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Characterization and application of activated carbon from biomass and coal wastes for naphthalene removal

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Activated carbons were prepared from different waste materials (coal tar pitch and apricot stones) by pyrolysis in the presence of water vapor. The adsorption of naphthalene from aqueous solution at 298 K on the obtained activated carbons was studied. It was established that the adsorption capacity of the activated carbons depends on theси surface area and porosity. It was found that naphthalene adsorption follows Langmuir isotherms. The adsorption capacity of activated carbon obtained from coal tar pitch/furfural was 18.75 mg/g and for activated carbon from apricot stones - 29.95 mg/g.

Keywords: coal tar pitch, furfural, apricot stones, adsorption, naphthalene.

1. INTRODUCTION

Solving the problems of pollution of ground water, which is the principal source of drinking water in most countries of the region, is an action of special importance that has already been globally discussed. Increasing the number of the existing water treatment facilities and construction of new facilities will be needed to improve drinking water quality because of human health concern. Industry generates a variety of pollutants which have negative impact on ecosystems and humans (toxicity, carcinogenic and mutagenic properties) [1, 2].

In order to ensure consistent protection of surface waters, the European Parliament and the Council of the European Union issued Directives on the environmental quality standards in the field of water policy. The European Environmental Agency (EEA) has included PAH compounds in the list of priority pollutants to be monitored in industrial effluents - Directive 60/EC and Directive 2008/105/EC [3,4].

Adsorption is a powerful technique for treating domestic and industrial pollutants. Activated porous carbons constitute one of the most important types of industrial carbons. The term activated carbon defines a group of carbon adsorbents with highly developed internal surface area and porosity. Activated carbons are extremely versatile adsorbents of industrial significance and they are used in a wide range of applications, principally related to the removal of undesired species, in order to effect purification or recovery of chemical constituents. Industrial waste is a potential low-cost source for preparation of activated carbons. Generally, industrial wastes are generated as a by-product of various industrial and agricultural production. Since these materials are locally available in large quantities, they are inexpensive. Such wastes are different agricultural by-products, wastes from coal conversion, different polymer wastes, etc. [5-12].

In our days the scientists worldwide are focused on searching of novel effective methods and new carbon materials for water purification from different toxic organic compounds. In this sense, a combination of various waste materials for production of activated carbons, for example wastes from coals and biomass materials, is suitable, and adsorption seems to be an attractive approach.

In this study naphthalene was adopted as a representative model compound of polycyclic aromatic hydrocarbons. Their static adsorption from aqueous solution on two types of adsorbents synthesized from different waste materials - coal and biomass (mixture of coal tar pitch/furfural and apricot stones) - was investigated.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Preparation of activated carbon from coal tar pitch and furfural. A mixture of coal tar pitch and furfural (50:50 wt. %) was treated with concentrated H_2SO_4 (drops of H_2SO_4 were added under continuous stirring) at 120 ºC until

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solidification. The obtained solid product was heated up to 600 ºC in a covered silica crucible with a heating rate of 10 ºC min^{-1} in nitrogen atmosphere. The carbonized solid material was further submitted to water steam activation at 800ºC for 1 h. The obtained carbon adsorbent is noted ACCF.

2.1.2. Preparation of activated carbon from apricot stones. Apricot stones (100 g) were heated in a laboratory installation in a flow of water vapor (120 ml/min) with a heating rate of 15ºC/min to a final carbonization temperature of 800ºC. The duration of treatment at the final temperature was 1 h. After treatment the sample was allowed to cool down. The obtained carbon adsorbent is noted ACA.

2.2. Porous and chemical structure analyses

The 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 overnight. The isotherms were used to calculate specific surface area S_{BET}, total pore volume V_T, micropore volume $W_{o.}$ (using the DR formulism) [13]. The samples were further characterized by elemental analysis and chemical character of the surface was determined. A procedure based on Boehm's method [14] was used to quantify total and individual acidic oxygen groups on the adsorbent surface. The basic group content was determined by titration with HCl [15].

2.3. Adsorption measurements

Adsorption measurements of naphthalene from aqueous solutions on the carbon adsorbents were performed at ambient temperature in a stirred batch system, thermostatically controlled by an external circulating bath. Kinetic studies revealed that the adsorption equilibrium was established after 30 minutes. The determinations were performed by introducing 50 ml portions of naphthalene solution into a series of conical flasks containing 100 mg amount of adsorbent. After 2 h the content of the flasks was filtered through a microporous filter and naphthalene was determined spectrophotometrically on a UV spectrometer Pfaro 300 at a wavelength of 275.5 nm. The amount of adsorbed mass (q_e) per unit of adsorbent was evaluated from the equation:

$$q_e = V(C_o - C_e)/m ,$$

where V (ml) is the volume of the solution, m (g) - the mass of the adsorbent, and C_o and C_e are the initial and equilibrium concentrations of the aromatic compound in the liquid phase (mg l^{-1}), respectively.

A Langmuir isotherm study was carried out with initial concentrations of naphthalene: 5, 10, 15 and 20 mg/l and adsorbent mass of 100 mg/50 ml at pH 5.80.

3. RESULTS AND DISCUSSION

3.1. Chemical composition and textural properties of the activated carbons.

The chemical composition data for the raw precursor and the prepared activated carbons (AC) are presented in Table 1. The preliminary results from the elemental analysis showed that the activated carbons are suitable for adsorption of pollutants, probably due to their low ash content. Activation with water vapor leads to a considerable increase in the oxygen content of the activated carbon obtained from the coal tar pitch/furfural mixture, in comparison with the activation of apricot stones, where a considerable decrease in the oxygen content was established. Both activated carbons have similar contents of carbon, hydrogen, nitrogen and sulphur.

The elemental analysis data indicated that the amount of oxygen containing structures in the pitch is not high. It can be seen that the introduction of furfural in the process of preparing the AC leads to aproximately 6-fold increase in the oxygen content. As furfural inserts oxygen in the precursor, the higher amount of furfural increased the content of oxygen in the synthesized carbon and made it more alkaline.

Table 1. Chemical composition of coal tar pitch, apricot stones and synthesized activated carbons

Sample	Ash (wt.%)	Volatiles (wt.%,daf)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)
Coal tar pitch	-	-	90.90	4.95	0.90	0.50	2.75
ACCF	0.80	1.90	81.59	2.56	0.28	0.59	14.98
Apricot stones	0.20	80.60	51.50	6.30	0.20	0.10	41.90
ACA	2.01	3.70	89.50	2.40	0.90	0.80	6.40

Table 2. Textural parameters of activated carbons produced by apricot stones

Sample	Iodine adsorption, mg/g	Surface area, BET m^2/g	Pore volume, m^3/g			
			Vmicro	Vmeso	Vmacro	Vtot
ACCF	1100	678	0.236	0.121	0.031	0.388
ACA	925	960	0.500	0.110	0.040	0.650

Previous studies carried out in our research group have shown that the composition of agricultural by-products has a strong influence on the final porous and chemical features of the solid products obtained by pyrolysis and subsequent activation [6]. It was found that the high lignin content favors the development of a macroporous structure, whereas cellulose yields predominantly microporous materials. Analysis of the chemical composition of the initial waste material showed that apricot stones, used as a carbon source, are mainly composed of cellulose and hemicellulose (30 wt % and 28 wt %, respectively), lignin (30 wt %) and a small amount of lipids (12 wt %), which makes this material suitable for preparation of carbons with well-developed microstructure.

In this work, coal tar pitch was selected as another carbon precursor. Earlier studies carried out in our research group have shown that furfural resin is a suitable oxygen-containing raw material for the production of carbon adsorbents with a large number of oxygen-containing groups on the surface [16]. The addition of furfural to the coal tar pitch used in the precursor mixture aimed to incorporate reactive structures in the carbon matrix, which induce polymerization and polycondensation reactions – this facilitates the solidification of the mixture. The resulting solid product was carbonized and submitted to steam activation to produce a suitable porous adsorbent.

Despite the large oxygen content, the synthesized carbon displays a strong alkaline character, as inferred from the pH value (Table 3).

The nitrogen adsorption isotherm of the activated carbons obtained from coal tar pitch/furfural and apricot stones are presented on Fig.1. The part of the isotherm in the range of the relatively lower pressures (a steep increase with a tendency for saturation) is typical for microporous adsorbents. The N_2 adsorption isotherm obtained corresponds to the IV type according to Brunauer *et al*. [15] (low pressure). Type IV isotherms are obtained for solids containing pores in the mesopore range. The shape of a type IV isotherm follows the same path as the type II at lower pressures. These adsorption isotherms have led to the development of the theory of capillary condensation. Broadly speaking, it is assumed that in the initial part of the isotherm the adsorption is restricted to a thin layer on the walls of the pores until capillary condensation begins in the smallest pores [15].

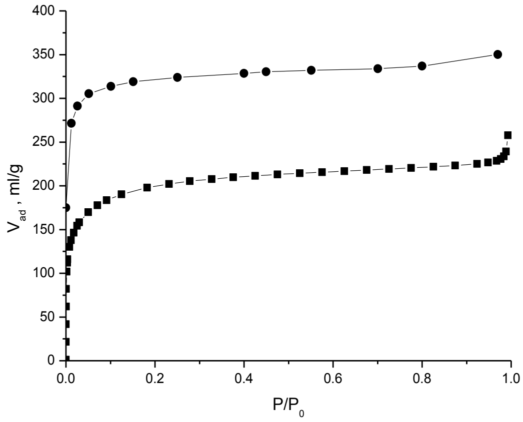

Fig. 1. N_2 adsorption isotherms at -196 ºC of the studied carbons (■ -activated carbon from coal tar pitch/furfural; ● -activated carbon from apricot stones).

Table 2 compares the porosity characteristics of activated carbons obtained from coal tar pitch/furfural and apricot stones. Both activated carbons possess close values of BET surface area.

The sample of activated carbon prepared from apricot stones has higher BET surface area and larger total pore volume with significant prevalence of the micropores, in comparison with activated carbon prepared from coal tar pitch and furfural.

In a previous work [17] about the effect of the ratio furfural:coal tar pitch in the carbon precursor, we have observed that the furfural content has a strong effect on the porosity of the resulting carbons. Low proportion of furfural give rise to activated carbons with a narrow microporosity, which is gradually opened in favor of large micropores and mesopores as the furfural content rises. Notwithstanding, the carbon yield also sharply decreases upon rising the furfural content, due to the reactivity of the precursor mixture. In this regard, if the sample ACCF is prepared with a low proportion of furfural in the precursor mixture (45 wt. %); it is characterized by a moderate value of BET surface area and well developed microporosity (Table 3). These porous features should be very suitable for the removal of aromatics from aqueous phase.

Table 3. Nature of the oxygen groups of the prepared carbons, obtained by Boehm titration

Sample	pH	Acidic groups ($meq.g^{-1}$)				Basic groups ($meq.g^{-1}$)
		Carboxylic	Lactonic	Phenolic	Carbonyl	Hydroxyl
ACCF	8.1	0.019	0.011	0.026	0.550	0.592
ACA	8.2	0.120	0.090	0.200	0.990	1.240

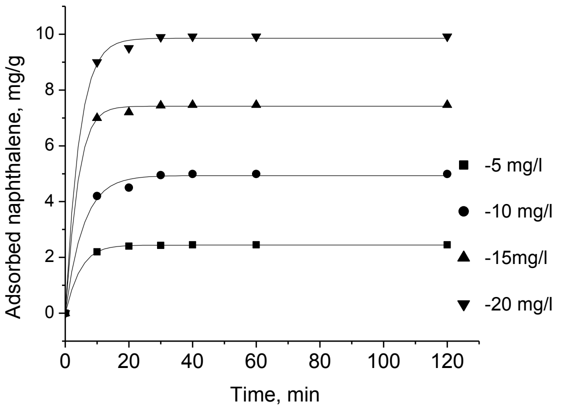

Fig. 2. Effect of contact time on adsorption of naphthalene on activated carbon from apricot stones. Conditions: carbon concentration: 100mg/50 ml; Naphthalene concentrations: 5mg/l(■) ; 10mg/l(●) ; 15mg/l(▲) ; 20 mg/l (▼).

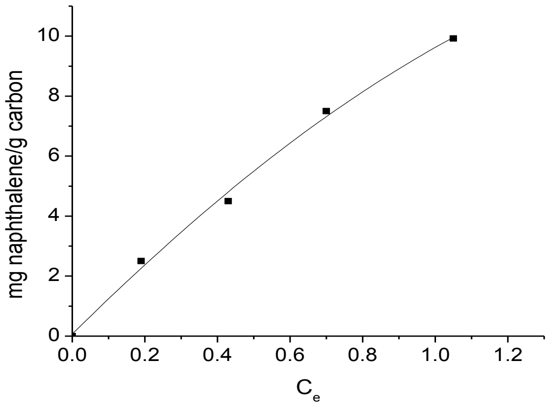

Fig. 3. Langmuir plots for adsorption of naphthalene on both activated carbons: (■- carbon from coal tar pitch/furfural; ● - carbon from apricot stones.

3.2. Surface functionalities of the activated carbons

The data of Table 3 show the nature of the surface functionalities created upon pyrolysis of the carbons. Analysis of the chemical composition of ACCF showed that along with the prevailing content of aromatic structures in the pitch, the resulting material has a relatively large oxygen content (Table 1). This corroborates 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. Despite the large amount of oxygen, the synthesized carbon displayed strong alkaline character, as inferred from the pH value. It was found that activated from apricot stones has a two times higher content of oxygen, carbonyl and basic groups than activated carbon from coal tar/pitch, despite the two-fold higher content of oxygen in the latter. This implies that the greater part of oxygen is inserted in the non-functional oxygen structures, which are obviously formed during the process of pyrolysis. The obtained data showed that the surface chemistry of carbons ACCF and ACA is characterized by carbonyl and phenolic functionalities, which render a basic character to the adsorbent.

3.3. Adsorption of naphthalene from aqueous solution

Initially, the adsorption kinetics of naphthalene on the studied carbons was evaluated in order to assess the time needed to attain equilibrium before determining the maximum adsorption capacity of each adsorbent. The kinetics of adsorption of naphthalene on both activated carbons ACA and ACCF from aqueous solution in concentrations ranging from 15 to 20 g/l are shown in Figure 2.

Equilibrium was attained for less than 1 h. The kinetic curves are smooth and continuous, and they lead to saturation, which suggests the possibility of the formation of monolayer coverage of naphthalene on the surface of adsorbent.

The Langmuir model [18] was tested and proved to fit the experimental data. The linear plot of the isotherm of the equation is an obligatory condition for the proper application of the theory of monomolecular adsorption. The linear plot of C_e/q_e *versus* C_e in Fig. 3 shows that the description of the adsorption of naphthalene on both adsorbents by the Langmuir isotherm model is satisfactory. Q_o and b were determined from the slope and intercept of the plot, respectively. The adsorption capacity of the coal/furfural adsorbent was 18.75 mg/g and that for the activated carbon from apricot stones - 29.55 mg/g. The estimated intensity of the adsorption parameter b varies from 0.4790 to 0.8735 (i.e.

between 0 and 1) [19], which implies favorable adsorption of naphthalene on the prepared carbons. For both adsorbents, excellent correlation coefficients were obtained when the data were fitted to the Langmuir theory. The Langmuir theory (1918) [20] is based on the assumption that all adsorption sites are equally "active", the surface is energetically homogeneous and a monolayer surface coverage is formed with no interactions between the adsorbed molecules. Hence, in aqueous media, the very good agreement with Langmuir equation indicated that the saturation limit was attained, which was also supported by the specific shape of the isotherms (Figure 4).

Figure 4 presents the isotherm of naphthalene in water – it has a typical L type shape (concave curvature at low concentrations) according to the Giles classification [21], which is characteristic for systems where the adsorbate has high affinity towards the adsorbent.

It is well known that the key factors influencing the adsorption capacity on activated carbons are the pore texture, surface chemistry and mineral content. The adsorption capacity of carbon materials is not connected in simple way with their surface area and porosity – the relation is complex. Generally the adsorption capacity depends on the access of the organic molecules to the inner surface of the adsorbents, which depends on their size. In our study, a good relation between the adsorption capacity and the porous and surface characteristics of the carbons was established. The activated carbon from apricot stones showed a higher adsorption capacity than that from coal tar pitch/furfural, because of its higher surface area

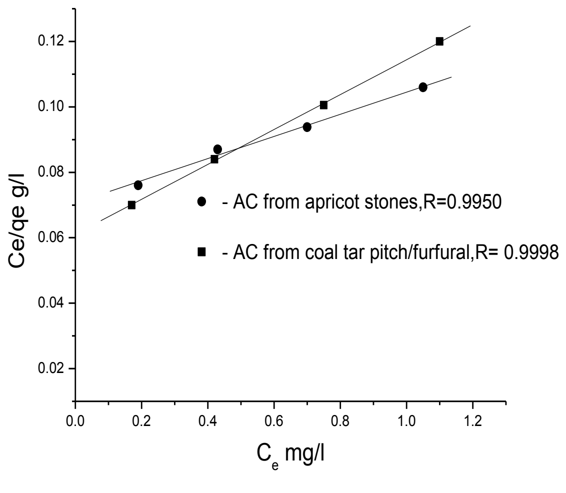

Fig. 4. Langmuir plots for adsorption of naphthalene on both activated carbons: Conditions: naphthalene concentrations, 5-20mg/l; treatment time - 120 min; carbon concentration - 100mg/50ml.

(BET), significant total pore and micropore volumes, as well as higher content of carbonyl and basic groups.

4. CONCLUSIONS

The present study shows that wastes from apricot stones and mixtures of coal tar pitch and furfural can be effectively used as raw materials for the preparation of activated carbons for removal of naphthalene. The carbons were characterized and utilized for the removal of naphthalene from water in the concentration range 5-20 mg/g. The maximum adsorption capacities were 18.75 mg/g for activated carbon from coal tar pitch/furfural and 29.95 mg/g for activated carbon from apricot stones. These results were found to be highly promising. It was established that the increase in adsorption affinity depends on both textural parameters and surface chemistry.

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ОХАРАКТЕРИЗИРАНЕ И ПРИЛОЖЕНИЕ НА АКТИВЕН ВЪГЛЕН ОТ БИОМАСА И ВЪГЛИЩНИ ОТПАДЪЦИ ЗА ИЗВЛИЧАНЕ НА НАФТАЛИН

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(Резюме)

Получени са активни въглени от различни отпадни материали (каменовъглен пек и кайсиеви костилки) чрез пиролиз в присъствие на водна пара. Беше изследвана адсорбцията на нафталин от водни разтвори при 298 K. Беше установено, че адсорбционният капацитет на активните въглени зависи от тяхната специфичната повърхност и порьозност. Беше установено, че адсорбцията на нафталин следва изотермите на Лангмюир. Адсорбционният капацитет та активният въглен получен от къменовъглен пек и фурфурол 18.75 mg/g, а за активния въглен от кайсиеви костилки - 29.95 mg/g.