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Adsorption of Diclofenac from aqueous solution using activated carbon prepared from olive stones

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ABSTRACT

Hydrogen is a valuable source of energy. However its storage is a major concern and means has to be developed for this purpose and where processes based on the technique of adsorption can be regarded as promising ways, particularly when using natural and with no cost solid materials.

The retention capabilities of this technique are shown through the present study which concerns the retention of a pharmaceutical compound, namely Diclofenac from aqueous solutions by adsorption onto activated carbon prepared from olive stones.

The first stage consisted of the preparation and determination of the physical and chemical characteristics of this material such as pH_{PZC}, porosity and specific area using known techniques of characterization. The functional groups present on the surface of this material were also determined by using Boehm method and by Fourier transform infra-red spectroscopy (FTIR).

The effects of contact time, pH, initial concentration of Diclofenac and adsorbent dose were investigated experimentally.

The results showed that the retention of the pollutant was rapid during the first minutes and then slowed down to reach equilibrium after 30 min. The maximum adsorption was reached at pH = 2.

Diclofenac adsorption kinetic was of the pseudo-second order controlled by the intra-particular diffusion phenomenon but is not the limiting step.

Basing on the obtained experimental data, the adsorption isotherm on the preset concentration range was well represented by the BET model.

Introduction

Hydrogen a non polluting energy vector requires great storage means. Different ways of hydrogen storage may be based on high and low pressures, liquefaction, involve chemical compounds that reversibly release H_2 upon heating, metal hydrides, etc. [1].

The present work is mainly devoted to the study of the retention capabilities of an activated carbon obtained from olive stones (ACOS), testing the elimination of pharmaceutical micropollutants, in the perspective to exploit this property for Hydrogen storage where porous carbon solid materials have

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shown great capabilities as H_2 sorbents due to their important specific surface area [2].

In fact pharmaceutical active compounds (PhACs) are a wide group of organic molecules, used for treating humans and animals and which may reach the aquatic environment via urine at very low concentrations of the order of μg/L and even ng/L [3,4]. They usually do not have acute toxic effects on aquatic fauna and flora, but can lead to long-term effects, representing a threat to both public health and the environment [5,6] due to their physicochemical properties, particularly polarity, water solubility, persistence, microbial resistance [7,8] and bioaccumulation in the food chain [9].

Different methods involving membrane filtration, advanced oxidation processes and adsorption [10] have been proposed for the removal of these compounds. The latter i.e. adsorption which is the main concern of the present work, has shown great capabilities, particularly when used with activated carbon [11]. However currently there are many developed adsorbents for the removal of drugs pollutants from aqueous solutions and industrial effluents.

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug used in human medical care as analgesic, antiarthritic and antirheumatic compound [12] and is one of the most extensively studied pharmaceuticals, for his potential toxic effects [13].

The present work is an opportunity to show the important factors to consider for a study of a solid material having a retention capacity of various compounds such as Hydrogen. This is shown through the example of the adsorption process of DCF using an activated carbon prepared from olive stones, evaluating, particularly, its physico-chemical characteristics and describing the retention kinetics.

Materials and methods

Materials

The olive stones were washed with slightly acidified water, to remove residual oils, and then dried in ambient air. An aqueous solution of 10% H_2SO_4 is mixed in the ratio 1:1with the olive pits for 24 h. The sorbent was washed with distilled water, dried at room temperature for more than 6 h, then at 110 °C for 24 h. The treated material was carbonized at 550 °C in a programmable oven (NUVE SANAYI) type (MF 120) for 1 h time. The carbonized sorbent was crushed into granules, sieved to different particle sizes, and then preserved in desiccators ready for use.

Adsorbate and chemical

Diclofenac sodium (DCF) (molecular weight = 318.1 g/mol; chemical formula $C_{14}H_{10}Cl_2NNaO_2$; pKa = 4.2) was purchased from Suzhou Ausun and its molecular structure is shown in Fig. 1. All other chemicals used were of analytical grades (Panreac, Cheminova, Fluka, Merck, Labosi et Biochem).

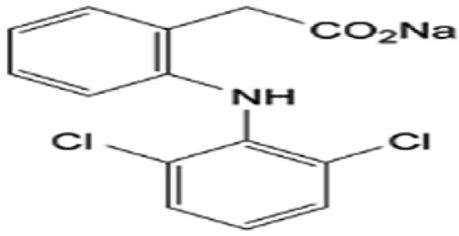

Fig. 1 – Molecular structure of Diclofenac.

Characterization techniques

Characterization of biosorbent was performed to obtain a better interpretation of the mechanism involved during the biosorption process.

Characterization of activated carbon prepared from stone olives required the use of several methods, mainly spectroscopic and volumetric.

Moisture was determined by drying the adsorbent in an oven at 105 °C until its weight remained constant. It is calculated by the following equation [14]:

$$H\% = \frac{m_0 - m_1}{m_0} \cdot 100 \quad (1)$$

where m_0 and m_1 are the adsorbent masses before and after drying, respectively.

Ash rate was assessed by the determination of the mass loss by combustion of material. For this 1 g of the dry adsorbent was introduced into a calcination crucible which was then placed in an oven at 600 °C for 45 min, After cooling the crucible was weighed. Ash rate is expressed by the following equation [15]:

$$\% = \frac{P_1 - P_2}{P_1} \quad (2)$$

where P_1 and P_2 are the weight (g) of the filled crucible before and after carbonization, respectively.

Porosity is due to the presence of pores of channels and cavities of different dimensions in the solid structure. The porosity influences the diffusion of the molecules inside the solid. It was determined as follows: a mass of material was introduced into a 50 ml container to the 35 ml graduation. Water was introduced into a test tube to the 10 ml graduation, and then it, water, was poured slowly and carefully in the first container until it reached exactly the solid level, noting the used amount of water. Porosity is given by the following relationship [16]:

$$\varepsilon = \frac{V_1}{V_t} \quad (3)$$

where m_2 and m_1 are the masses of the test tube filled with solid and water (g) and empty, respectively.

Surface area is related to the adsorption capacity of an adsorbent and its increase indicates a greater availability of binding sites for the adsorbate [17]. It was determined by the methylene blue method which consists in measuring the adsorption capacity for methylene blue, which is the amount of the dye necessary for a monolayer covering the external and internal surfaces of all particles present in 100 g of the