Novel polymer-based nanoporous carbon adsorbent for removal of pentachlorophenol from water

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Polyolefin material - polyolefin wax, a by-product from industrial production of polyethylene at low pressure - was used for preparation of nanoporous activated carbon. The adsorbent surface characterization revealed well-developed surface area and presence of high amount of surface functional groups, capable of binding the adsorbate molecules. The results suggest a possible use of polymer waste as a suitable precursor for production of nanoporous activated carbon, thus lowering the cost of wastewater treatment processes. The obtained activated carbon was applied for adsorption of pentachlorophenol (PCP) from aqueous solution. Batch adsorbing experiments were performed under different conditions, i.e. concentration of pentachlorophenol, pH, contact time, etc. The adsorption of pentachlorophenol was found to follow Langmuir equation, as well as Freundlich equation.

Keywords: Adsorption, activated carbon, pentachlorophenol, water purification, polymer waste

INTRODUCTION

Chlorinated phenols are widely used as flame retardants, solvents, herbicides, insecticides and fungicides [1]. Effluents from polymeric resin production and oil refining, steel, petroleum, paint, pharmaceutic, paper industries also contain chlorophenolic compounds [2]. Pentachlorophenol (PCP) is one of the seven industrially produced chlorophenols [1]. PCP is accumulated in sediments and aquatic systems, however it has slow biodegradation rate [1]. Pentachlorophenol is toxic and mutagenic for microorganisms and mammals; as it is an inhibitor of oxidative phosphorylation [2]. PCP uncouple oxidative phosphorylation via making cell membranes permeable to protons, resulting in dissipation of trans-membranes proton gradients and consequential electrical potentials [3]. Maximal PCP discharge concentration in industrial effluents is limited down to $1 - 2$ mg/l. [1].

There are several methods for PCP removal - oxidation, biological degradation, membrane filtration, ion exchange, reverse osmosis, photocatalytic degradation [4]. Adsorption is a simple and effective method and it has been widely applied for the removal of different organic and inorganic pollutants. Activated carbons (AC) are considered to be efficient adsorbents, however the industrial anthracite-based activated carbon are expensive. In the last years there is a special attention towards production of low-cost activated carbons from different waste materials - biomass (agricultural by products, different sources of plants, etc.), coal by-products, polymers wastes, etc.

Polymer by-products from production of different polymer materials are very promising raw materials for synthesis of activated carbons, due to their availability at a low price. Thermo-chemical conversion of plastic by-products has received attention of the researchers, which is connected with the potential of these materials to produce energy as well as activated carbon with very good characteristics [5-8].

There are some reports for PCP removal by different adsorbents – bentonite [9], activated sludge biomass, [2] spent mushroom compost [3], pine bark [10], almond shell residues [1], coal fly ash [11] and fungal biomass [12]. Till now activate carbons from waste polymers have not found suitable application. It is possible to use them for removal of different organic pollutants, especially different substituted phenol compounds like PCP, which is one of the aims of this research paper.

In the present paper, novel carbon adsorbent was synthesizes from polymer waste (a by-product at the producing of polyethylene at low pressure) by carbonization with sulfuric acid and subsequent hydro-pyrolysis.

Surface area, porosity and structural properties of obtained activated carbon were characterized in

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details. The adsorption of activated carbons towards pentachlorophenol was investigated.

EXPERIMENTAL AND THEORETICAL METHODS
Synthesis of activated carbon

The initial raw materials for synthesis of activated carbon are polyolefin wax and phenol-formaldehyde resin. Polyolefin wax is a waste material, obtained as a by-product from production of polyethylene at low pressure. The mixture of polyolefin wax and phenol-formaldehyde resin (50:50%) was heated up to the melting temperature (150°C) and then concentrated sulfuric acid was added until solidification. The solid product was cooled down and washed with water, then dried at 150°C, and carbonized at 600 °C in a covered silica crucible with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The obtained carbonizate product was subjected to hydro-carbonization at 800°C in a stainless steel vertical reactor for 1 h.

Surface measurements

Textural characterization was carried out by measuring the N$_2$ adsorption isotherms at -196 °C using Quantachrome NOVA 1200 apparatus. Prior to the adsorption measurements the samples were outgassed under vacuum at 300°C overnight, to remove any adsorbed moisture and gases. The isotherms were used to calculate specific surface area S$_{BET}$ and total pore volume V$_t$.

Micropore and mesopore volumes were obtained by applying the DFT model to the N$_2$ adsorption data, assuming a slit-shaped pore geometry [43].

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: water solutions of NaHCO$_3$, Na$_2$CO$_3$, NaOH and sodium ethoxide. About 0.5 g (the same quantity is used for all the basic solutions) of the activated carbon sample was put in contact with 100 ml of 0.05 N water base solutions 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 water solution. It was assumed that NaHCO$_3$ was capable of neutralizing all carboxylic groups, Na$_2$CO$_3$ - carboxylic and lactonic groups, NaOH - carboxylic, lactonic and phenolic groups, and sodium ethoxide was assumed to neutralize all acidic groups [14]. The total number of basic sites was determined by titration with 0.05 N HCl [15]. 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 water solution.

The point zero charge (pH$_{pzc}$) was determined by inserting six portions of 50 ml 0.1 M NaCl solutions in six closed Erlenmeyer flasks. The pH of the solutions (pH$_0$) in each flask was adjusted to values 2, 4, 6, 8, 10 and 12, respectively, by adding 0.1M HCl or 1 M NaOH solutions. Furthermore six portions of 0.2 g adsorbent were added and agitated in a shaker for 1 h, and allowed to stay for 48 h (with intermittent manual shaking) to reach equilibrium. Then, the final pH vaues (pH$_f$) of supernatant liquids were measured [16]. The value of pH$_{pzc}$ is determined in the case when pH$_0$ = pH$_f$.

The infrared measurements were performed by *Bruker Tensor 27* FTIR Spectrometer in the range 4000 - 400 cm^{-1} with a resolution of 1 cm^{-1} by means of reflection technique using an *MIRacle-Diamond/ZnSe Crystal Plate* ATR accessory (Pike technology).

pH determination

The following procedure was carried out: 4.0 g of carbon was put into a 250 cm^3 beaker and 100 cm^3 of distilled water was added. The beaker was covered with a watch glass and heated to a boiling temperature for 5 min. The mixture was then set aside and the supernatant liquid was poured off at 60°C. The decanted portion was cooled down to room temperature and measured to the nearest 0.1 pH value [17].

Adsorption measurements

The adsorption capacity of the carbon toward PCP was determined by the following procedure: 0.1 g portions of the activated carbon were added to four aqueous solutions (50 cm^3) of PCP with different concentrations - 0.01, 0.02, 0.025, 0.03 g/l, respectively. The initial and equilibrium concentrations of the PCP in the solution were determined spectrophotometrically by UV spectrophotometer Pharo 300 at 305 nm. The effect of pH on PCP removal was studied using 0.1 g activated carbon and 0.03 g/l water solution of PCP. The pH is adjusted by HCl and NaOH water solutions.

RESULTS AND DISCUSSION
Chemical characterization

The chemical analysis of activated carbon is presented in Table 1. The results show that hydro-pyrolysis increases carbon and oxygen content. The activated carbon sample has very low ash content and high hydrogen content, whereas sulfur content decrease two times during hydro-pyrolysis.

Table 1. Chemical characterization of activated carbon.

Sample	W^a wt.%	A^d wt.%	C wt.%	H wt.%	N wt.%	S wt.%	O wt.%
AC	2.02	2.78	84.54	2.18	1.65	0.02	11.52

W^a – water content, ash free basis; A^d – ash content, dry basis

Textural characterization

Porosity has strong effect on the adsorption properties of activated carbon. The pore structure of obtained activated carbon was investigated by N_2 gas adsorption. Textural characterization was carried out by measuring the N_2 adsorption isotherms at −196°C. The nitrogen adsorption isotherms of the activated carbon are presented in Fig. 1. Analysis of nitrogen adsorption data shows that activated carbon from mixture of polymer waste and phenol-formaldehyde resin has high surface area (S_{BET}) and well-developed pore structure. The part of the isotherms in the range of the relatively lower pressures has a steep increase with a tendency for saturation, which is typical for microporous adsorbents. The obtained N_2 adsorption isotherms correspond to IV type, according to Brunauer classification at low pressure [13]. The main textural parameters of the prepared carbon, obtained from the analysis of the nitrogen adsorption isotherms, are complied in Table 2.

Our results show that using precursor mixture of polyolefin wax and phenol-formaldehyde resin (containing oxygen) leads to activated carbon with high surface area. The pore volume analysis show that this activated carbon has prevailing content of micropores.
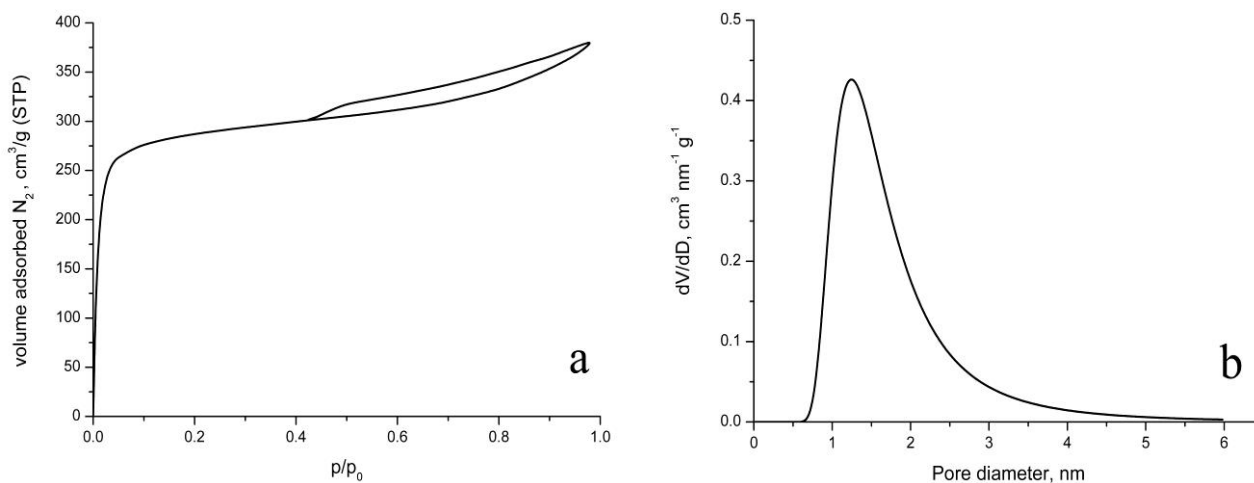

Fig.1. N_2 adsorption isotherm (a) and pore size distribution (b) of activated carbon at 196 ºC.

Table 2. Physico-chemical characteristics of the activated carbon.

Sample	BET surface area S_{BET}, m^2/g	Microporous surface area S_{mi}, m^2/g	External surface area S_{ext}, m^2/g	Total pore volume V_t, cm^3/g	Total pore volume V_{mi}, cm^3/g	Average pore diameter D_{av}, nm
AC	870	729	141	0.59	0.38	2.7

Oxygen-containing groups

The chemical character of the surface of the activated carbon was investigated by determining the amount of oxygen functional groups, and also by pH measurements and IR spectra. The oxygen-containing functional groups are very important specific characteristics of the activated carbon, because they have strong effect on its adsorption properties. The identification and quantification of the oxygen groups for the investigated carbon sample are shown in Table 3. 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 are detected on the surface of activated carbon, prepared from the mixture of polyolefin wax and phenol-formaldehyde resin. The activation with water

Table 3. Quantification of oxygen groups on carbon surface (mEquiv/g)

Sample	Carboxylic groups	Lactonic groups	Phenolic groups	Carbonyl groups	Basic groups	pH
	$NaHCO_3$	Na_2CO_3	NaOH	EtONa	HCl	
AC	0.050	0.047	0.050	2.021	0.4	8.31

vapor leads to considerable increase of the amount of basic groups, which is in a good agreement with the pH measurements. It should be mentioned that this distribution of the amount of different oxygen groups is logical, because in principle the application of the hydro-pyrolysis leads to formation of activated carbon with basic character of the surface.

IR spectroscopy

The IR spectroscopy results confirm the presence of oxygen-containing groups on the surface, which increase the adsorption properties of activated carbon.

IR spectra of the activated carbon sample are presented in Fig. 2. Stretch vibrations of associated –OH groups around 3400–3230 cm^{-1} were detected. The bands at 3000- 2800 cm^{-1} are due to aliphatic stretching vibrations. C-H stretching vibrations in the region of 3000– 2800 cm^{-1} are related to aliphatic structures. The band at 1709 cm^{-1} could be related to the stretching of C=O in linear aliphatic aldehydes, ketones and carboxyls [18, 19]. The bands around 1660 cm^{-1} cannot be interpreted unequivocally. They could be due to: 1) aromatic ring stretching coupled to highly conjugated carbonyl groups (C=O); 2) stretching vibrations of C=C bonds in aromatic structures; 3) OH groups [18, 19]. The bands in the region of 1200–1000 cm^{-1} are due to C–O in complex ethers and ring structures.
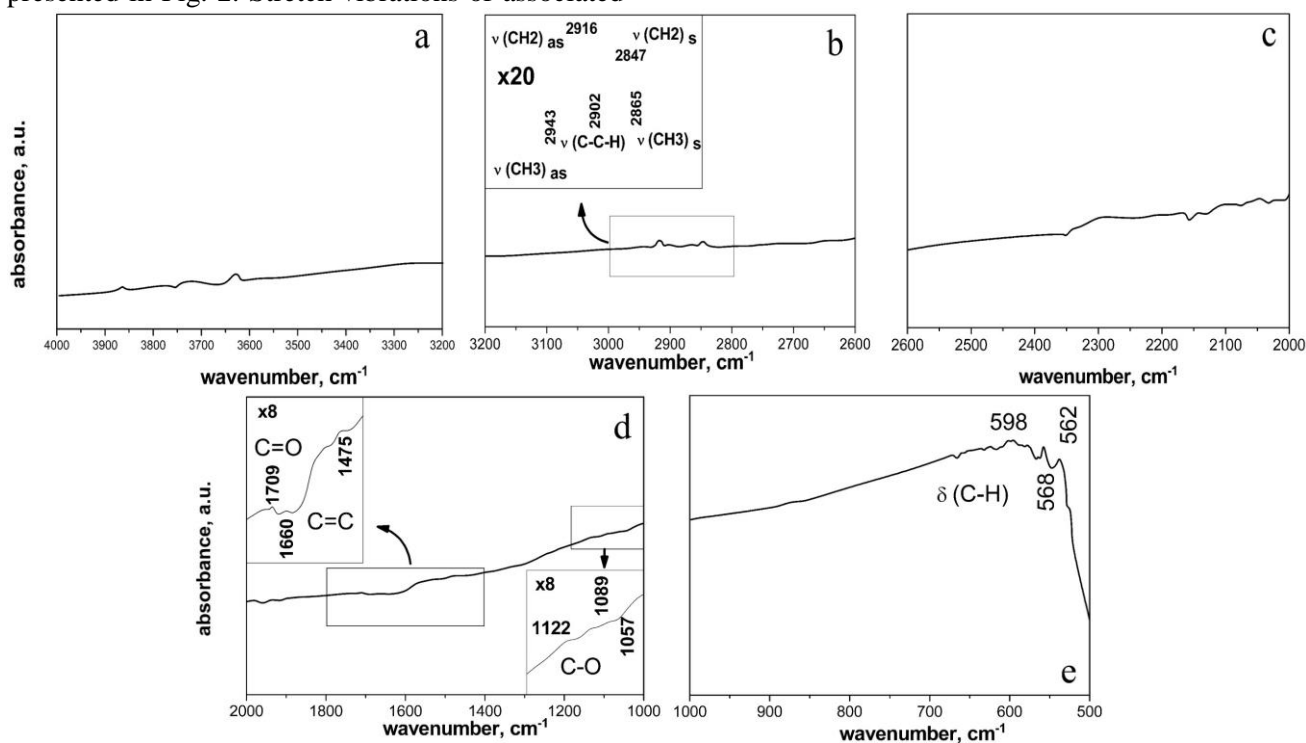

Fig. 2. IR spectrum of activated carbon: 4000-3200 cm^{-1} (a); 3200-2600 cm^{-1} (b); 2600-2000 cm^{-1} (c); 2000-1000 cm^{-1} (d); 1000-500 cm^{-1} (e).

Adsorption of PCP from water solution. Adsorption kinetics

The kinetic curves in Fig. 3 show the adsorption behavior of PCP on the synthesized activated carbon from water solution with PCP concentrations of 0.01–0.03 g/l. PCP adsorption increases sharply at short contact time. The adsorption process is quite fast and efficiently illustrates that the adsorption of PCP is completed almost on the whole surface of activated carbon. Furthermore, the adsorption capacity increases slowly and the adsorption equilibrium is established within 10 min. The removal curves are smooth and continuous, leading to saturation, suggesting the possibility of formation of monolayer coverage of PCP on the surface of the adsorbent [20]. However, the low amount of basic functional groups and saturation of less accessible adsorption sites could lead to delay of the adsorption process.
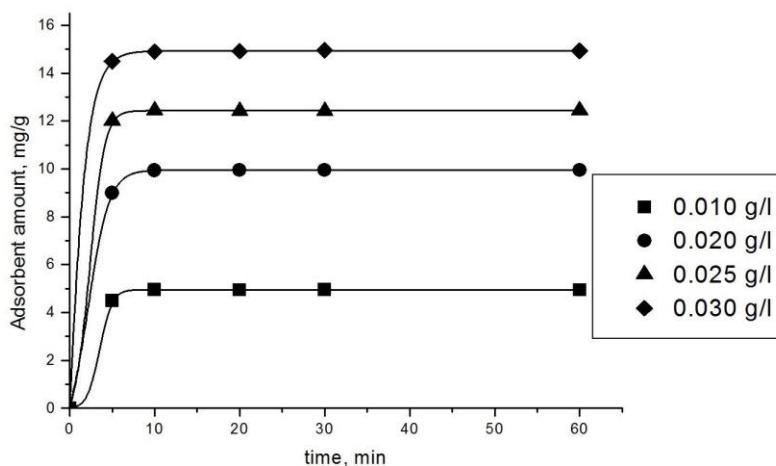
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Fig. 3. Effect of treatment time and initial PCP concentration on the adsorption of PCP. Conditions: activated carbon amount - 0.1 g per 50 ml solution; PCP concentrations - 0.01, 0.02, 0.025, and 0.03 g/l.

Adsorption of PCP from water solution. Adsorption isotherms

The isotherms are obtained using a similar procedure as for the adsorption experiments previously mentioned. The adsorption capacity was investigated for different initial concentrations (0.01-0.03 g/l) for PCP for 60 min (Fig. 4). The adsorption isotherm for PCP was described by the well-known adsorption isotherm models of Langmuir and Freundlich. The Langmuir model isotherm based on monolayer adsorption is expressed as follows [21]:

$$C_e/q_e = C_e/q_m + 1/(b\, q_m) \qquad (1)$$

where q_e is the equilibrium PCP concentration on the adsorbent (mg/g), C_e - the equilibrium PCP concentration in the solution (mg/l), q_m - the monolayer adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption equilibrium constant (l/mg), related to the free energy and the affinity of adsorption.
Freundlich isotherm for sorption on a heterogeneous surface is expressed as follows:

$$\log Q_e = \log K_f + (1/n)\log C_e \qquad (2)$$

where K_f is a constant related to the adsorption capacity, and n is an empirical parameter, corresponding to adsorption intensity, which depends on adsorbent homogeneity (Fig. 5).
The values of the applied equations of the models are presented in Table 4.
The maximum adsorption capacity calculated from Langmuir equation is 29 mg/g, which is the highest value in comparison with other activated carbons, obtained from different raw materials [25, 26].

Table 4. Data for PCP adsorption obtained from Langmuir and Freundlich plot

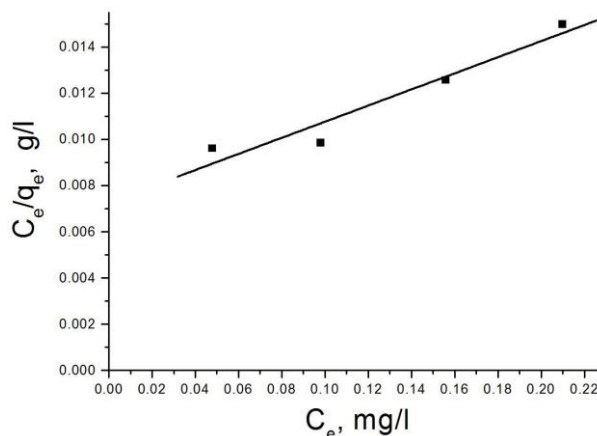| Model	Parameters	R (linear regression coefficient)
Langmuir	$Q_o = 29$ mg/g ; $b = 4.74$ l/mg	0.97144
Freundlich	$K_f = 63.68$; $n = 0.9143$	0.98261

Fig. 4. Langmuir plot for PCP adsorption on activated carbon. Conditions: PCP concentrations - 0.01, 0.02, 0.025, 0.03 g/l; 60 min contact time; activated carbon amount - 0.1 g per 50 ml solution.

Effect of pH on adsorption

The pH of the solution is related to the surface chemistry of adsorbent and chemistry of adsorbate. In order to find optimum pH for maximum PCP removal onto activated carbon, the experiments were performed in the pH range from 2 to 10, using adsorbent amount of 0.1 g activated carbon and 0.03 g/l PCP water solution. The pH is adjusted by addition of hydrochloric acid and NaOH. The results are presented in Fig. 6.
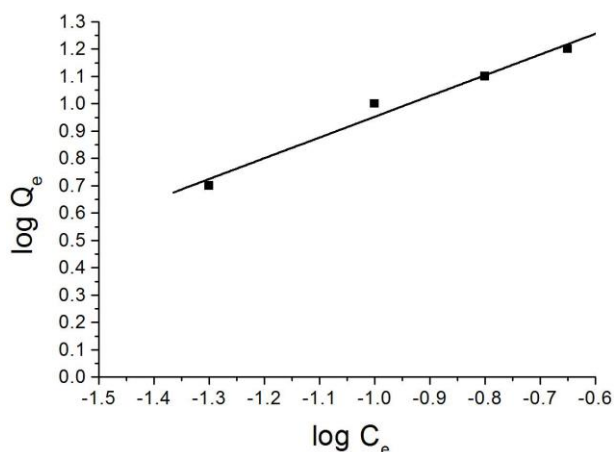
Fig. 5. Freundlich isotherm of PCP adsorption. Conditions: activated carbon amount 0.2-0.8 g; time of treatment 60 min.
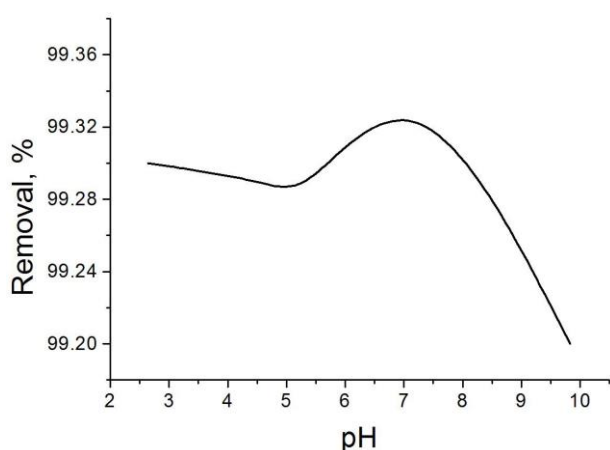

Fig. 6. Effect of pH on PCP removal. Conditions: time of treatment - 60 min, activated carbon amount - 0.1 g per 50 ml solution; PCP concentration - 0.03 g/l.

The effect of pH on PCP removal by the activated carbon can be explained by the surface chemistry of the adsorbent and the chemistry of PCP in solution. The carbon surface is positively charged at pH < pH_{pzc} and negatively charged at pH > pH_{pzc} [22]. It is also important to mention that PCP is the strongest acid among phenol derivates, with pKa value of 4.75 [23]. Thus, PCP in water solution will be mainly in protonated form at pH < pK_a, and in deprotonated form at pH > pK_a [22].

As can be seen from Fig 6, the maximum uptake of PCP by activated carbon was achieved at pH = 7. At pH = 7 PCP is dominantly in deprotonated form. Therefore attraction forces appear between PCP ions and the adsorbent surface. According to [24], at pH ~7 the adsorbent will tend to adsorb preferably cations, due to the cooperative effect of the net negative surface charge.

At pH values lower than adsorbent pH_{pzc}, the removal of PCP by activated carbon was minimal because of the repulsive forces existing between the positively charged activated carbon surface and the PCP present in water solution in its protonated

form. The removal of PCP by activated carbon decreased sharply at pH > 7. This observation was attributed to the fact that at pH values higher than pHpzc, the adsorbent surface will be negatively charged. At the same time, PCP in the water solution exists entirely in the anionic form at neutal and basic pH. Therefore electrostatic repulsion between the negatively charged adsorbent surface and the anionic form of PCP in water solution will appear at lower adsorption.

CONCLUSIONS

Activated carbon prepared from polymer waste (polyolefin wax) and phenol-formaldehyde resin has been successfully used as adsorbent for the removal of PCP from aqueous solution. The adsorption of PCP attains equilibrium in a short time of 10 minutes. The adsorption was found to follow Langmuir and Freundlich equations, as the Langmir model showed better fit to the experimental data. The maximum adsorption capacity calculated from Langmuir equation is 29 mg/g, which is the highest value in comparison with other reported activated carbons obtained from different raw materials.

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НОВ НАНОПОРЕСТ ВЪГЛЕРОДЕН АДСОРБЕНТ НА ОСНОВАТА НА ПОЛИМЕР ЗА ОТСТРАНЯВАНЕ НА ПЕНТАХЛОРФЕНОЛ ОТ ВОДИ

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(Резюме)

Полиолефинов материал - полиолефинов восък, страничен продукт от производството на полиетилен при ниско налягане - бе използван за получаването на нанопорест активен въглен. Повърхностните характеристики на адсорбента демонстрират добре развита повърхност и наличие на много повърхностни функционални групи, склонни да свързват молекулите на адсорбата. Резултатите показват възможност за използване на полимерния отпадък като подходящ прекурсор за производството на нанопорест активен въглен, като по този начин се намаляват разходите за пречистване на отпадните води. Полученият активен въглен бе използван като адсорбент на пентахлорфенол от воден разтвор. Адсорбционните експерименти бяха проведени при различни условия: концентрация на пентахлорфенола, pH, време на контакт, и др. Резултати от адсорбцията на пентахлорфенола съвпадат много добре с изотермите на Лангмюир и Фройндлих.