

Effective removal of estrone and β -estradiol from aqueous solutions using macadamia nutshell activated carbon as a novel adsorbent

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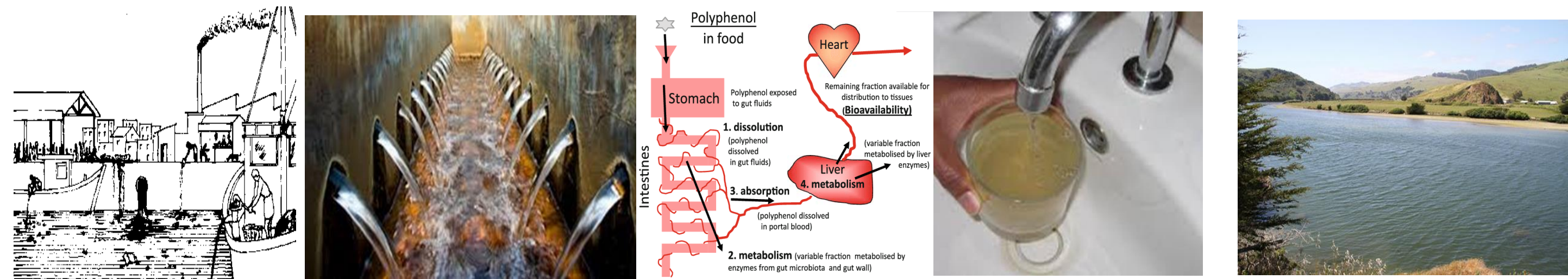
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INTRODUCTION

Steroid hormones are a class of medications that are prescribed for diverse human and veterinary purposes. 17β -estradiol is extensively utilized as a human contraceptive pill for the birth regulator, and as a growth stimulator in feedlot ration of livestock animals [1-3]. Different steroid hormones are used in veterinary medications, and as constituents of livestock animal feed, for example, cattle, poultry, and pigs [4-6]. Essential portions of steroid hormones administered to humans and animals are not fully metabolized by the body [7]. The excess is spilled over and passed out as waste, either in the form in which they are administered or as derivatives of the parent compound [3-6]. Due to the challenge posed by the presence of steroids and other pollutants in water, researchers have been working towards developing low-cost materials that can be used to remove unwanted contaminants from water system [3-5]. This has led to the usage of biomaterials from agricultural waste and nanomaterials for environmental pollutants [6,7] like organics and dyes.

Activated carbons (AC) have been widely adopted in the industrial fields for air, water, and sewage clean up to remove odour in the air and contaminants in water, taking advantage of their absorptivity [7]. The use of macadamia nutshell activated carbon as an effective adsorbent for the removal of endocrine-disrupting chemicals like estrone (E₁) and β -estradiol (E₂). The activated carbon material was characterized by Fourier transforms infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). Adsorbent factors such as pH, contact time, initial steroids concentration, temperature, and adsorbent dosage were considered.



MATERIALS AND METHODS

All solvents such as estrone and β -estradiol were delivered by Sigma-Aldrich (Johannesburg, South Africa). The chemical structures of estrone (E₁) and β -estradiol (E₂) are shown in Figure 1.

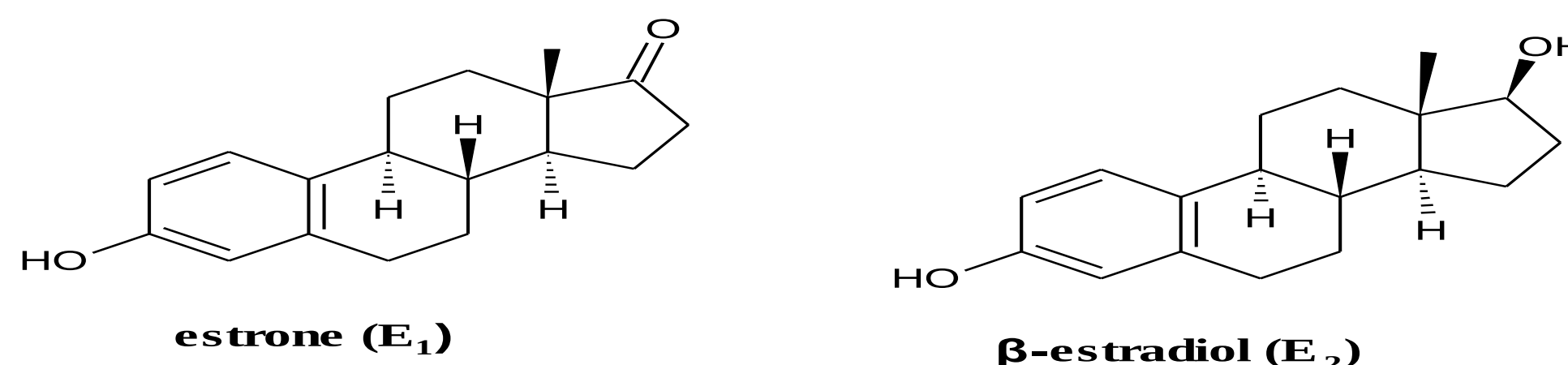


Fig. 1. The chemical structures of estrone (E₁) and β -estradiol (E₂)

Macadamia nutshell activated carbon (MAC) with the surface area of about 1000 m²/g, was obtained commercially from Filtatech (Johannesburg, South Africa), and utilized without additional purification.

Characterization Methods: FT-IR, TGA / DTA, SEM

Batch Adsorption Experiments

Batch adsorptions of the selected estrone (E₁) and β -estradiol (E₂) onto the adsorbent (MAC) was performed using a Multichannel agitator MS-53 M model Jeio Tech (Seoul, Korea).

The tests were carried out using 50.0 mL of estrone or β -estradiol solutions under the following:

- Initial concentration (1, 2, 6, 8, 10 mg/L);
- Different contact times (10, 30, 90, 180, 360 min);
- Adsorbent dosage (0.1, 0.4, 1, 1.2, 1.6 g/L),
- pH values (2, 4, 6, 7, 8, 10),
- Different temperature (20, 25, 30, 35 °C).

RESULTS AND DISCUSSION

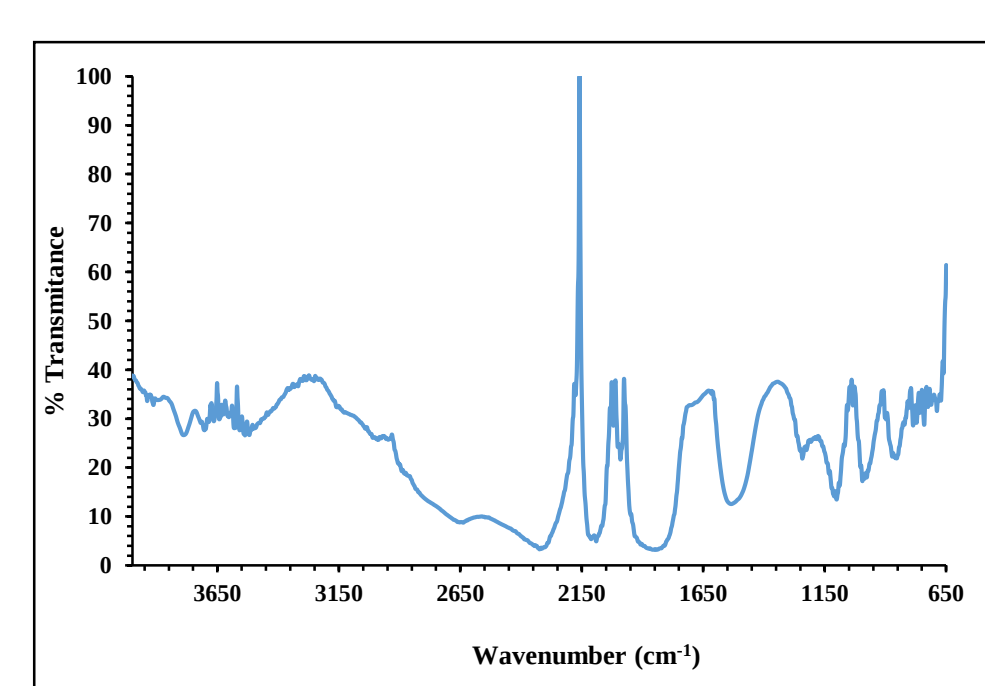
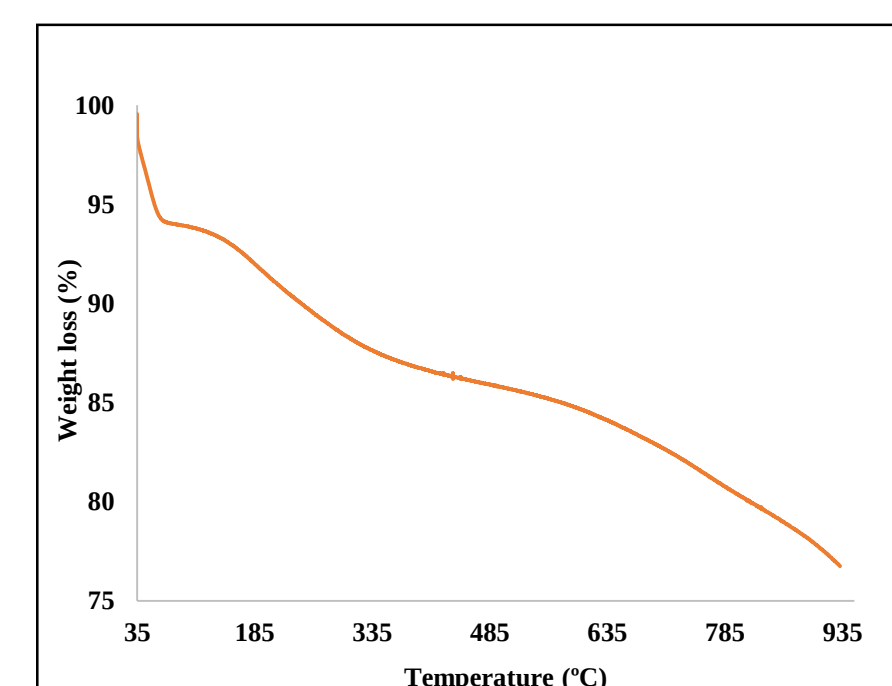
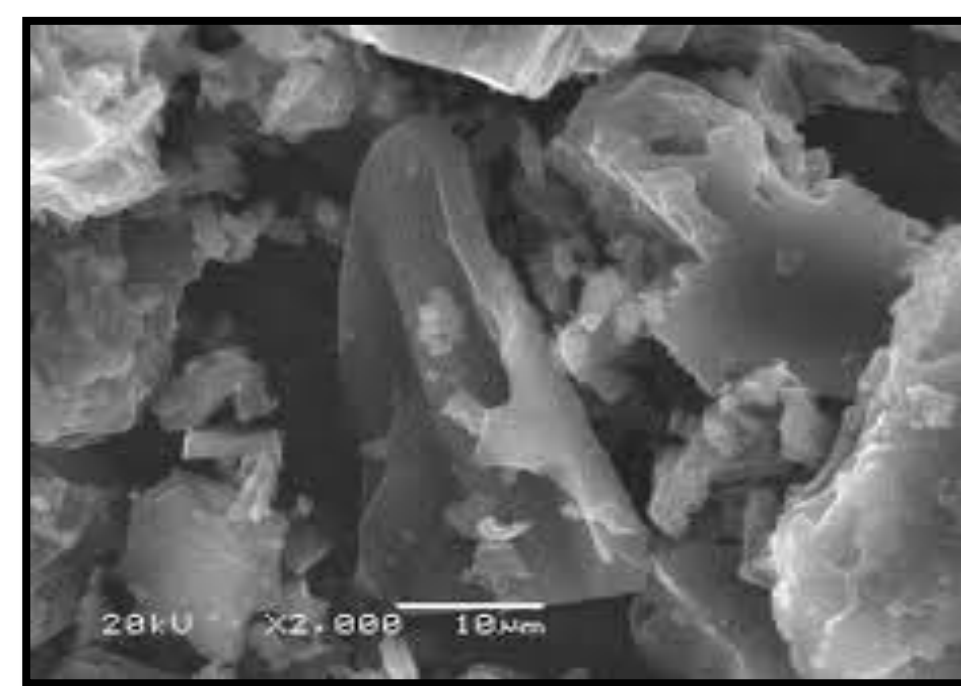


Fig. 2. FTIR-spectra and TGA of Macadamia activated carbon (MAC)

Fig. 3. Scanning electron microscopy images of MAC



The spectra of MAC (Fig. 2) showed an alkyl aromatic/aliphatic activated carbon structure within the regions 3000 – 2800 cm⁻¹ and 900–700 cm⁻¹, an abundant oxygen-containing hydroxyl groups: ν (-OH) around 3700 – 2000 cm⁻¹, ν (-COOH) a shoulder around regions 2600 cm⁻¹ and 1700 cm⁻¹.

The FT-IR spectra of GMAC show that the alcohol structure ν (O-H) stretching is sharp and broad around 3385 – 3268 cm⁻¹ and ν (-COOH) stretching at 2628 cm⁻¹. The high-pitched peaks within the regions 2950 – 2850 cm⁻¹ could be ascribed to the stretching alkane ν (-CH₃/-CH₂) band (Fig. 1).

The third weight loss was slowly noticed between 482 – 926 °C, and this is attributed to the main compound cellulose, hemicelluloses and partial lignin loss from the various materials [7-9].

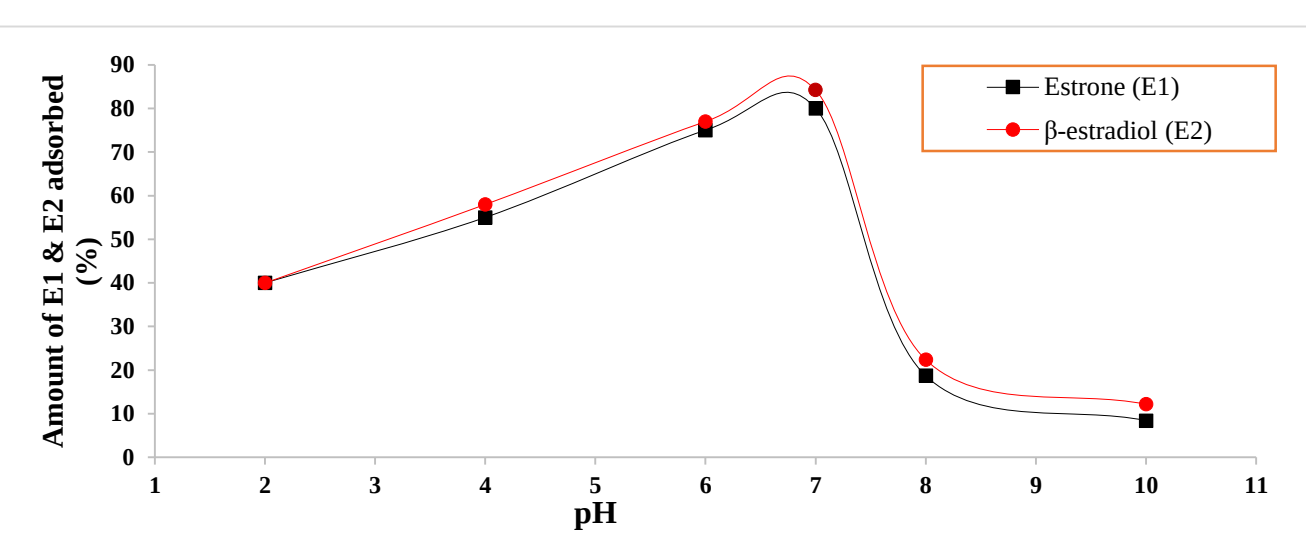
The SEM image revealed that the macadamia activated carbon consists of flaky long fold-like structure with visible porosity in the materials.

The analysis of the sample showed that the structural backbone was not significantly transformed since they retained their flakiness, signifying that the handling was not disproportionately severe towards destroying the texture of the material.

The penetrable exterior of the produced activated carbon is critical for fascinating in adsorbate molecules or particles during the adsorption trials [8-10].

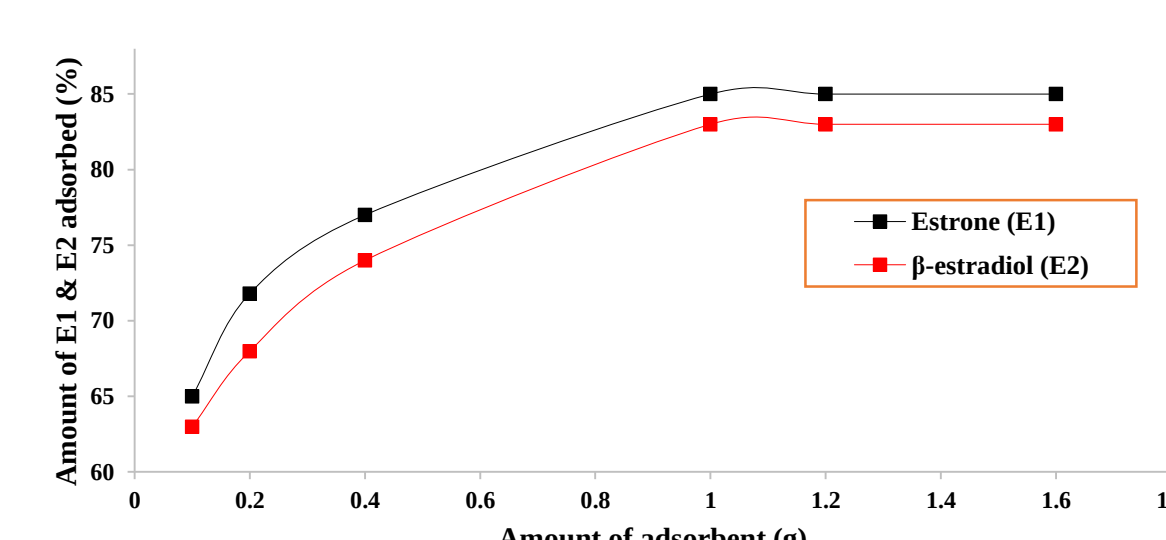
Effect of selected parameters on the steroids adsorption onto MAC

Effect of pH



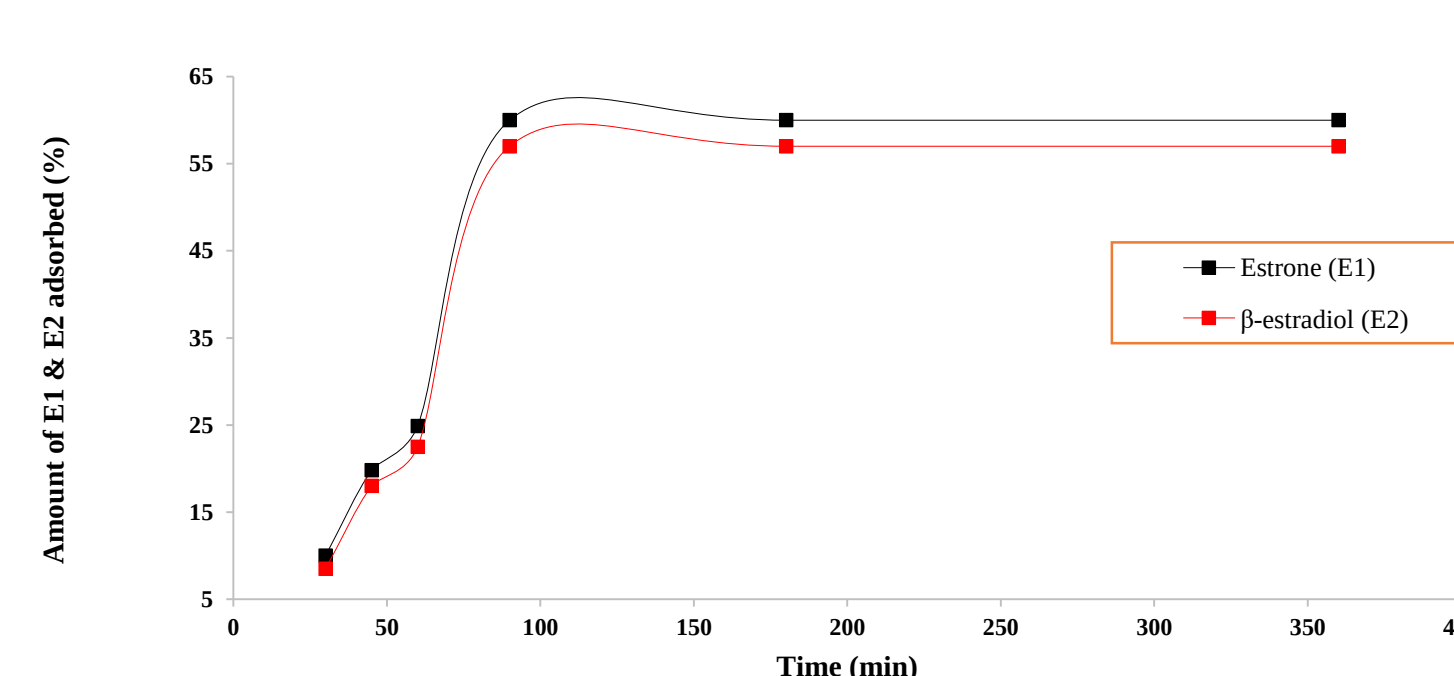
The percentage of E₁ and E₂ adsorbed was observed at lower and neutral pH (4, 6, and 7). The number of steroids adsorbed was found to be maximum at pH = 7 for both E₁ and E₂ are neutral and occur in non-ionic molecular form; hence, they were readily adsorbed onto the activated carbon [8-10].

Effect of adsorbent dosage



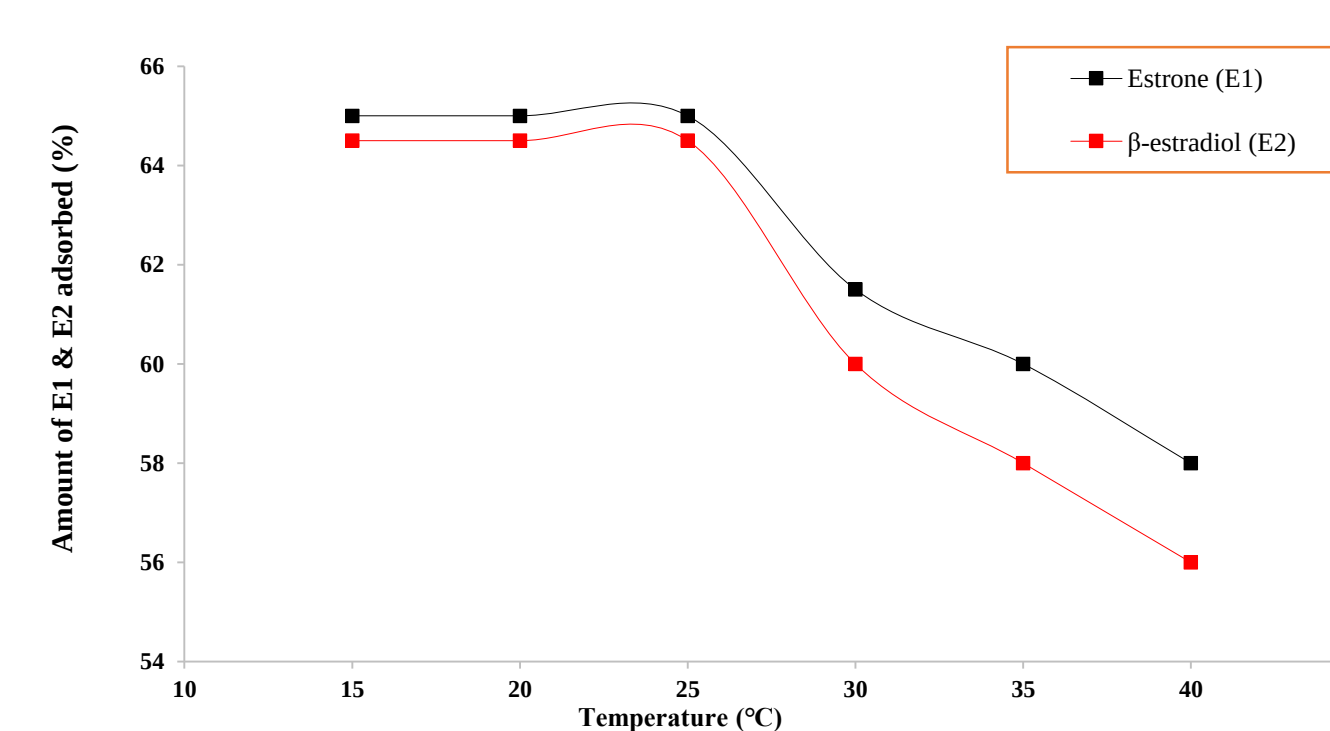
It was observed that at 1.0 g of the adsorbent dose, the % removal of β -estradiol (E₂) reached about 83%, while about 3% more reaching 85% depict the extraction of estrone (E₁). Thus 1.0 g/L of activated carbon was considered as the optimum dose and utilized in further experiments [9,10].

Effect of contact time

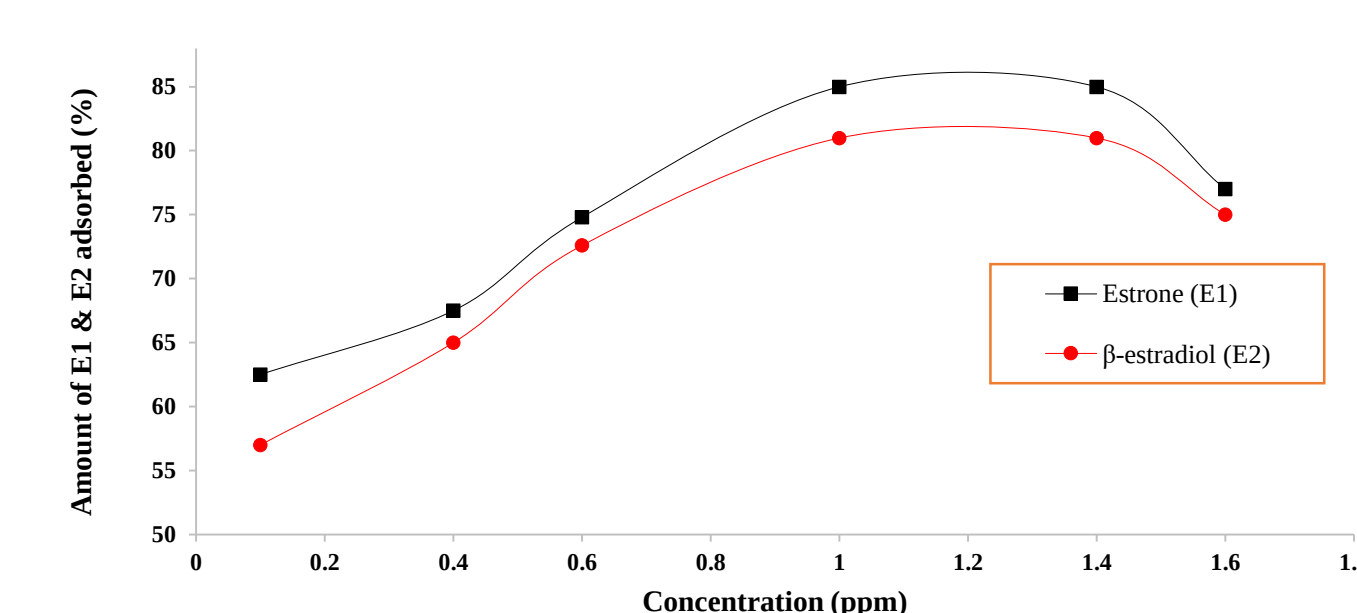


The adsorption of estrone and β -estradiol onto macadamia activated carbon (MAC) increased with increasing contact time. Moreover, the sorption was very rapid in the first 25 min; hence the % removal reaching 60% for estrone (E₁) and 58% for β -estradiol (E₂). The adsorption of E₁ and E₂ increased progressively during the following 45 min until equilibrium is reached at about 90 min.

Adsorbent dose effect



Effect of concentration



The calculations revealed that almost 85% of estrone and 82% of β -estradiol removal was achieved at low levels (0.1–1.0 mg/L). Once the concentration was increased further from 1.0 to 1.6 mg/L, the percentage removal of E₁ and E₂ reduced to about 76-77%, while adsorption ability rises with an increase in concentration. With the rise in the initial level, the mass transfer driving force increases, thereby resulting in a higher estrone (E₁) and β -estradiol (E₂) adsorption.

The plot shows that % adsorption by the activated carbon at variable temperatures with optimal sorption of 65% for estrone (E₁) and 64.5% for β -estradiol (E₂) taking place at low temperature (15–20 °C). This is because room temperature is suitable for the binding of steroids on the surface of the adsorbent.

The equilibrium sorption decreases from 65 to 58 %, with an increase in temperature. These observations could be due to the propensity of steroids molecules to seepage from the solid phase to bulk phase with an upsurge in temperature of the solution [7-10]

Adsorption Kinetic and Thermodynamic Parameters

Batch studies kinetic data were analysed by pseudo-first-order (PFO) and pseudo-second-order (PSO) models for steroids adsorption are described in Equations (1) and (2).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \dots\dots\dots (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots (2)$$

Calculations from the thermodynamic equilibrium constant, K_o with temperature were utilized for the evaluation of thermodynamic parameters like the free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°).

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \dots\dots\dots (3)$$

The exothermic nature of steroids sorption by MAC was confirmed by the negative values of ΔH , an indication that electrostatic interactions occurred between the steroids and the MAC adsorbent, thereby supporting physisorption mechanisms [4-8].

CONCLUSION

Steroid-MAC system adsorption was achieved through the characterized MAC with confirmed mesoporous texture and highly carbonaceous nature. The results of the batch studies showed that the maximum percent 85% of estrone and 82% of β -estradiol removal was accomplished at low concentrations (0.1–1.0 mg/L), time (120 min), pH 7, and dosage (0.1 g), temp. (25 °C), and a solution volume of 25 mL. The kinetics studies confirmed that the pseudo-second-order kinetics model could explain the steroids-MAC adsorption system. Thermodynamic factors: ΔG° values of -1.223 to -1.308 kJ/mol, $\Delta H^\circ = -11.72$ kJ/mol, and $\Delta S^\circ = 37.34$ J/mol K of steroids adsorbed onto MAC indicate that the adsorption was spontaneous, proceeded favourably at lower temperature and exothermic in nature. Overall thermodynamic parameters analysis indicates that electrostatic interactions occurred between the steroid and the MAC samples, thereby support physisorption mechanisms.

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