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Adsorption of endocrine disruptor bisphenol A by carbonaceous materials: influence of their porosity and specific surface area

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ABSTRACT

Three carbonaceous materials of different textural and surface properties were investigated as suitable adsorbents of bisphenol A (BPA), for comparison reasons, to examine the role of pore size distribution and surface acidity/basicity in bisphenol A adsorption. Typical adsorption isotherms, kinetic, and thermodynamic studies were carried out and the relative parameters as: initial pollutant concentration, solution pH, ionic strength, temperature, desorption, were calculated. Attention was particularly paid to the effect of the carbon structure, examined by BET analysis and surface chemistry examined by potentiometric titration and Fourier Transform Infrared Spectroscopy, in order to elucidate the removal mechanism. Desorption tests of loaded samples followed, with water and organic solvents of varying polarity.

Keywords: Activated carbons; BPA removal; Desorption; Textural properties; FTIR; Surface charge.

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1. Introduction

Urban and industrial wastewaters are generally highly hazardous and toxic due to the presence of organic micropollutants. Various processes are usually applied for their treatment such as biodegradation, oxidation, catalysis, and adsorption [1]. For the latter process, activated carbon constitutes certainly the typical sorbent, which is produced from various sources and usually taking advantage of low cost materials. In order also to reduce global warming, the recycling of organic by-products into carbon materials without disposing of them was examined; the produced materials were successfully applied to remove endocrine disruptors and it was concluded that carbonaceous materials produced from organic by-products could be used as adsorbents [2]. Activated carbons demonstrated high adsorption capacity to remove organic micropollutants detected in wastewater, due to the presence of active sites on their surfaces, which increased the dispersive interactions between the activated carbon graphene layers and the aromatic ring of compounds [3]. A preliminary study of our Lab in this area involved the use of activated carbons developed by pyrolysis and chemical activation of biomass, originated from potato peels [4]. A promising adsorption capacity of about 455 mg bisphenol A/ g (denoted hereafter as BPA) was reported; hence, encouraging for the present in-depth investigation.

A fluidized powdered activated carbon pilot was studied for tertiary treatment in conventional wastewater plants [5]. Granular activated carbons were also tested, in column tests, for endocrine disrupting chemicals [6].Most commercial powdered activated carbons have a predominance of micropores, which might not be easily penetrated by BPA molecules; while ordered mesoporous carbons, as CMK-3 are mainly mesoporous [7].

The presence of endocrine disrupting compounds (EDCs) in the water cycle (wastewaters-aquatic systems-drinking water) is considered as major environmental issue. In the analysis of environmental samples, BPA is usually determined along with other xenoerstogens. Bisphenol A is one of the highest volume of chemicals produced worldwide

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for plastics and epoxy resins that may present an unreasonable risk to the environment on the basis of its for long-term adverse effects on growth, reproduction, and development in aquatic species and is subjected for possible identification as priority hazardous substance in water. Due to widespread application of BPA, it is commonly found in sewage effluents, industrial wastewaters and surface waters [8–11]. A survey conducted in Ontario on emerging organic contaminants that included pharmaceuticals, hormones and Bisphenol A showed that 27 of 48 target pollutants were detected in source water, finished drinking water, or both [12].

As stated, activated carbons have been successfully tested for the adsorption of BPA. In this work, three carbonaceous materials were strictly selected for their distinguished differences in pore distribution and SSA in order to testify the role of the pore size distribution and the surface area in the BPA adsorption for the first time, to the best of our knowledge. Additionally, the role of surface acidity and/or basicity was also studied. The aim of this study was also to point out that under the term activated carbons or carbonaceous materials is included a great variety of materials with completely different properties that present completely different BPA adsorption efficiency and to try a correlation between properties and efficiency to be presented. Adsorption experiments resulted in isotherm, kinetic and thermodynamic results in order to clarify the factors that may affect the adsorption process as well as to elucidate the adsorption mechanism. Moreover, possible environmental impact due leaching of BPA from loaded carbons was investigated by employing water and various organic solvents of different polarity.

2. Experimental

2.1. Materials and methods

Bisphenol A,$(CH_3)_2C(C_6H_4OH)_2$4,4′-(propane-2,2-diyl) diphenol (the IUPAC ID), i.e. an endocrine disrupting chemical waste organic micropollutant examined here, to be possibly sorbed and removed by activated carbon. The batch tests were conducted in the normal manner [13]. Three carbonaceous materials were examined:

a) a highly ordered mesoporous carbon with hexagonal structure, CMK-3, synthesized with silica as the template - previously applied for reactive dyes sorption [14].
b) an activated carbon prepared in the laboratory from waste biomass, potato peels, ppH4. Potato peels after being washed with water and deionised water, were hydrothermally treated for 24 h and then the biochar prepared was thermally activated with phosphoric acid at 400°C for 2 h.
c) a commercial wood-based activated carbon (NUCHAR BAX-1500, from Mead Westvaco) – used also for lead ion removal [15] sample B. Before the use the activated carbon was washed in a Soxlet apparatus to remove water soluble admixtures. The under examination materials were denoted hereafter as CMK-3, ppHP4 and B respectively.

The surface area and pore size distribution of the carbonaceous materials were determined by the nitrogen adsorption–desorption isotherms at liquid N_2 temperature (77 K), measured by the AS1Win (Quantachrome Autosorb-1C automated adsorption instrument). Prior to analysis, 0.25 g of each sample was overnight degassed at 120°C in a vacuum system at 10^4 Torr. From the isotherms the Specific Surface Area, SSA, total pore volume, V_t, volume of micropores, V_{mic} and volume of mesopores, V_{mes} were calculated.

The surface functional groups of the carbonaceous materials, were qualitative determined by Fourier transform infrared (FTIR) spectra. The FTIR spectra of the samples were taken by a FTIR-spectrometer (model FTIR-2000, Perkin Elmer, Dresden, Germany) using KBr disks. The spectra were recorded from 4000 to 400 cm^{-1} and were presented at transmittance mode.

The surface pH, that provides information about the acidity or the basicity of the surface of the carbonaceous samples, was also determined. 0.4 g of dry material was added to 20 mL of water, the suspension was stirred overnight at room temperature and then, the pH of the solution was measured [16].

Potentiometric titration was conducted with a Mettler Toledo T50 automatic titrator. 0.1 g of carbon was placed in 50 mL of $NaNO_3$ supporting electrolyte solution (0.01 mol/L) and after overnight stirring was titrated with NaOH (0.1 mol/L) under N_2 saturation over a wide range of pH. The total surface charge, Q (mmol/L), was calculated as a function of pH by the equation Eq. (1) [16]:

$$Q = \frac{C_A + C_B + \left[\mathrm{OH^-}\right] + \left[\mathrm{H^+}\right]}{W} \tag{1}$$

where C_A and C_B are the acid and base concentrations (mol/L), respectively, $[H^+]$ and $[OH^-]$ are the equilibrium concentrations of these ions (mol/L), and W is the solid concentration (g/L).

2.2. Adsorption experiments

Adsorption of BPA onto the carbonaceous materials was studied by batch experiments that were run in triplicate and the mean values are presented. The effect of initial pH, ionic strength, initial concentration of BPA solution, temperature, contact time and desorption were investigated.

In order to investigate the effect of initial solution pH on the adsorption of BPA, the initial pH values of solutions of 100 mg/L with the same volume (0.02 L) and the same amount of sorbent (0.01 g), were adjusted with a pH-meter (CRISON basic 20) to different values by using microaditions of dilute NaOH or HCl solutions and shaken at 160 rpm for 24 h at a temperature controlled water bath with a shaker (JULABO SW-21C). The residual BPA concentrations after adsorption and filtration through a 0.45 lm pore size of cellulose membrane (purchased by SchleicherSchuell MicroScience), were determined by using UV spectrophotometer (Hitachi U2000) at 283 nm. The amount of BPA uptake at equilibrium Q_e (mg/g) was calculated using the mass balance equation [Eq. (2)]:

$$Q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where m (g) is the mass of adsorbent, and V (L) the volume of adsorbate.

The optimum pH found to be pH = 3.

For testing the effect of the initial concentration on BPA adsorption and temperature, a certain amount of carbonaceous material (0.01 g) and 0.02 L of BPA solution of different initial concentrations (0–300 mg/L) were placed in capped volumetric flasks. The suspensions were shaken for 24 h at pH = 3 at 25, 45, and 65°C and agitation rate = 160 rpm, in the temperature controlled water bath for 24 h. After adsorption experiments, the samples were measured for the remaining BPA concentrations as previously described.

Kinetic experiments were performed by mixing 0.01 g/L of carbons with 0.02 L of BPA solution (C_o = 100 mg/L). The suspensions were shaken at optimum pH = 3 in water bath at 25°C and agitation rate = 160 rpm in a temperature controlled water bath with a shaker. Samples were collected at fixed intervals (5–45 min, 1–72 h), filtered and measured.

Desorption experiments were carried out by mixing in capped flasks the collected, amount of BPA-loaded materials, after adsorption, with 20 mL of deionized water (same amount of sorbent and same volume as in the adsorption step) over a pH range between 2 and 12, at 25°C for 24 h. The evaluation of desorption was done as desorption percentage. Additionally, some organic solvents were also tested as eluent. The tested organic solvents were: diethyl ether–methanol 9:1 v/v, ethanol, acetonitrile and methanol. The collected, after adsorption, amounts of BPA-loaded carbonaceous sorbents were mixed in flasks, with the same amount of sorbent and same volume as in the adsorption step, for 24 h

The supernatants were collected, filtered and measured spectrophotometrically. The evaluation of desorption again, was calculated as desorption percentage. This procedure was made to determine the organic solvent that could eluent the greater amount of BPA from the BPA-loaded carbonaceous materials.

3. Results and discussion

3.1. Characterisation of carbonaceous materials

The selection of the three carbonaceous sorbents was made having as criterion their different characteristics, specifically the specific surface area and porosity and mainly the pore size distribution. In Fig. 1a the nitrogen adsorption-desorption isotherms are presented while the calculated parameters are presented in Table 1. Differences were observed in these isotherm curves of the carbons. That of ppHP4 was characteristic of curve type I, according to IUPAC classification [17], showing that the material was purely microporous. The isotherm curve of CMK-3 was of type IV according to IUPAC classification, creating a hysteresis in nitrogen desorption, appearing the existence of mesopores and consequently, the capillary condensation of adsorbed nitrogen inside them. As for the B isotherm, it appeared characteristics both of curves type I and IV. In its initial part, one may see the apparent nitrogen intake of type I, which shows the existence of micropores. At higher relative pressures, however, the isotherm was characterized of type IV, being typical of a mesoporous material. It was so concluded that the sorbent B had micro- and mesopores [18–20]. The specific surface area of B was found to be 2143 m^2/g, of CMK-3 1178 m^2/g and of ppHP4 156.5 m^2/g.

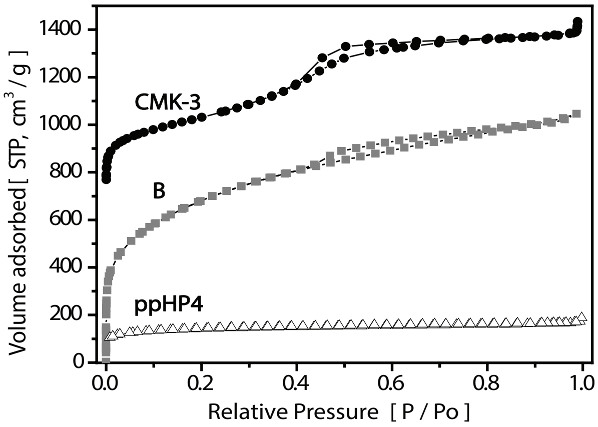

Fig. 1a. Nitrogen adsorption curves for B, CMK-3 and ppHP4 carbonaceous materials.

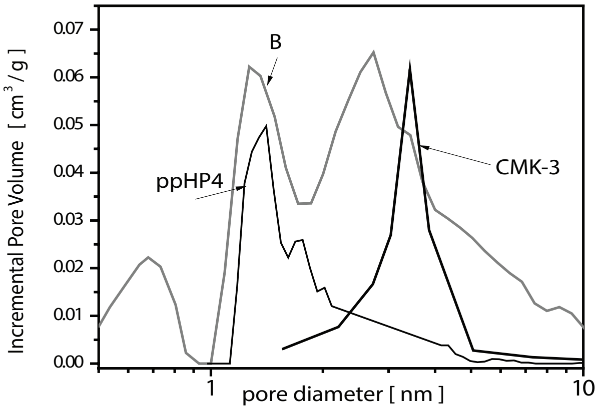

Fig. 1b. Pore size distribution of CMK-3, ppHP4 and B carbonaceous materials.

Table 1
Parameters of the carbons pore structure calculated from nitrogen adsorption isotherms

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{meso} (cm^3/g)	V_{mic} (cm^3/g)	V_{meso}/V_t
B	2143	1.494	0.696	0.798	0.465
CMK-3	1178	1.28	1.23	0.050	0.961
ppHP4	156.5	0.099	0.010	0.089	0.101

The pore size distributions of the three materials are presented in Fig. 1b. From the figure it was observed that CMK-3 sample was a pure mesoporous carbon with a pore diameter centered at 3.5 nm, ppHP4 was a pure microporous with a pore diameter at 1 nm while the B one was a micro-mesoporous carbon (pore diameter 1.5 and 3 nm respectively).

3.2. Adsorption experiments

3.2.1. Effect of pH

Bisphenol A sorption on activated carbon was studied batchwise. The solution pH may have a role in BPA removal, because it could influence the electrostatic charge between the carbon surface and the adsorbing species [21]. It controls initially the ionization level of BPA and then, the activated carbon capacity [22]. The pH influence of pH on BPA adsorption is shown in Fig. 2a, for 100 mg/L initial concentration and 0.01 g added carbonaceous material. The percentage removal is estimated by Eq. (3):

$$R\% = \frac{C_o - C_e}{C_o}100 \tag{3}$$

where C_0 and C_e are the initial and equilibrium concentration of BPA respectively.

The maximum removal was observed at the pH value of 3 for all carbonaceous samples.

With the increase of pH, a small reduction in BPA removal was observed (of 5% for the B material, up to 15% for the ppHP4). BPA at pHs < 9 exists in the molecular form; in this case, BPA can be sorbed onto carbon surface by π-π electronic and hydrophobic interactions [23]. Increasing the pH from 3 to 9, the dissociation of BPA occured, explaining the aforementioned reduction; Bautista-Toledo et al. [23] presented its aqueous speciation. The first deprotonation of bisphenol A (to its mono-anion $HBPA^-$) started at around pH 8.0 and the second one at around pH 9.0, to its divalent anion BPA^{2-}.

In Fig. 2a it was observed that adsorption remained increased and relatively uninfluenced when pH did not exceed BPA's pKa (being 9.9–11.3). At pH values over 10, ~80% the substance is negatively charged ($HBPA^-$), while at pH > 12 it exists as BPA^{2-}. Therefore, due to the repulsive electrostatic interaction among the negatively charged carbon surface and BPA anion, adsorption was reduced. Similar observations have been also traced in the literature [22,24].

3.2.2. Effect of ionic strength

Ionic strength is an important parameter in the relative studies; industrial wastes are known to contain high concentrations of salts together with the pollutants, a fact that could influence the effectiveness of adsorbents to remove pollutants. The results of this effect on the BPA removal by carbons sorption are given in Fig. 2b. The effect noticed with the ionic strength variation was not quite considerable, as also reported elsewhere [22].

3.2.3. Effect of contact time

Molecules and ions that have been sorbed on fine adsorbent particles tend to desorb returning to the aqueous solution; hence, time passing a thermodynamic equilibrium is established. In order to predict the sorption behavior a kinetic investigation is necessary. The latter will describe the amount of pollutant uptake on the material surface and control mass transfer and system's equilibrium in relation with contact time. Pseudo-first and pseudo-second-order kinetic models have been usually applied on typical experiments, to describe the sorption process [25].

The following parameters are expressed in the aforementioned kinetic models: k_1 (min^{-1}) and k_2 ($min^{-1}(mg/g)^{-1}$) that are the rate constants for the linear form of the pseudo-first [Eq. (4)] and pseudo-second order [Eq. (5)] equations respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{5}$$

Examining the effect of time on the BPA removal, it was apparent that BPA sorption was succeeded up to 80% in 30 min and completed in less than 3 h (data not shown). The application of 1st order kinetic equation on the experimental results gave the parameters q_e and k_1 with time, but with a very low correlation coefficient (of 0.643). The application of the pseudo-2nd order kinetic equation for the B carbon gave for $q_e = 192.30$ and $k_2 = 0.00777$, with a coefficient of $R^2 = 0.999$; where the slope of the relative plot ($1/q_e$) and the intercept ($1/k_2q_e^2$) were used. Hence, the pseudo-2nd order model described better the experimental results. Similar conclusions have been often found in the literature [25–27].

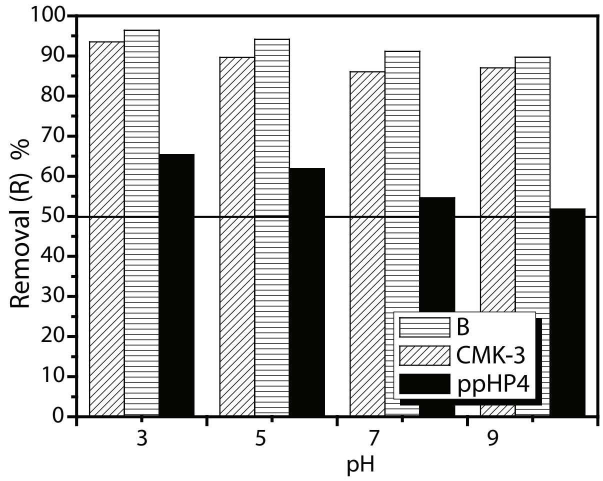

Fig. 2a. Effect of pH on BPA adsorption on B, CMK-3 and ppHP4 carbonaceous materials.

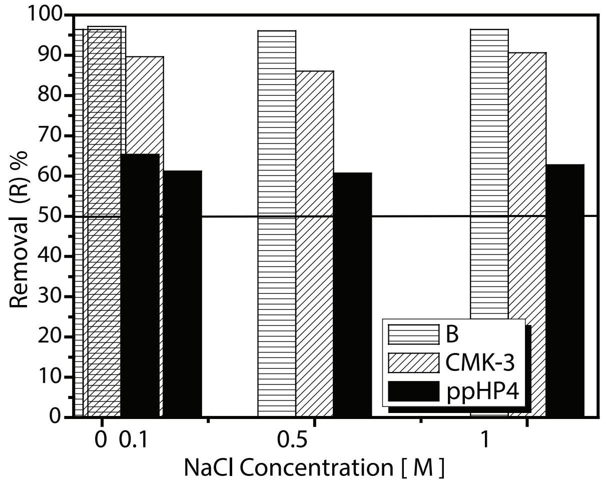

Fig. 2b. Effect of Ionic Strength on BPA adsorption on B, CMK-3 and ppHP4 carbonaceous materials.

3.2.4. *Effect of initial concentration of BPA*

The equilibrium is generally characteristic of the system studied, depending on many parameters such as the properties of the adsorbing medium and the respective pollutant, the solution type, temperature, pH, and presence of antagonistic ions. So, often adsorption is other misconstrued for a given temperature, i.e. a diagram that gives the quantity of adsorbing substance per mass unit of adsorbent as a function of its equilibrium in the solution. The experimental results were described by two of the most known adsorption models, namely the Langmuir [29] and the Freundlich [30] models. The Langmuir adsorption isotherm is expressed by Eq. (6):

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{6}$$

where Q_e (mg/g) is the equilibrium BPA concentration in the solid phase; Q_{max} (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant;

The Freundlich adsorption isotherm is expressed by Eq. (7):

$$Q_e = K_F C_e^{1/n} \tag{7}$$

where K_F ($mg^{1-1/n}$ $L^{1/n}$/g) is the Freundlich constant representing the adsorption capacity, and n (dimensionless) is the constant depicting the adsorption intensity.

Fig. 3a presents the experimental data expressed by the Langmuir adsorption model for the three activated carbonaceous materials tested (CMK-3, ppHP4 and B).

The adsorption parameters following the Langmuir and Freundlich isotherm equations, including the maximum adsorption capacity (Q_{max}), are presented in Table 2. From the R^2 values, it is seen that the results were fitted better to the Langmuir model. From which, it may be deduced that BPA's adsorption on the activated carbons tended to a monolayer adsorption.

3.2.5. *Effect of temperature*

The study of the effect of temperature on BPA adsorption could assist to decide whether adsorption is an exothermic or endothermic process [26]. This examination was conducted at temperatures of 25°, 45° and 65°C and the results are presented in Table 2; for the B carbon the effect of temperature is presented in Fig. 3b. For the activated carbons B and ppHP4, it was found that the adsorbing ability for BPA was lowered with the increase of temperature, showing that the adsorption on carbon's surface was an exothermic reaction. This reduction of adsorbing ability with temperature perhaps is owed to the weakening of sorptive forces among the adsorbent active sites and the adsorbing substance during the process [26].

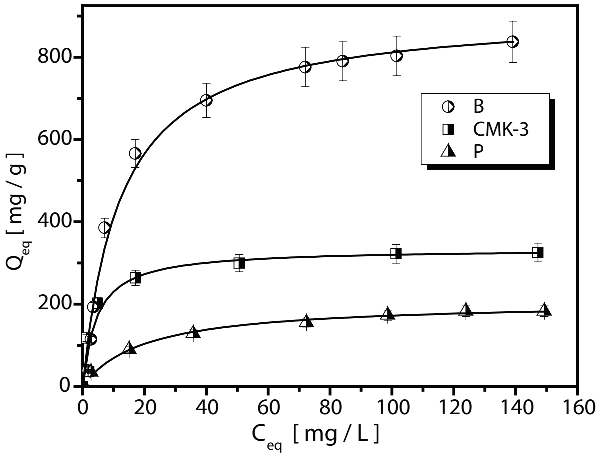

Fig. 3a. Adsorption isotherms for B, CMK-3 and ppHP4 carbonaceous materials.

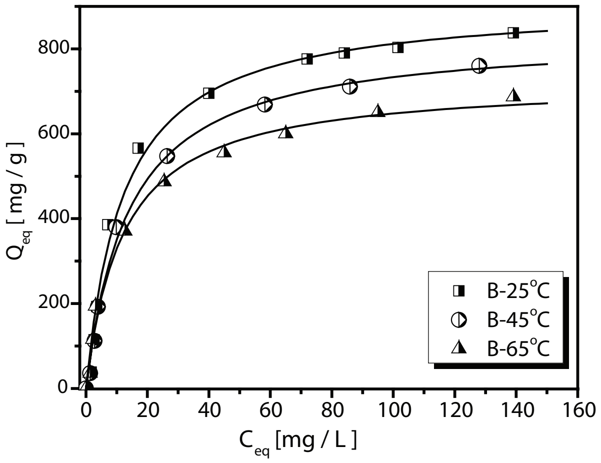

Fig.3b. Effect of temperature on B activated carbon.

3.2.6. *Thermodynamics study*

Information on the adsorption mechanism can be also taken from the Gibbs free energy (ΔG°), the enthalpy difference (ΔH°) and the entropy change (ΔS°). Thermodynamic analysis was also realized based on the equilibrium data of isotherms at three different temperatures for the calculation of the respective parameters (ΔG°, ΔH°, ΔS°) [30]. The Gibbs free energy change (ΔG°, kJ/mol) of the adsorption process is expressed by the Van't Hoff equation [Eq. (8)]

$$\Delta G^\circ = -RT \ln(K_c) \tag{8}$$

The equilibrium constant K_c (dimensionless) can be calculated from Eq. (9):

$$K_c = \frac{C_s}{C_e} \tag{9}$$

where C_s (mg/L) is the amount adsorbed at equilibrium and R = 8.314 J/mol/ K is the universal gas constant.

The change in entropy (ΔS^0, kJ/mol K) and the heat of adsorption (ΔH^0, kJ/mol) at a constant temperature T (K) was calculated by the equation (Eq. (10)):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

Table 2
Equilibrium parameters for the adsorption of BPA at various temperatures onto the three activated carbons

		Langmuir model			Freundlich model		
		Q_{max}		R^2	K_F	$1/n$	R^2
25°C	B	910.75	0.0819	0.9859	156.65	0.3612	0.9066
	CMK-3	334.39	0.2209	0.9015	110.42	0.2343	0.8052
	ppHP4	206.26	0.0505	0.9904	34.57	0.3448	0.9742
45°C	B	834.71	0.0722	0.9936	132.47	0.3522	0.9339
	CMK-3	364.37	0.2563	0.9917	153.15	0.1839	0.9524
	ppHP4	180.31	0.0457	0.9807	31.70	0.3178	0.9827
65°C	B	725.79	0.0829	0.9907	128.07	0.3856	0.9224
	CMK-3	389.82	0.2842	0.9957	125.01	0.2486	0.9347
	ppHP4	167.33	0.0351	0.9875	25.97	0.3353	0.9765

Hereafter, from Eqs. (7)–(9):

$$\ln(K_c) = -\frac{1}{RT}\Delta H^\circ + \frac{1}{R}\Delta S^\circ \tag{11}$$

The values of ΔH^0 and ΔS^0 were calculated from the slop and intercept of the plot between $\ln(K_c)$ versus 1/T.

The calculated values are presented in Table 3. The total free energy change ΔG° during the adsorption process of BPA onto the three sample materials was negative for the examined temperature range; a fact that proved it is spontaneous. The noticed reduction in the negative values of ΔG° with the temperature increase from 25 to 65°C proposes that adsorption is less favored at increased temperature. The negative values of ΔH° for B carbon and ppHP4 carbons show the exothermic nature of the adsorption. The enthalpy change values were calculated 10.44, 6.81 και 4.91 kJ/mol for the carbons B, CMK-3 and ppHP4 respectively, values indicative of physi-sorption [30]. The values for the entropy change were found to be positive indicative of a randomness increase at the solid/solution interface during BPA adsorption on activated carbon surfaces. So, there is a faster reaction between the π electrons of BPA with the π electrons of benzene rings of the carbonaceous materials' surface. These positive ΔS° values also prove the increased relationship of the adsorbent with BPA, and the increase of the freedom degrees of the adsorbing species [26,32].

Furthermore, the negative values of ΔG° show that the adsorption process was spontaneous, while randomness increased with temperature. The increase of these negative values with temperature indicates that lower temperature results in easier adsorption [32]. Similar results were previously reported by other authors [22,31].

3.2.7. Desorption experiments

The effectiveness of water and various organic solvents for BPA elution from the loaded activated carbons was also investigated in order to assess the environmental safety of loaded materials. On the other hand, a successful desorption certainly means the possible reuse of the adsorbent itself in a next cycle.

Table 3
Thermodynamic parameters for BPA adsorption on the activated carbons

Samples	T(K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
B	298	–15.9666	–10.44	0.0199
	308	–16.4712		
	318	–17.375		
ppHP4	298	–7.34709	–6.81	0.0027
	308	–8.33289		
	318	–7.26841		
CMK–3	298	–15.2139	4.91	0.0733
	308	–18.0972		
	318	–20.1065		

Deionised water was at first tested, at pH varying from 2 to 10; Fig. 4a shows the B sample results. The maximum percentage desorption obtained for all carbonaceous samples, was less than 10%. The maximum desorption was noticed at pH 10, where the BPA retention forces were leaned, contrary to adsorption. In other words, the adsorption bonds of the substance onto the carbon pores were strong enough; the electrostatic repulsions created between the ionised BPA and the adsorbent at alkaline pH were not capable to destroy these bonds. So, the activated carbons were rather environmentally safe.

Oganic solvents were also tested, selected according to their increased polarity and the results are shown in Fig. 4b, for the B carbon. The following order for these solvents exists with respect to their dielectric constant: n-hexane 1.9%, diethyl-ether 4.3%, ethanol 24.3%, methanol 32.6% and acetonitrile 37.0%. It was observed that a complete (100%) desorption was taken by a mixture 9:1 of diethyl-ether/methanol.

Methanol was effective (at 85%), followed in decreasing order by acetonitrile, ethanol, sodium dodecyl-sulphate, water (at pH 10), and n-hexane. The aforementioned stands are in agreement in literature [33].

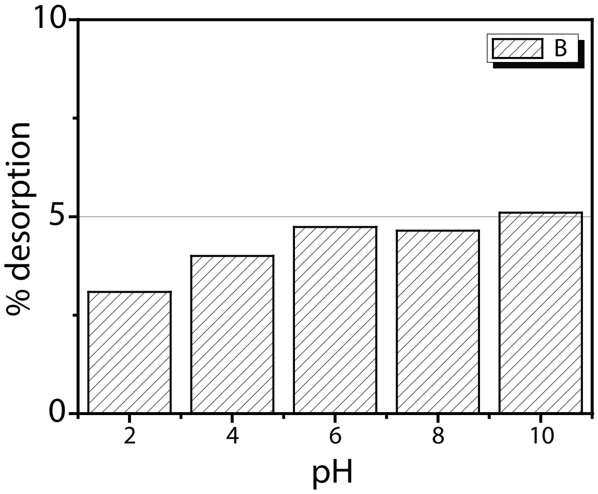

Fig. 4a. Desorption of BPA in different pH values.

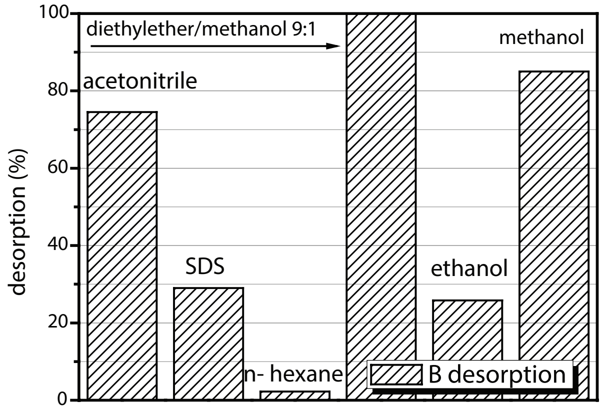

Fig. 4b. Desorption of BPA in different organic solvents.

3.3. *Effect of the texture of the carbonaceous materials*

From the adsorption experimental results it was apparent that there was a quite linear relation between the specific surface area, S_{BET}, of the adsorbents applied to BPA removal and its maximum capacity for bonding the pollutant, as it is presented in Fig. 5; the greater the material's specific surface, the larger was the adsorbing capacity. Activated carbon B had maximum adsorbing capacity 910 mg/g and the maximum specific surface of 2143 m^2/g. It was, therefore, concluded that the specific surface of the carbon sample was intensely influencing the adsorption capacity.

3.4. *Effect of surface chemistry*

Apart of the specific surface area and porosity, the surface chemistry also plays an important role in the characterization and adsorbing ability of carbon materials. BPA sorption besides being correlated to the distribution of BPA species at different pH values can be also correlated to the pHpzc values of under examination carbonaceous materials, that were evaluated from the titration curves and presented in Fig. 6a. From the figure it is revealed that ppHP4 carbon and CMK-3 were acidic at the pH range from 3 to 10, while B activated carbon presented a pH_{pzc} at about 6.5. At pH > 8, the surface of adsorbents is negatively charged while bisphenol A is deprotonated into its anionic forms ($HBPA^-$, BPA^{2-}), therefore, repulsive electrostatic adsorbent–adsorbate interactions were developed between the carbons and the substance, having as result the reduction of adsorption at these pH values. The maximum adsorption was attained at pH of 3.0 for all carbonaceous materials where repulsive electrostatic interactions are not established between adsorbent and adsorbate and BPA can be adsorbed on the carbon surface by electron dispersion at p-conjugated systems [4].

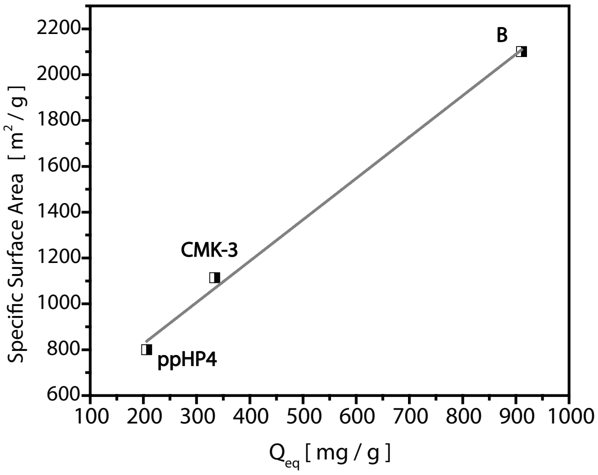

Fig. 5. Correlation of specific surface area and maximum adsorption capacity of the carbonaceous materials.

From the obtained titration data the amount of basic groups were calculated for the three studied activated carbons and are presented in Table 4. A linear proportional relation was apparent among the carbons adsorbing capacity and the existing basic surface groups, which were mainly phenolic; the results are presented in Fig. 6b.

FT-IR spectra provided information related with the chemical interactions of adsorbents and adsorbed surface groups, as well as for the functional groups of the adsorbent. In this way, it is possible to find out the mechanism of BPA sorption that may be accomplished observing the shift of precise peaks presented in FTIR spectra for the raw carbon samples and their counterparts after BPA adsorption. This will mean that the specific characteristic group of the material interacts with the pollutant's species; for this reason, spectra before and after BPA adsorption were taken for the three carbonaceous materials and are presented in Fig. 7.

The main characteristic peaks of the samples were observed at:

(i) 3100–3400 cm^{-1}, that can be attributed to O-H stretching vibration,
(ii) 1720 cm^{-1}, attributed to the bond C=O stretching vibration mainly due to carboxylic groups,

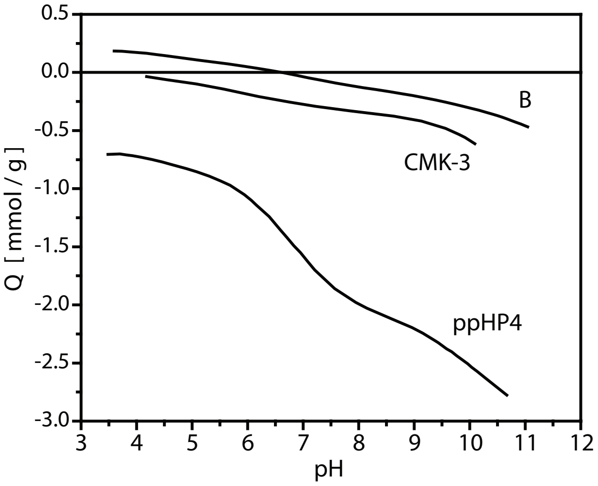

Fig. 6a. Potentiometric titration curves of the carbonaceous materials.

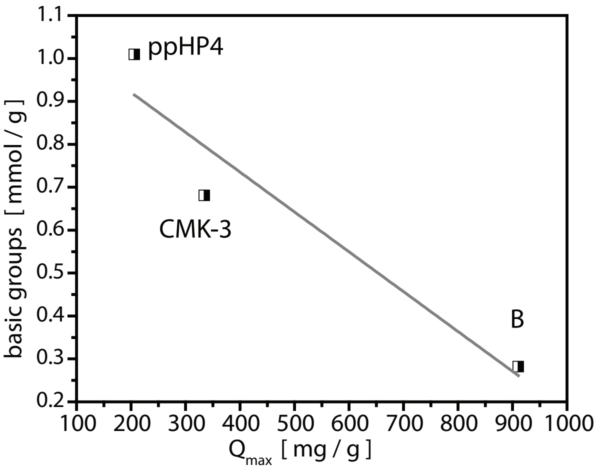

Fig. 6b. Correlation of the amount of basic groups of the carbonaceous materials and their maximum adsorption capacity.

(iii) 1615 cm^{-1}, attributed to the C=C of aromatic rings and also the conjugated systems, such as diketone, ketoester, quinone (1550–1680 cm^{-1}), and

(iv) 1050 cm^{-1}, attributed to the C-O-C surface oxygen groups.

Comparing the obtained spectra of the materials, new peaks are apparent after BPA adsorption. For all the carbons, the peak appearing at ~1600 cm^{-1} in the initial samples and being characteristic of the aromatic rings of the carbons was slightly shifted following adsorption. This shift may be ascribed to the π-π stacking interactions between the electrons of the aromatic ring of the adsorbed substance (i.e. BPA) and the electrons of the aromatic rings of the carbonaceous materials [34]. The wide peak of increased intensity observed at ~1200 cm^{-1} for the carbons following BPA adsorption may be due to the phenolic surface groups of BPA adsorbed on carbons surface [4].

Table 4
Results of potentiometric titration; amount of acid and basic surface groups of carbonaceous samples (in mmol/g).

Samples	Acidic groups (mmol/g)	Basic groups (mmol/g)
B	0.271	0.282
CMK-3	0.272	0.681
ppHP4	1.356	1.009

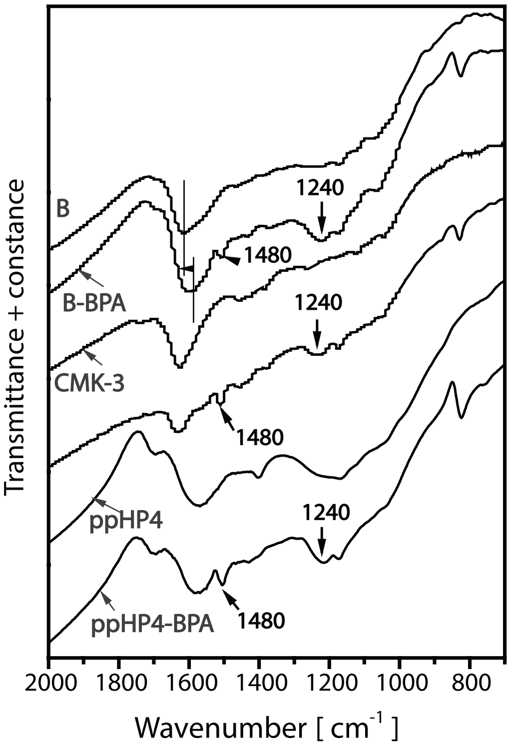

Fig. 7. FTIR spectra of the carbonaceous materials and their counterparts after BPA adsorption.

Consequently, certain absorption changes came of attention for the bonds C-O and O-H of all the BPA-loaded carbon samples. These changes in the FTIR spectra revealed the presence of aromatic rings and hydroxylic groups on the carbons after adsorption and hence, lead to the conclusion that the process mechanism could be described by the creation of π-π bonds, of the π electrons of BPA with the π electrons of the carbon aromatic rings and hydrogen bonds, between carbon hydroxyls and BPA.

4. Conclusions

The adsorption efficiency of three activated carbonaceous samples, of different structure and surface chemistry, towards bisphenol A (BPA) was investigated by employing batch experiments. Their capacity was observed to be straightly related with the specific surface area of the material. The maximum adsorbing capacity of 910 mg/g was achieved by activated carbon B with a specific surface area of 2143 m^2/g, a micro-mesoporous carbon with pore diameter 1 and 3 nm respectively.

The solution pH and ionic strength was not found to affect adsorption. The process was better described by the Langmuir isotherm model and pseudo-2nd-order kinetic model. With the temperature increase, a reduction of adsorbing capacity was observed. Adsorption was found to be physical, exothermic and spontaneous. BPA when was adsorbed on the carbonaceous materials could not get desorbed in aqueous solutions of varying the pH but could get desorbed in organic solvents. The adsorption of BPA on activated carbons may be attributed to the creation of π-π bond and hydrogen bonds, too.

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