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Application of fractional factorial and Doehlert designs for optimizing the preparation of activated carbons from Argan shells

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ABSTRACT

A high quality activated carbon has been obtained, by physical activation with steam, from a Moroccan agricultural by-product (Argan shells) and their characteristics were investigated. In order to optimize experimental conditions of the preparation, a combination of a fractional factorial design and a Doehlert design was applied. In the first step of this work, a two-level fractional factorial design $2^{(5-1)}$ was used to study effects and first order interactions of various factors such as atmosphere in carbonization step, carbonization time at 400 °C, activation temperature, activation time and steam flow. The results reveal that the most influential factors on the yield and the methylene blue adsorption are activation temperature, activation time, steam flow and the presence of a significant interaction between activation temperature and activation time in both cases. In the second step, activation temperature and activation time were optimized using Response Surface Methodology with a Doehlert design, and Desirability function. The optimal conditions for the preparation of activated carbon have been identified to be an activation temperature of 880 °C, an activation time of 96 min and steam flow fixed at this positive level of 0.2 $cm^3\ min^{-1}$. The characteristics of prepared activated carbon obtained at the optimal conditions were determined using adsorption capacity of methylene blue, iodine and phenol, BET surface area, pHpzc, and surface functions based on Boehm method. Those characteristics (MB adsorption: 608.9 mg g^{-1}, iodine adsorption: 1026.4 mg g^{-1}, phenol adsorption: 633.3 mg g^{-1}, BET surface area: 1292 $m^2\ g^{-1}$) were shown greater than those of a commercial activated carbon used in water treatment and those reported by other researchers studying activated carbon preparation from various solid wastes by steam activation method. On the other hand, this work showed that Argan shells are a good precursor for the production of activated carbon, by steam physical activation, with high performance to be used in water treatment applications.

1. Introduction

Activated carbons are of great interest. They are highly effective adsorbents that are extensively used in a wide range of applications such as medical uses, industrial applications, gas storage, removal of pollutants and odor from gaseous and liquid phases, catalysis, gas purification and separation... [1–6]. Activated carbon can be manufactured, by physical or chemical activation, from different lignocellulosic raw materials like wood, coconut, turf, mineral coal, bone, wool, cotton, synthetic polymers... [7–9]. However, the high cost (including production from expensive and non-renewable precursors, regeneration and reuse) restricted its widespread use. To date, there has been an increasing interest in the preparation of activated carbon from by-products of agriculture and from industrial wastes [10–20]; the utilization of those biomass wastes for activated carbon production has a positive impact in reducing organic solid wastes, production of materials with high added value and on environmental protection.

The main objective of this study is to determine the optimal conditions to prepare a new activated carbon, by physical activation with steam, from an agricultural by-product (Argan shells) which is a cheap precursor, abundant and underused. The Argan tree (*Argania spinosa*) is an endemic species in the Southwestern region of Morocco, and its seeds are used to produce oil of value for culinary and cosmetic uses. The Argan oil process produces large quantities of biomass residues that are mainly used for heating purposes.

The preparation of activated carbon is influenced by many factors. For this reason experimental designs have been used to control the different factors which influence and interfere in preparation, in order to optimize experimental conditions. In the first step of this work, a fractional factorial design was used to study the effects of these factors on the preparation in order to extract the most important ones. In the second step, the most influential factors are optimized using Response Surface Methodology and multicriteria optimization with a Doehlert design [21] and desirability function.

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Once the activated carbons were obtained, the optimal sample was characterized by different methods to determine surface area, pore size distribution, surface functions and point of zero charge. Additional information on pore size distribution and efficiency was obtained by the adsorption characteristics for different adsorbates such as methylene blue, iodine and phenol. The results were compared with those of a commercial activated carbon used in drinking water treatment.

2. Materials and methods

2.1. Preparation of activated carbon

2.1.1. Raw material

Argan shells were obtained from Argan oil processing in the region of Essaouira, Morocco. This residue was crushed and sieved. A fraction with a particle size of 1–2 mm was selected for the preparation.

2.1.2. Two step preparation (carbonization/activation)

The carbonization of raw material is a method for eliminating volatile products by the degradation of organic material in such a way as to keep, in addition to mineral elements, only a carbonized skeleton. The operational conditions which are used during carbonization determine the porous texture.

The dried residue was carbonized in a tube furnace (Carbolite 1200C, UK) with a temperature control under a flow of N_2 gas (300 $cm^3\ min^{-1}$) at a heating rate of 10 °C min^{-1} at carbonization temperature for the desired time, before it was activated (heating rate of 10 °C min^{-1}) at desired activation temperature for the desired time under steam (0.2 $cm^3\ min^{-1}$) and cooled to room temperature. After activation, the activated carbons were boiled for 30 min in distilled water, dried, ground and sifted to obtain a powder with a particle size smaller than 50 μm. This powder was then dried at 105 °C until constant weight and kept in a hermetic bottle for future tests.

2.1.3. One step preparation (activation)

The activation of the raw material was conducted in a tube furnace (carbolite) with a temperature control as at a heating rate of 10 °C min^{-1}. At the activation temperature, the steam (0.2 $cm^3\ min^{-1}$) was injected using a steam generator placed at the entrance of the reactor. The other steps were the same as in Section 2.1.2.

2.2. Characterization of activated carbon

2.2.1. Characterization techniques

The samples were characterized by using nitrogen adsorption at 77 K using AUSORB IQ from Quantachrome Instruments with embedded software (Quantachrome® ASiQwin™). The BET equation was applied to the N_2 adsorption isotherms, from which the nitrogen surface area was obtained using a value of 0.162 nm^2 for the molecular area of N_2 at 77 K.

The chemical property analyses were done by measuring the point of zero charge or pH_{PZC} determined using the pH drift method [22]. While for quantifying total acidity and the total basicity, titration method was carried out based on Boehm method [23].

2.2.2. Adsorption tests from aqueous solutions

The adsorption capacity is one of the essential parameters in the process design of a specific adsorbate–adsorbent system.

To have maximum adsorption capacities of the activated carbon samples for methylene blue, iodine and phenol, the adsorption isotherms were determined. The choice of these molecules is justified by their properties. Thus, the mesopores and large micropores of carbon are often studied by methylene blue adsorption and this also serves as a model compound for adsorption of organic contaminants from aqueous solution [24]. The iodine molecule gives information on the surface area contributed by pores larger than 1 nm [25]. The determination of the iodine number is a simple and fast test giving a good indication to the internal surface area of an activated carbon; in many activated carbons the iodine number is closed to the BET surface area [26]. The phenol index serves as a model for adsorption of aromatic micropollutants from aqueous solutions.

These isotherms were determined by adding 0.01 g of carbon to flasks containing 100 cm^3 of aqueous solutions, prepared from distilled water (pH = 6, $\chi = 2\ \mu S\ cm^{-1}$), with different initial known concentrations of solute (2–500 mg L^{-1}). These flasks were kept in a thermostat shaker bath at (20 ± 2) °C. When the equilibrium time (determined by kinetic tests; 2 h for iodine, 4 h for methylene blue, and phenol) was reached, the suspensions were filtered (0.45 μm, Whatman cellulose nitrate membrane) and the equilibrium concentrations (C_e) were then determined. The concentrations of methylene blue and phenol were determined by spectrophotometric method at the maximum absorbance wavelength (660 nm for methylene blue and 270 nm for phenol). The iodine concentrations were determined using the sodium thiosulfate volumetric method [27].

The adsorption capacity Q_e at equilibrium was defined as the amount of adsorbate per gram of adsorbent (in mg g^{-1}) and was calculated using following equation:

$$Q_e = (C_0 - C_e)\, V/\, m \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations in aqueous solution, respectively, V (L) is the volume of the solution and m (g) is the mass of the adsorbent.

The maximum adsorption capacities of the carbon samples for all the adsorbates studied were calculated applying the Langmuir equation [28].

$$Q_e = Q_m \frac{KCe}{1 + KCe} \tag{2}$$

where Q_e is the equilibrium adsorbate loading onto the adsorbent (mg g^{-1}), C_e the equilibrium liquid-phase concentration of the adsorbate (mg L^{-1}), Q_m the monolayer adsorption capacity (mg g^{-1}), and K the Langmuir constant (L mg^{-1}).

The parameters of these equations were calculated by using a non-linear regression fitting method. The results reported were the average from the values of at least three tests. In all the cases, the standard errors were lower than 5%.

Control tests were made for each solution, shaken during the equilibrium time without activated carbon, filtered and measured. They will be used to account for possible adsorption of the solute on the membrane or on the walls of the vials.

2.3. Chemical used

All used chemicals were of analytical reagent grade, greater than 99% purity, obtained from VWR BDH Prolabo®, Methylene blue ($C_{16}H_{18}ClN_3S$), Phenol (C_6H_6O), Iodine (I_2), Potassium Iodide (KI), Sodium thiosulfate ($Na_2S_2O_3{,}5H_2O$), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Sodium chloride (NaCl)…

3. Results and discussion

3.1. Study of the influence of factors on preparation of activated carbon

The aim of this study was to determine the optimal conditions for the preparation of activated carbon from Argan shells. The objective of the preliminary step was to quantify the influence of five parameters (atmosphere in carbonization step (U_1), carbonization time at 400 °C (U_2), activation temperature (U_3), activation time (U_4) and steam flow (U_5)), taking into account the potential first order interactions between these factors. These variables with their respective domain (Table 1) are