



Synthesis and characterisation of activated carbon from agroindustrial waste—Preliminary study of 17 β -estradiol removal from aqueous solution



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ABSTRACT

In this study, new activated carbons from coffee, wood and apple pomace wastes were synthesised by pyrolysis and subsequent acid wash under reflux. These materials were characterised by a combination of spectroscopic and chemical techniques including SEM, BET, TGA, WCA, FT-IR, and pH_{PZC} . The carbons prepared were applied as adsorbents in the removal of 17 β -estradiol (E2) from aqueous solutions. In general, the results of characterisation of the manufactured adsorbents showed that the surfaces properties size and pore distribution are dependent on the precursor used. Furthermore, the leaching of inorganic compounds with HCl causes structural modification, which leaves the materials more active in interactions with 17 β -estradiol. The highest percentage of E2 removal was obtained for samples from coffee and wood wastes, where the percentage of E2 removal was 100%, with exception of CS sample. For activated carbon from apple pomace, the activation process increased its adsorption capacity about two-fold (39.2–81.6%) ($\text{E2} = 0.500 \text{ mg L}^{-1}$). In addition, amount of E2 adsorbed were: CS, ACCSA7, ACCSA10 and ACM = 0.33 mg g^{-1} ; AP = 0.13 mg g^{-1} ; ACAP7 = 0.27 mg g^{-1} ($\text{E2} = 0.500 \text{ mg L}^{-1}$) and ACCSA7, ACCSA10 and ACM = 5.07 mg g^{-1} ; CS = 4.95 mg g^{-1} ; AP = 2.05 mg g^{-1} and ACAP7 = 2.35 mg g^{-1} ($\text{E2} = 7.60 \text{ mg L}^{-1}$). These aspects demonstrate the potential of activated carbon from agroindustrial wastes as new adsorbents for the removal of 17 β -estradiol in aqueous solution.

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1. Introduction

Activated carbon is known as an excellent adsorbent for the removal of organic contaminants due to its large adsorption capacity [1,2]. However, due to its high cost of production, there is increased interest in organic matrix precursor alternatives which could reduce the total production cost of activated carbons. Lignocellulosic materials originating from agroindustrial wastes are widely employed for this purpose [3]. These agricultural wastes have proved to be promising precursors for the production of activated carbons because they are renewable sources available at low cost [4]. Thus, activated carbon can be prepared from a large number of lignocellulosic raw materials, especially agroindustrial waste such as grape seeds [5], grape stalks [4], sugarcane bagasse [6], cocoa shells [7], marigold straw [8], sour cherry stones [9], waste walnut shells [10], rice husks [11,12], cotton woven waste

[13], reedy grass leaves [14], bamboo [15], apple waste [16], Van apple pulp [17], spent coffee grounds [18], coffee husks [2], coffee wastes [19,20] and red mud [21].

The process for manufacturing of activated carbons from lignocellulosic materials involves two procedures, carbonization and activation, and can be performed in one or two steps depending on the activation method (physical or chemical). Specifically, when the carbonization is carried out in an inert atmosphere the process is called pyrolysis [22]. According to Mohamed and collaborators [23], the pyrolysis of lignocellulosic materials gives rise to three phases: char, oils (tars) and gases. However, in the pyrolysis of lignocellulosic raw materials, a rudimentary porosity is obtained on the char fraction as a consequence of the release of most of the non-carbon elements such as hydrogen, oxygen and nitrogen in the form of gases and tars, leaving a rigid carbon skeleton formed by aromatic structures [22].

When activated carbons are prepared by chemical activation, the precursor is impregnated with an activating agent such as

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ZnCl₂, H₃PO₄, KOH, NaOH, CaCl₂, H₂SO₄ or K₂CO₃ [4,24,25], in aqueous medium. The resulting material is subsequently dried in an oven and carbonized (400–800 °C). Inorganic material (activating agent) can be excluded using water or solutions of acid. The solution of acid (HCl) removes the inorganics from the carbon adsorbent, leaving holes and voids within the adsorbent material and consequently increasing the porosity [26]. Although the characteristics of the prepared activated carbon depend to some extent on the precursor used, the most significant factors are those related to preparation conditions such as the carbonization time (C_t) and carbonization temperature (C_T) [24]. According to the literature [24,27], the optimum conditions varied widely depending on the method of evaluation where optimum C_T varied between 400–800 °C and C_t varied between 0.5–3 h.

In this paper, new activated carbons from coffee, wood and apple pomace wastes were prepared by pyrolysis and subsequent acid wash/leaching of inorganic material. The carbon materials manufactured were characterised by a combination of chemical and spectroscopic techniques including SEM, BET, TGA, WCA, FT-IR, and pH_{pzc}. In addition, preliminary studies on the removal of the estrogen 17 β -estradiol (E2) by the prepared activated carbons were performed. Nowadays, some studies have been reported about the removal of the estrogens from aqueous solution, but in most of the cases, commercially available activated carbons were employed. Only few studies have shown the use of agroindustrial waste in the synthesis of activated carbon and application as adsorbents in the removal of 17 β -estradiol (E2) from aqueous solutions. This contaminant was chosen because it is the primary metabolite with the highest estrogenic potency, compared with other estrogens [28,29]. E2 is used in human medicine, particularly in hormone replacement therapy (HRT) and for the treatment of other gynecological disorders. It is also used in the treatment of prostate and breast cancer in men and breast cancer in post-menopausal women [28,30]. The estrogen 17 β -estradiol is used industrially for the synthesis of 17 α -ethinylestradiol (EE2), a commonly used active ingredient in oral contraceptive pills [29]. However, E2 at the usual low concentrations found in aquatic systems has a negative impact on the performance of water and wastewater treatment plants. In fact recent studies carried out in several countries indicate that industrial and domestic wastewaters are major sources of E2 release to the environment [28,31].

2. Experimental method

2.1. Materials

Acetonitrile (gradient grade) was supplied by J.T. Baker (Phillipsburg, NJ). A standard of the estrogen 17 β -estradiol (E2) ($\geq 98\%$ pure) was purchased from Sigma–Aldrich (St. Louis, USA) (Scheme 1 please see Supplementary material). Sodium nitrate (analytical grade) and hydrochloric acid (37% weight; analytical grade) were purchased from Neon (São Paulo, Brazil). Sodium hydroxide, calcium oxide, sodium carbonate (analytical grade) were obtained from Vetec (Rio de Janeiro, Brazil). Potassium bromide (analytical grade ($\geq 99\%$ pure)) was obtained from Acros Organics (New Jersey, USA). Activated carbon was purchased from Merck (Darmstadt, Germany). A stock solution of the standard at a concentration of 150 mg L⁻¹ was prepared by dissolving the compound in acetonitrile and stored at 4 °C in a refrigerator. An aqueous solution of 13.0 mg L⁻¹ was prepared from the stock solution. Working aqueous solution was prepared daily by diluting of the 13.0 mg L⁻¹ solution with water, to attain the required concentration for calibration measurement. The water used in this work was Milli-Q.

2.2. Carbons adsorbents preparation

Initially, two carbon adsorbents were prepared employing mixtures of agroindustrial wastes. 50.0 g sample of coffee waste was mixed with 50.0 g of wood sawdust, 100.0 g of calcium oxide, 100.0 g of soya oil and water were added to obtain a homogeneous paste. Use of calcium hydroxide aims to catalyse the oxidation reactions and serve as fondant on sintering of clay minerals to form high porosity materials. The soya oil in combination with coffee waste and sawdust leaves the amorphous material that in the presence of calcium oxide to be removed the latter increases considerably the surface area and formation of active sites for adsorption. This sample was named Mcoffee:sawdust. Finally, for the second carbon adsorbent, 100.0 g sample of apple pomace waste was mixed with 10.0 g corn starch and water to obtain a homogeneous paste. This sample was named Mapple. These pastes were placed in a cylinder mould 4.8 cm in diameter and 14.0 cm in height (253.34 cm³). The resulting materials were wet-shaped and dried at room temperature for 24 h. Then, the dried cylinders were placed inside a stainless steel reactor Fig. 1 to allow symmetric gas distribution and ensure a homogeneous gas exchange rate (nitrogen at 100 mL min⁻¹), in order to avoid the formation of heterogeneous carbon composite adsorbents. The reactors were then heated inside a tubular furnace at 20 °C min⁻¹ up to 800 °C, remaining at this temperature for 30 min. Afterwards, the adsorbents were cooled down to room temperature under argon (25 mL min⁻¹). Each carbonized cylinder was then milled and sieved to a particle size $\leq 150 \mu\text{m}$ and stored in an appropriate flask. These carbon adsorbents named CS (coffee waste and sawdust) and AP (apple pomace waste).

Subsequently, the leaching of inorganic components of the carbon adsorbents was performed by treatment with acid. This procedure was carried out using 25.0 g of CS or AP to 500 mL of HCl 6.00 mol L⁻¹ in a flat-bottomed flask. The mixture was allowed to reflux for 24 h at 100 °C [26]. Afterwards, the mixture was filtered and washed with water and sodium carbonate solution at 0.100 mol L⁻¹ to achieve a final pH of 7. Finally, the material was oven dried for 24 h at 100 °C, and sieved to a particle size $\leq 150 \mu\text{m}$. These activated carbon adsorbents were named ACCSA7 (coffee waste and sawdust) and ACAP7 (apple pomace waste).

Another activated carbon was prepared from the adsorbent ACCSA7 by washing with water and sodium carbonate solution at 0.100 mol L⁻¹ to a final pH of 10, to evaluate the influence of pH on activation process the carbon. The material was oven dried for 24 h at 100 °C, and sieved to a particle size $< 150 \mu\text{m}$. This activated carbon adsorbent was named ACCSA10. The activated carbon purchased from Merck was named ACM.

2.3. Characterisation

The samples were characterised by scanning electron microscopy (SEM) using a JEOL-JSM 6060 microscope (USA), operating at 15 kV. The samples were first coated with a thin platinum layer in a sputtering system before analysis [19].

The N₂ adsorption-desorption isotherms of the samples were determined at the boiling point of liquid nitrogen (77 K) using a Nova 1000 surface analyser and a Micrometrics Instrument model TriStar II 3020 (USA). Previously, the samples were degassed for 10 h at 150 °C under vacuum. The specific surface areas were evaluated using the BET (Brunauer-Emmett-Teller) multipoint technique [32] and the pore size distribution was obtained using the BJH (Barret, Joyner and Halenda) method [33].

Thermogravimetric analyses (TGA) were recorded in a thermogravimetric analyser SDT Q600 produced by TA Instruments (New Castle, USA). Dried samples (~ 10 mg) were analysed under a

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