Abstract

Adsorption of two widespread emerging water contaminants (atrazine and paracetamol) onto three different activated carbons was investigated. The carbons were characterized and the influence of their physicochemical properties on the adsorption performance of atrazine and paracetamol was evaluated. The adsorption equilibrium data were fitted to different adsorption isotherm models (Langmuir, Freundlich, and Dubinin-Radushkevich) while the adsorption rates were described using three different kinetic models (pseudo second order, intraparticle diffusion and a new approach based on diffusion-reaction models). The results indicated that hydrophobic character of the compounds does not affect the sorption capacity of the tested carbons but does influence the uptake rate. The model proposed, based on mass balances, lead to interpret and compare the kinetic of different adsorbents in contrast to classical empirical models. The model is a simple and powerful tool able to satisfactorily estimate the sorption capacities and kinetics of the carbons under different operation conditions by means of only two parameters with physical meaning. All the carbons studied adsorbed paracetamol more effectively than atrazine, possibly due to the fact that sorption takes place by H-bonding interactions.

Keywords: adsorption, paracetamol, atrazine, kinetics, diffusion model, sludge activated carbon

Introduction

The emission of so-called “emerging contaminants” has arisen recently as an environmental problem. This group is mainly composed of compounds used in large quantities in everyday life, such as human and veterinary pharmaceuticals, personal care products, surfactants, pesticides and different industrial additives. Removal of some emerging contaminants in wastewater treatment plants (WWTP) was found to be rather low due to the fact that most of them are resistant to biological degradation. Consequently sewage effluents are one of the main sources of these compounds and their metabolites, which can potentially end up in finished drinking water (Petrovic et al. 2003; de Ridder et al. 2010).

One effective way to eliminate these recalcitrant compounds could be to introduce an adsorption step before dumping WWTP effluents. Activated carbons are widely used to adsorb organic substances from gases or liquids. They are commonly obtained from various organic precursors such as bituminous coal, peat, wood, coconut shell (Marsh and Rodriguez-Reinoso, 2006). In recent years, there has been a growing interest in converting organic waste materials with high carbon content into activated carbon (Schröder et al. 2011). Sludge is waste material produced in large volumes in the sewage treatment plants.

It can be recycled by composting and used in agricultural land, incinerated or used in landfills. Nowadays, new environmentally benign alternatives for this residue are being sought. In this sense, sewage sludge has been investigated as an attractive precursor for activated carbon production (Smith et al. 2009).

The adsorption capacity of an activated carbon depends on its physic-chemical characteristics (e.g. surface area, pore size, functional groups,..) and the nature of the adsorbate (e.g. molecular weight and size, hydrophobicity, polarity, functional groups (Mohamed et al. 2011). In the literature, several solute properties that influence organic solute adsorption onto activated carbon have been discussed. Some authors have tried to directly relate octanol–water coefficient (Kow) to adsorption capacity (De Ridder et al. 2010). A good relation between this property and adsorption was found for most of the hydrophobic contaminants onto activated carbons. However, a poor correlation was shown when the solutes were small and hydrophilic (Westerhoff et al., 2005) or when they were aromatic compounds (Chen et al., 2007). In the case of aromatic compounds several authors have suggested that they can be adsorbed on activated carbons by dispersion interactions between the π-electrons of the aromatic ring and those of the graphene layers (Li et al., 2009). Functionalization of either the adsorbent or the adsorbate profoundly affects these dispersion interactions. On the other hand, if the aromatic compounds have hydrogen-bonding functional groups, hydrogen bonding can contribute to the compound adsorption. (Moreno- Castilla 2004, Terzyk 2000). However, the specific mechanisms, through which adsorption of aromatic compounds occur are still not well established.

In this work, we study the adsorption of two widespread water emerging contaminants, atrazine (1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)) and paracetamol (N-acetyl-p-aminophenol) onto different activated carbons prepared from various raw materials: a bituminous coal, a lignite and sewage sludge. To understand interactions between the sorbents and the target contaminants, the texture and chemical properties of active carbons were characterized. This research aims to provide new information for a better understanding of the factors and the mechanism involved in the adsorption process. Moreover, a new kinetic model, based on mass balances and description of transfer processes, has been proposed to describe with physical interpretation the sorption kinetic, overcoming the limitation of classic kinetic empirical models.

Material and Methods

Adsorbates

The adsorbates used were a pesticide, atrazine (Sigma-Aldrich, Germany) and a pharmaceutical, paracetamol (Fagron, Spain). Table 1 shows physico-chemical properties of these two compounds.

Paracetamol stock solution (200 mg/L) was prepared with ultra-pure water (Milli-Q). Atrazine stock solution (1000 mg/L) was prepared with acetone (Scharlau, Spain). From these solutions, samples for calibration and sorption experiments were obtained by dilution.

Adsorbents

Three activated carbons were evaluated. Two of them were commercial activated carbons. Filtrasorb-400 (F-400) was supplied by Chemviron (Belgium) and obtained from a bituminous coal. Norit PK 1-3 (NPK) was produced from peat by Norit Americas Inc. (USA). The third carbon was a sludge-based activated carbon-like material (SBC) prepared from sludge from WWTP through the methodology described by Smith and Fowler (2011).

Textural and chemical carbons characterization methods

The texture of the three carbons was characterized by N_2 adsorption isotherm at -196 ºC, in a conventional volumetric apparatus (ASAP 2420 from Micrometics). Before each experiment, the samples were outgassed under vacuum at 120ºC overnight to remove any adsorbed moisture and/or gases. The N_2 isotherms were used to calculate the specific surface area (S_{BET}), total pore volume, (V_{TOT}), at a relative pressure of 0.95, and pore size distribution. The pore size distribution (PSD) was evaluated using the density functional theory (DFT), assuming slit-shape pore geometry.

The carbons were further characterized for their elemental analysis using a LECO CHN-2000 and a LECO Sulphur Determination S-144-DR. The ash content and humidity were determined according to the methods described in ISO 1171 and ISO 5068.

FTIR technique was applied in order to determine the main functional groups on the surface carbons. For this purpose spectra were determined between 4000 and 400 cm^{-1} using an FTIR spectroscope (Spectrum 65 FT-IR, PerkinElmer).

Adsorption assays

For kinetics studies, 50 mg of adsorbent were added to 250 mL of 40 mg/L atrazine or paracetamol solutions. Mixtures were stirred at 25ºC in a multipoint agitation plate. At different times (from 1 to 48 hours), samples were taken and filtered through a cellulose acetate filter (0.2 μm diameter pore) and the remaining concentrations were analyzed in a UV/Vis spectrophotometer (Lambda 25 PerkinElmer) at 242 nm for paracetamol and 224.9 nm for atrazine. The detection limit for paracetamol was 144 ppb and for atrazine 220 ppb. The paracetamol and atrazine uptake (q_t) was calculated by:

$$q_t = \frac{(C_0 - C_t)\,V}{W} \qquad (1)$$

Where q_t is the amount (mg/g) of atrazine or paracetamol adsorbed at time t, C_0 is the initial concentration (mg/L), C_t is the concentration at time t (mg/L), V is the volume (L) of the adsorbate solution and W is the weight (g) of carbon used.

Equilibrium adsorption studies were made at 25ºC varying the atrazine or paracetamol concentration (1-150 mg/L). The remaining atrazine and paracetamol concentrations after equilibrium time were determined as described above and the uptake was calculated using Eq. (1).

Adsorption modeling

Isotherms experimental data were fitted to two-parameter isotherm models: Langmuir (Eq.2), Freundlich (Eq.3) and Dubinin-Radushkevich (DR) (Eq. 4,5 and 6)

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (2)$$

$$q_e = K_f {C_e}^{1/n} \qquad (3)$$

$$ln\ q_e = ln\ q_{max} - \beta \mathcal{E}^2 \qquad (4)$$

$$\mathcal{E} = RT\ ln\ (1 + 1/C_e) \qquad (5)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

Where q_e (mg/g) is the amount of compound adsorbed per mass unit of activated carbon, C_e (mg/L) is the organic compound concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, K_L (L/mg) is a constant related to the affinity between the pollutant and the adsorbent, K_f ((mg/g) (L/mg) $^{1/n}$) is the Freundlich sorption constant and "n" is a constant related to adsorption intensity. $\mathcal{E}$ is the Polanyi potential, R is the gas universal constant (J/(molK)), T is temperature (K) and β is a constant related to free energy (E) of adsorption (J/mol) of the adsorbate.

Kinetic modeling in sorption processes has been described for different approaches (Clark 1987; Wolborska 1989; Yan et al. 2001, Ho et al 1998). In the present work, the different kinetic models such as pseudo-second order (Eq. 7), intraparticle diffusion (Eq. 8), and the diffusion-adsorption model were used to describe the non-equilibrium stage of adsorption.

$$\frac{\partial q_t}{\partial t} = k_2 (q_e - q_t)^2 \quad (7)$$

$$q_t = k_p t^{0.5} + A \quad (8)$$

Where k_2 (L/(mg min)) is the rate constant, k_p is the intraparticle rate constant (mg/(L·min$^{0.5}$)) and A is the intercept (mg/L).

The diffusion-adsorption model is based on the well-known diffusion-reaction mathematical model (Cultip and Shacham, 2008) which has been successfully used in a wide range of chemical engineering related systems (Dorado et al. 2014). The model proposed is based on the following assumptions:

1.-Isothermal conditions across the batch system and over time.

2.-Planar geometry and perpendicular diffusion through the solid are used to derive to the model equations.

3.-The aqueous-solid interface resistance is negligible.

4.-Aqueous-solid interface equilibrium is described by Langmuir's isotherm, according to previous results (Tab. 4).

5.-There is a maximum penetration depth for the pollutant into the solid phase.

Isothermal conditions are needed to define the isotherm equilibrium and they are ensured by means of controlled room temperature. Planar geometry only influences in the coordinate system used for solving the differential equations. The assumption that interface resistance is negligible is consistent with the operation conditions used in the experimental work since an optimal stirring was ensured. Finally, the concept of maximum penetration is employed for comparing the behavior of the system under different conditions and the boundary set is in concordance with the size of the particles.

According to the above specifications, the mass balance in the liquid phase can be formulated as:

$$\frac{\partial C_t}{\partial t} = -\frac{D * a_s}{\mathcal{E}_D}\left(\frac{\partial C_s}{\partial x}\right)\Big|_{x=0} \qquad (9)$$

for the initial conditions: t=0, $C_t = C_0$

Where D is the diffusion coefficient (m^2/min), $a_s$is the effective specific surface area (m^2/m^3), $\mathcal{E}_D$ is the fraction of liquid in the total volume, C_s and C_t (mg/L) are organic compound concentrations in the solid and liquid phases, respectively and x is the depth from the sorbent material surface (m).

The mass balance in the solid phase is described by the following equation (10)

$$\frac{\partial C_s}{\partial t} = -D\left(\frac{\partial^2 C_s}{\partial x^2}\right) \qquad (10)$$

With the following boundary conditions:

$$at\ x = 0, \qquad C_s = \frac{q_{max} k_L C_e}{1 + k_L C_e} \qquad (11)$$

$$at\ x = \delta, \qquad \frac{\partial C_s}{\partial x} = 0 \qquad (12)$$

Where δ is the maximum penetration depth for the pollutant into the solid phase (m), q_{max} and k_L are the Langmuir constants shown in Tab. 4. The set of partial differential equations was discretized in space in eight nodes along the sorbent thickness (Dorado et al. 2014).

The parameter estimation of the different isotherm and kinetic models were solved using MATLAB, minimizing the objective function (OF) given in the equation (13).

$$OF = \sqrt{\sum_{i=1}^{N} [q(P_1, P_2) - q^*]^2} \qquad (13)$$

Where N is the number of measurements realized, q* is the experimental solute uptake, q (P_1, P_2) is the predicted uptake by the model, P_1 and P_2 are the different estimated parameters. In the case of Langmuir, the parameters are q_{max} and K_L, for Freundlich K_f and n, for DR q_{max} and β, for second order k_2 and q_e, for intraparticle K_p and A and for the adsorption diffusion model D and a_s.

Results and discussion

Activated carbons characterization

The results of elemental analysis, ash and humidity of the three carbons (F-400, NPK and SBC) are listed in Table 2. Data shows that the elemental composition is similar for F-400 and NPK which have high carbon content (about 90%) and differs significantly from those of SBC, which has a carbon content of only 41%. On the other hand, SBC has the highest ash content. High ash content is a common feature of materials prepared from sewage sludge due to the chemical composition and mineral content of this precursor material (Lillo-Rodenas et al. 2008).

Carbons textural properties determined from N_2 adsorption isotherms data are summarized in Table 3. It can be seen that F-400 has the maximum S_{BET} (1234 m^2/g), approximately twice as high as those of NPK (782 m^2/g), whereas the BET surface area of SBC was, by far, the lowest (260 m^2/g). This low BET value of sludge based activated carbon could be attributed to the low carbon content and the high ashes content of their sludge precursor (Anfruns et al. 2011; Smith et al. 2009).

With regards to the adsorption isotherm results (Fig. 1), the F-400 carbon presents the largest nitrogen adsorption followed by the NPK carbon. The N_2 adsorption onto NPK and F-400 takes place, fundamentally, at low relative pressures which is typical of microporous materials. Their isotherms show a gradually upward increase from relative pressures above 0.2, indicating the presence of well-developed mesoporosity. Moreover these isotherms show a hysteresis loop, more important for NPK sample, which is associated to capillary condensation inside the mesopores. The adsorption isotherms present a type I-IV hybrid shape according to the BDDT classification, with a sharp knee at low relative pressures for NPK material suggesting that the microporosity of this sample is mainly composed of pores of a small

diameter. The broad knee present in the F-400 isotherm indicates that this carbon has micropore sizes greater than those assigned to NPK. The shapes of hysteresis loops have often been related to specific pore structures. In this respect, the shape of the loop in the nitrogen isotherms of the activated carbons is Type H4, according to the IUPAC nomenclature, which is often associated with narrow slit-like pores. On the other hand, the SBC material shows a small N_2 adsorption capacity with an incipient hysteresis loops. The isotherm belongs to Type I in the BDDT classification, with a clear sharp knee at low relative pressures indicating that the microporosity of this sample is mainly composed of pores of small diameter.

The total pore volume values (V_{TOT}) are shown in Table 3. The F-400 exhibits the highest V_{TOT} (0.615 cm^3/g) whereas the lowest was obtained for SBC (0.161 cm^3/g). The pore size distribution was calculated by means of the DFT method and the results are presented in Table 3 and the corresponding plots in Fig. 2. An intensive peak at the pore diameter range between 0.6 nm and 0.8 nm can be observed for F-400 and NPK carbons (Fig. 2) indicating the presence of narrow micropores or ultramicropores. This is confirmed by the value of ultramicropore volume obtained for these two carbons, ≈ 0.155 cm^3/g, (Table 3). Nevertheless, the contribution of medium-sized microporosity (0.7 nm-2 nm) is much more important in the F-400 activated carbon (0.221 cm^3/g) than in NPK carbon (0,064 cm^3/g). In contrast, the activated carbon obtained from sewage sludge presents a low value of both, ultramicropore volume (0.049 cm^3/g) and medium-size microporosity (0,023 cm^3/g).

Regarding mesoporosity, NPK presents the highest mesopore volume (0.120 cm^3/g) which is significantly higher than those of F-400 (0.077 cm^3/g) and SBC (0.049 cm^3/g) carbons.

The carbons were also characterized by infrared spectroscopy in order to get information about the main functional groups on the carbons surface. The three IR spectra exhibit a similar profile as can be seen in Fig. 3. However, there are some significant differences among them. In regards to the common bands, the broad band in the 3500-3200 cm^{-1} region due to O-H stretching vibration can be seen. This band appears in all three recorded spectra, but it is considerably more intense in F-400 and NPK than in SBC. This hydroxyl function could belong to an alcohol, phenol or carboxylic group. However, for F-400 spectra, the absence of a peak at approximately 1750-1680 cm^{-1} characteristic of C=O stretching vibrations rules out the presence of carboxylic group. In contrast, NPK and SBC spectra show a weak band at 1741 cm^{-1} that indicates the presence of carbonyl function.

The two closest and acute bands at 2925 and 2853 cm^{-1} also appear in the three spectra and correspond to asymmetric and symmetric C-H stretching vibrations of aliphatic groups, $-CH_3$ and $–CH_2-$. These bands are more intense in the two commercial activated carbons than in the SBC. Their corresponding bending vibrations are observed between 1470 and 1380 cm^{-1}. The overlapped bands at the 1585-1650 cm^{-1} region, also common for the three carbons, are due to C=C stretching vibrations in sp^2 hybridized carbons in polyaromatics rings. This band is substantially stronger in F-400 activated carbon than in NPK and exhibits a very low intensity in SBC. An important point of difference between the two commercial activated carbons and SBC appears at 1000-1111 cm^{-1} region cm^{-1}. This strong band, only present in SCB activated carbon spectra, could be attributed to Si-O stretching vibration of mineral matter contained in the carbon (silicates). This result is in agreement with the high ash content found in SCB activated carbon.

Adsorption isotherms

Adsorption isotherms for atrazine and paracetamol sorption on F-400, NPK and SBC activated carbons are shown in Fig. 4. According to their initial slopes, the NPK and SBC isotherms can be classified as L-type, whereas the F-400 isotherm is H-type according to Giles' classification (Giles et al. 1974a,b). This suggests that F-400 has a high affinity for atrazine and paracetamol.

The experimental data were fitted to two-parameter isotherms (Langmuir, Freundlich and Dubinin-Radushkevich). The constants obtained from these three models and the objective function (OF) values are listed in Table 4. According to the OF values, the Langmuir equation provides a better description of the atrazine and paracetamol adsorption onto F-400 and SBC activated carbons, while the Freundlich model explains better the adsorption of these compounds on NPK. DR isotherm shows a lower fitting (higher values of OF) for all the studied cases, indicating this model does not offer a satisfactory description of the experimental behavior. As can be seen from Fig. 4, the NPK experimental isotherm presents two steps: a first step with a short plateau, followed by an increase in the amount of the micropollutant adsorbed and then, a second plateau. This profile, which is more pronounced for atrazine sorption, could be related to the higher mesoporosity of NPK carbon. Konda et al. (2002) showed that the sorption behavior of some organic pesticides on soil could be described by a two-step isotherm and they pointed out that this shape might represent the occurrence of a different type of adsorption mechanism.

F-400 exhibits the highest adsorption capacities (q_{max}) for the two adsorbates (Table 4). Moreover, the higher value of K_L for F-400 compared to those of NPK and SBC indicates that F-400 has a greater affinity for the two contaminants. The different behaviors of the three carbons can be attributed not only to their different surface area but also to their different size pore distribution, functional groups and mineral matter content (Moreno-Castilla 2004; Haydar et al. 2003).

To assess the influence of pore size distribution on atrazine and paracetamol adsorption, the maximum adsorption capacities (q_{max}) were correlated with the meso, micro and ultramicroporous volumes of the three activated carbons (Table 5). As it can be seen, the maximum adsorption capacity (q_{max}) shows a good linear correlation with the micropore volume values in the 0.7-2 nm width range, suggesting that sorption occurs predominantly in this kind of pores. These results agree with those obtained by other authors studying similar micropollutants sorption on different activated carbons (Moreno-Castilla 2004; Li et al. 2009; Pelekani and Snoeyink 2002). In this sense, the high adsorption of the F-400 carbon could be ascribed to its higher microporous content compared to the other two carbons. The low adsorption capacity of SBC is due to its lower surface area. In addition, the high amount of SBC mineral matter might have a negative effect on the sorption process because mineral matter is able to block the pores of the carbon matrix by adsorbing water due to its hydrophilic character (Moreno-Castilla 2004). In this sense, Dorado et al. (2010) observed for the same material (SBC) a decrease of around 60% in the sorption capacity for the organic compounds due to the competition with water for the active sites. However, when comparing the sorption capacity for the same specific surface area, the amount of paracetamol adsorbed per square meter of adsorbent material (0.207 mg/m^2) is higher than that of NPK (0.192 mg/m^2) and even similar to that of F-400 in the case of atrazine (0.175 and 0.172 mg/m^2 respectively).

When the two compounds adsorptions are compared, it can be seen that paracetamol is more adsorbed than atrazine onto the three activated carbons (Table 4). The adsorption of organic compounds is influenced by different molecular features such as the size, the hydrophobicity and the nature of the functional groups which determine the interaction between the adsorbent and adsorbates (π-π interactions, Hydrogen bounds) (Moreno-Castilla 2004).

Although paracetamol is slightly smaller than atrazine, its molecular dimensions are very similar (0.65 nm for paracetamol and 0.72 nm for atrazine) (Rossner et al 2009). Thus, the two molecules are

small enough to access the micropores with widths in the 0.7 to 2 nm range. Consequently, the differences found in sorption capacities cannot be attributed to size exclusion effects.

It is well known that the nonpolar surface of activated carbons preferably adsorbs hydrophobic compounds with a high octanol/water coefficient (K_{ow}). The K_{ow} may be regarded as an initial indicator of the sorption onto activated carbon (Westerhoff et al. 2005). Mohamed et al. (2011) studied the adsorption of four substituted phenols and concluded that the compound's hydrophobicity is the main factor determining a higher adsorption capacity. The same behavior was observed by Li et al. (2009) for simple aromatic compounds. According to these studies, as atrazine has a higher K_{ow} coefficient than paracetamol (Table 1), a higher adsorption might be expected for atrazine if hydrophobic interactions were the main sorption mechanism. However, in our study paracetamol was more adsorbed than atrazine onto the three carbons. These results are in accordance with the findings of other authors. Pan and Xing (2008) reported no explicit relationship between the sorption constants on carbon nanotubes and K_{ow} for different organic compounds. De Ridder et al. (2010) developed a model to predict equilibrium carbon loading on a specific activated carbon for different solutes that refleted a wide range of solute properties. They concluded that hydrophobic partitioning was the dominant removal mechanism for solutes with log $K_{ow} > 3.7$. However, solutes with a relative low log K_{ow} and with groups which are capable of forming H-bonds (such as the compounds tested in the present study) showed higher carbon loading at similar log K_{ow} values than the solutes without these groups. This means that K_{ow} is not always a determinant factor in adsorption.

Several works indicate that the π-stacking interaction between aromatic π-systems in organic compounds and in sorbents is a key mechanism in adsorption processes (Moreno-Castilla 2004; Cotoruelo et al. 2011; Keiluweit and Kleber 2009). Atrazine and paracetamol have different aromatic rings in their structure. Inductive and resonance effects of the substituents affect the charge distribution within aromatic molecules. The –NHR and –OH groups in paracetamol causes an electron density addition to the aromatic ring so that it can act as a π-donor. Conversely, atrazine is a π-deficient N-heterocyclic compound and has a –Cl substituent which is electron-withdrawing. These two features make atrazine a π-acceptor compound. On the other hand, the IR analyses showed that the F-400 and NPK carbons have -OH aromatic groups which increase the electron density of the activated carbon graphitic planes. This makes activated carbon a surface π-donor. It was therefore expected that atrazine

(π-electron acceptor) would have more affinity for these activated carbons than paracetamol. However, our experimental results do not support this theory.

Another possible mechanism proposed for organic compounds sorption is that based on H-bonding interactions (De Ridder et al. 2010; Moreno-Castilla 2004; Terzik 2000; Villaescusa et al 2011 and Welhouse and Bleam 1993). O-H groups present on the surface of the activated carbons can form H-bonds with N-H in Atrazine and O-H in paracetamol. Because OH-OH interactions are more intense than OH-NH interactions, this adsorption mechanism could explain the fact that paracetamol was more adsorbed than atrazine. Furthermore, in the case of atrazine, the steric effect of side-chains might hinder the formation of hydrogen bonds between the molecule and the functional groups of the activated carbons. This proposed mechanism is in agreement with Terzyk 2004 which proposed different adsorption mechanisms for different organic molecules (paracetamol, aniline, phenol and acetanilide) depending on pH conditions. At neutral pH paracetamol was adsorbed via OH group in carbon and carbon modified with NH_3, and via amide group on modified carbons with acid (H_2SO_4 and HNO_3). On the other hand, the interaction of aniline with surface groups was via weak hydrogen bonds (NH) as suggested by the small value of enthalpy adsorption.

Adsorption kinetics

A series of kinetic studies was performed to compare the rates of sorption of both organic compounds on the activated carbons F-400, NPK and SBC. The kinetics describes the pollutant uptake, which in turn controls the residence time. This is the key to designing further appropriate sorption treatment processes. Concentration profiles over time are shown in Fig. 5 together with the kinetic models tested. The sorption capacity of the carbons influences the abatement rate since the concentration gradient is the driving force of the process. In this sense, the initial removal rate of both compounds on F-400 is significantly higher than on NPK and much superior to that on SBC. In order to compare the kinetic characteristics of each carbon, the parameters that define the three models tested (pseudo second order, intraparticle diffusion and diffusion-adsorption model) were determined by fitting them to the experimental concentrations measured (Table 6). The OF values indicate the degree of agreement between the model predictions and experimental data. According to the results, the best fitting (the lower OF value) was achieved for the pseudo second order and the diffusion-adsorption models

In the case of the pseudo second order model, the k_2 value is proportional to the sorption rate on the materials. An analysis of this parameter shows that, although F-400 and NPK have a higher sorption capacity, the kinetic constant is significantly higher in SBC than in the two other carbons (up to 2.8 and 2.3 times higher than F-400 for atrazine and paracetamol, respectively). These results indicate that with its similar sorption capacity, SBC could become an interesting economic alternative by reducing the time required to achieve equilibrium by more than half.

An analysis of the results from the intraparticle model, although the model predictions diverge slightly from those of the other models, helps to explain the number of stages that occur in the sorption of each compound (Fig. 6). Whereas three stages were detected in the sorption of atrazine on F-400 and NPK, only two were observed for SBC. Similarly, SBC was one of the carbons with fewest stages in the sorption of paracetamol (three as against the four stages for NPK). It is thought that when there are three stages, the first one corresponds to the external mass transfer, followed by intraparticle diffusion and finally the equilibrium achievement (Ruiz et al 2010). The higher number of stages observed in the NPK carbon illustrate the different behavior of the sorption process through mesoporous and microporous according to the previous characterization of the material.

The model developed in the present work, based on the classic diffusion-adsorption reaction models, allows a quantitative comparison of the behavior of different materials by means of only two parameters with physical meaning, in contrast to the previous empirical models. The coefficient diffusion (D) value denotes the relative rate of transfer through the material (i.e. sorption rate) and the effective area (a_S) is the relative amount of area involved in the process. Thus, the most relevant information obtained from this model is that SBC, although it shows the lowest specific surface area, in terms of kinetic behavior has an effective area of the same order of magnitude as F-400 and NPK. In view of the specific surface area of the three materials (Table 6) the percentage of effectiveness was found to be between 11% for F-400 and 50% for SBC.

In comparison, for the same carbon and without any exception, the diffusion coefficient of atrazine is always higher than for paracetamol. Although the sorption capacity for atrazine (more hydrophobic) is lower than paracetamol (Table 4), atrazine is adsorbed onto the carbons at a higher rate (and, thus, in a shorter contact time).

Conclusions

The characterization of the three activated carbons revealed that F-400 has the highest total microporous volume, containing mainly medium-sized micropores (0.7 nm-2 nm). NPK was found to have the highest mesopore volume whereas its microporosity consists fundamentally of ultramicropores (<0.7 nm). SBC shows low micro and mesoporosity, probably due to its precursor characteristics. F-400 has the highest aromaticity. In contrast, NPK and SBC are richer in carboxylic groups.

The Langmuir equation describes the atrazine and paracetamol adsorption onto the F-400 and SBC activated carbons whereas the Freundlich model explains the adsorption of these compounds onto NPK carbon better. The NPK isotherm present two steps and this behavior seems to be related with its higher mesoporosity. F-400 exhibits the highest adsorption capacities and a great affinity for the two adsorbates.

Several kinetic models have been used for predicting the uptake rate of emergent contaminants by carbons. The new approach model, presented here, based on diffusion-reaction equations provides the best description of the experimental data. The good agreement with model predictions confirms the feasibility of representing the complex phenomena occurring during sorption by means of relatively simple models. This model provides a powerful predictive tool together with relevant process parameter values (effective area and diffusion coefficient), which allow the characterization and comparison of different materials by means of fitting parameters with physical meaning (e.g. relation between diffusion coefficient and size of pores). Similarly, different surface coatings, carbon activation processes and carbon origins, among others, could be assessed, focusing not only on sorption capacities but also on kinetic limitations. For instance, these kinetic studies have shown SBC to be a promising sorbent material if the specific surface area can be enhanced. The hydrophobic character of the compounds does not show any correlation with the sorption capacities of carbons but it directly relates with the uptake rate, which is a decisive parameter if contact time is a critical factor.

Irrespective of the pore structure and surface chemistry, the three activated carbons showed a higher adsorption capacity for paracetamol than for atrazine. Taking into account the characteristics of these compounds, hydrogen bonding is likely to be the main mechanism governing the sorption of the two contaminants.

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Tables captions

Table 1. Physico-chemical properties of atrazine and paracetamol.

Table 2. Elemental analysis, ash and humidity of the activated carbons.

Table 3. BET area, total pore volume, ultramicropore, medium-sized micropore, total micropore and mesopore volumes of F-400, NPK and SBC activated carbons.

Table 4. Isotherm parameters for atrazine and paracetamol sorption on F-400, NPK and SBC.

Table 5. Coefficient of determination (r^2) for linear regression between maximum sorption capacity (q_{max}) and pore volumes.

Table 6. Kinetic parameters for atrazine and paracetamol sorption on F-400, NPK and SBC.

Figure captions

Figure 1 N_2 adsorption isotherms at -196 ºC for F-400, NPK and SBC carbons.

Figure 2 Pore size distribution of the activated carbons, obtained by application of the DFT model to the N_2 adsorption data at −196 °C.

Figure 3 IR spectra of SBC, NPK and F-400 carbons.

Figure 4 Experimental data and model predictions for a) atrazine and b) paracetamol adsorption onto the different activated carbons.

Figure 5 Kinetic experimental data and models of a) atrazine, b) paracetamol adsorption onto different activated carbons.

Figure 6 Intraparticle-diffusion plots adsorption of atrazine and paracetamol on the different activated carbons.

Table 1. Physico-chemical properties of atrazine and paracetamol.

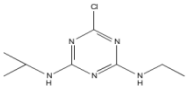
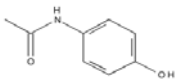
Compound	Atrazine	Paracetamol
Molecular structure		
Molecular formula	$C_8H_{14}ClN_5$	$C_8H_9NO_2$
Molecular weight (g mol^{-1})	215.69	151.16
Log K_{ow}	2.43	0.46-0.49
pK_a	2.27	9.86
Molar volume (cm^3 mol^{-1})	169.8	120.9

Table 2. Elemental analysis, ash and humidity of the activated carbons.

	F-400	NPK	SBC
Elemental analysis (Dry basis, wt%)			
Carbon	91.00	88.09	41.62
Hydrogen	0.34	0.54	0.62
Nitrogen	1.01	0.88	1.57
Sulfur	0.69	0.24	0.47
Ash	6.92	8.57	55.37
Humidity (wt%)	2.17	5.58	3.97

Table 3. BET area, total pore volume and of ultamicropore, micropore and mesopore of F-400, NPK and SBC activated carbons.

	S_{BET} (m^2/g)	V_{TOT} (cm^3/g)	V_{umi} (cm^3/g)	V_{mi-umi} (cm^3/g)	V_{mi} (cm^3/g)	V_{meso} (cm^3/g)
F-400	1234	0.615	0.154	0.221	0.375	0.077
NPK	782	0.489	0.155	0.064	0.219	0.120
SBC	260	0.161	0.049	0.023	0.073	0.049

Table 4. Isotherm parameters for atrazine and paracetamol sorption on F-400, NPK and SBC.

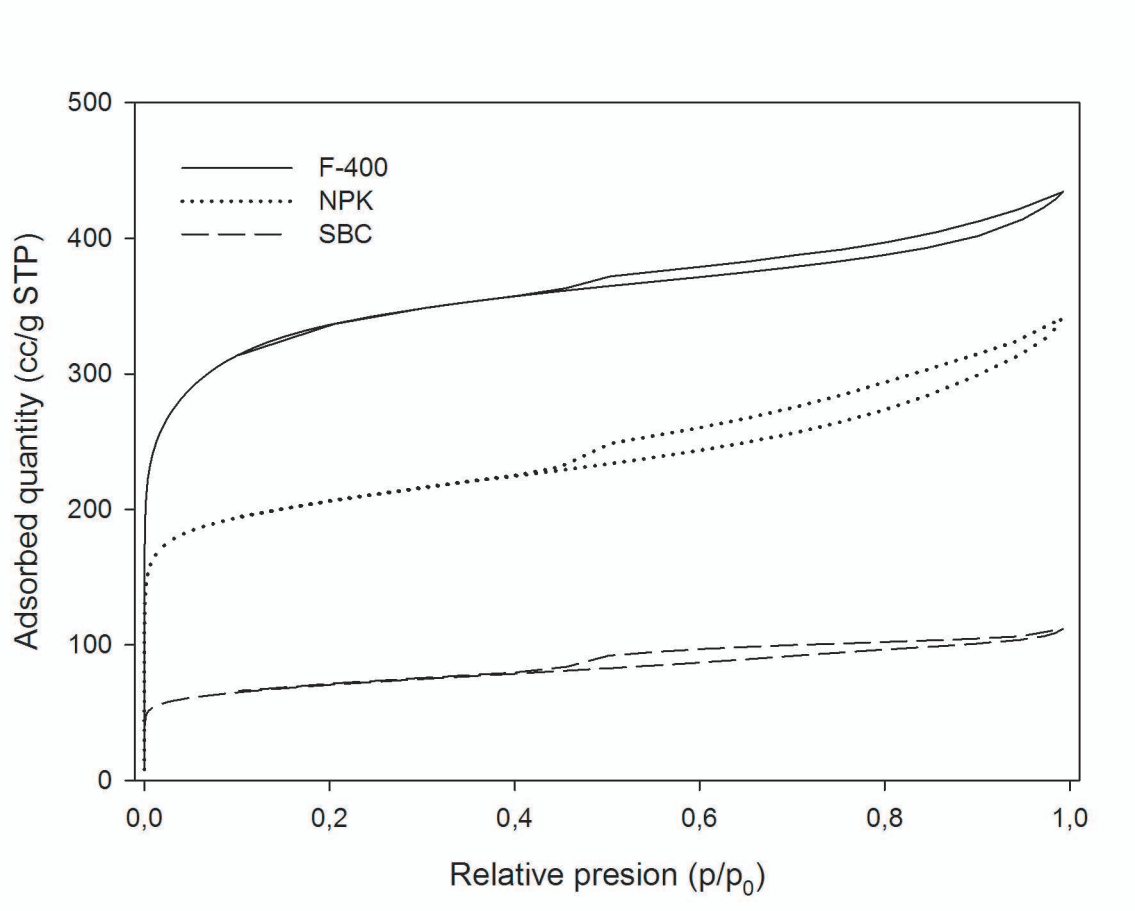
		Atrazine			Paracetamol		
		F 400	NPK	SBC	F 400	NPK	SBC
Langmuir	q_{max}	212.26	119.45	45.49	261.04	150.08	53.75
	K_L	0.31	0.09	0.05	0.35	0.06	0.15
	OF	26.79	45.80	9.65	135.10	37.14	12.89
Freundlich	Kt	69.57	22.28	5.99	157.07	28.79	19.04
	n	3.42	2.59	2.23	9.35	3.06	4.69
	OF	44.45	38.65	9.09	138.29	29.57	16.82
DR	β	0.01	0.02	0.13	0.02	0.09	0.015
	q_{max}	181.76	87.96	32.02	245.18	116.97	45.97
	OF	74.43	63.58	15.09	136.52	68.78	22.54
	E	7.45	4.77	1.93	4.90	2.34	5.87

Table 5. Correlation of determination (r^2) for atrazine and paracetamol sorption capacity (q_{max}) with pore volume.

	Correlation coefficient (r^2)	
	atrazine	Paracetamol
Ultramicropores (< 0.7 nm)	0.680	0.707
Micropores (0.7-2 nm)	0.934	0.920
Mesopores (2-50 nm)	0.109	0.125

Table 6. Kinetic parameters for atrazine and paracetamol sorption on F-400, NPK and SBC.

		Atrazine			Paracetamol		
		F-400	NPK	SBC	F-400	NPK	SBC
Second order	$k_2 \times 10^{-4}$	1.41	3.50	3.94	1.52	2.16	3.70
	qe (calc) (mg/g)	195.2	93.55	43.70	190.10	110.30	46.20
	OF	4.69	1.69	1.04	3.31	3.52	1.16
Intraparticle	k_{p1}	1.99	0,61	0,27	1,51	1,03	0,35
	A_1	-7.13	1.06	-0.44	-2.86	-2.86	-1.21
	k_{p2}	1.41	0.31	$-4.5*10^{-3}$	0.37	0.32	0.21
	A_2	-2.36	7.28	7.05	20.69	6.74	0.54
	k_{p3}	0.13	$4.2*10^{-3}$	-	0.03	0.61	$3.8*10^{-3}$
	A_3	28.60	16.19	-	32.99	-1.42	7.79
	k_{p4}	-	-	-	-	$1.3*10^{-3}$	-
	A_4	-	-	-	-	20.24	-
	OF	7.45	4.83	4.63	8.26	3.84	3.16
Adsortion_difusion	$D \times 10^{-10}$	7.86	9.29	5.64	7.48	5.90	4.72
	a_s	135.15	112.77	131.34	110.95	109.29	124.75
	OF	4.43	1.48	1.02	3.23	4.15	1.20


F-400
NPK
SBC
Adsorbed quantity (cc/g STP)
Relative presion (p/p0)
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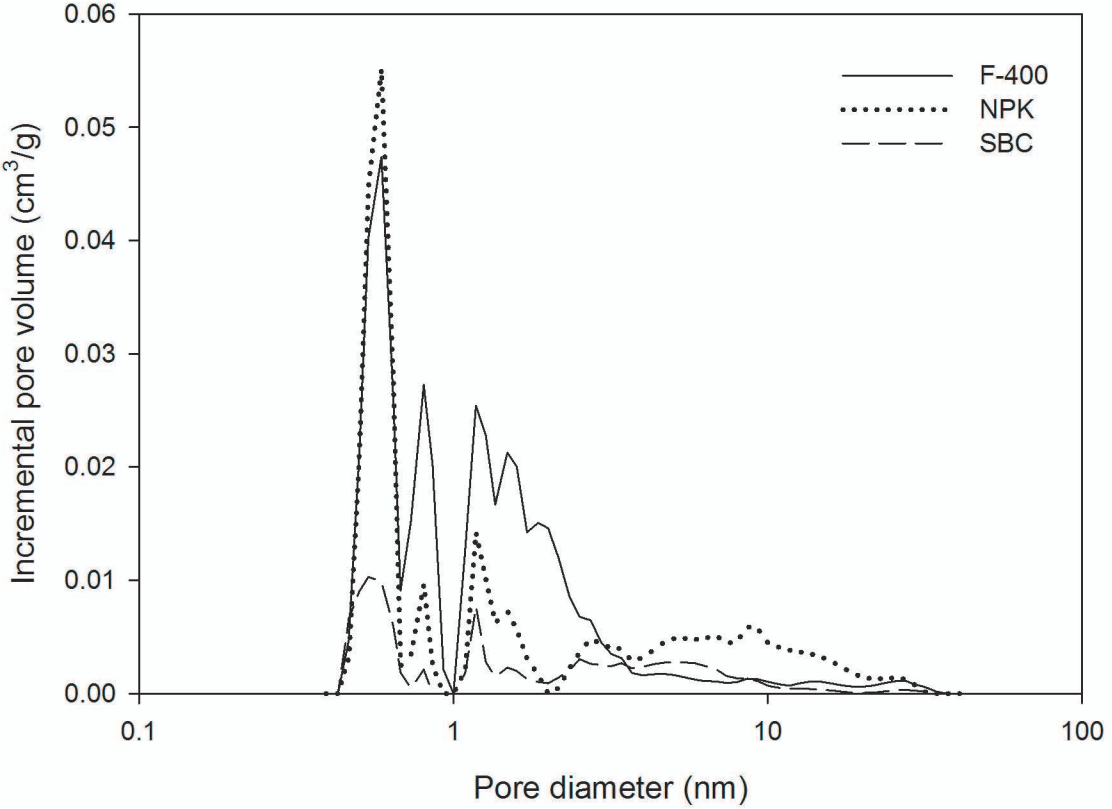
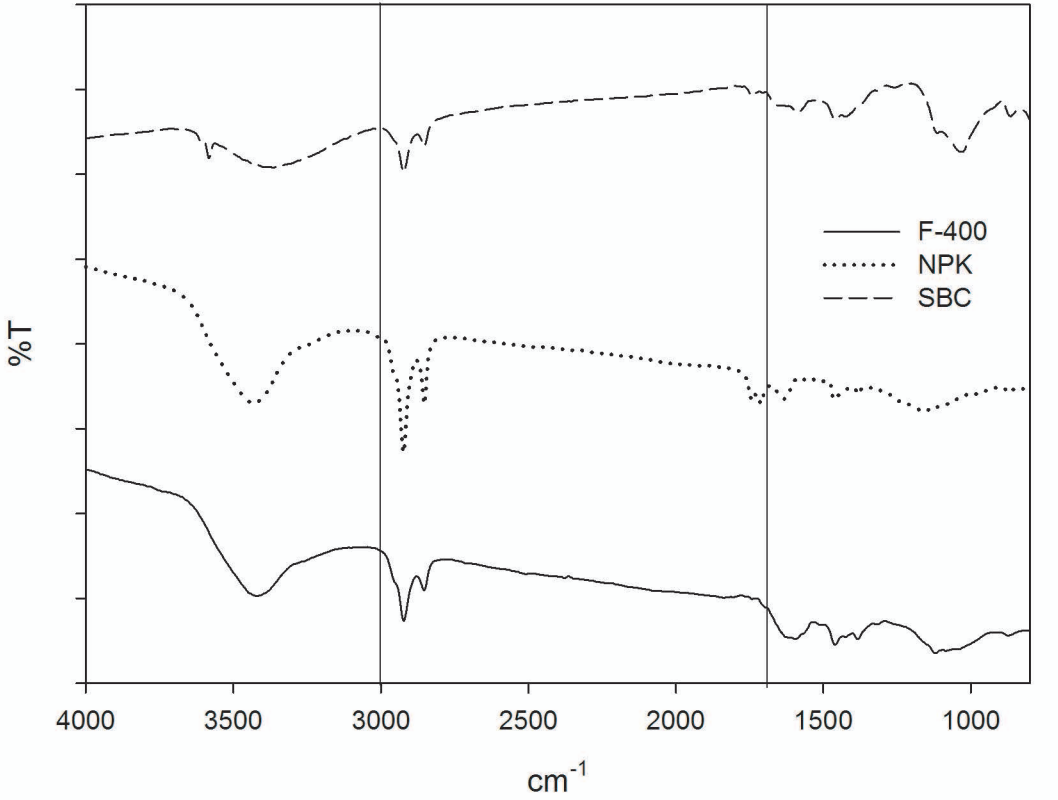
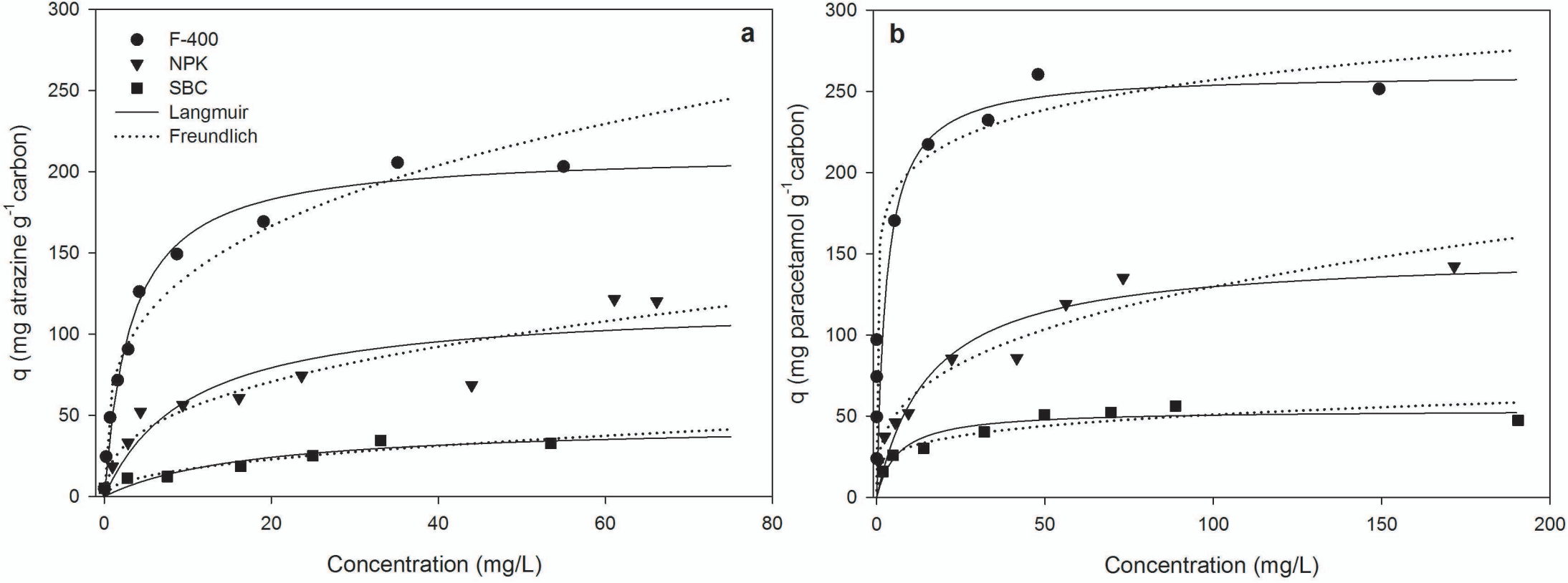
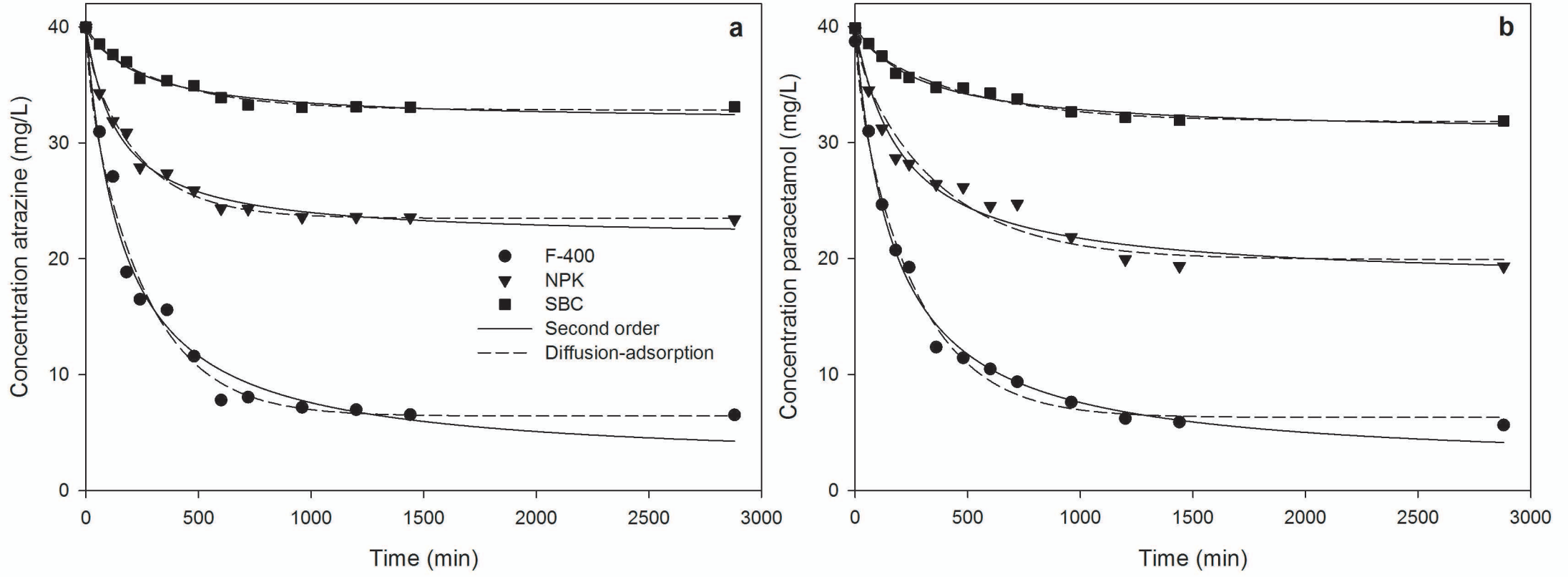
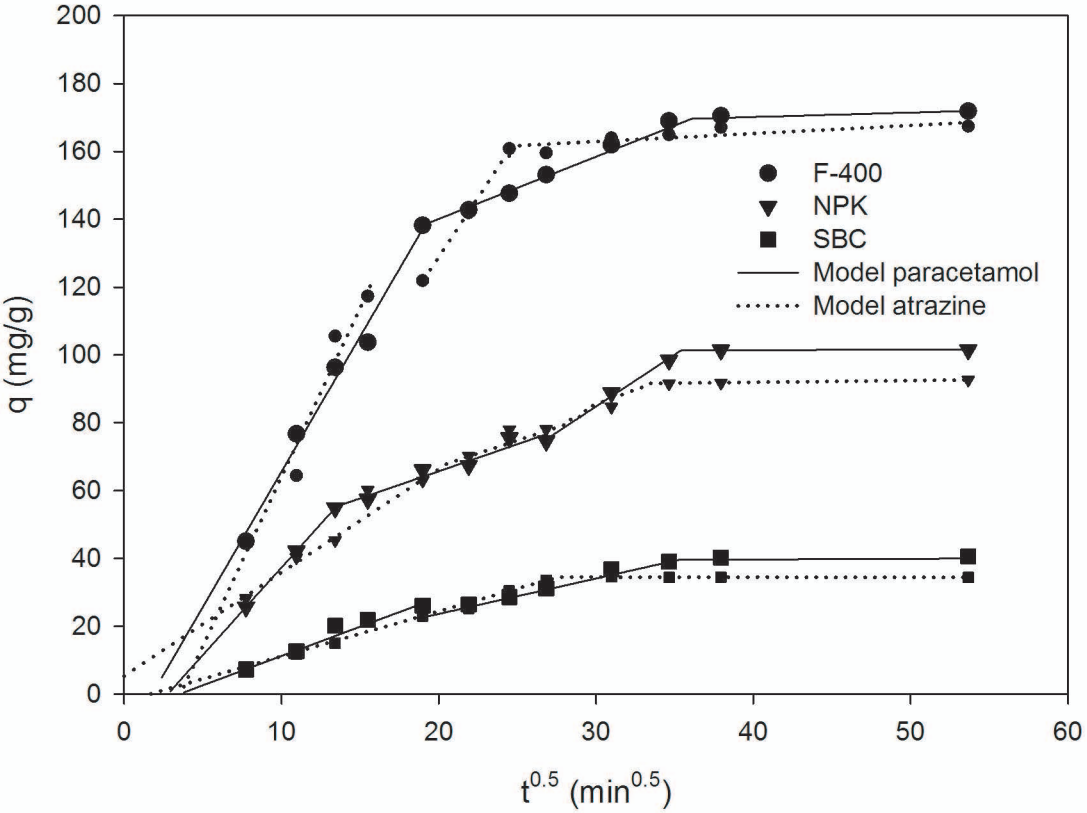
100
200
300
400
500
0,0
0,2
0,4
0,6
0,8
1,0


0.06
0.05
0.04
0.03
0.02
0.01
0.00
Incremental pore volume (cm3/g)
0.1
1
10
100
Pore diameter (nm)
F-400
NPK
SBC


F-400
NPK
SBC
%T
4000
3500
3000
2500
2000
1500
1000
cm-1


a
b
F-400
NPK
SBC
Langmuir
Freundlich
q (mg atrazine g-1carbon)
q (mg paracetamol g-1carbon)
Concentration (mg/L)
Concentration (mg/L)
0
50
100
150
200
250
300
0
20
40
60
80
0
50
100
150
200


a
b
Concentration atrazine (mg/L)
Concentration paracetamol (mg/L)
Time (min)
Time (min)
F-400
NPK
SBC
Second order
Diffusion-adsorption
0
10
20
30
40
0
500
1000
1500
2000
2500
3000


200
180
160
140
120
100
80
60
40
20
0
q (mg/g)
0
10
20
30
40
50
60
t0.5 (min0.5)
F-400
NPK
SBC
Model paracetamol
Model atrazine