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Removal of aromatic hydrocarbons from water by activated carbon from apricot stones

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ABSTRACT

Production of carbon adsorbent from agricultural waste (apricot stones) and its application for water purification from organic pollutants are investigated in the paper. Activated carbon (AC) is prepared by pyrolysis of the biomass materials at 700 °C in a flow of steam. Steam pyrolysis is a process, which creates both energy liquid and gaseous products, as well as high-grade activated carbons. The produced AC as solid product is used for removal of phenol and p-nitrophenol. It was found that the adsorption capacity is 152 mg/g for phenol and 179 mg/g for nitrophenol. An hybrid adsorptive-membrane purification of water from phenol is performed, and it is established that this combination considerably increases the effectiveness of the water purification from phenol.

1. Introduction

Wastewater pollution has become a serious problem nowadays. Chemical pollution of surface water presents a threat to the aquatic environment with hazardous effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystems and loses of habitats and biodiversity, as well as a threat to human health. As a matter of priority, causes of pollution should be identified and emissions should be stopped from the source, in the most economically and environmentally effective manner. The environment and human beings are exposed to hazards of different pollutants (organic, metal ions, etc.) from wastewater. These chemical pollutants present a large number of components exhibiting great diversity in their structure and in their chemical and biochemical activities.

Organic pollutants (phenol and phenolic compounds, polycyclic hydrocarbons, etc.) constitute an important class of highly toxic environmental pollutants, which are metabolized into derivatives, capable of reacting with DNA to promote mutagenic and carcinogenic responses [1]. In recognition of their mobility and long persistence in environment, the World Health Organization has recommended limits for aromatic substances in drinking water [2], and the European Environment Agency (EEA) has included these compounds in its list of priority pollutants to be monitored in industrial effluents [3,4].

Great efforts have been made in the last years to modify the water technologies for removing the phenol and phenolic compounds from waste waters. Although the different methods have been used for phenol removal from water: chlorination [5], ozonation [6] catalytic and photocatalytic oxidation [7,8], adsorption [9], nano-filtration [10], reverse osmosis [11], each of them possesses some limitations. Thus, chlorination of phenol containing water leads to formation of chlorphenolic substances, which are well known as poisonous and carcinogenic [12]; ozonation and catalytic oxidation are related with use of high doses of active oxidants [6]; phenol removal by adsorption is a prolonged process, additionally a high price of commercial activated carbon decrease the economic efficiency of such treatment [13]; due to solute diffusion through polymer membranes matrix phenol is poorly rejected even with high selective reverse osmosis membranes [14].

Therefore a search of novel effective methods for water purification from phenolic compounds is still of recent interest. In this sense a combination of various physico-chemical methods of water treatment with membrane purification seems to be an attractive approach [14,15].

In the last years there is special attention towards production of low-cost activated carbons from different natural materials. The attention has focused on various solid materials, which are able to remove the pollutants from the contaminated wastew-

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ater at low cost. In this connection, a number of works report thermo-chemical conversion of agricultural by-products and other sources of biomass as alternative precursors for the preparation of carbon-based adsorbents [16–20]. Agricultural by-products are very promising raw material for the production of activated carbons because of their availability at a low price. The thermo-chemical conversion of agricultural residues has received an enormous amount of attention as a consequence of its availability and its potential to produce energy as well as activated carbons with good adsorption properties [21].

In this paper we will focus on the investigation of the adsorptive properties towards phenol and p-nitrophenol of activated carbon, obtained by pyrolysis in the presence of water vapor of wide-spread agricultural by-product (apricot stones), as well as on the studying of a combined adsorption-membrane approach for water purification from phenolic compounds.

2. Materials and methods

2.1. Materials

Initially, the chemical composition (organic matter fractions) of the carbon precursor was analyzed. Details on the experimental procedure has been described elsewhere [22]. A wet-chemical method was used, yielding four fractions: soluble in a toluene–ethanol mixture (50:50, v/v), soluble in 0.94 mol L^{-1} sulfuric acid, soluble in 13.5 mol L^{-1} sulfuric acid and insoluble in 13.5 mol L^{-1} sulfuric acid. The lipids were solubilized by the first extraction step, the proteins and hemi-cellulose by the second step, and cellulose by the third step. The lignin remained in the residual fraction.

2.2. Preparation of activated carbon

Apricot stones were used as carbonaceous precursor for the preparation of activated carbons. 100 g apricot stones was heated in a laboratory installation in a flow of pure water vapor (120 ml/min) with a heating rate of 15 °C/min to a final carbonization temperature of 700 °C. The duration of treatment at the final temperature is 1 h. After the treatment the sample is left to cool down.

2.3. Porous structure analyses

The porous structure of carbon adsorbents was studied by N_2 adsorption at 77 K. The N_2 surface area and mesopore size distribution were determined using the BET equation [23] and a procedure developed by Barret et al. [24], in which the apparent pore radius was calculated by the Kelvin equation [25]. The total pore volume (V_{total}) is derived from the amount adsorbed at a relative pressure 0.95, assuming that the pores are then filled with liquid adsorbate. The Dubinin–Radushkevich equation was used to calculate the micropore volume (V_{micro}). The volume of macropores (pore size larger than 50 nm) was deduced from mercury porosimetry.

2.4. Oxygen functional groups

The content of oxygen-containing functional groups with acidic character on the carbon surface was determined applying the Boehm method by neutralization with bases of increasing strength: $NaHCO_3$, Na_2CO_3, NaOH and sodium ethoxide [26]. About 0.5 g (±0.0001 g) of the carbon was put in contact with 100 ml of 0.05 N base solution in sealed flasks. The suspensions were shaken at least 16 h, and then filtered. The excess of base remaining in the solution was determined from back titration after adding an excess of standard HCl solution. It is accepted that $NaHCO_3$ was capable of neutralizing all carboxylic groups, Na_2CO_3 – carboxylic and lactonic groups, NaOH – carboxylic, lactonic and phenolic groups, and sodium ethoxide was assumed to neutralize all acidic groups.

The total amount of basic sites was determined with 0.05 N HCl [27]. The procedure is the same as above mentioned, as back-titration of the excess of HCl was performed using titration with 0.05 N NaOH solution.

2.5. pH measurements

The pH of the carbons was measured according to the following procedure: exactly 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 as hot as possible but not below 60 °C. The decanted portion was cooled to ambient temperature and its pH was measured to the nearest 0.1 pH unit.

2.6. Adsorption measurements

The adsorption process from aqueous solutions of phenol and p-nitrophenol on activated carbon was carried out at 298 K. For this purpose, aqueous solutions with different initial known concentrations were used, as model water phenol solutions in the range from 100 mg/l to 300 mg/l. Adsorption isotherms were determined by using stoppered flasks, containing 0.1 g of carbon in 50 cm^3 of solution. They are agitated by a mechanical shaker for predetermined time intervals at room temperature to reach equilibrium conditions—60 min for phenol and nitrophenol, respectively, as the measurements are performed at 120 min to be sure that the equilibrium conditions are reached. The concentrations are determined spectrophotometrically, at maximum adsorption wavelength $\lambda = 269$ nm for phenol, and $\lambda = 316$ nm for nitrophenol, using spectrophotometer Pfaro 300 UV spectrometer.

The amount of adsorbed pollutant per unit gram of adsorbent, q_e, was evaluated from the equation:

$$q_e = \frac{V(C_o - C_e)}{M}, \tag{1}$$

where V is the volume of solution, C_o is the initial concentration of the adsorbate solution, C_e is the concentration of the solute in the bulk phase at equilibrium and M is the mass of the adsorbent.

Average of three measured values was taken for every adsorption measurement.

The linear form of the Langmuir equation [28] is applied to calculate the adsorption capacity of activated carbons:

$$q_{eq} = \frac{Q_o b C_{eq}}{1 + b C_{eq}}, \tag{2}$$

where C_{eq} is the residual (equilibrium) pollutant concentration left in solution after binding (mg/l), q_{eq} is the amount of pollutant bound to the adsorbent (mg/g), Q_o is the maximum amount of the pollutant per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/l), and b is the constant related to the affinity of binding sites (l/mg).

2.7. Adsorption-membrane purification of water from phenol

The experiments were conducted in 200 ml dead-end membrane cell with the area of 26.4 cm^2 at constant stirring of 300 rpm. Polyamide nanofiltration OPMN-P(Vladipor) [29] and low pressure polyamide reverse osmosis ESPA-1(hydronautics) membranes [30] were used in the study.

The operating pressure of 0.08–0.14 MPa in the cell was created by compressed nitrogen. The efficiency of water purification E is

Table 1
Proximate and ultimate analysis of the raw precursor and activated carbon, produced by steam pyrolysis.

Sample	Proximate analysis (wt%)		Ultimate analysis (wt%, maf)[a]				
	Ash	Volatiles	C	H	N	S	O^{diff}
Apricot stones	0.2	80.6	51.5	6.3	0.2	0.1	41.9
Activated carbon	2.0	3.7	89.5	2.4	0.9	0.8	6.4

[a] maf—moisture, ash free base.

determined as:

$$E\,(\%) = \frac{C_o - C_e}{C_o}, \qquad (3)$$

where C_o and C_p, mg/L^3—phenol concentrations in initial solution and after purification, respectively.

The productivity (J, L/(m^2 h)) of baromembrane purification is determined as follows:

$$J_v = \frac{V}{S\tau}, \qquad (4)$$

where J is the membrane flux, V is the permeate volume (L) passed through the membrane with an area of S (m^2), within time—τ (h), at operating pressure of ΔP (MPa).

3. Results and discussion

3.1. Chemical composition

Analysis of the chemical composition of the initial waste material showed that apricot stones, used as carbon source, is mainly composed of cellulose and hemicellulose (30 wt% and 28 wt%, respectively), lignin (30 wt%) and a small amount of lipids (12 wt%).

From ultimate and proximate analyses (Table 1) it was observed that agricultural waste apricot stones contain relatively high volatile matter along with a large oxygen content (almost 42 wt%).

Previous studies 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 from pyrolysis and activation [17]. It was found that the high content of lignin favors the development of a macroporous structure, whereas cellulose yields predominantly microporous materials. Apricot stones possess a combination of large quantities of cellulose and lignin, which shows that from apricot stones as a source, can be obtained an activated carbon with well-developed porous structure.

The data for the proximate and ultimate analysis of the raw precursor and the activated carbon are presented in Table 1.

The raw source (apricot stones) is suitable material for thermochemical treatment aiming production of activated carbon—after pyrolysis the content of carbon increased, while the content of oxygen decreased. As expected the content of hydrogen has decreased after carbonization. It should be noted that activated carbon from apricot stones has relatively low ash content and low sulfur content, which makes it appropriate material for purification processes.

3.2. Oxygen functional groups content

The presence of different oxygen-containing functional groups on the surface of activated carbon is a very important specific characteristic, because they have strong effect on the adsorption properties. The identification and quantification of the oxygen groups presented in the prepared carbons are shown in Table 2. The Boehm titration reveals that various oxygen-containing groups with different chemical properties are present on the activated carbon surface. A large amount of carbonyl groups, as well as only insignificant amount of strong acidic (carboxylic or lactone-like binding structures) are detected on the surface of activated carbon prepared from apricot stones. The activation with water vapor leads to the considerable increase of the amount of basic groups, which is in a good agreement with the pH value. It should be mentioned that this distribution of the amount of different oxygen groups is logical, because the application of the process of steam pyrolysis as activation method leads to the preparation of activated carbons with basic character of the surface.

3.3. Textural parameters

The porosity has a strong effect on the adsorption properties of the activated carbon. Data in Table 3 give the detailed characteristics of the pore structure of the activated carbon. Analysis of the nitrogen adsorption data using several equations indicated that the pyrolysis of apricot stones in the presence of water vapor brings about a large apparent surface area (S_{BET}) and micropore volume. The nitrogen adsorption isotherm of activated carbon obtained from apricot stones is presented in 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 is corresponded to IV type according to Brunauer et al. (low pressure). Type IV isotherms are obtained for solid containing pores also in mesopores range. The shape of the Type IV isotherm follows the same path as the type II at lower relative pressures. These adsorption isotherms have led to the development of the theory of capillary condensation. Broadly speaking it is assumed that along

Table 2
Quantification of oxygen groups on activated carbons surface (mequiv./g).

Parameter	pH	Acidic groups				Total basic groups
		Carboxyl	Lactonic	Hydroxyl	Carbonyl	
Carbon	8.2	0.120	0.090	0.200	0.990	1.24

Table 3
Textural parameters of the activated carbon produced by apricot stones.

Sample	Iodine adsorption, mg/g	Surface area, m^2/g	Pore volume, cm^3/g			
			Micro	Meso	Macro	Total
Activated carbon	900	1175	0.50	0.11	0.32	0.93

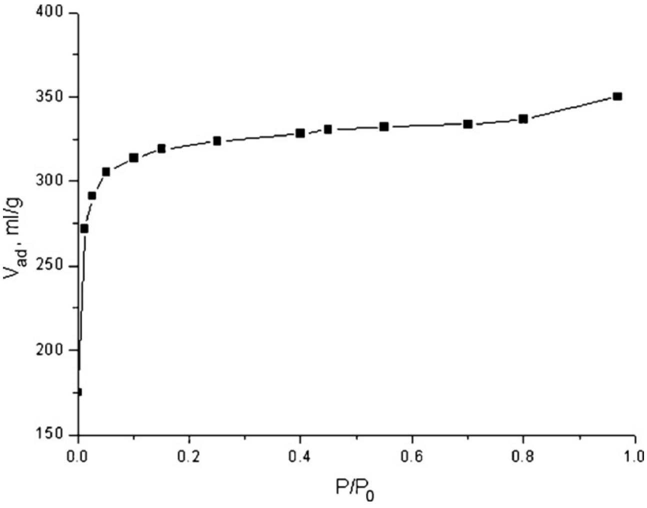

Fig. 1. N_2 (77 K) adsorption isotherm of carbon obtained from apricot stones.

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 [31].

The observed characteristics corroborate the presence of considerable volume of micropores, where the adsorption proceeds on the principle of the condensation in pore volume and this is in accordance with the high adsorption capacity of the sample. The relatively high microporosity of the carbon from apricot stones can be partly attributed to the higher content cellulose content of the raw material. The lignocellulosic material of the initial precursor has a large effect on the pore structure of activated carbon prepared by one-step pyrolysis activation process.

3.4. *Adsorption of phenol and nitrophenol from water solution*

3.4.1. *Effect of contact time*

Adsorption is a well known equilibrium separation process for treatment of water containing organics.

Fig. 2 a and b shows the effect of time of treatment on the removal of phenol and nitrophenol with concentrations of 100–300 mg/l by activated carbon. Data indicate that the removal of phenol and nitrophenol increase with time and attains equilibrium in 60 min for all initial concentrations. Organic adsorption increases sharply for a short time and slows gradually when equilibrium is approached. The plots show that the amounts of phenol and nitrophenol vary in a single smooth and continuous curves, leading to saturation and suggesting the possibility of the formation of monolayer coverage of pollutants on the surface of the adsorbent.

3.4.2. *Langmuir isotherms*

The adsorption isotherms of phenol and nitrophenol of activated carbon are presented in Fig. 3. The amounts of pollutant adsorbed at equilibrium per carbon mass unit are presented as a function of the equilibrium phenol concentration. The type of isotherm shapes and their initial slopes belong to type L in Giles classification [32]. The phenol adsorption isotherm shows a plateau value at high adsorbate concentration (subgroups 1 and 2) suggesting that the sorbate uptake proceeds via monolayer complexion. The development of a second layer was not observed in any cases of phenol retention.

The nitrophenol adsorption isotherm belongs to the type L too, although the data obtained show difference at highest concentrations (250 and 300 mg/l). This suggests that the adsorption of nitrophenol was more closely related to the textural characteristics of the carbon than to its surface chemistry.

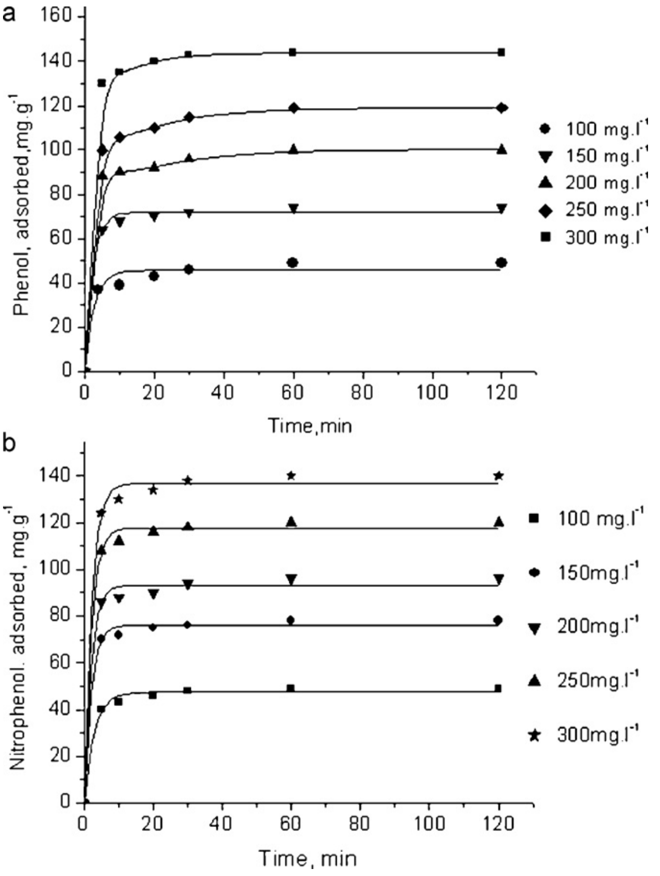

Fig. 2. (a) Effect of treatment time and initial concentrations on the adsorption of phenol. Conditions: carbon concentration 100 mg/50 ml; phenol concentrations: (●) 100 mg/l; (▼) 150 mg/l; (▲) 200 mg/l; (♦) 250 mg/l; (■) 300 mg/l. (b) Effect of treatment time and initial concentrations on the adsorption of nitrophenol. Conditions: carbon concentration 100 mg/50 ml; nitrophenol concentrations: (●) 100 mg/l; (▼) 150 mg/l; (▲) 200 mg/l; (♦) 250 mg/l; (■) 300 mg/l.

The linear plot of C_e/q_e versus C_e shows that adsorption obeys the Langmuir isotherm model for investigated pollutants (Fig. 4). The calculated values of Q_o and b are presented in Table 4.

Q_o represents the practical limiting adsorption capacity when the surface is fully covered with pollutant molecules.

All these isotherms are fitted to the investigated adsorption data. Correlation coefficients, calculated for these isotherms by using lin-

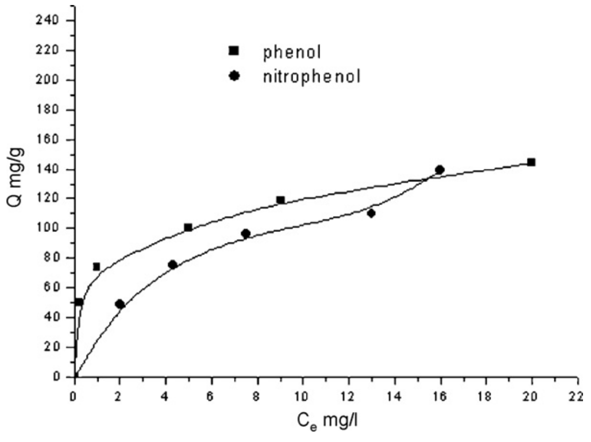

Fig. 3. Phenol and p-nitrophenol isotherm on activated carbon: (■) phenol; (●) nitrophenol. Conditions: concentration 100–300 mg/l; treatment time, 120 min; carbon concentration, 100 mg/50 ml.

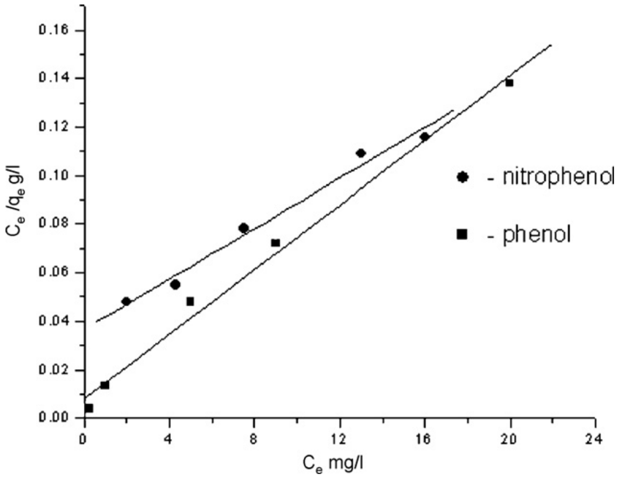

Fig. 4. Langmuir plot for adsorption of phenol and p-nitrophenol on activated carbon: (■) phenol; (●) p-nitrophenol. Conditions: concentrations: 100–300 mg/l, time, 120 min, carbon concentration, 100 mg/50 ml.

Table 4
Data for phenol and nitrophenol adsorption obtained from Langmuir plots.

No.	Type of pollutants	Q_o, mg/g	b, l/mg	R^2
1.	Phenol	152	0.00644	0.99202
2.	p-Nitrophenol	179	0.17340	0.99002

R^*—correlation coefficient.

ear regression procedures, show that the Langmuir isotherms fit excellent to the experimental data.

The adsorption maximum capacity of 152 mg/g for phenol, and 179 mg/g for p-nitrophenol, for activated carbon, produced after pyrolysis of apricot stones in water vapor, were established. Data for calculated maximum adsorption capacity (Table 4) of activated carbon towards phenol and p-nitrophenol show that, due to NO_2 group, p-nitrophenol has more powerful withdrawing properties than phenol. The presence of NO_2 group in nitrophenol obviously leads to more strong withdraw of π-electron density from aromatic ring, since the latter constitutes an electron-acceptor group itself. The adsorption of nitrophenol was still greater than that the corresponding retention of phenol.

Some physical characteristics of the adsorbed pollutants are presented in Table 5.

p-nitrophenol, which possesses lower water solubility (Table 4), is adsorbed to a greater extent than phenol, which has higher solubility in water. Mattson and Mark established that that the mechanism of adsorption of phenolic compounds is determined not only by "π–π interactions" and "donor–acceptor complex formation", but also by so-called "solvent effect" [34]. This usually neglected effect, together with two effects above mentioned, occur simultaneously during adsorption, and this determines strongly adsorption properties of carbon towards phenol. When a porous carbon comes into contact with a phenol solution, water molecules first are adsorbed on the hydrophilic polar oxygen groups, including these groups located at the micropore entrances [35,36]. A possible reason for this is that water molecules can form H-bonding with the surface oxygen groups, as well as water molecules are more competitive than phenol towards adsorption sites, especially at neutral pH and at extremely low concentrations [37,38]. The adsorbed water molecules will be further associated with each other to form water clusters, which are remarkably stabilized in micropores, reducing the accessible surface area, and impeding with or even preventing phenol adsorption. Thus the lower adsorption of phenol by activated carbon in comparison with nitrophenol may be due to not only the more powerful withdrawing NO_2 group, but also the influence of the water molecules.

Table 5
Physical characteristics of phenolic compounds [33].

Phenol compound	λ (nm)	pK_a at 298 K	Solubility at 298 K (g/100 g H_2O)
Phenol	269	9.96	9.3
p-Nitrophenol	316	7.13	1.7

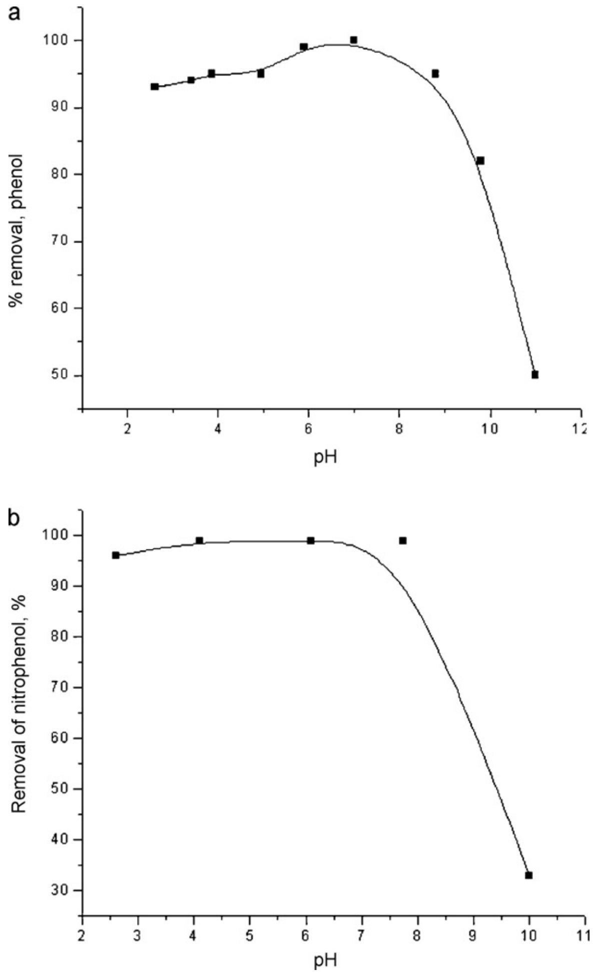

Fig. 5. (a) Effect of pH on phenol removal on carbon. Conditions: treatment time, 120 min; carbon concentration, 100 mg/50 ml; phenol concentration, 100 mg/l. (b) Effect of pH on p-nitrophenol removal on carbon. Conditions: treatment time, 120 min; carbon concentration, 100 mg/50 ml; phenol concentration, 100 mg/l.

The comparison of the adsorption capacity of activated carbon from apricot stones towards phenol and p-nitrophenol with other low cost adsorbents, obtained from different waste materials – rice husk, wood FA, rice husk, char, coke breeze, pyrolyzed residue from animal bones, etc. [9] – shows, that adsorption capacity of the activated carbon, prepared by steam pyrolysis of apricot stones, is higher for these adsorbent materials. Our results, obtained for adsorption ability of activated carbon from apricot stones, are comparable with some commercial activated carbons. It has been reported that the maximum phenol and p-nitrophenol adsorption capacity of activated carbon from different types of coals are from 97 to 152 mg for phenol, and from 127 to 232 mg/g for nitrophenol [39]. Having in the mind, that apricot stones material for producing activated carbon is not expensive, as well as the simplified method for preparation, it is reasonably to assume that the adsorption process towards these pollutants has to be more advantageous.

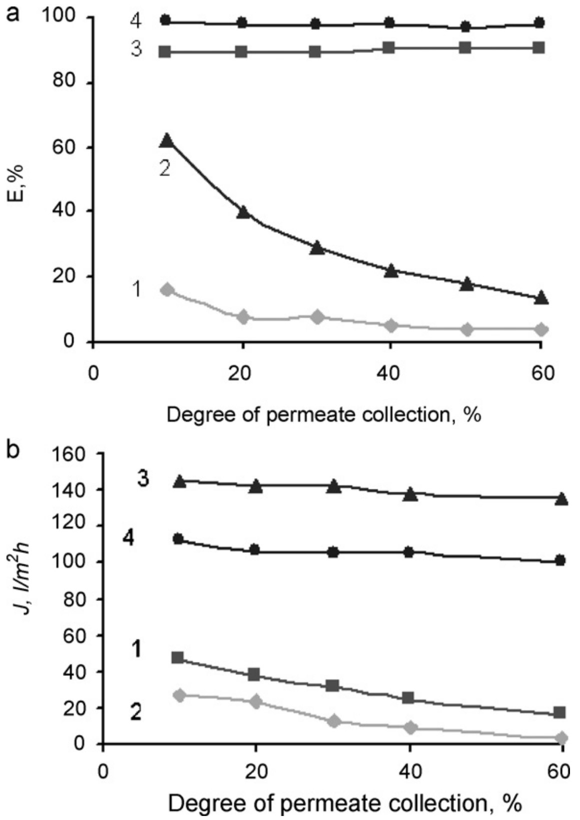

Fig. 6. Dependencies of efficiency (a) and productivity (b) of water purification from phenol with membranes: OPMN-P (1 and 3) and ESPA-1 (2 and 4) at different degrees of permeate collection: without sorbent (1 and 2) and with addition of activated carbon (3 and 4). Operating pressure ΔP is 0.8 MPa, pH of the phenol solution is 9.6. Concentration of activated carbon is 1 g/l.

The effect of the pH of the external solution on the extent of adsorption of phenol and nitrophenol can be seen in Fig. 5a and b. pH is one of the key factors, that control the adsorption process, because it influences the electrostatic interaction between the adsorbent and the adsorbate. At acidic pH the amount of phenol adsorbed, Q_o, remains constant or increases slightly with pH, and at a certain value of pH, the value of Q_o begins to decrease, which continues while pH increases. The results indicate, that the phenolic compounds are preferentially adsorbed on the surfaces of the activated carbon in their molecular form, because at acidic pH value they are not dissociated. The phenol compounds start to dissociate at a pH close to their pK_a (Table 5), which is 9.96 for phenol and 7.13 for p-nitrophenol. The decrease of the phenol adsorption begins at pH 8.5, while for p-nitrophenol at pH 7.6 (nearly one pH unit lower). When pH increases from 2.5 to 11, activated carbon progressively acquires negative charge from the external to the internal surface of the pores.

In order to speed up the water treatment process, as well as to increase the efficiency of water purification from phenol compounds, especially at high pH values, we used combined adsorption-membrane method. As seen in Fig. 6, an addition of activated carbon in phenol solution, with following membrane filtration, increases sharply the phenol removal from water, for example, from 16.08% up to 90.89% with OPMN-P membrane, and from 62.18% to 99.97% for ESPA-1 membrane. Obviously, this occurs due to simultaneous realization both adsorption and membrane mechanisms of water purification. It should be noted, that the addition of activated carbon enhances the membrane flux, even at high degrees of permeate collection (40–60%).

So positive effects of the sorbent addition on the rejection and membrane flux obviously may be explained by formation of a barrier layer from the deposited sorbent particles on the membrane surface during nanofiltration. This layer prevents a penetration of phenol molecules in the membrane porous structure, and therefore minimizes its fouling, and enhances the membrane flux. On the other hand the operating pressure, used as driving force in nanofiltration, promotes the penetration of the pollutants in the porous structure of the activated carbon, thus reducing contact time needed for adsorption and facilitates the adsorption process in whole. It appears that combined adsorption-membrane approach possesses some beneficial features, comparing with traditional adsorption filters, for which large loadings of sorbents and rather long contact time are needed for deep water purification. Thus, with this investigation, it was shown that hybrid adsorption-membrane method allows rising the efficiency and productivity of water purification from organic pollutants.

4. Conclusions

The present investigation showed that waste of apricot stones can be effectively used as a raw material for the preparation of activated carbon for removal of phenol and nitrophenol. This carbon was characterized and utilized for the removal of phenol and nitrophenol from water in the range of concentrations of 100–300 mg/l. The maximum adsorption capacities are 152 mg/g for phenol and 179 mg/g for nitrophenol. These results are found to be highly promising. It is established that the adsorption affinity increases with the electron-withdrawing of the substituent of phenol. The adsorption capacity of the activated carbon depends on the pH solution. At acidic pH the amount adsorbed remained practically constant, or increased slightly with increasing pH. When pH increased further, there was a decrease in the amount of phenol adsorbed.

Applying the hybrid adsorptive-membrane method of water purification from phenolic compounds improved the efficiency of water treatment.

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