Elimination of persistent anthropogenic pollutants by micro-mesoporous carbon xerogels. Natural organic matter on surface water and textural properties influences.

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Abstract

The increase of emerging pollutants (pesticides, pharmaceuticals, iodinated contrast media (ICM), …) in surface and groundwater is a threat to the environment and to human health due to its toxicity and its persistence in water. In this work, the removal of pharmaceuticals and ICM by adsorption onto carbon xerogels and commercial activated carbons with different physicochemical properties is studied. Carbon xerogels have similar micropore volume and BET surface area (0.152±5 cm3g-1 and 625±25 m2g-1, respectively), with macropore and mesopore volume up to 0.63 cm3g-1 and 1.09 cm3g-1 and an average pore diameter from 8.8 to 45.6 nm. YAO activated carbon present the highest micropore volume and BET surface area (0.357 cm3g-1 and 1092 m2g-1, respectively). Small pores favour the pharmaceuticals adsorption and larger pores the uptake of ICM. The presence of polymeric groups in the carbon xerogels and ashes in the HYDC and YAO activated carbons (26.27% and 4.87%, respectively) provides a basic surface for enhancing the adsorption of acidic compounds. All adsorbents have a basic pH (9.3-11.6). The hydrophobicity or hydrophilicity of the adsorbates influences in different ways the adsorption process on porous carbon materials. Natural Organic Matter (NOM) influences in the retention of the pollutants by the carbon materials. There is a competition between the NOM and ICM for the large pores of the carbon xerogels (overall, r>0.98 amount ICM adsorbed *vs*. Hg volume intrusion in mesopores). Electrostatic interactions between the natural organic matter and the salicylic and diatrizoic acids have the effect of reducing the quantity adsorbed.

Keywords: Iodinated Contrast Media; Pharmaceuticals-pollutants; Micro-mesoporous Carbon Xerogel; Surface Water; Natural Organic Matter; Adsorption.

1.- Introduction

The great increase in the world population and the development of emerging countries over the last few decades has led to a massive use of pharmaceuticals, personal care products, hormones, pesticides... whose residues generate the called emerging pollutants and consequently to environmental problems such as water pollution [1,2]. The emerging pollutants are a new class of chemicals whose effects on human health and the environment are still not sufficiently known. In general, these pollutants are mostly toxic, persistent and bioaccumulative. Among the dangerous pharmaceuticals detected in the aqueous media are: contraceptives, analgesics, anti-inflammatory substances, steroids, antibiotics and contrast media used in diagnostic scans.

Since the beginning of this century, Dr. Barceló's research team has been studying the presence of emerging pollutants in several Spanish rivers, one of which is the River Llobregat [3,4], whose waters have been used in the present study. In wastewater treatment plants (WWTPs) many most organic pollutants are eliminated by primary (physical-chemical) and secondary (biological) treatments. However, some pharmaceuticals and Iodinated Contrast Media (ICM) compounds are only partially eliminated due to they are recalcitrant compounds with a great resistance to be degradated by biological methods [5]. So, it is necessary to resort a tertiary treatment (ozonation, activated carbon filtration, UV degradation, adsorption, ...) or advanced technologies, such as nanofiltration/ultrafiltration, reverse osmosis, advanced oxidation processes to guarantee a more efficient elimination.

Many radiology and imaging studies in medicine require the use of contrast media to increase the differences in density between the different tissues and structures of the organism. The pharmaceuticals used to generate bio-images represent an extensive and complex group of substances. Among them, ICM such as diatrizoate (DTZ), iodixanol (IDX), iohexol (IHX), iomeprol (IMP), iopamidol (IPM) and iopromide (IPR) are frequently employed. Margot et al. [5] investigated the limited removal of ICM during wastewater treatment. The physico-chemical properties of ICM (high stability, hydrophilic properties, high molecular size, ...) make the

removal of these organic compounds extremely difficult in WWTPs with a high cost associated [6]. Moreover, in the process of chlorinating water for human consumption, the simultaneous presence of ICM and natural organic matter (NOM), causes the formation of by-products or unwanted compounds such as iodinated trihalomethanes that are potentially carcinogenic [7].

A promising alternative for the removal of recalcitrant emerging pollutants is the adsorption on adequate adsorbents materials. Kovalova et al. [8] compared and predicted the elimination efficiency for 56 organic micropollutants (pharmaceuticals, human metabolites, and industrial chemicals) by applying post-treatment technologies (ozonation, UV and powdered activated carbon) to hospital wastewater. They found that most compounds were eliminated efficiently by powdered activated carbon and ozone treatment, whereas elimination was much lower with UV; ICM adsorption on activated carbons was less effective. Álvarez et al. [9] studied the removal of two emergent pollutants, caffeine and diclofenac, using two mesoporous carbon xerogel materials and compared the results with those obtained with a commercial microporous activated carbon. They concluded that mesoporous materials need much less time to reach equilibrium and that mesopores appears to be more conducive for the adsorption process, since the transport of the molecules within the pores is not limited by steric hindrance.

Carbon xerogels are polymeric synthetic materials whose properties can be tailored according to their final application by controlling the synthesis parameters [10,11]. Thus, it is possible to design the size of the pores and adapt the porous texture to the final application. Currently microwave treatment is also applied for obtaining these materials [12].

The presence of Natural Organic Matter (NOM), a complex matrix of heterogeneous organic material present in all natural waters mainly formed by humic and fulvic acids, can play an important role in the removal of organic micropollutants due to its adsorption onto porous carbonaceous materials [13]. The simultaneous presence of NOM and pharmaceutical contaminants in water implies a competition for the adsorption sites onto the large pores of carbonaceous adsorbent materials [14,15]. Furthermore, NOM can obstruct the microporosity of

the adsorbent making it less effective. NOM adsorption depends on factors such as pore volume, pore structure, electrostatic attractive and repulsive forces, specific interactions between the NOM and the surface of activated carbons and access to the positive adsorption sites, temperature and contact time [16].

This research work was undertaken in order to investigate the influence of the chemical and textural properties of carbon adsorbents (mesoporous carbon xerogels and commercial microporus activated carbons) on the removal of different emerging pollutants. Six pharmaceutical compounds and six ionidated contrast agents were selected according their different molecular size, acid dissociation constant (pKa), solubility and molecular weight. The adsorbent materials used were broadly characterized to try to find out the relationship between their chemical-textural properties and their effectiveness in the pollutant adsorption process. The influence of the presence of NOM in the water on the adsorption capacity of the target pollutants was also assessed.

2.- Materials and Methods

2.1 Adsorbents materials

Three different carbon xerogels (CX-A, CX-B and CX-C) were synthesized using the methodology of the *Microwave and carbon technological applications* group in INCAR described in the works of Rey-Raap et al., Moreno et al. and Calvo et al. [12, 17-22] with collaboration of Xerolutions Company.

Following that methodology, the organic xerogels were synthesized by polycondensation of resorcinol and formaldehyde using deionized water as solvent and a sodium hydroxide solution (1 M) as basification agent. The resorcinol/formaldehyde molar ratio and the dilution ratio were 0.5 and 5.7, respectively. Three solutions, with different pH ($5 < pH < 7$) [17-20], were heating in a microwave oven (85 ºC, 3 h) to allow gelation. Gel water excess was removed by heating in

the oven (mass loss ≈ 50%). After a drying step, the xerogels were carbonized (N_2 flow 500 ml/min, 50 ºC/min, 700 ºC, 2 h at final temperature) in a horizontal tubular furnace [21-22].

Two commercial activated carbons were selected according to their origin, shape and texture for comparing purposes. Hydrodarco C, powder (HYD C, lot M-1847), was produced from a lignit coal by Norit Americas Inc (USA). YAO, a coconut powder activated carbon (YAO, lot M325 2855), was supplied by Eurocarb Products Ltd (The United Kingdom). Both activated carbons were obtained by physical activation.

2.2 Adsorbates

Six pharmaceuticals (acetaminophen, caffeine, diclofenac sodium, levodopa, phenol and salicylic acid) and six ICMs (DTZ, IDX, IHX, IMP, IPM and IPR) were selected based on several criteria, such as, molecular weight, pKa, hydrophobicity, solubility, molar volume and molecular dimensions (Table SI 1) [20]. The molecule dimensions (the closest fitting "box" around the molecule) were calculated using Hyperchem 8.0 software [23]. Their molar volumes were obtained from Basic PhysiChem Properties (Advanced Chemistry Development, Inc. (ACD/Labs)).

Different stock solutions of each compound (100 mg L^{-1}) were prepared with ultra-pure water obtained by Milli-Q purification systems (Millipore academics). From these solutions, samples for calibration and sorption experiments were obtained by dilution with ultra-pure water (Milli-Q).

2.3 Characterization of the materials

The different adsorbents materials were characterized from their ultimate analysis and ashes. The ash content was determined according to the method described in ISO 1171 norm [24]. The ultimate analysis was carried out on a LECO CHN-2000 and a LECO Sulphur Determination S-144-DR. The pH of the slurry was determined by preparing a 10% aqueous suspension of samples.

The suspensions were stirred for 30 minutes, allowed to stand for 24 h, after which their pH was measured using a pH-meter.

FTIR technique was applied in order to determine the main functional groups on the surface of the carbon xerogels. For this purpose spectra were determined between 4000 and 400 cm^{-1} using an FTIR spectroscope (Nicolet 8700 Fourier Transform Infrared Spectromoeter with DGTS Detector).

The surface morphology of the different carbon xerogels was examined using a scanning electron microscope (FEI, Quanta FEG 650 Model) equipped with an Energy X-ray analyzing system (Ametek-EDAX, Apollo X detector).

The textural properties of the different adsorbents were characterized from N_2 adsorption isotherms 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 BET specific surface area (S_{BET}) [25], total pore volume, (V_{TOT}) at a relative pressure of 0.99, and pore size distribution (PSD). The PSD was evaluated using the density functional theory (DFT), assuming slit-shape pore geometry. Mercury porosimetry was used to determine the volume of mesopores and macropores and the percentage of porosity in these pore sizes. Mercury porosimetry was carried out using a Micrometrics AutoPore IV 9500 Series apparatus, which provided a maximum operating pressure of 228 MPa. Mercury porosimetry analysis was based on Washburn's intrusion theory (the contact angle being set to 130° and the surface tension to 485 dym/cm).

2.4 Single adsorption assays

For the single adsorption equilibrium studies, 20 mg of adsorbent was added to 100 mL of different organic compound solutions with various concentrations (10-100 mg L^{-1}). The mixtures were stirred for 24h at 25 ºC on a multipoint agitation plate [26, 27]. Then, samples were taken and filtered through a cellulose acetate filter (0.2 μm diameter pore). The remaining

concentrations were analyzed in a UV/Vis spectrophotometer (Lambda 25 PerkinElmer) at the corresponding wavelength of each compound (Supporting Information (SI) Table SI 1). The Organic compound uptake (q) was calculated by the following equation:

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

where q is the amount (mmol g^{-1}) of organic compounds adsorbed at equilibrium, C_0 and C_f are the initial and final concentrations (mmol L^{-1}), respectively, V is the volume (L) of the adsorbate solution and W is the weight (g) of the adsorbent used.

2.5. Adsorption modelling and statistical analysis

The experimental results were fitted to two parameter isotherm models: Langmuir (Eq. (2)) and Freundlich (Eq. (3)) [26, 28]

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

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

where q_e (mmol g^{-1}) is the amount of compound adsorbed per mass of unit adsorbent, C_e (mmol L^{-1}) is the organic compound concentration at equilibrium, q_{max} (mmol g^{-1}) is the maximum adsorption capacity, K_L (L $mmol^{-1}$) is a constant related to the affinity between the pollutant and the adsorbent, K_f ((mmol g^{-1}) (L $mmol^{-1})^{1/n}$) is the Freundlich sorption constant and n is a constant related to the intensity of the adsorption.

The parameter estimation of the different isotherms was solved using MATLAB software and minimizing the objective function (OF) (Eq. (4)) according to the methodology employed in the work [26]

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

where N is the number of measurements performed, q^* is the experimental solute uptake, q (P_1, P_2) is the uptake predicted by the model, P_1 and P_2 are the different estimated parameters. In the case of the Langmuir model, the parameters are q_{max} and K_L and for Freundlich K_f and n.

Statistical study was performed with the different experimental data and the estimated parameters. Linear correlation coefficient calculations were performed using Sigma Plot software (Sigma Plot 12.3, exact graphs and data analysis).

2.6. Multi adsorption assays

The experiments were conducted in ultra-pure water (Mil·li Q) and surface water collected from Cardener River (Barcelona, Spain). The surface water had a TOC of 3.75 mg C/L and a DOC of 3.23 mg C/L (determined by TOC Multi N/C 3100, Analytical Jena).

Solutions of the six pharmaceuticals and the six ICM mixed together in three different concentrations (0.1 μmol L^{-1}, 1 μmol L^{-1} and 10 μmol L^{-1}) were prepared with both ultra-pure water and surface water. The multi-adsorption process was conducted in the same way than the single adsorption assays (20 mg adsorbent, 100 ml sample, 24 h stirring and then filtered at 0.2 μm). The remaining concentration of the 12 compounds after the adsorption assays was analyzed using a UPLC-HRMS (Waters ACQUITY UPLC system coupled to a Orbitrap Q Exactive (Thermo Fisher Scientific, San Jose, CA, USA)).

The different multisolutions (pharmaceuticals and ICM) were analysed following the procedure described and performed in a previous work [29]. The details of the method were described in the Supplementary Information (SI Analytical method).

3. Results and discussion

3.1. Chemical and surface analysis of the carbon xerogels and activated carbons

The carbon xerogels used as adsorbents (CX-A, CX-B and CX-C) have a high carbon content (~97%), low hydrogen, nitrogen and oxygen content (<1.7%) and no sulphur, no ash or humidity are detected (Table 1). These results are according to their synthetic origin.

Table 1

Regarding commercial activated carbons, YAO, is characterized by its high carbon and oxygen content (90.92% and 2.74%, respectively) while HYDC shows the highest ash content (26.27 %). Moderate or high ash content is a common feature in the activated carbons obtained by physical activation of low-rank coal due to the high content of the mineral matter present in the precursor. In general, the activated carbons obtained by chemical activation process have a lowest ash content than their precursors (coal, industrial biomass wastes,..) [30, 31].

As it can be seen in Table 1, all adsorbents used have a basic pH (between 9.3 and 11.6), indicating a low level of acidic surface groups and/or the predominance of surface basic groups or perhaps the presence of mineral matter [32]. Depending on the pH of the medium and the pH of the carbon porous materials, the surface may be positively or negatively charged. According to Menendez et al. [33], in a neutral aqueous solution, (i.e., where the $pH_{solution} < pH_{adsorbents}$) the basic sites of the carbon materials combine with protons from the medium to leave a positively charged surface.

The carbon xerogels are also characterized by infrared spectroscopy in order to get information about the main functional groups on the surface. The different IR spectra are shown in Fig. 1. The main bands observed in the three carbon xerogels are a broad band between 3550-3200 cm^{-1} region which is attributed to the presence of –OH groups [34]. The two closest bands at 2910 and 2850 cm^{-1} correspond to asymmetric and symmetric C-H stretching vibrations of aliphatic groups (CH_3, CH_2). Other important peaks are approximately located at 1600 and 1450 cm^{-1}. According to Fuente et al. [35], these two bands can be attributed to hydroxyl groups terminating the zigzag edges of the carbon materials and C-O-H deformation with simultaneous carbon ring vibrations. The bands at 1230-70 cm^{-1} and ~840 cm^{-1} are related to oxirane ring system (C-O-C) whose

stretching vibration band is found at 3000-50 cm^{-1} [34]. Furthermore, the oxane ring system bands are observed at 1105 and ~815 cm^{-1}. According to Montes-Morán et al. [32], etheric rings are one of the functional groups that give a basic character to the surface of the carbon material.

Figure 1

The images obtained by scanning electron microscopy (SEM) of the synthesized carbon xerogels are shown in Fig. 2. In these SEM images it can be especially appreciated the shape and size of the clusters in the synthesized carbon xerogels.

Figure 2

3.2. Textural analysis of the carbon xerogels and activated carbons

The textural properties of the carbon xerogels and the commercial activated carbons were characterized by means of the nitrogen adsorption-desorption isotherms (Fig. SI 1,). As can be seen, the three carbon xerogels show a hybrid adsorption isotherm of type I-IV according to the BDDT classification of the International Union of Pure and Applied Chemistry (IUPAC) [36]. The N_2 adsorption capacity at low relative pressure ($p/p^0 < 0.1$), indicative of the presence of micropore (pore size smaller than 2 nm), is the same for all the carbon xerogels. The N_2 isotherms of these materials differ in the type of hysteresis loop they display (Fig. SI 1a), with CX-A showing a H2 type loop, CX-B an H1 type whereas CX-C may be of type H3 as it does not show any limiting adsorption at a high p/p^0 [36, 37]. The type-H2 hysteresis loop, present in CX-A, is typical of complex pore structures in which network effects are important and can be associated with pore blocking where the size distribution of neck widths is large. The H1 hysteresis loop, present in CX-B, is typical in materials which exhibit a narrow range of uniform mesopores. The H3 hysteresis loop type, present in CX-C, is typical of non-rigid aggregates of plate-like particles but also when the pore network consists of macropores which are not completely filled with pore condensate.

To try to understand the differences in the behavior of the three carbon xerogels during the adsorption process the PSD was calculated (Fig. 3. and Table 2). The carbon xerogels show practically the same microporosity (with pore diameters ranging from 0.9 to 1.7 nm approx.) with micropore volume around of 0.155 $cm^3\ g^{-1}$, while the mesoporosity of each carbon xerogel is very different and so CX-B have a mesopore volume of 0.914 $cm^3\ g^{-1}$ versus CX-C with only 0.273 $cm^3\ g^{-1}$. The BET specific surface area of the carbon xerogels is very similar with values between 594 – 651 $m^2\ g^{-1}$.

Figure 3

Table 2

The commercial activated carbon YAO, exhibits a nitrogen adsorption-desorption type I isotherm (Fig. SI 1) suggesting the development of microporosity without mesopores. On the other hand, HYDC shows a type I-IV nitrogen isotherm with a small degree of microporosity and the steep slope of the isotherm as well as the hysteresis loop reflect the development of mesoporosity (Fig. SI 1). The type-H4 hysteresis loop present in HYDC is often associated with narrow slit-like pores [37].

As can be seen in Table 2, YAO is the adsorbent with the highest microporosity and BET specific surface area (micropore volume of 0.357 $cm^3\ g^{-1}$ and 1092 $m^2\ g^{-1}$, respectively). This BET is almost twice the value of the other adsorbents. The three carbon xerogels have a similar micropore volume and in all the cases the contribution of this volume to the total porosity is lower than 25%. However, YAO is chiefly microporous with more than 90% of the pore volume composed of pores less than 2 nm in width (Table 2 and Figure SI 2). HYDC shows a high mesopore volume (0.198 $cm^3\ g^{-1}$) which implies more than 55% of its total porosity, being lower to the mesopore volume that present the carbon xerogels (from 273 $cm^3\ g^{-1}$ up to 0.914 $cm^3\ g^{-1}$).

The macro and mesopore volume of carbon xerogels was determined by Mercury porosimetry (Fig. 4, and Fig. SI 3 and Table SI 2). The CX-C is the carbon xerogel which present the higher

values of macro and mesopore volume ($V_{macropore}$ = 0.63 cm^3 g^{-1} and $V_{mesopore}$ = 1.09 cm^3 g^{-1}) and the average pore diameter (45.6 nm). On the other hand, CX-A and CX-B showed a low macropore volume (up to 0.08 cm^3 g^{-1}) and average pore diameters of 8.8 and 19.3 nm, respectively.

Figure 4

3.3 Pharmaceutical and ICM equilibrium studies

The adsorption isotherms corresponding to the adsorption of the twelve organic compounds onto the carbon xerogels and activated carbons are shown in Fig. SI4 and Fig. SI5. According to Giles classification [38] the pharmaceutical and ICM isotherms corresponding to the carbon xerogels and HYDC are types L (group 2), which means that these adsorbents have a good affinity for these compounds. The isotherms corresponding to phenol, salicylic acid, acetaminophen and DZT are also types L (group 2) for YAO, whereas the rest of pharmaceutical and ICM isotherms for YAO are type H showing a higher affinity.

Tables SI 3 (a-e) shows the different parameters values obtained from the experimental data fitted to the isotherm models Langmuir and Freundlich and the objective function (OF). In the case of the minimum OF values, the Freundlich equation provides a better description for most of the pharmaceutical and ICM compounds in the carbon xerogels except salicylic acid and IDX. Both compounds are explained by the Langmuir model suggesting the formation of a monolayer. Respect the activated carbons, Langmuir and Freundlich models indicate a good fit depending on the pharmaceutical or ICM adsorbed.

The Freundlich parameter n indicates that the adsorption of the twelve organic compounds is favorable onto the carbon xerogels and activated carbons because this value is between 1 and 10 [39]. The highest maximum adsorption (q_{max}) for the pharmaceutical and most of ICM is provided by the activated carbon YAO. In the case of IDX and IPR, carbon xerogels get a better adsorption around 0.14 and 0.10 mmol g^{-1} respectively. In addition, the adsorption of

ICM in CX-A is higher than CX-B and CX-C suggesting that the mesopore diameter can influence on the adsorption process.

3.3.1. Effect of the nature of the adsorbate

The adsorption selectivity of the pharmaceutical compounds on carbon xerogels follows the order: phenol > (≈ similar in CX-A) salicylic acid > acetaminophen > caffeine > levodopa > diclofenac. In the case of ICM is: IDX > IMP ≈ IPM > IPR > IHX > DTZ, except for CX-C that the adsorption of IPR is higher than IMP and DTZ than IHX. Both orders are compared with the physical-chemical properties of the compounds (Table SI 1) and the adsorption process of the activated carbons in order to establish which properties of the organic compounds would have influence on adsorption.

The linear correlation coefficient (Tables SI 4 and SI5) between q_{max} and the different physical-chemical properties of the compounds shows that pKa and solubility do not play a significant role in the adsorption of pharmaceutical and ICM. However, the highest dimension of the molecule deserves to be considered. As it is shown in Fig. 5, the smaller the size of pharmaceutical, the greater quantity of compound is adsorbed (negative strong $r \geq 0.838$) on carbon xerogels. This trend changes for ICM, which an increase of the size leads to a higher adsorption (positive $r > 0.643$).

Figure 5

It would be expected that adsorption of phenol could be higher than salicylic acid due to the its molecular size. In this study, the adsorption of phenol is similar (in carbon xerogels) or lower (in YAO) than salicylic acid. So, the chemical groups in the aromatic ring can probably influence on the adsorption process. The dispersive/repulsive mechanism adsorption (π-π dispersion interaction, electron donor-acceptor complex formation, hydrogen-bond formation [40]) has to be considered. Phenol has a donor group activating the aromatic ring while salicylic acid presents a withdrawing group deactivating the aromatic ring. The lower adsorption of phenol suggests

dispersion effects due to the electron donating group in this compound. Moreover, the withdrawing groups of salicylic can play an attraction interaction with YAO and carbon xerogels surface groups.

Another comparison between similar size molecules is the adsorption of caffeine and levodopa. Both compounds are similarly adsorbed onto YAO, but in carbon xerogels, caffeine exhibits a higher q_{max} than levodopa. One of the different physico-chemical properties between these molecules is the logKow. So, hydrophobicity can play an important role to the adsorption onto carbon xerogels. It can be classified as high (3.5 < log Kow), moderate (2 < log Kow < 3.5), low (log Kow < 2) [41] and hydrophilic (log Kow < -0.5). A high positive linear correlation (r>0.9, different carbon xerogels, table SI 4, Fig. 5) between q_{max} and log Kow is observed in a low – moderate hydrophobicity pharmaceutical compounds (Diclofenac is excluded). In the case of ICM compounds, the trend is negative (Fig. 5), indicating the higher hydrophilic the greater adsorption. Furthermore, hydrophobicity is also highly correlated to the adsorption intensity of Freunlich (n) in carbon xerogels (Fig. 6 and Fig. SI 7). The more negative (hidrophylic compounds) or lower log Kow value (low hydrophobic compounds), the higher adsorption intensity (n). In the case of activated carbon, there is only a negative correlation in low hydrophobic compounds. The trend changes in ICM compounds suggesting that other factor like carbon mesoporosity and chemical interactions can affect the adsorption process. These results are partially in agreement with Nam et al. [42] which concluded that high hydrophobic compounds were better fitted to Freundlich than low hydrophobic.

Figure 6

3.3.2. Effect of the pore distribution and carbon surface chemistry.

To assess the influence of pore size distribution on the adsorption of pharmaceutical and ICM compounds, the maximum adsorption capacities (q_{max}) for each compounds have been correlated with the different pore volumes ($V_{u\text{-}mic}$, V_{micro}, V_{meso}, Table 2). The results (Table SI 6) indicate that the adsorption of pharmaceutical and DTZ occurs in ultramicropore (r>0.76) and in

the total micropore (r>0.93). On the other hand, it is observed a negative correlation on the mesopore, suggesting the supermicropore is the main site of adsorption. These results are in agreement with Marques et al [43] and Vadenyapina et al. [44] which studied the adsorption of acetaminophen onto activated carbons. They concluded that the presence of a mesopore network does not have an impact in the diffusion of small compounds when it is an important volume of supermicropores.

The adsorption of IPM, IMP and IHX probably occurs on the micropore (good correlation total micropore, r>0.73), IDX in the mesopore (r ≈ 0.8) and there is no clear correlation for IPR. In order to correlate the adsorption of the different ICM (q_{max}) onto different size of mesopore, different pore volume cross-sections are performed on the mesopores using data from the PSD (Table SI 7). In this case, IHX, IMP and IPM are better adsorbed in the 1.3-5 nm diameter pore (r>0.87, table SI 8). These results are in accordance with the works of Mestre et al. [45,46] that studied the adsorption of IPM in activated carbons. They concluded IPM adsorption took place on supermicropores and mesopore creating a dimmer or trimmer form of IPM depending on the texture of the adsorbent. Ge et al. [47] proposed a physisorption of IPM (q_{max}≈800 mg g^{-1}) onto the micro and mesopore activated carbon (S_{BET}=1951 m^2 g^{-1} and V_{meso} = 1.57 cm^3 g^{-1} (BJH model)) In the case of IDX and IPR, the adsorption probably occurs in the interval 5-10 nm of the mesopore (higher positive correlation than the global mesopore 2-10 nm). Both compounds show the largest dimension and it may hinder to access the narrower mesopores (2-5 nm). On the other hand, the presence of a suitable macropore and mesopore structure in carbon xerogels allows large molecules to be adsorbed to this range of pores. In the case of HYDC and YAO, a lower adsorption of ICM compounds can be due to the absence of macroporosity, low quantity of mesopore and the presence of mineral matter (or ashes) blocking the access of ICM in the mesopores. Beside the pore distribution of adsorbents, chemical interactions might be occurred between the surface of the adsorbents and the pharmaceutical and ICM compounds.

According to Lorenc-Grawobska et al. [40], phenol adsorption occurs on the micropore by three different mechanisms. One of them is based on the formation of an intracomplex between the

hydroxyl group of phenol and the external surface oxygen groups blocking the pore entrance [41 48]. In this study, the adsorption of phenol might be reduced due to competition with water molecules for the same sites in presence of oxygen (≈ 1% carbon xerogels, 2.74% in YAO) via hydrogen bonding (groups –OH on carbon xerogels).

As regards the adsorption of acidic compounds with a low pKa (salicylic acid and DZT), it may be affected by the net positive charge of the different absorbents due to the basic character of the adsorbent (pH>9.2, Table 1). At neutral pH solutions, acidic compounds are dissociated and electrostatic interactions with the positive surface favours the adsorption of these compounds [31]. In fact, it might be one of the reasons that explains why salicylic acid, even having larger size, is similar or higher adsorbed than phenol in carbon xerogels and YAO. The presence of high content of mineral matter in HYDC has different effects on the adsorption of different organic compounds studied, negative on salicylic acid and positive on levodopa. According to Moreno-Castilla [49], mineral matter is able to adsorb water, blocking the pores and affecting hydrophobic compounds as the case of salicylic acid and could enhance the adsorption of hydrophilic compounds as levodopa. Despite differences in adsorption between caffeine and levodopa due to their hydrophobicity, acid - basic oxygen functional groups on the surface adsorbents can affect their adsorption process. Quesada- Peñate et al. [50] observed that the adsorption of levodopa was increased by basic groups on the surface of activated carbons and reduced due the presence of acidic groups giving a more hydrophilic character to the adsorbent and a possible water adsorption. Alvarez et al. [9] and Batista et al. [51] observed a higher affinity of caffeine towards to different adsorbents with basic surface, with high density of surface positive charge due to the predominance of nitrogenated functionalities over oxygenated groups. This fact enhanced the interaction between the active adsorption sites with the lone pairs of the nitrogen atoms of caffeine. Similar conclusions were obtained by Ptaszkowska-Koniarz et al. [52] which modified carbon xerogels with amine groups and copper obtaining different adsorbents with acid and basic oxygen functional groups. They observed the highest caffeine adsorption on the adsorbents with the highest content of basic oxygen groups and the lowest with onto those with acidic groups.

They suggested an interaction via hydrogen bonding of the heterocyclic-N caffeine group and hydrogen of the surface carbon xerogels (-NH_2, -OH, -COOH).

Regarding the adsorption of acetaminophen and diclofenac, different mechanisms can be involved depending on the adsorbents and increasing the amount adsorbed. The most common are van der Waals force [53], electrostatic interactions, n-π and π-π interaction [9, 54] hydrophobicity and hydrogen bonding [55].

There is little information about chemical interactions of ICM with different adsorbents. Mestre et al. [56] observed that in aqueous solutions (at pH 5), iopamidol is a neutral molecule thus π-π interactions can take part in the adsorption on a slightly negative charged surface. Kim et al. [57] proposed different mechanism involving electrostatic interactions, hydrophobic interactions and hydrogen bonds for IPR adsorption.

In the present study, it seems that physisorption can be the dominant mechanism in carbon xerogels due to the linear correlation with adsorption and micro-mesopores. In addition, the hydroxyl groups (-OH, Fig. 1) and basic oxygen groups can support the adsorption process of different pharmaceuticals via dipole-dipole H-bonding. In the case of ICM adsorption, it is required thorough investigation for ICM chemical interactions in future studies.

3.4. Multiadsorption and influence of NOM

ICM and pharmaceutical compounds are not expected to appear isolated in wastewater and surface water. Thus, the removal of a mixture of all compounds (ICM and pharmaceutical) in a surface water is studied, as well as in ultrapure water (Mil·li Q water) for comparison purposes. This can also help to a better understanding of the effect of NOM present in water on the multiadsorption process in different concentrations (0.1, 1 and 10 μmol L^{-1}). The total concentrations of the pharmaceutical and ICM studied compounds (before and after the adsorption experiment), together with the percentage of removal in Mil·li Q and river water are

listed in table 3. In addition the percentages removals of each compound are shown in figures SI 8, SI 9 and SI 10.

Table 3

As can be seen in ultrapure water and at low concentrations, the removal of almost all pharmaceuticals and ICM are higher than 87.8% and 98.9%, respectively. The only exception is phenol removal, that exhibits the lower adsorption (60-90% adsorbed, Fig. SI 8a), suggesting that chemical interactions between carbon materials and water occur through hydrogen bonding, and as a result of the called solvent effect [58].

At 1 μmol L^{-1} concentration in ultrapure water, ICM compounds (except IDX) compete for the narrow of mesopores as can be seen the progressive reduction of amount adsorbed according to the diameter of mesopore carbon xerogel. For example, the percent of IHX adsorbed is 85%, 77% and 60% for CX-A, CX-B and CX-C, respectively (Fig. SI8a). Similar progression (93%, 87% and 78%) is observed for the bulkiest IDX at the highest concentration (10 μmol L^{-1}). On the other hand, the total amount of pharmaceuticals removed (Table 3) diminishes to the same extent on all three carbon xerogels, indicating that the microporority may be saturated. Whereas the amount of ICM adsorbed decreases drastically in line with the total mesoporority and pore diameter.

The presence of NOM affected on the adsorption process at the different concentrations. The first remarkable result is the lower adsorption of DTZ and salicylic acid (at highest concentration) onto the carbon xerogels according to the pore diameter (Figure SI 8b) and respect to the other ICM and pharmaceutical in ultrapure and surface water. Similar results were obtained by different authors [5, 8, 59] that the DTZ remove was around 15% in wastewater treatment plants respect IHX, IPM, IMP and IPR (between 50-80% elimination). NOM is a complex mixture of organic compounds that is negatively charged at neutral pH, so electrostatic interactions may favour or oppose the adsorption with adsorbents and the other compounds [16]. DZT and salicylic acid at neutral solutions is negative charged, as a consequence electrostatic repulsion is produced with NOM reducing the amount adsorbed.

The adsorption of IHX, IMP, IPM and IPR also are affected by the presence of NOM at 1 μmol L^{-1} (and IDX at 10 μmol L^{-1}). High linear correlation (r>0.87) is observed between the difference amount adsorbed of ICM in ultrapure and surface water and the volume intrusion Hg mesopores of carbon xerogels (Fig. 7 and Table 4).

Figure 7

Table 4

As can be observed, NOM is adsorbed along the entire mesopore regardless of their size without being affected by the presence of a macropore structre (lower linear correlation with total meso-macropore, Table 4). In consequence, ICMs are directly competing with NOM for the same active narrow mesopore pores. In addition, molecule size also affects in ICM adsorption since the higher the dimension the less the amount adsorbed, as in the case of IPR compared to IHX, IMP and IPM.

Acetaminophen, caffeine and diclofenac are practically removed by the carbon xerogels at 1 μmol L^{-1}. This suggests that both compounds are adsorbed on the micropore without direct competition with NOM. At 10 μmol L^{-1} these pharmaceuticals are adsorbed higher than 60% and ICM lower than 17% (Fig. SI 10b), indicating that carbon xerogels are losing their efficiency due to the high concentration of pollutants and presence of NOM.

4.- Conclusions

Carbon Xerogels (CX-A, CX-B and CX-C) and commercial activated carbons (HYDC and YAO) were successfully used as adsorbents of six pharmaceuticals and six Iodinated Contrast Media (ICM) selected for pollutant removal in aqueous phase. The chemical characterization of the carbon materials revealed that all adsorbents used have a basic pH (between 9.3 and 11.6), indicative a low level of acidic surface groups and/or the predominance of surface basic groups or the presence of mineral matter. The textural characterization indicated that YAO is the more microporous adsorbent (micropore volume of 0.357 cm^3 g^{-1}) and that the carbon xerogels are

fundamentally meso and macroporous materials (mesopore volume up to 1.09 cm^3 g^{-1} and macropore volume up to 0.63 cm^3 g^{-1} by mercury porosimetry). In relation to the adsorption process the main results are:

- The sorption coefficients of the pharmaceuticals and ICM fitted the Freundlich and Langmuir models well. Adsorption of the pharmaceuticals took place mainly in the total microporosity, whereas that the adsorption of IPM, IMP and IHX occurred on the wider micropores and mesopores (1.3 – 5 nm), IPR on the mesopores (preferably 5-10 nm) and IDX on the total mesopores. ICM adsorption depended specially on the mesopore width of the carbon xerogels.
- The adsorption intensity (n) and partitioning constants (Log Kow) maintained a negative correlation with the hydrophobic compounds in all the adsorbents. In the case of hydrophilic compounds the correlation depended on the mesopore structure of the carbon xerogels and differed from that of the commercial activated carbons.
- The adsorption of salicylic acid was mainly due to electrostatic interactions and was greater than that of phenol. The adsorption of phenol was affected by water competing for the same adsorption sites (solving effect). A high quantity of mineral matter or ashes (in the case of HYDC) influenced positively the adsorption of levodopa.
- The presence of natural organic matter reduced the adsorption of ICM due to the competition for mesopores. A high correlation of the difference of ICM adsorbed (between mil·liQ and surface water) with the total mesopore volume of the carbon xerogels was observed. Furthermore, different repulsion interactions were produced between acid ions and NOM (negative charged) decreasing the quantity adsorbed.

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Figure captions

Figure 1 IR spectra of carbon xerogels

Figure 2. SEM photographs of the synthesized carbon xerogel at different magnifications (5000X, 15000X and 60000X, respectively).

Figure 3. Pore size distribution obtained by application of the DFT model to the N_2 adsorption data of carbon xerogels

Figure 4. Log differential Mercury intrusion volume *vs* pore diameter on the carbon xerogels

Figure 5. Trend of adsorption capacity (q_{max}) *vs* the largest dimension compound and logkow onto carbon xerogels (CX-A, CX-B and CX-C a) pharmaceuticals, b) ICM

Figure 6. Relation between the intensity of adsorption (n) Freundlich and logkow on carbon xerogels: a) CX-A, b) CX-B, c) CX-C

Figure 7. Difference of ICM adsorbed between Mil·li Q and surface water at 1 μmol L^{-1} vs Hg volume intrusion mesopores (cm^3 g^{-1})