени – окислен въглен (126 mg g^{-1}) и въглен, термически обработен (117 mg g^{-1}) до 1300 °C. Адсорбционният капацитет спрямо фенол на термически обработения активния въглен е много близък до капацитета на окисления въглен, независимо от по-ниската стойност на специфична повърност и обема на порите. Това вероятно се дължи на образуването на водни асоциати. Резултатите показват, че адсорбцията на фенол върху активен въглен, получен от смес нафурфурол и каменовъглен пек, корелира със специфичната повърхност и обема на порите.