Removal of pollutants present in pharmaceutical industry water by coal-based activated carbons

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Abstract

Several studies have demonstrated the presence of pollutants from the pharmaceutical industry in surface and groundwater. The main inputs of pollutants come from households, hospitals and the industry and many of these compounds are not completely removed by WWTPs. The purpose of this research is to study the adsorption of paracetamol, phenol and salicylic acid using coal-based activated carbons. A lignite from Mequinenza (M) and an anthracite from Coto Minero Narcea (CN) from Spain were chemically activated with alkaline agents obtaining two activated carbons (MAC and CNAC). Two commercial activated carbons widely used in water treatment (F400 and NPK) were selected for comparison purposes. The activated carbons were characterized and the results showed a high surface BET (1839 m^2 g^{-1}) and total pore volume (0.83 cm^3 g^{-1}) on CNAC while MAC was characterized by high sulphur content (6%). Vapour isotherms indicated a chemical interaction between the surface functional groups of MAC and the water molecules. The highest uptake of the three pharmaceutical compounds was achieved by CNAC. MAC showed a high affinity for anion salicylates (at pH 4-8). The maximum adsorption capacity of the pollutants onto the activated carbons followed the order salicylic acid > phenol > paracetamol which can be explained by hydrophobicity.

Keywords

Pharmaceutical-pollutants, modelling-adsorption, activated-carbon, lignite, anthracite.

1. Introduction

In recent years, the emission of emerging contaminants (pharmaceuticals, pesticides, personal care products) has been causing serious environmental problems in aqueous media. These pollutants and their metabolites have been found in high concentrations in wastewater treatment plants (WWTPs) effluents, due to their resistance to biological degradation (Osorio et al. 2012; Postigo et al. 2010).

Among these emerging contaminants, by the end of the 20th century pharmaceuticals were identified as a cause of great concern (Ayscough et al. 2000; Halling-Sørensen et al., 1998; Sebastine and Wakeman, 2003). The discovery of a variety of pharmaceutical substances (such as antidepressants, antibiotics, antihistamines, analgesics and other medicines) in surface, ground, and drinking waters (Mompelat et al. 2009) is raising concern about the potentially adverse

environmental consequences of these contaminants (García-Mateos et al. 2015; Kümmerer, 2001; Méndez-Diaz et al. 2010; Petrie et al. 2015).

Previous studies have demonstrated that the use of conventional treatment systems, as activated sludge (Carballa et al., 2004; Gracia-Lor et al. 2012) is not sufficient to effectively remove this type of organic compounds. It is therefore necessary to investigate new technologically viable and economically feasible alternatives to effectively remove these pharmaceutical pollutants from water. Currently, the solutions under investigation are focused primarily on improving the purification process and use of activated carbon, ozone treatment or the ultraviolet radiation. Activated carbon is an adsorbent material with a high adsorption capacity used in a wide range of liquid and gas phase applications, including water treatment, air purification, solvent vapour recovery, food and beverage processing and pharmaceutical industry. In the future, apart from the traditional areas of application, several new purposes for activated carbon are expected to emerge due to strict governmental regulations related with water quality.

More than 50% of the activated carbon manufactured in USA and China is based on coal (Roskill, 1998). Coal is a carbon-rich sedimentary rock that is formed from plants subjected to high pressure and heat over millions of years. During its formation and transformation, it incorporates different mineral matter including sulphur and heavy metals. The degree of change undergone by a coal as it matures from peat to anthracite is known as coalification. Coalification has an important influence on physical and chemical properties (e.g. carbon content) of the coals and is referred to as the 'rank' of the coal (peat (from 50% to 64% of carbon content), lignite, sub-bituminous, bituminous, anthracite (92-96% of carbon) (Kural, 1994)).

Coal has a direct important role as an energy resource. It generates 41% of the total world electricity supply and is needed to produce 66% of the world’s steel (Schernikau, 2015). However, the combustion of coal generates pollutant and greenhouse gas emissions (CO_2, SO_2, NO_x...), making coal a problematic fuel from environmental point of view (Spörl et al., 2013). So, carbons with a high content in sulphur are no suitable for combustion and it would be necessary to find different alternatives for coal such as activated carbons manufacturing.

The adsorption of pollutants on activated carbon depends on the physic-chemical characteristics of the adsorbent (e.g. functional groups, surface area, mineral matter) and the nature of the adsorbate (e.g. .molecular size, functional groups,...) (Moreno-Castilla, 2004). The presence of mineral matter (or ashes) can enhance the adsorption of water by means hydrogen bonds, and decrease the adsorption of the aromatic pollutants. Moreover, the presence of oxygen, nitrogen, and/or sulphur groups and aromatic rings on the surface of the activated carbon and the functional groups of the aromatic molecules can produce different dispersion interactions between aromatic rings.

The aim of this work is the modelling of the adsorption of common pharmaceutical industry compounds present in aqueous solutions using coal-based activated carbons. With this purpose, two activated carbons from lignite (M), from the Mequinenza basin in Zaragoza (Spain), and from anthracite (CN), from Coto Minero Narcea in Asturias (Spain), will be developed for adsorption of emerging pollutants in water. In addition, two commercial activated carbons, F400 and NPK obtained from bituminous coal and peat respectively and widely used in waste water treatment, were selected for comparison purposes. The four activated carbons were characterized on the basis of elemental composition, texture and water vapour isotherms for the purpose of establishing the factors involved in the adsorption of three emerging compounds and pollutants from the pharmaceutical industry (paracetamol, phenol (antiseptic, for sore throat pain) and salicylic acid). Furthermore, the influence of pH upon the adsorption of the different organic compounds was investigated.

2. Materials and methods

2.1. Adsorbents

In this study, two activated carbons (CNAC and MAC) were prepared from different evolved coals (rank): an anthracite (CN) from Coto Minero Narcea, Asturias, Spain, and a lignite (M) from the Mequinenza basin in Zaragoza, Spain (Cabrera et al., 2002).

The precursors (CN and M) were activated by chemical activation using alkaline hydroxides (NaOH and KOH). The coals were mixed with the activated agent in solid state (physical mixture). Powdered alkaline hydroxides were selected as they would favour contact between the carbonaceous precursor and the activating agents (Ros et al., 2006). The physical mixing method is a very easy procedure that simplifies the first step in the preparation of activated carbons by chemical activation. It is widely used in the preparation of activate carbons from very different such as coals and terrestrial and marine biomass (Ferrera-Lorenzo et al., 2014; Gil et al., 2014; Lillo-Ródenas et al., 2001). Mixtures expressed as mass ratio (activating agent:precursor) were the following, 3:1 (NaOH:CN) and 1:1 (KOH:M). The mixtures were introduced in a horitzontal cylindrical furnace (Carbolite CTF 12/65/550, and heated up to 830 ºC in a 400 ml min^{-1} nitrogen flow in the case case of the anthracite (CN) and up to 750 ºC in a 150 ml min^{-1} nitrogen flow for the lignite (M), at a heating rate of 5 ºC min^{-1}. The maximum temperature was held for 1 hour in both cases. After chemical activation, in order to remove the activation products and any mineral matter blocking porosity, the adsorbent materials were washed with a 5M hydrochloric acid solution and subjected to a series of deionised water (Milli-Q) rinses. Finally the samples were dried at 105 ºC. The activated carbons obtained from the anthracite and lignite (<200 micrometers) were named CNAC and MAC, respectively. The pH of the activated carbons was determined using the methodology of Ros (Ros et al., 2006).

The experimental conditions of chemical activation of these coals were different in order to develop activated carbons with different pore size distribution with a view to studying their behaviours during the removal of pollutants present in pharmaceutical industry wastewater. From studies conducted Girón (Giron et al., 2015) on the influence of the alkaline activating agent upon the activation of the forest biomass fly ash, it can be inferred that under the same experimental conditions NaOH contributes more to the development of mesoporosity than KOH (Girón et al., 2015). One of the conclusions of this work is: "In general, mesoporosity is favoured by chemical activation using NaOH in high concentrations". Perrin (Perrin et al., 2004), in the work on the activation of an anthracite, observed that the development of mesopore volume was favoured by using a high NaOH concentration and a high activation temperature (830ºC). In the present study, with the objective of obtaining the largest possible mesopore volume and micropores of large size in an anthracite-based activated carbon, NaOH was used as activating agent with mass ratio of 3:1 and high temperature of 830ºC. By contrast for the activation of lignite, KOH was selected as activating agent at a mass ratio of 1:1 and an activating temperature of 750ºC, experimental conditions that favour the development of micropore volume (Girón et al., 2015).

Two commercial activated carbons commonly used for the treatment of water were also evaluated, Filtrasorb-400 (F400) and Norit PK 1-3 (NPK). F400 was developed by Chemviron (Feluy, Belgium) from a bituminous coal by physical activation (steam water). NPK was produced by Norit Americas Inc. (Marshall, USA) through steam-water activation of a peat.

2.2. Adsorbates

The organic pollutants evaluated were phenol (CAS 108-95-2, 98.5%, cod. 141322, Panreac, Spain), salicylic acid (CAS 69-72-7, 99.5%, Batch32347/2948, Scharlau, Spain) and paracetamol (CAS 103-90-2, 98%, lot L08100275, Fagron, Spain). Table 1 shows the physico-chemical properties of the three compounds (Bolton et al., 2008). The molecule dimensions (the close fitting "box" around the molecule), surface areas (grid and approximate) and volume were calculated using Hyperchem 8.0 (De Ridder et al., 2012).

TABLE 1

Phenol, salicylic acid and paracetamol stock solutions (100 and 150 mg L^{-1}) were prepared with ultra-pure water from Milli-Q purification systems (Millipore academics). The samples for calibration and for the sorption experiments were obtained from these solutions by dilution with ultra-pure water (Milli-Q).

2.3. Characterization of the activated carbons

The activated carbons were characterized for their elemental analysis (content of C, H, N and S) using a LECO CHN-2000 and a LECO Sulphur Determination S-144-DR. Ash content was determined according to ISO 1171 procedure. The texture of the activated carbons was characterized by a 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 (ca. 10^{-3} Torr) at 120 ºC overnight to remove any adsorbed moisture and/or gases. The amount used in the N_2 adsorption analysis is around 0.2-0.5 g. The isotherms were used to calculate the BET specific surface area (S_{BET}) by using the standard method of Brunauer, Emmett and Teller (BET theory, Brunauer et al., 1938, 1940 and Brunauer, 1970). The p/p^0 points used to calculate the S_{BET} are within the BET range and in general are in $p/p^0 < 0.10$ with a correlation coefficient of 0.99999. Also the N_2 isotherms were used to calculate the total pore volume (V_{TOT}) at a relative pressure of 0.95. The pore size distribution (PSD) was calculated on the basis of the density functional theory (DFT), assuming slit-shape pore geometry.

Water-Vapour sorption isotherms of the samples were determined at 25ºC for water activity (a_w) from 0 to 1. Water activity was evaluated by means of a Hydrosorb HS-12-HT model instrument (Quantachrome Instruments). The equilibrium moisture content was expressed as mmol per g of dry solid.

An SEM analysis (TM 1000 Tabletop microscope, Hitachi) was carried out to evaluate surface texture and porosity.

2.4. Adsorption assays

For equilibrium adsorption studies, 50 mg of adsorbent was added to 250 mL of organic compound solutions in different concentrations (1-150 mg L^{-1}). The mixtures were stirred at 25ºC using a multipoint agitation plate. After 24 hours, the samples were taken out and filtered through a cellulose acetate filter (0.45 μm pore diameter) and the remaining concentration of adsorbate was analyzed in a UV/Vis-visible spectrophotometer (Lambda 25 PerkingElmer) at 242 nm for paracetamol, 269.9 nm for phenol and 295 nm for salicylic acid. The paracetamol, phenol and salicylic acid uptake, q, was determined by means of the formula:

$$q = \frac{(C_0 - C_f)\,V}{m} \qquad (1)$$

Where, q is the amount (mmol g^{-1}) of organic compounds adsorbed, C_0 and C_f are the initial and final concentration (mg dm^{-3}), respectively, V is the volume (L) of adsorbate solution and m is the weight (g) of activated carbon used.

The effect of the pH upon the adsorption of the organic compounds was investigated over a pH range of 2-10, adjusting the pH by adding 0.1 M HCl or 0.1 M NaOH in 250 ml of 40 mg L^{-1} solutions.

2.5. Adsorption modelling

The experimental results were fitted by the models described in Table 2. The parameter estimation of the different isotherms was solved using MATLAB by minimizing the objective function (OF) in equation (4) (Lladó et al., 2015):

$$OF = \sqrt{\sum_{i=1}^{N} [q(P_1, P_2) - q^*]^2} \qquad (4)$$

where, N is the number of measurements taken, 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 used are q_{max} and K_L and for Freundlich K_f and n.

TABLE 2

3. Results and discussion

3.1. Characterization of the activated carbons

The chemical composition of the precursors (M and CN) and the activated carbons are summarized in Table 3. As can be seen, the anthracite (CN) is characterized by a high carbon content (90.6 %) and a low ash content (4.4 %), whereas the lignite (M) has a low carbon content (56.6 %) and a high ash and sulphur content (16.2 % and 5.35% respectively).

TABLE 3

The activated carbons, MAC and CNAC, obtained from lignite and anthracite respectively, have a higher carbon and lower ash content than their corresponding precursors (Table 3). It is worth

nothing that there is a significant reduction in ash content in the activated carbons obtained, especially in the lignite-based activated carbon (16.20% and 6.94% for M and MAC respectively). During the chemical activation process new inorganic compounds are formed. These are soluble in hydrochloric acid and water and can mostly be eliminated in the final step by means of a washing process. The washing process with acid gives an acidic behaviour to MAC and CNAC (pH 3.9 and 4.0 respectively). On the other hand, the commercial activated carbons (F400 and NPK) have a basic pH due to the physical activation with steam and the presence of ashes (Montes-Morán et al., 2012).

It is worth nothing the high sulphur content in MAC (6%). This fact makes this adsorbent a potentially suitable material for some environmental applications such as the mercury elimination in gas streams (Lopez Anton et al., 2015a, Lopez Anton et al., 2015b).

If the commercial carbons are compared with MAC and CNAC, their carbon content order is CNAC > F400 > NPK > MAC. It was expected that MAC would have higher carbon content than NPK because MAC is from lignite while NPK is from peat. However, the ash content of the activated carbons is NPK > MAC > F400 > CNAC in inverse proportional to the coalification of the coal precursor.

Fig. 1 shows the nitrogen adsorption-desorption isotherms at -196 ºC of the four activated carbons. The textural properties (S_{BET}, V_{TOT} and PSD) of the four activated carbons as determined from the N_2 adsorption isotherms are summarized in Table 4.

FIGURE 1.

TABLE 4

All the isotherms are hybrid-shaped and belong to type I-IV according to the IUPAC classification (Thommes et al. 2015). Although the isotherms have a similar shape, some differences can be appreciated. The adsorption of N_2 took place fundamentally at low relative pressures (p/p^0 <0.1), which is typical of microporous solids. The anthracite-based activated carbon (CNAC) shows the highest nitrogen adsorption and the peat-based activated carbon (NPK) the lowest (Fig. 1). The knee of the isotherms is different for the coal-based activated carbons of different rank. The isotherms of CNAC and F400 present a broad knee at low relative pressures (p/p^0<0.2) which signifies the presence of wide micropores while the isotherms of MAC and NPK show a more pronounced knee which signifies that there is a narrower pore distribution (Fig. 1

and Table 4). The presence of a hysteresis loop (type H4 which is associated with narrow slit-shaped pores (Sing, 1982)) and an increase in the slope of the isotherm indicate a developed mesoporosity. These features are especially evident in NPK, which has the highest mesoporosity.

Moreover, in Table 4, it can be observed that CNAC exhibits the highest total pore volume at p/p^0=0.95 (V_{TOT} = 0.830 cm^3g^{-1}) and specific surface area BET (S_{BET} = 1839 m^2g^{-1}) followed by F400, MAC and NPK. MAC presents a BET surface value of 1100 m^2g^{-1}, slightly higher than that obtained by T. Depci in the chemical activation with zinc chloride from Gölbaşi lignite (Turkey) (Depci, 2012).

The four activated carbons are basically microporous materials, although NPK has a high degree of mesoporosity (≈36%). Regarding the pore volumes, the ultramicropore volume ($V_{ultramicro}$ = volume corresponding to pore with < 0.7 nm) is similar for all the activated carbons (between 0.154 and 0.184 cm^3 g^{-1}). With respect to supermicropore volume ($V_{supermicro}$ = volume corresponding to pore width 0.7-2 nm), CNAC shows the highest value (0.394 cm^3g^{-1}) while NPK has the lowest (0.064 cm^3g^{-1}) and F400 and MAC have intermediate values (0.221 and 0.173 cm^3g^{-1}). Finally, the mesopore volume (V_{meso} = volume corresponding to pore width 2 - 50 nm) is similar for CNAC and NPK (0.113 and 0.120 cm^3g^{-1}) while for F400 and MAC this value is very low.

To gain a better understanding of the different pore volumes of the activated carbons, their pore size distribution was studied (Fig. 2). The main difference is in the mesopore region where CNAC shows mesopores of a small size (2-4 nm) while the NPK mesopores range between 2 and 20 nm.

FIGURE 2.

The effect of the thermochemical process on the texture of the coal-based (lignite and anthracite) activated carbons of different rank, MAC and CNAC, is clearly revealed by scanning electron microscopy, Figure 3.

FIGURE 3.

MAC (Fig. 3c, 3e and 3g) has a wide pore network structure as a result of chemical activation. The precursor of MAC is low-evolved coal (lignite, M, Fig. 3a) with a high volatile matter and

ash content. Its chemical activation involves the thermal decomposition of the carbonaceous material, the elimination of volatile matter and as consequence the generation of a macroporous structure with the formation of large vacuoles in the final material, as can be seen from the images under different magnifications (Fig. 3c, 3e and 3g). In contrast, CNAC (Fig. 3d, 3f and 3h) has a dominant laminar structure like its precursor, which is a highly evolved coal (anthracite, CN, Fig. 3b),with a well-ordered structure and a low volatile matter content. Because its volatile matter content is low, chemical activation takes place preferably in the interlaminar areas of the anthracite generating thereby a macroporous structure with large cracks, as can be seen from the images under different magnifications (Fig. 3d, 3f, 3h).

The water vapour adsorption isotherms serve to clarify the chemical interactions with the surface groups and the physical adsorption between the water molecules and the material used (Alcaliz-Monge et al., 2002; Vartenetyan et al., 1986), Figure 4.

FIGURE 4

Figure 4a shows the water vapour adsorption-desorption isotherms for the four activated carbons. The four isotherms are of type V, which is characteristic of weak adsorbate-adsorbent interactions. This type of isotherm is generally observed in microporous materials and often reported for activated carbons (Lopez-Anton et al., 2015a; Lopez-Anton et al., 2015b). At low relatives pressures ($p/p^0 < 0.3$) of water vapour adsorption (Fig. 4b), the chemical interaction between the surface groups of the activated carbon and the water molecules are higher in MAC than the rest of activated carbons, which suggests the presence of hydrophilic surface mainly from sulphur groups (Table 3). Chemical interaction with the surface groups is lower in NPK and the water adsorption can be due by the presence of ashes or mineral matter. Finally, chemical interaction is negligible in CNAC and F400 suggesting the disappearance of surface groups due to maturity of the raw materials and the severe activation conditions (such as the high temperature and high ratio of the activating agent). As the pressure increases (Fig. 4a) physical adsorption (pore filling) becomes more important due to the influence of the textural development. Therefore the CNAC isotherm presents the highest water adsorption (approx. 40.1 mmol/g), followed by F400 and MAC whereas NPK showed the lowest adsorption. These results are accord with the order of increase adsorption of the obtained nitrogen adsorption isotherms (CNAC > F400 > MAC > NPK) (Fig. 1).

3.2. Influence of pH

The influence of the pH of the solution on the adsorption of the three pollutants (paracetamol, phenol and salicylic acid) is shown in Figure 5.

FIGURE 5.

As can be seen, there are no significant variations in the adsorption of paracetamol and phenol by the four activated carbons with respect to the pH (Fig. 5a and 5b). The molecules remain undissociated at a pH lower than pKa (9.99 or 9.38) and therefore the removal is constant.

On the other hand, the adsorption of salicylic acid (Fig. 5c) shows a significant decrease with increasing pH. When the pH is lower than the salicylic pKa (2.97), the carboxylic groups are undissociated. This favours the adsorption of salicylic acid because, under acidic conditions, the chemical groups on the activated carbon cause a decrease in the total negative charge. Conversely, at high pH, salicylic acid dissociates as well as acidic functional groups in the carbon surface. Therefore, repulsion forces between negative charges arise between salicylates and carbon surface, impeding the adsorption process.

It can also be seen in Figure 5c that between pH 4 and 8 the adsorption of salicylic acid by MAC is higher than in the others activated carbons. This behaviour can be explained by the presence of different functional groups on the surface of MAC as it can suggest the results on the chemical adsorption showed at low pressures in the water vapour isotherm (Fig. 4). Mui and Valix (Mui et al., 2010; Valix et al., 2006), suggested that depending on the acid-base nature of the carbon suspension, which is often affected by the elemental composition of carbon (particularly heteroatoms such as nitrogen, oxygen and sulphur), the adsorbent can be positively or negatively charged as shown below:

(Positive surface) $C=S^{\delta+}OH + H^{+} \rightarrow C= S^{\delta+} + H_2O$ (5)

(Negative surface) $C=O^{\delta-}H^{+} \rightarrow C=O^{\delta-} + H^{+}$ (6)

Here the salicylate can be expected to be adsorbed favourably onto the positively-charged carbon surface due to the presence of the high sulphur content. Therefore in the pH range of 4-8, the attraction of opposite charges between the surface and dissociated salicylic acid may contribute to the increase adsorption onto MAC.

3.3. Adsorption isotherms and modelling

The experimental adsorption isotherms of the three pollutants on the four activated carbons are shown in Figure 6.

FIGURE 6

According to their initial slopes and Giles' classification (Giles et al., 1974a; Giles et al., 1974b), the NPK isotherm can be classified as of type L2, whereas the MAC, F400 and CNAC isotherms are of type H2. This suggests that the three carbons have a high affinity for paracetamol, phenol and salicylic.

The experimental data were fitted to two different two parameter isotherms (Langmuir, Freundlich). Table 5 shows the constants obtained and the objective function (OF) values for the two models. According to the OF values, paracetamol adsorption is best represented by the Freundlich model, whereas salicylic acid is best fitted by the Langmuir model, except on MAC. Phenol behaviour depends on the activated carbon used (F400 and MAC by Langmuir, CNAC and NPK by Freundlich). If the q_{max} from the Langmuir model for the four activated carbons are compared, the adsorption capacity follows the order CNAC>F400>MAC>NPK which is the same order as some textural development characteristics (S_{BET} and total pore volume V_{TOT}). The highest adsorption equilibrium constant values (K_L) are achieved for the adsorption of paracetamol onto the four activated carbons. This indicates that the four activated carbons have a high affinity for this compound. Moreover, K_L value for salicylic on MAC is higher than the rest of activated carbons, indicating that the presence of sulphur on MAC can increase the affinity. On the other hand, K_L for phenol is higher on F400 then the rest of the activated carbons.

TABLE 5

With respect to the Freundlich model, the parameter 1/n is a measure of adsorption intensity or surface heterogeneity. According to Navasivayam and Senthilkumar, (Namasivayam and Senthilkumar, 1998), n indicates favourable adsorption when $1<n<10$. The highest n value, within this range, the highest adsorption intensity (Chantawong et al., 2003). In this study, the different n values observed are between 2 and 7. The highest n value obtained for paracetamol adsorption onto CNAC indicating the most favourable adsorption among all.

As can be seen in Figure 6, the highest pollutant adsorption capacities are obtained with CNAC. This high performance could be due to the high BET area and the development of the micropore and mesopore structure. A comparison of the different pore volumes and the compound sizes, would lead one to expect that molecules smaller than 0.7 nm (in the case of phenol and salicylic acid) would be adsorbed by ultramicropores. Although MAC show a higher microporosity respect F400, the máximum adsorption capacity (qmax, Table 5) is achieved by F400.–Therefore, the adsorption process must take place not only on the ultramicropores but also on the supermicropores. In other words, the supermicropores also have a pore filling role. Regarding the mesopores, CNAC and NPK show the same amount of mesoporosity but the mesopores differ in their diameter. Depending on the characteristics of the activated carbon, the mesopores allow the access of pollutants (Dabrowski et al., 2005), or they make little contribution to the capture of molecules depending on the mechanism of adsorption on the active sites (Cai et al., 2014; Fierro et al., 2008). In this study, it was found that mesopores of NPK (with a large diameter of 2-20 nm) only make a small contribution adsorption due to the presence of surface groups (water vapour isotherm) and they allow the access. On the other hand, the small diameter mesopores of CNAC (2 - 4 nm) and the low chemical interactions with the surface groups can suggest a pore-filling adsorption mechanism.

Regarding the effect of the nature of the adsorbate, the single component isotherms (Figure 5) and the modelling results (Table 5) show that the highest adsorption capacity corresponded to salicylic acid followed by phenol and paracetamol. This order cannot be explained on the basis of the size of the compounds (Table 1) because the salicylic acid is larger than the phenol and smaller than the paracetamol. Galhetas (Galhetas et al., 2014) studied the adsorption of paracetamol on different activated carbons and concluded that paracetamol might form dimmers and its adsorption occurred on wider and some of the narrow micropores. By this sense, the paracetamol might be adsorbed less due to higher dimensions of the dimmer. Another aspect to be considered is solubility. Moreno-Castilla (Moreno-Castilla et al., 1995) observed that their adsorption capacity increased with the decreasing water solubility of phenolic compounds. In our study, this parameter seems to be of secondary importance since paracetamol was less easily adsorbed than phenol.

Hydrophobicity (high logKow) might also explain the order of adsorption capacity of the different pollutants. According to Mohammed (Mohammed et al., 2011), activated carbons are mainly hydrophobic and display a strong affinity for organic molecules with a limited solubility in water. Hydrophobic compounds tend to be attracted to the adsorbent surface and hence they are more easily adsorbed than hydrophilic compounds. In this study, salicylic acid is the most hydrophobic pollutant followed by phenol and paracetamol.

4. Conclusions

Activated carbons obtained from anthracite (CNAC) and lignite (MAC) were successfully used as adsorbents for paracetamol, phenol and salicylic acid pollutant removal in aqueous phase.

- A high decrease in the ash content was observed in the activation of the lignite (from 16.2% in M to 6.94% in MAC). On the other hand, CNAC had very low ash content making this activated carbon suitable for water treatment.
- At low relative pressures in the water vapour isotherms, MAC showed a higher vapour uptake than the rest of activated carbons due to the presence of sulphur functionalities (6% Sulphur content on MAC).
- The adsorption of salicylic acid showed a strong dependence with the variations in the pH solutions. Maximum salicylic acid adsorption was observed at pH = 2 onto the different activated carbons. At the pH range 4-8, the adsorption of anion salicylates was favoured onto MAC suggesting that the presence of sulphur functionalities of the activated carbon favours the ionic interactions.
- The highest adsorption capacity of the three pharmaceutical pollutants was achieved by CNAC followed by F400, MAC and NPK. This order coincides with their BET surface, the total micropore volume and the total pore volume
- A study of pollutant adsorption on the different activated carbons showed that hydrophobicity (higher log Kow) was the main reason for the higher adsorption capacity of salicylic acid. Moreover, the adsorption of salicylic acid onto MAC can also governed by ionic interactions

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FIGURE CAPTIONS

Figure 1. N_2 adsorption isotherms at -196ºC for CNAC, F400, MAC and NPK.

Figure 2. Pore size distribution (DFT) of the activated carbons

Figure 3. Scanning electron microscope (SEM) of the materials: a) "Mequinenza" lignite (M) at 1000x; b) "Coto Minero Narcea" anthracite (CN) at 1000x; c) lignite based activated carbon at 400x; d) anthracite based activated carbon at 400x; e,g) lignite based activated carbon at 5000x; f,h) anthracite based activated carbon at 5000x.

Figure 4. a) Water vapour adsorption-desorption (at 25ºC) of the materials b) water vapour adsorption at low pressures (0-0.4)

Figure 5. pH effect on the adsorption equilibrium a) phenol, b) paracetamol and c) salicylic acid

Figure 6. Pharmaceutical compounds adsorption onto the coal-based activated carbons: a) CNAC, b) F400, c) MAC and d) NPK