Fluoxetine adsorption from aqueous solution onto activated carbons

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Introduction

The potential toxicity of pharmaceutical compounds in the environment has lead to the increased interest in finding efficient methods to remove them. The disposal of these products to the terrestrial or aquatic environment is a major pollution problem, in particular the introduction of such endocrine disruptors on food chain via the aquatic environment, mainly due to their physico-chemical characteristics (such as solubility, polarity, low volatility...) [1]. One of the most used pharmaceutical compounds is the selective serotonin reuptake inhibitors (SSRIs), which are used to treat a variety of major psychiatric pathologies. The active principle of SSSIs is fluoxetine and the most common commercial drug is commercialized under the brand name Prozac®.

Activated carbons (ACs) have been widely used in wastewater and drinking water treatment plants for the removal of various pollutants via adsorption processes, in particular for the adsorption of some pharmaceutical compounds. ACs can be produced from a great variety of raw materials; however, the possibility of using agriculture or industrial residues for preparing ACs is interesting since it allows the reduction of production costs.

With these premises, this work aimed to prepare ACs from almond tree pruning by physical activation processes with steam and carbon dioxide, under different temperature conditions. Selected samples were impregnated with triethylenediamine (TEDA, 5%wt.) by sublimation. The ACs characterization was made by N_2 adsorption at 77 K (AUTOSORB-1, Quantachrome), mercury porosimetry (AUTOPORE 4900 IV, Micromeritics), helium stereopycnometry (Quantachrome), FT-IR spectroscopy (Perkin Elmer model Paragon 1000PC) and pzc determination. The fluoxetine adsorption was studied under neutral pH at 25 ºC. Stock solutions of fluoxetine HCl (0.5 and 1 gL^{-1}) were prepared in deionized water with variable amounts of ACs (0.010 and 0.200 g), maintaining the contact during 420 min. The determination of fluoxetine HCl was done by ultraviolet absorption at 274 nm (Perkin Elmer Lambda 850 Uv–Vis spectrophotometer).

Discussion of Results

The precursor showed a higher reactivity towards steam in comparison to CO_2 activation, which can be attributed to the greater diffusivity of the former agent. Table 1 shows the textural characteristics of the ACs prepared, as determined from N_2 adsorption isotherms at 77 K. From this Table it can be inferred that the adsorption capacity of the ACs is increased with temperature with both activating agents, up to a certain burn-off degree in which a decrease in the pore volumes is found. All ACs exhibited type I isotherms, typical of microporous solids [2]. Also, the relative proportion micro/mesopores showed a slight widening when increasing temperature with both activating agents. However, the temperature conditions which caused the destruction of porosity also brought up a decrease in the external surface contribution, probably due to external burning.

With respect to TEDA impregnated ACs, it was found that impregnation process caused a significant decrease (of approximately 50%) of the apparent surface available to N_2 at 77 K, mainly due to the micropore blockage. With regards to their surface chemistry, all ACs were basic with pzc decreasing in the sequence: C900/60>S650/60>C900/60/T>S650/60/T, which shows that the impregnation caused a decrease on the pzc value.

Table 1. Textural parameters determined from N_2 adsorption at 77 K

	Burn-off (%)	S_{BET} ($m^2\ g^{-1}$)	V_{mi} ($cm^3\ g^{-1}$)	V_{me} ($cm^3\ g^{-1}$)	S_{EXT} ($m^2\ g^{-1}$)
C700/60	16.5	399	0.22	0.03	30
C750/60	17.3	391	0.22	0.03	30
C800/60	21.3	432	0.23	0.04	36
C850/60	27.6	547	0.28	0.07	61
C900/60	32.4	710	0.37	0.13	138
C950/60	37.4	565	0.29	0.09	94
S650/60	33.6	651	0.34	0.14	122
S700/60	44.8	755	0.38	0.18	143
S750/60	62.8	870	0.44	0.26	224
S800/60	66.6	841	0.43	0.22	173
S850/60	82.0	768	0.37	0.17	148

Figure 1 shows the fluoxetine adsorption isotherms for selected ACs. The higher fluoxetine uptake of C900/60 in comparison to S860/60 can be associated to the greater presence of microporosity found in the former sample, rather than to a higher chemical affinity, since C900/60 has a higher value of pzc (which would not favor the adsorption process considering fluoxetine basic character). With respect to impregnated ACs, it was found that TEDA deposition induced modifications on the adsorption mechanism. On the one hand, fluoxetine adsorption was in some extent inhibited at low C_e (maybe because of the existence of competitive adsorption with water molecules). On the other hand, a significant increase in fluoxetine adsorbed volume was found as C_e increases, which could be related to the existence of some chemical interactions TEDA-fluoxetine by means of weak forces such as hydrogen bonds. In the case of samples S650/60 and S/650/60/T, impregnation caused an increase in the fluoxetine adsorption capacity, despite its lower value of apparent surface.

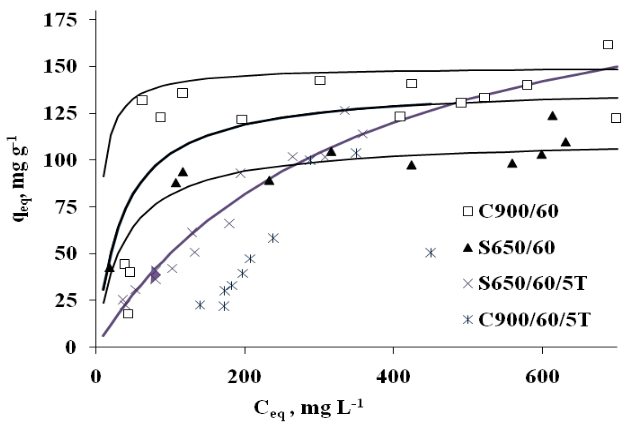

Figure 1. Fluoxetine adsorption isotherms.

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