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Development of a new adsorbent from agro-industrial waste and its potential use in endocrine disruptor compound removal

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HIGHLIGHTS

- Development of a new adsorbent from agro-industrial waste.
- Characterization by chemical and spectroscopic methods.
- Alternative for the treatment of effluents that contain estrogens.
- The AC adsorbent was successfully employed as solid phase adsorbent for the preconcentration of E2 and EE2 from aqueous solutions.

GRAPHICAL ABSTRACT

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ABSTRACT

A new activated carbon (AC) material was prepared by pyrolysis of a mixture of coffee grounds, eucalyptus sawdust, calcium hydroxide and soybean oil at 800 °C. This material was used as adsorbent for the removal of the endocrine disruptor compounds 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) from aqueous solutions. The carbon material was characterized by scanning electron microscopy (SEM), infrared spectroscopy (FTIR), N_2 adsorption/desorption curves and point of zero charge (pH_{PZC}). Variables including the initial pH of the adsorbate solutions, adsorbent masses and contact time were optimized. The optimum range of initial pH for removal of endocrine disruptor compounds (EDC) was 2.0–11.0. The kinetics of adsorption were investigated using general order, pseudo first-order and pseudo-second order kinetic models. The Sips isotherm model gave the best fits of the equilibrium data (298 K). The maximum amounts of E2 and EE2 removed at 298 K were 7.584 (E2) and 7.883 mg g^{-1} (EE2) using the AC as adsorbent. The carbon adsorbent was employed in SPE (solid phase extraction) of E2 and EE2 from aqueous solutions.

1. Introduction

In recent years, public concern about the environmental occurrence of consumer products (detergents, pharmaceuticals, hormones) has been increasing. These substances may interfere with the normal functioning of the endocrine system in humans and wildlife by: (i) mimicking the effect of endogenous hormones; (ii) antagonizing the effect of endogenous hormones; (iii) disrupting the synthesis and metabolism of endogenous hormones, or (iv) disturbing the synthesis of specific hormone receptors [1–5]. Since the magnitude of the risks associated with their presence in the environment is difficult to predict, great concern exists about these substances, known collectively as "endocrine disrupting compounds" (EDCs). Even though they are found in very low

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concentrations (in the ng L^{-1} range) there is still a lack of knowledge about the long-term risks of EDC for non-target organisms as well as for human health [6,7].

Currently, many methods have been described for effectively monitoring and detecting EDCs in the environment. Liquid chromatography (LC) coupled with a fluorescence detector, tandem mass spectrometry and ultraviolet detectors have all been used in these studies. Due to the low concentration level of EDCs in environmental water, the samples must be preconcentrated. Since these enrichment procedures also concentrate matrix constituents, samples must be cleaned-up prior to analysis in order to eliminate interfering compounds [8]. Solid phase extraction (SPE) is one of the most widely used sample preparation techniques for preconcentration and clean-up of EDCs due to its advantages of simplicity, rapidity, minimal consumption of organic solvents, high preconcentration efficiency and sample throughput [9–15].

The most commonly used adsorbent material for SPE is chemically bonded silica, usually with a C_8 or C_{18} organic group. On the other hand, the most commonly used polymeric resin in SPE is porous polystyrene [16]. Despite its advantages, some of these adsorbent materials do not satisfactorily remove the interfering matrix, resulting in inadequate selectivity and sensitivity. In order to solve this problem, there is a demand for new adsorbents for SPE that may improve analyte recovery, sorptive capacity and selectivity. In recent years, increasing attention has been paid to preparations of activated carbon for the removal of EDCs and the results illustrate the potential of these materials to extract the analytes effectively [17–22]. The advantages of using activated carbon include its large surface area, pore structure, and thermostability, all of which improve its ability to remove contaminants from various aqueous media [23,24].

Activated carbon generally demonstrates a high capacity to adsorb EDCs [20,25,26]. However, most studies have employed commercially available carbons, which carry a high cost, hindering their use. Thus, attempts have been made to develop inexpensive activated carbon utilizing agro-industrial and municipal waste materials. Baccar and collaborators [18] prepared an activated carbon from a Tunisian agricultural by-product and applied it to the adsorption of ibuprofen, ketoprofen, naproxen and diclofenac. The results demonstrated that large quantities of drugs could be adsorbed from a mixture, demonstrating the ability of the prepared adsorbent to adsorb multiple drugs. Another study presented by Mestre and co-authors [27] assessed the potential of activated carbons prepared by chemical activation of sisal with K_2CO_3 to removal of organic pollutants. They observed that prepared samples attained values comparable to a commercial carbon.

In Brazil, the agricultural-industrial waste products represent unused resources being widely available and environmentally friendly so they have a great potential to be used as adsorbents. Their application in adsorption processes can be a way to help manage them. In this context, this study aimed to develop a new cost-effective activated carbon from agro-industrial waste to remove the endocrine disruptors 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) from aqueous solutions. For this purpose, the adsorbent material was first prepared from a mixture of coffee grounds, eucalyptus sawdust, calcium hydroxide and soybean oil by pyrolysis. Use of calcium hydroxide aims to catalyze the oxidation reactions and serve as fondant on sintering of clay minerals to form high porosity materials. Then, the adsorption of these EDCs was assessed regarding its kinetic and equilibrium aspects. Ultimately, the activated carbon was evaluated as a packing adsorbent for extraction and concentration of the estrogens studied.

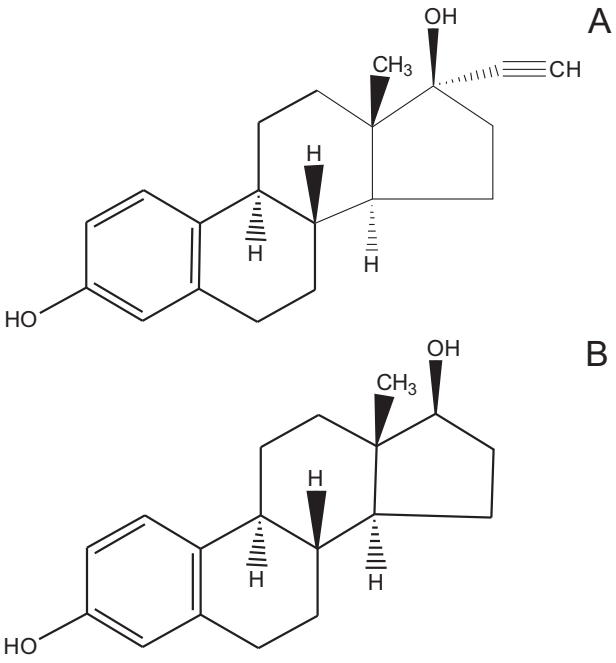

Fig. 1. (A) Structural formula of EE2; (B) structural formal of E2.

2. Experimental

2.1. Chemicals and reagents

Acetonitrile (gradient grade) was supplied by J.T. Baker (Phillipsburg, N.J.). Standards of the estrogens 17β-estradiol (>98% pure) and 17α-ethinylestradiol (>98% pure) were purchased from Sigma–Aldrich (St. Louis, USA) (Fig. 1). Sodium nitrate (analytical grade) and hydrochloric acid (37% weight; analytical grade) were purchased from Neon (São Paulo, Brazil). Sodium hydroxide and calcium hydroxide (analytical grade) were obtained from Vetec (Rio de Janeiro, Brazil). Potassium bromide (infrared grade) was supplied by Acros Organics (Fair Lawn, N.J.). Stock solutions of the individual standards at a concentration of 200 mg L^{-1} were prepared by dissolving the compounds in acetonitrile and were stored at 5 °C. Working aqueous solutions of the standards were prepared daily by diluting the stock solution with water to attain the required concentrations for calibration measurements. The water used in this work was de-ionized.

2.2. Preparation and characterisation of activated carbon adsorbent

The activated carbon adsorbent was prepared using the following procedures (Fig. 2): a 50.0 g sample of coffee grounds was mixed with 50.0 g of eucalyptus sawdust and 100.0 g of calcium hydroxide. To obtain a homogeneous paste 100.0 g of soybean oil and water were added. This paste was placed in a cylinder mould 4.8 cm in diameter and 14.0 cm in height (253.34 cm^3). Subsequently, the resulting material was wet-shaped and dried at room temperature for 24 h. Afterward, the dried cylinders were placed inside a stainless steel reactor (Fig. 2) to allow symmetric gas distribution and ensure a homogeneous gas exchange rate (argon at 100 mL min^{-1}), in order to, avoid the formation of heterogeneous carbon composite adsorbents. The reactor was then heated inside the tubular furnace at 20 °C min^{-1} up to 800 °C, remaining at this temperature for 30 min. Subsequently, the adsorbent material was cooled down to room temperature under argon (25 mL min^{-1}). Each carbonized cylinder was then milled and sieved to a particle size ≤150 μm, and