

## ON THE USE OF LOW COST ADSORBENTS FOR THE REMOVAL OF ENDOCRINE DISRUPTORS FROM WATER: A CASE STUDY WITH BISPHENOL A

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### Abstract.

*The present paper is focused on the use of low cost adsorbents for the removal of endocrine disruptors from water. This class of organic compounds has been recently considered of increasing environmental concern because of the adverse health effects. Among them, bisphenol A (BPA), widely used for the plastic production, is considered as a critical contaminant due to its harmful effects. The adsorption efficiencies of four types of activated carbons, commonly used in the drinking water treatment, on the bisphenol A removal were investigated using batch adsorption experiments. Based on kinetic and mass transfer considerations the activated carbon F400 gives the best results and was selected for further adsorption studies. The obtained results showed that the BPA isotherm experimental data are well described by Freundlich isotherm and demonstrated the excellent performance of the selected adsorbent. Thus, F400 can be considered of a potential practical interest for the BPA pollution control purposes.*

**Keywords:** adsorption, carbonaceous adsorbents, drinking water, endocrine disruptors.

### Introduction

According to the US Environmental Protection Agency, endocrine-disrupting compounds (EDCs) are exogenous agents interfering with synthesis, secretion, transport, metabolism, binding action, or elimination of natural blood-borne hormones that are present in the body and are responsible for homeostasis, reproduction, and developmental processes. These agents act through various types of receptors such as nuclear receptors, nonnuclear steroid hormone receptors, nonsteroid receptors, enzymatic pathways involved in steroid biosynthesis and/or metabolism, etc. (Diamanti-Kandarakis et al., 2009).

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EDCs can occur naturally in the environment or as a result of industrial activities. Estrone and 17 $\beta$ -estradiol (natural female hormones), for example, are ubiquitous in the aquatic environment receiving sewage inputs. They are sufficiently stable to survive sewage treatment processes and are reactivated through deconjugation. These two compounds are among the most potent of all EDCs being involved in causing adverse effects in fish adjacent to sewage outfalls (Zhang and Zhou, 2005).

Synthetic EDCs consist of a wide range of crop protection products (pesticides, chlorinated insecticides), antifouling compounds, pharmaceuticals and personal care products, industrial chemicals (polychlorinated biphenyls, alkylphenols and their ethoxylates), etc. (Zhou et al., 2010). Exposure to synthetic EDCs has been associated with adverse reproductive outcomes including reduced female fecundity, longer time to conception, higher miscarriage rates and decreased sperm motility (Frye et al., 2011).

Bisphenol A (BPA) is one of the most known endocrine disruptors. It is an organic compound, essential in plastic and plastic additive synthesis such as polycarbonate (Goyal et al., 2000; Liao et al., 2010; Wang et al., 2014) and epoxy resins (Niu et al., 2013; Tomuta et al., 2013), frequently used for food packaging systems (bottles, dishes, cans), for compact discs production or for self-adhesive labels, fax paper and dental sealants fabrication (Guida et al., 2015). Various studies have shown that BPA presents harmful effects on human health and wildlife. Behavioural changes, altered growth, early secondary sexual maturation (Erler and Novak, 2010), infertility or breast cancer (Benachour and Aris, 2009) have been reported. Human exposure to BPA action may occur, for example, through contamination of food and beverages contained in polycarbonate bottles and cans, which are internally coated with epoxy resin, due to migration phenomena of BPA unbound monomers (Kang et al., 2006; Simoneau, 2013; Vandenberg et al., 2007). In addition, low concentration of BPA in water can eventually lead to high human exposure through the food chain (Wu et al., 2015). Currently, many studies are carried out to develop effective methods for the removal of this molecule from the aquatic environment in order to reduce its health and environmental impacts.

Methods such as adsorption (Dong et al., 2010; Han et al., 2012; Kim et al., 2011; Kitaoka and Hayashi, 2002; Nguyen-Huy et al., 2014), biological treatment (Froehner et al., 2011; Melcer and Klecka, 2011), ultrasonication, ozonation, advanced oxidation (Guerra et al., 2015) and photodegradation technology (Li et al., 2006; Peng et al., 2008; Tanizaki et al., 2002; Wang et al., 2007) were investigated for this purpose. Among them, adsorption was found to be an interesting solution for the removal of BPA from water systems in terms of low cost and ease of operation. Moreover, the process can be easily implemented

using different materials as adsorbents (Nguyen-Huy et al., 2014) without leading to harmful secondary products. Several studies with activated carbons reported that adsorption efficiency of BPA depends on the physical-chemical properties of pollutants and adsorbents (Bautista-Toledo et al., 2005). However, to the best of our knowledge no relevant work about the removal of low concentration of BPA by low cost adsorbents has been carried out.

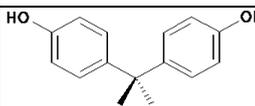
The aim of this work was to study the removal of BPA from aqueous solutions by adsorption using low cost adsorbents. Four activated carbons, commonly used in drinking water treatment for the removal of micro-pollutants were chosen to be tested and their adsorption efficiencies under concentration conditions closer for a real water contamination were investigated. Adsorption isotherms studies were carried out in order to determine the maximum adsorption capacities and model isotherm were used to analyse the obtained experimental data and to determine the specific adsorption parameters. In addition, this research provides new information allowing a better understanding of the mechanism involved in the BPA adsorption process.

## Materials and methods

### Adsorbate

The adsorbate used in this study was Bisphenol A (CAS number 80-05-07, 99% purity) purchased from Sigma Aldrich Chemical Company. According to the literature, BPA is one of the most targeted compounds, due to its toxicity and occurrence in the environment. Indeed, this molecule is often found in industrial and domestic waste and drinking water and surface water. Table 1 presents some physical-chemical characteristics of the endocrine disruptor (EDC) used in this work.

**Table 1.** Physical-chemical properties of the target compound

<i>Name of molecule (full name and abbreviation)</i>	<i>Use</i>	<i>Molecular weight (<math>g\ mol^{-1}</math>)</i>	<i>Log <math>K_{ow}</math></i>	<i>Solubility in water (<math>mg\ L^{-1}</math>)</i>	<i>pK<sub>a</sub></i>	<i>Structure</i>
Bisphenol A (BPA)	plasticizer	228.1	3.3	110	9.6-10.2	

Stock solutions are prepared by dissolving the compound in ultrapure water. The solution was then stirred for three days in the dark until complete dissolution

based on the low solubility in water of BPA. Prior to use, the stock solution was filtered through a 0.2  $\mu\text{m}$  membrane filter to remove the undissolved BPA particles and then diluted to prepare the working solutions for the adsorption isotherms study. For the HPLC analysis of BPA a stock solution was prepared with methanol and then the working solutions were obtained by dilution with ultrapure water.

Moreover, it will be noticed that all solvents and chemicals used in this work were commercially available and of analytical grade.

#### ***Activated carbons and adsorbent preparation***

Four activated carbons Filtrasorb-400 (F400 Calgon Carbon Corp., Pittsburgh, PA, USA), Picactif NC 60, NC 90 and TE 60 (Pica Corp.) widely used in the drinking water treatment were tested in this work.

Prior to use, the adsorbents were crushed to powder to obtain particles of an average diameter of less than 80  $\mu\text{m}$ . The resulting powder was then washed several times with ultrapure water (EUP; ELGA DV25,  $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ ,  $\text{COT} < 10 \mu\text{g C}\cdot\text{L}^{-1}$ ,  $\text{pH} = 5.5$ ) to eliminate the fines (i.e. particles floating on the surface of washing water) and then were suspended in EUP for at least four hours to remove the alkaline substances and eventually pre adsorbed organic compounds.

**Table 2.** The main characteristics of investigated activated carbons

<i>Name</i>	<i>Aspect</i>	<i>Origin</i>	<i>Median diameter (mm)</i>	<i>Specific area (<math>\text{m}^2\cdot\text{g}^{-1}</math>)</i>	<i>Apparent density (<math>\text{g}\cdot\text{cm}^{-3}</math>)</i>
Picactif NC 60	granular	coconut	3.80	1240	0.52
Filtrasorb-400	granular	fossil	2.32	1200	0.54
Picactif NC 90	granular	coconut	1.72	1596	0.45
Picactif TE 60	granular	coconut	1.15	1153	0.73

Finally, the washed carbons were dried in an oven at  $150^\circ\text{C}$  for 24 hours and then stored in a desiccator until use. Some characteristics of the used adsorbents are listed in Table 2.

#### ***Batch adsorption experiments***

BPA adsorption isotherm experiments were conducted in batch mode with the bottle-point method. The adsorption isotherms balances are carried out with powdered activated carbons. Increasing amounts of powder activated carbon (PAC) ( $1\text{-}7 \text{ mg}\cdot\text{L}^{-1}$ ) accurately weighed are introduced into 5 Erlenmeyer flasks of

2.5 L. Each flask was filled with 2 L of working solution at a fixed initial concentration, sealed, covered with aluminium foil (to avoid photodegradation reaction during the experiment) and magnetically stirred for 7 days to reach the adsorption equilibrium. The experiments were conducted at 25°C and without pH adjustment. After the equilibrium was reached the liquid phase residual concentrations were measured by liquid chromatography (HPLC) and the amount of adsorbed BPA was deducted from the mass balance. Randtke and Snoeyink (1983) provide many details on the conduct of the isotherms. For each test, blank included to determine the initial target compound concentration. All experiments were done in duplicates.

### ***Analytical method***

The concentration of BPA was determined by high performance liquid chromatography (HPLC) with a reverse phase partition column. It was performed on a Waters® Alliance 2695 system configured with a Waters® Scanning Fluorescence Detector 474 at an excitation wavelength of 280 nm and an emission wavelength of 310 nm. Indeed, most of the EDCs are amendable to fluorescence detection based on the fact that most of EDCs contain aromatic moieties.

Separation of the target compound was carried out with a Waters® C<sub>18</sub> BEH X-Bridge column (250 x 4.6 mm d.i., dp = 5 µm). The analysis was done under isocratic conditions. The used mobile phase composition was: 55% of 10 mM H<sub>3</sub>PO<sub>4</sub> solution and 45% of acetonitrile. The run time was of 10 min, the flow rate of 1 mL·min<sup>-1</sup> and the injection volume was maintained at 50 µL. The calibration was obtained from the analysis of BPA standard solutions (5-250 µg·L<sup>-1</sup>).

### ***Theoretical aspects on mass transfer***

#### *Hypothesis of external mass transfer as limiting factor: $k_f$ determination.*

In order to quantify and compare the adsorption efficiencies of the selected activated carbons the characteristic coefficients of the adsorption kinetics were determined. Thus, in order to characterise the adsorption kinetics of a given compound with a given activated carbon in the hydrodynamic conditions external mass transfer ( $k_f$ ) and surface diffusion coefficients ( $D_s$ ) were calculated. ( $k_f$ ) is generally estimated by semi-empirical equations and its value is conditioned by the particle size and not by the nature of porosity of the adsorbent. On the contrary, ( $D_s$ ) depend on the nature of the activated carbon, its structure and preparation method but also on the nature and size of the adsorbed molecule.

Considering mass transfer as a dominant mechanism, these coefficients were calculated separately. These hypotheses were verified by using the dimensionless Biot's number.

If the activated carbon particles are considered as being spherical and the material flow at the surface of the grain as being continuous, the mass transfer equation of solute ( $i$ ) from the liquid phase to the solid one can be expressed by Eq. (1), where: ( $C_s$ ) is function of  $q(t)$  (at  $t = 0$ ,  $C_s = 0$ ), ( $R_p$ ) is the radius of the coal particle and ( $\rho_p$ ) is the dried activated carbon density.

$$\frac{dq(t)}{dt} = \frac{3k_f}{R_p \rho_p} (C - C_s) \quad (1)$$

The batch stirred reactor commonly referred as “batch” reactor is characterised by a lack of input and output flows. Assuming that before all experience the initial charge of a solute is zero within the activated carbon, the balance equation of the batch reactor liquid phase is according to Eq. (2) (production = accumulation).

$$C_0 - C_b(t) = Wq_i(t) \quad (2)$$

As a result, Eq. (3) can be deduced:

$$\frac{dC_b(t)}{dt} = -W \frac{dq(t)}{dt} \quad (3)$$

at  $t = 0$ ,  $C_b(t) = C_0$  and  $q(t) = 0$

Considering the concentration  $C_{si}$  zero in the first moments of the kinetics, it is possible to determine the coefficient  $k_f$  by Eq. (4), where ( $W$ ) is the adsorbent concentration in the reactor. The equation can be applied when  $t$  tends to 0.

$$\left. \frac{dC_b(t)}{dt} \right|_{t=0} = -W \frac{3k_f}{R_p \rho_p} C \quad (4)$$

*Hypothesis of surface diffusion coefficient as limiting factor:  $D_s$  determination.*  
The determination of surface diffusion coefficient  $D_s$  can rely on the relation developed by Crank (1956) which can be applied to discontinuous batch reactors (i.e. the concentration of the solute in the solution decreases during adsorption), according to Eq. (5), where ( $P_n$ ) is given by the non-zero roots of Eq. (6), with

$$E = \frac{C_0 - C_e}{C_0}$$

$$\frac{q(t)}{q_e} = 1 - 6 \sum_{n=1}^{\infty} \frac{\exp(-D_s P_n^2 \frac{t}{R_p^2})}{9 \frac{E}{(1-E)} + (1-E) P_n^2} \quad (5)$$

$$\tan P_n = \frac{3P_n}{3 + (\frac{1}{E} - 1)P_n^2} \quad (6)$$

Once both coefficients were determined, the calculation of the dimensionless Biot number will allow the establishing of the dominant mechanism of solute adsorption on activated carbon. The Biot number is defined by Eq. (7), where ( $q_0$ ) is the adsorption capacity for  $C_e = C_0$

$$Biot = \frac{k_f R_p C_0}{D_s \rho_p q_0} \quad (7)$$

Traegner and Suidan (1989) identified several typical cases:

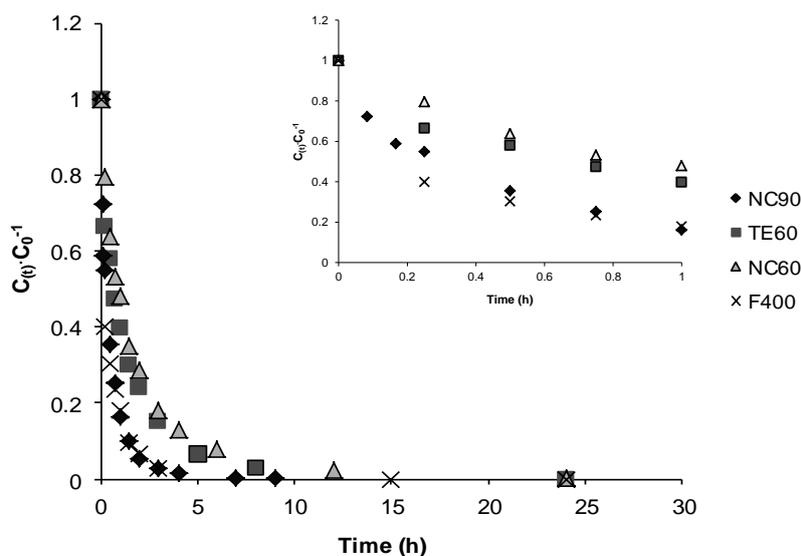
- Biot  $\ll 1$ , the external mass transfer is the dominant mechanism and only  $k_f$  value is significant;
- Biot  $\gg 100$ , the surface diffusion is the dominant mechanism and only  $D_s$  value is significant;
- $1 \leq Biot \leq 100$ , both mechanisms are important:  $D_s$  and  $k_f$  values are significant.

## Results and discussion

### *Investigation of the adsorption performance*

Four different activated carbons named F400, TE60, NC60, NC90 commonly used in the drinking water treatment were selected and investigated in this work in order to determine their capability to remove the target pollutant from water but also to find the minimum contact time for the experiments. For this purpose, a series of bisphenol kinetic adsorption experiments were performed on each activated carbon in order to select the most efficient adsorbent. The experimental

protocol used in these experiments was quite similar to the one of adsorption isotherms. Here only two conical flasks were used. The first one served as control sample while in the second one, the kinetics of the pollutant adsorption on activated carbon was followed for 24 h. Aliquots were taken at different time intervals and analysed by HPLC-Fluo for the residual pollutant concentration monitoring.



**Fig. 1.** Normalised concentration profiles of bisphenol A (initial concentration of  $100 \mu\text{g}\cdot\text{L}^{-1}$ ) onto various activated carbons (PAC dose  $50 \text{mg}\cdot\text{L}^{-1}$ )

The kinetic study was carried out by adding  $50 \text{mg}\cdot\text{L}^{-1}$  of PAC to a solution of bisphenol of  $100 \mu\text{g}\cdot\text{L}^{-1}$ . Figure 1 shows the obtained the normalised concentrations profiles versus time for bisphenol A with the tested adsorbents. It was observed that the target compound was more quickly adsorbed onto F400 and NC90 carbons with an apparent equilibrium reached after 4 days. For the other adsorbents the adsorption equilibrium was essentially obtained after 10 days.

Moreover, as stated before in order to quantify and compare the adsorption efficiencies of the selected activated carbons the mass transfer characteristic adsorption coefficients were also determined for each compound-activated carbon couple.

#### *Calculation of external mass transfer coefficient $k_f$*

It is well-known that the external mass transfer describes the geometry of the activated carbon grains and the hydrodynamics in which the adsorption takes place. It allows understanding how the solute reaches the liquid film bonded to the

adsorbent. This coefficient has a significant value at the beginning of the adsorption kinetics but it is less correlated to the specific adsorption properties of a given carbon. However, if the external mass transfer is the dominant phenomenon in kinetics, the four activated carbons will be classified with respect to this coefficient.

The calculation is done from the tangent between the first kinetics two points (between  $t = 0$  and  $t = 0.25$  h). The external mass transfer coefficients calculated for the four activated carbons are summarised in Table 3.

**Table 3.** Estimated external mass transfer coefficients of bisphenol A onto the investigated adsorbents

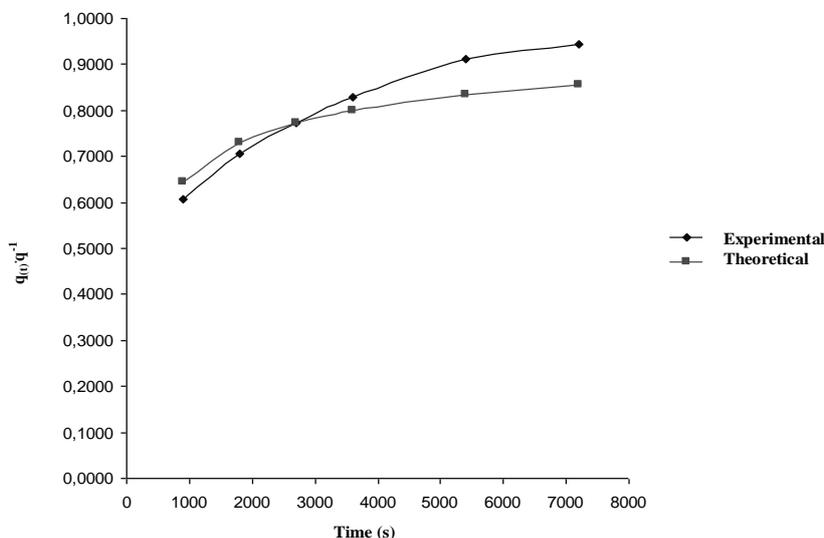
	<i>NC90</i>	<i>TE60</i>	<i>NC60</i>	<i>F400</i>
$k_f$	0.94E-01	0.81E-01	0.48E-01	1.33E-01

The results summarised in Table 3 show clearly that the F400 carbon has the most important external mass transfer coefficient.

*Calculation of surface diffusion coefficient  $D_s$ .*

As mentioned above, the surface diffusion coefficient ( $D_s$ ) explains the phenomenon occurring just after a molecule is adsorbed on a support. The molecule diffuses to activated carbon surface in the adsorbed state until it fixes on a site. The compound distribution can be correlated to the adsorbent nature. In this case, the geometry of the activated carbon particles and the system hydrodynamics does not influence the coefficient.

$D_s$  coefficient was calculated as the optimised average value allowing to minimise the difference between the theoretical ratio  $q(t)/q_e$  and the experimental one.  $q(t)$  and  $q_e$  are the adsorbate amount adsorbed per unit of mass adsorbent at time  $t$  and at equilibrium. When the experimental data and the theoretical ones are in good agreement (error is minimal) the  $D_s$  value is accepted. Figure 2 shows the obtained curves for bisphenol A/F400 system.



**Fig. 2.** Representations of the theoretical and experimental profile of  $q(t)/q_e$  for bisphenol A/F400 system

The other experimental data of adsorption of BPA onto the considered adsorbents were treated in the same manner. Table 4 lists the identified  $D_s$  values of BPA for the four investigated activated carbons.

**Table 4.** Surface diffusion coefficients  $D_s$  of bisphenol A on different activated carbons

	<i>NC90</i>	<i>TE60</i>	<i>NC60</i>	<i>F400</i>
$D_s$	2.57E-13	0.56E-13	0.34E-13	3.31E-13

As for the external mass transfer coefficient, the obtained data clearly indicates that the activated carbon F400 has the best coefficient of surface diffusion. Thus, this adsorbent allows a better diffusion of BPA in its pores. This can be mainly due to its larger pore volume as indicated previously by Choi et al. (2005).

*Biot number estimation*

The Biot number is proportional to  $q_0^{-1}$ .  $q_0$  value is determined using the equation relating  $q_e$  to  $C_e$  following different models. For a given model, the constants of the equation are determined experimentally. In this study, only the parameters of bisphenol A adsorption on F400 activated carbon have been established. The calculated Biot number is presented in Table 5. Its value, well

above 100, allows us to consider that the surface diffusion phenomenon is dominant in the kinetics of adsorption of bisphenol A.

**Table 5.** Biot number calculated for bisphenol A on F400 activated carbon

	<b>F400</b>
Biot number	1.08E+03

Given the fact that  $D_s$  and  $k_f$  values obtained for bisphenol A on the other three activated carbons were similar to those obtained for F400, we can assume that the Biot number will be also similar. Consequently, the surface diffusion can be also considered as dominant phenomenon. The adsorption isotherms will allow us to calculate other values of the Biot number and to confirm this hypothesis.

Based on the obtained value of  $D_s$  for the activated carbon F400 it can be supposed that this adsorbent allows a better diffusion of solute in its pores. In addition, as previously determined this adsorbent has the best characteristics in terms of adsorption kinetics. Therefore, taking into account these results F400 was selected for further BPA adsorption studies.

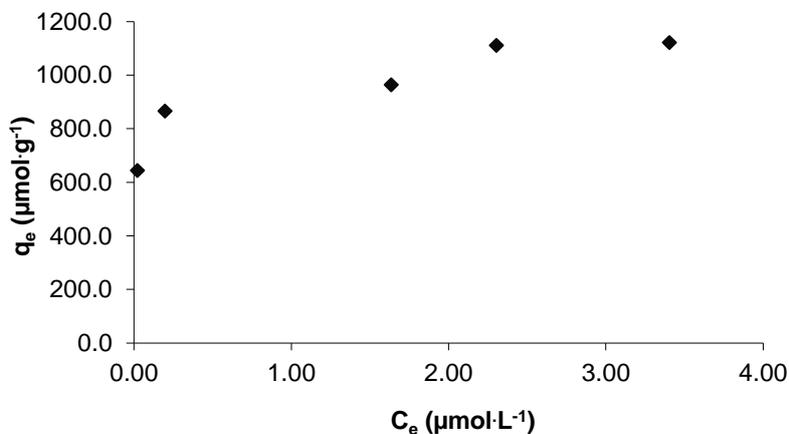
#### ***Adsorption isotherms of BPA***

After selecting the activated carbon, various tests were carried out in order to determine the initial concentration at equilibrium.

The experimental values of the equilibrium concentration ( $C_e$ ) obtained for each BPA/activated carbon system serve to determine the corresponding BPA amount adsorbed via the mass balance, expressed by Eq. (8), where:  $C_0$  and  $C_t$  ( $\text{mgL}^{-1}$ ) are the liquid phase concentrations in BPA at time 0 and  $t$ , respectively.  $V$  (L) is the volume of solution and  $W$  (g) the adsorbent weight.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (8)$$

Figure 3 presents the adsorption capacity at equilibrium expressed in  $\mu\text{mol}\cdot\text{g}^{-1}$  depending on the concentration in the liquid phase for the activated carbon F400.



**Fig. 3.** Adsorption isotherm for bisphenol A over the activated carbon F400

$q_m$  value gives indications on the optimal adsorption potential of activated carbon when all adsorption sites are occupied by bisphenol A. It can be seen that the adsorption capacity of F400 increased with increasing BPA equilibrium concentration. Moreover, the isotherm shape tends towards an experimental asymptote.

Generally, adsorption isotherms describe the interaction between an adsorbate and an adsorbent when the adsorption process reaches equilibrium. Thus, it is of practical importance to determine the most appropriate methods allowing the analysis of experimental equilibrium results. Adsorption isotherm models are used to characterise such interactions. Indeed, the linearization of this isotherm according to a known model allows us to obtain the characteristic parameters for the considered coal/solute system. These settings will be used to evaluate the considered system.

In this work, two isotherms equations, Langmuir and Freundlich models were employed in order to analyse the isotherm experimental data and to select the most appropriate one for this work. Indeed, these ones are the most used in water treatment applications for describing the adsorption characteristic of carbons (Kumar and Sivanesan, 2005).

The Langmuir model assumes a monolayer adsorption onto the adsorbent surface which consists of a finite number of active sites with a uniform energy (Tan et al., 2007; Hasan et al., 2012) while, the Freundlich model is an empirical equation based on multilayer adsorption on heterogeneous surfaces (Equation 10). The Langmuir isotherm is described by Eq. (9), where  $q_e$  is the adsorbed BPA amount per gram of adsorbent,  $C_e$  is the equilibrium concentration of BPA,  $b$  is

the Langmuir constant, related to the affinity of binding sites and  $q_m$  is the maximum adsorption capacity (saturation capacity) of the considered compound on the adsorbent at the isotherm temperature.

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (9)$$

The Freundlich model is given by Eq. (10), in which  $K$  and  $n$  are the Freundlich constants.

$$q_e = K C_e^{1/n} \quad (10)$$

The parameters of these mathematical equations can be identified using their linear forms. Thus, linear regression analysis of isotherm data using the linearized forms of these equations was done firstly. For the Langmuir model two linear forms are frequently used to describe the adsorption of an organic compound in water (Ho, 2004; Kumar and Sivanesan, 2005) expressed by Eqs. (11, 12).

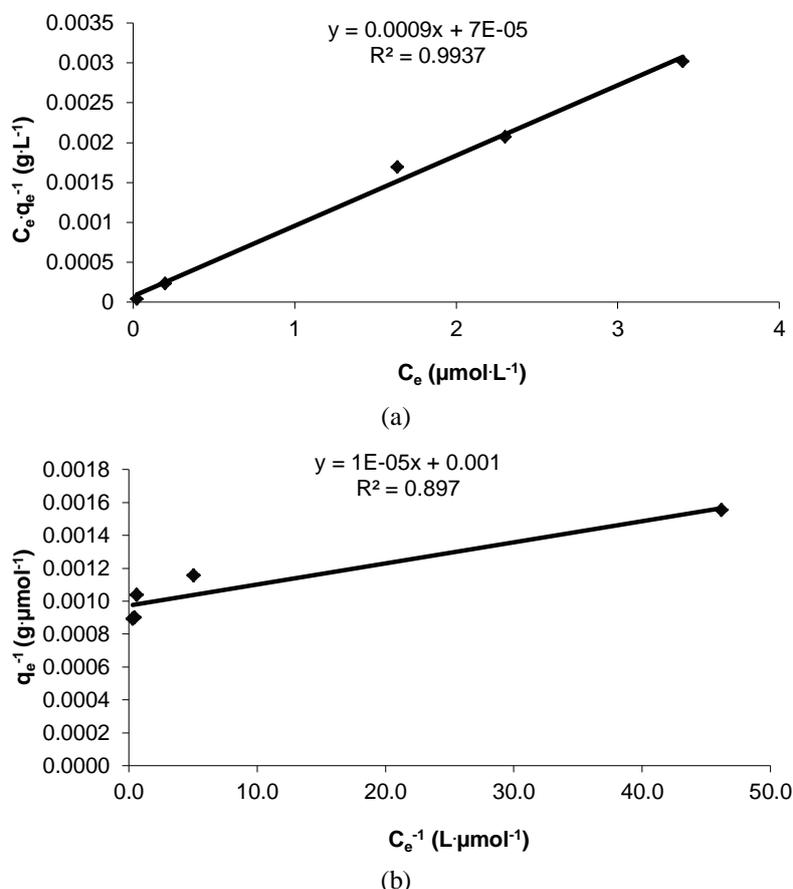
$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} = a' + b'C_e \quad (11)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} \cdot \frac{1}{C_e} \quad (12)$$

The linear form of the Freundlich model is according to Eq. (13).

$$\ln(q_e) = \ln(K) + \frac{1}{n} \ln(C_e) \quad (13)$$

Thus, it is possible to determine the corresponding isotherm parameters. The values found for the maximum adsorption capacity for the activated carbon F400 and the Langmuir constant were  $q_m = 1133.7 \mu\text{mol}\cdot\text{g}^{-1}$  and  $b = 11.8 \text{ L}\cdot\mu\text{mol}^{-1}$ , respectively.

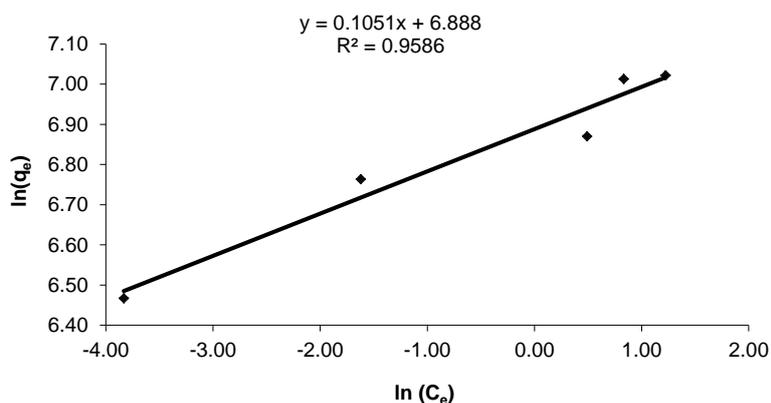


**Fig. 4.** Langmuir linearization according to equations 11 (a) and 12 (b)

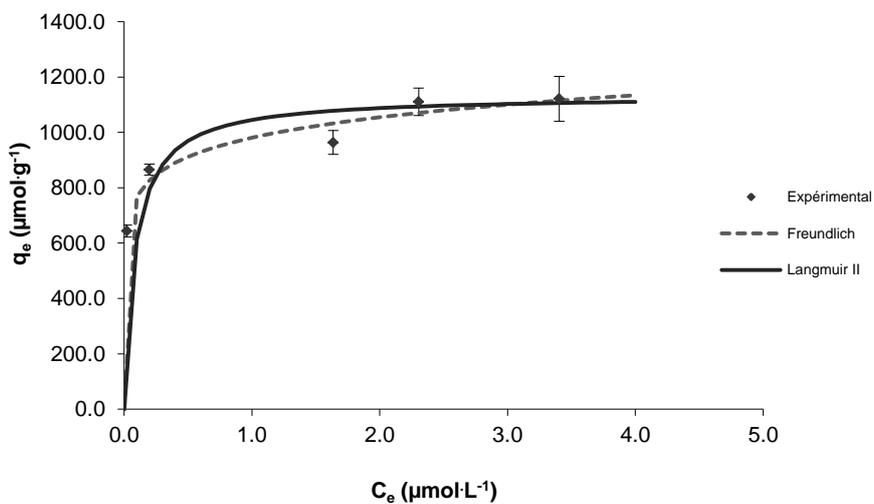
Figure 5 shows the linearization of the adsorption isotherm of BPA onto the activated carbon F400 using the Freundlich model. The process leads to a linear regression with a good correlation coefficient ( $R^2 = 0.9588$ ). The obtained  $K$  and  $n$  parameters offer indications for the affinity between the activated carbon and the bisphenol A and for the interaction energy occurring between the adsorbate molecule and the inner surface of the pore, respectively.

Figure 6 shows the Langmuir II and Freundlich experimental and theoretical isotherms.  $q_e$  parity diagrams for both models presented below show that the Freundlich model is more similar to the obtained experimental results (Figure 7). Even though the Langmuir linearization (Eq. 11) has a higher correlation coefficient, it seems that Freundlich model describes more accurately the adsorption of bisphenol A on F400 activated carbon. In other words, for this study

it can be considered that the adsorption of BPA by F400 took place in a multilayer adsorption manner.



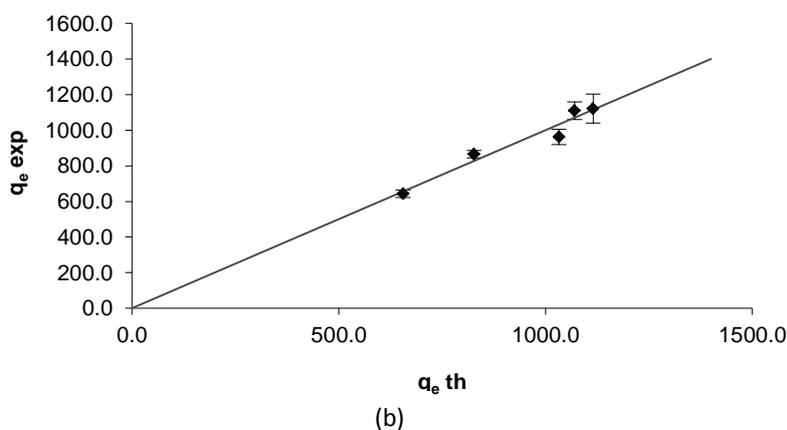
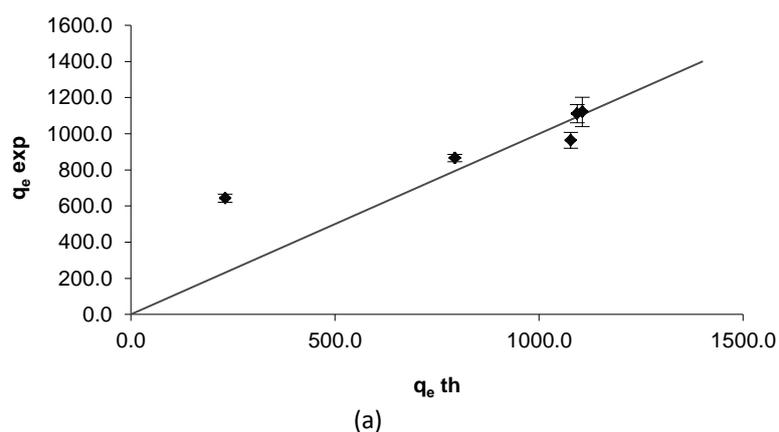
**Fig. 5.** Linearization of Freundlich adsorption isotherm of bisphenol A onto the activated carbon F400



**Fig. 6.** Freundlich and Langmuir fits of experimental data for bisphenol A adsorption onto the activated carbon F400

*Discussion of adsorption parameters determined with the Freundlich model*

Table 6 shows the Freundlich isotherm parameters for bisphenol A adsorption on F400 activated carbon. The calculated  $K$  value confirms the high adsorption capacity of the used adsorbent with microporous structure.



**Fig. 7.**  $q_e$  parity diagrams of Langmuir (a) and Freundlich (b) models

The high value of  $n$  parameter shows that the energy distribution of the adsorption sites of the F400 is heterogeneous and that the density of the high energy sites is important. As a consequence, it can be supposed that the activated carbon F400 will be very efficient for very low pollutant concentrations. Indeed, for very dilute solutions, a previous study carried out on pesticides reported that

the molecules adsorption occurs firstly on the most high-energy sites (Abiven, 2002).

**Table 6.** Parameter values calculated for the Freundlich model

<i>F400</i>	
<i>K</i>	980.5 ( $\mu\text{mol}\cdot\text{g}^{-1})(\mu\text{mol}\cdot\text{L}^{-1})^{-1/n}$
<i>n</i>	9.52

In 2002, Abiven reports *K* values for the adsorption of pesticides from pure water on F400 activated carbon powder ranging from 821.8 to 1201.5 ( $\mu\text{mol}\cdot\text{g}^{-1})(\mu\text{mol}\cdot\text{L}^{-1})^{-1/n}$ . The initial pesticides concentration was of 600  $\mu\text{g}\cdot\text{L}^{-1}$  and the activated carbon powder doses were between 2 and 8  $\text{mg}\cdot\text{L}^{-1}$ , respectively. The values obtained for *n* ranged from 3.44 to 5.07. For three of the pesticides on which Abiven worked in his study, the parameter *K* has higher values compared to those obtained in our study. This observation can be explained by the fact that bisphenol A is at least two times more soluble in water than the three pesticides which will therefore be more likely adsorbed on the activated carbon.

Tsai et al. studied in 2006 the adsorption of bisphenol A on two activated carbons: one based on coconut (PCB) and one based on coal (BPL) with a surface area slightly smaller than F400 (916  $\text{m}^2\cdot\text{g}^{-1}$  and 1060  $\text{m}^2\cdot\text{g}^{-1}$ , respectively). They modelled Langmuir and Freundlich isotherms. For a bisphenol A concentration of 60 to 100  $\text{mg}\cdot\text{L}^{-1}$  and a carbon level of 0.25  $\text{g}\cdot\text{L}^{-1}$ , Freundlich parameters are those shown in Table 7.

**Table 7.** Freundlich coefficients for bisphenol A obtained by Tsai et al. (2006)

	<i>K</i> ( $\mu\text{mol}\cdot\text{g}^{-1})(\mu\text{mol}\cdot\text{L}^{-1})^{-1/n}$	<i>n</i>
BPL	811.7	7.1
PCB	904.1	13.9

*K* and *n* values obtained in our study are consistent with those reported by Tsai et al. (2006) especially with those registered for BPL coal which has the same origin as the F400 activated carbon. However, the *K* value slightly inferior to ours might be explained by the fact that BPL coal has a slightly smaller specific surface area, resulting in a diminished adsorption capability. The same can be inferred for the PCB coal. However, in this case *n* has a value much higher than in our study. The activated carbon PCB being of different origins, this difference could be explained by the higher proportion of pores whose size is close to that of bisphenol A or by the different surface functions generating more connection points in the pores.

## Conclusions

The aqueous adsorption of bisphenol A, a representative molecule of the endocrine disruptors group, under conditions similar to the environmental ones was investigated in this work using low cost adsorbents. As stated before an efficient removal of such a molecule is of environmental importance taking into account its harmful effect.

The adsorption capacities of several activated carbons, commonly used in the drinking water treatment, were studied at laboratory level in detail based on adsorption kinetics and mass transfer considerations. The obtained data showed clearly that the activated carbon F400 is the most efficient one.

Moreover, the exploitation of experimental results of the adsorption isotherm was used to characterise the selected system coal/pollutant in the non-competitive conditions. The adsorption results obtained in pure water were interpreted according to the parameters  $K$  and  $n$  of the Freundlich model. The calculated value of parameter  $n$ , suggested that bisphenol A develops a great heterogeneity of interaction energies with the activated carbon F400, with a significant fraction of high-energy sites. The obtained parameter  $K$  gives us an idea of the adsorption capacity of the activated carbon and further to quantify the natural organic matter competitive effect for the tests that will be conducted in the near future, in natural water.

The obtained results are interesting and clearly suggested the feasibility of the use of low-cost adsorbents (especially powdered activated carbons) for the removal of BPA from drinking water.

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