


Removal of 17 α -ethinylestradiol (EE2) from aqueous solutions by peanut shells (*Arachis hypogaea*): adsorption kinetic, isothermal, and thermodynamic studies

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ABSTRACT

This study evaluated the potential of using raw peanut shells as an adsorbent to remove the hormone 17 α -ethylestradiol (EE2) from water. High-performance liquid chromatography with fluorescence detection was used in the determination of EE2. Kinetics data were tested with the pseudo-first-order, pseudo-second-order, and Elovich models, whereas isothermal data were tested with the Langmuir, Freundlich, and Sips models, and the parameters (ΔG° , ΔH° and ΔS°) were evaluated. A maximum removal rate of approximately 90% was observed in a solution with an initial EE2 concentration of 263.2 $\mu\text{g L}^{-1}$, under the best experimental conditions (stirring speed = 500 rpm, pH = 6, and adsorbent mass = 2 g in 24 h), and showed an adsorption capacity of 17.3 $\mu\text{g g}^{-1}$ at 306 K. The pseudo-first-order model adjusted better to the data in the studied temperature range, presenting a potential barrier of 16.69 kJ mol^{-1} (E_a) for adsorption kinetics. The Freundlich model and Sips model adjusted better to the data in the studied temperature range. The negative value of ΔG° ($-15.87 \text{ kJ mol}^{-1}$ at 306 K) confirmed the viability and spontaneity of the adsorption process. The positive value of ΔH° (168.9 kJ mol^{-1}) characterized the chemical nature of the adsorption process.

Key words: 17 α -ethinylestradiol, adsorption, endocrine disruptors, peanut shells

HIGHLIGHTS

- Removal of 17 α -ethinylestradiol (EE2) from aqueous solutions by peanut shells.
- Adsorption kinetic, isothermal, and thermodynamic studies were evaluated.
- The isothermal data were treated with the Langmuir, Freundlich and Sips models.
- The Sips model adjusted better to the data.
- Adsorption on peanut shells is an accessible and simple process for possible wastewater treatment containing EE2.

INTRODUCTION

Contamination of water bodies caused by chemical substances is a global challenging issue for humankind. Since the 20th century, rapid progress in industrialization and urbanization, uncontrolled population growth and climate change have led to the unsustainable use of water. These factors, combined with anthropogenic actions threaten and affect significantly the quality of ecosystems, biodiversity, food, energy and the mineral and water resources of the planet (Hejazi *et al.* 2011; Silva *et al.* 2014; Barbosa *et al.* 2015). The availability of clean water is one of the most threatening issues that our society has been facing. Unfortunately, it has affected more than 3.3 billion people around the world who do not have access to drinking water and/or live with water scarcity and this number may increase 52% by 2025 (Hejazi *et al.* 2011; Okoli *et al.* 2017; Olu-Owolabi *et al.* 2017).

Part of environmental contaminations are related to the emerging contaminants (ECs), which include a wide range of substances capable of causing harm to the surroundings and human health, even in small amounts (ng L^{-1} to $\mu\text{g L}^{-1}$) (Han *et al.* 2010; Choina *et al.* 2013; Candido *et al.* 2016). ECs are chemical compounds present in several commercial products (pharmaceuticals, pesticides, personal care products, hormones, illicit drugs,

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nutritional supplements, diagnostic agents, among others) or microorganisms that can be found in environmental matrices at trace levels. These compounds are hardly monitored and can provide a potential risk to human health and to the environment (Collins & Silva 2011; Choina *et al.* 2013; Birch *et al.* 2015; Patiño *et al.* 2015; Candido *et al.* 2016).

Endocrine disruptors (EDs), organic micropollutants, are compounds capable of causing undesirable biological effects in live organisms and serious damage to the environment (Choina *et al.* 2010; Barreiros *et al.* 2016; Monneret 2017; Wan *et al.* 2022). In this context, removing EDs from water has been attracting the attention of activist groups, the global scientific community, government agencies, and the private sector. They are able to deregulate, alter or affect the functions of the endocrine system in the following ways: blocking, imitating or minimizing the normal effect of a specific hormone (Dezotti & Bila 2007; Jardim & Ghiselli 2007; Braga *et al.* 2011; Fernandes *et al.* 2011; Ifeiebuegu 2012; Silva *et al.* 2012; Dzieweczynski & Hebert 2013).

Within this class are steroid estrogens (natural or synthetic), a group of biologically active compounds and highly persistent in aquatic environments. They are continuously released into water bodies by human urinary and/or fecal excretions, partially or totally metabolized (Ifeiebuegu 2012; Choina *et al.* 2013; Sadowski & Kopciuch 2013; Birch *et al.* 2015; Candido *et al.* 2016; Leonard *et al.* 2017). Synthetic estrogen, 17 α -ethinylestradiol (EE2), the target substance of this study, proceeding from natural estrogen 17 β -estradiol (E2), found in pharmaceuticals, mainly in contraceptive pill formulations and hormone replacement therapies for menopause, osteoporosis treatment, menstrual disorders and cancer of the prostate cancer is considered a potent ED (Sodré *et al.* 2007; Mazellier *et al.* 2008; Choina *et al.* 2010; Fernandes *et al.* 2011; Silva *et al.* 2012; Han *et al.* 2013; Aris *et al.* 2014; Laurenson *et al.* 2014; Barreiros *et al.* 2016; Leonard *et al.* 2017). Furthermore, EE2 has been found in various environments (wastewater, surface water or groundwater), and is a problematic pollutant for aquatic systems because it is highly environment persistent and bioaccumulates in living organs (De Wit *et al.* 2010; Liu *et al.* 2021; Wan *et al.* 2022).

Recent studies have shown that environmental issues due to ED contamination are associated with water and effluent treatment plants (Sodré *et al.* 2007; Birch *et al.* 2015; Wan *et al.* 2022). Therefore, efficiency of treatment plants in removing EE2 is greatly important in combating pollution and reducing EE2 contamination by humans and the environment. According to Wan *et al.* (2022), several EE2 removal studies in effluent treatment plants are performed all over the world. They use inefficient or inappropriate treatment methods for the complete removal of these pollutants, therefore, the search for alternative and sustainable technologies, processes and techniques becomes a continuous and arduous task (Jardim & Ghiselli 2007; Ifeiebuegu 2012; Richardson & Ternes 2014; Patiño *et al.* 2015; Diagboya & Dikio 2018).

Several technologies have been employed for removing organic pollutants from water, such as filtration, coagulation, chemical precipitation, ion exchange, reverse osmosis, membrane technology, electrochemical, enzymatic treatment, photocatalysis, photolysis, solvent extraction, advanced oxidative processes, activated sludge, ozonation, adsorbents, among others (Aquino *et al.* 2013; Patiño *et al.* 2015; Diagboya & Dikio 2018). Tang *et al.* in a review study report occurrence and removal of EE2 in municipal wastewater treatment plants (WWTPs), totaling 282 WWTPs in 29 countries. 64% of WWTPs use the activated sludge process, anaerobic-anoxic-oxic/anoxic-oxic 6%, oxidation ditch 5%, member bioreactor 3%, biofilm 6%, stabilization pond 7%, primary treatment 3% and other processes 6%, with EE2 removal averages in the range of 47.5–83.6%, and observed that the main mechanisms of EE2 removal in municipal WWTPs include mainly adsorption and biodegradation. Another review study reports that several physical, chemical, biological and hybrid processes applied as treatment methods for endocrine disrupting compounds have been extensively studied, in addition to promising adsorption technologies, especially those that use agricultural residues as adsorbents. Other works on EE2 removal, degradation and adsorption can be found in the literature (Heo *et al.* 2011; Ifeiebuegu & Ezenwa 2011; Valladares Linares *et al.* 2011; Ifeiebuegu *et al.* 2015; Li *et al.* 2016; Goswami *et al.* 2018; Liu *et al.* 2019; Procópio *et al.* 2020).

However, unconventional techniques like the adsorption methods have emerged with great potential and economic viability for the treatment of effluents and contaminated water, mainly involving natural adsorbents from wastes from agro-industrial activities and biodegradable materials from by-products from agricultural and industrial operation (Fernandes *et al.* 2011; Han *et al.* 2013). Removal of EE2 and EDs has always been difficult to perform and the use of these materials as a cost-effective alternative, robustness, ease of use and application, good efficiency are of great interest to the scientific community and a great option for traditional adsorbents (Braga *et al.* 2011; Fernandes *et al.* 2011; El-Sayed *et al.* 2014; Barros *et al.* 2017). However, they are discarded in large quantities, making them viable, renewable and ecologically correct, reducing the direct release of

pollutants into the environment and assisting in the wastewater treatment. China and USA are the world's largest producers of peanut shells and generate huge amounts of tons of by-products per year and at low cost (Brown *et al.* 2000; Zhu *et al.* 2009; Al-Othman *et al.* 2012).

In this context, the objective of this work was to evaluate the use of peanut shells, a lignocellulosic agro-industrial residue, as an alternative means of effective biomass adsorption and low cost, for the removal of the synthetic hormone EE2 from the aqueous medium. Furthermore, experimental data were analyzed using pseudo-first-order, pseudo-second-order and Elovich adsorption kinetic models, and kinetic constants were calculated as a function of temperature. Adsorption equilibrium was expressed by Langmuir, Freundlich and Sips isotherms. Activation energy of the adsorption process, which is a very important indicator, was also evaluated.

With the results obtained in this work, it is possible to show the technical potential that the material has for removing contaminants emerging from the aqueous medium. In addition, it is possible that it is an economically viable alternative, since it is an industrial waste that is normally discarded.

EXPERIMENTAL

Reagents and solutions

Ultrapure deionized water (18.2 M Ω *cm 298 K resistivity) was obtained from a Direct-Q (Millipore[®]) purification system. 0.1 mol L⁻¹ of HCl solution and 0.1 mol L⁻¹ of NaOH solution were used to adjust pH of the solutions. Acetonitrile (ACN) [\geq 99.9%, HPLC grade] and methanol [\geq 99.9%, HPLC grade] were purchased from Sigma-Aldrich[®], and the EE2 standard [\geq 99.4% purity] was purchased from Fluka Analytical[®]. Standard EE2 solution of 10 mg L⁻¹ in methanol was prepared for the evaluation of the experimental parameters (selectivity, linearity, precision, accuracy, detection limit, quantification limit, and robustness) of the chromatographic methodology. 10.00 mg of the EE2 standard was weighed, dissolved in methanol, and quantitatively transferred to a 100.00-mL volumetric flask, completing the volume with methanol and homogenizing. Subsequently, a 10.00 mL aliquot of the standard solution, previously prepared, was pipetted into a 100.00-mL volumetric flask, completing the volume with methanol and homogenizing. For the adsorption experiments, a solution of EE2 was obtained from Ciclo 21 contraceptive (União Química[®]). One pill was macerated and dissolved with deionized water, and then transferred to a 100.00-mL volumetric flask. According to the manufacturer, each tablet contains 0.03 mg of EE2, however, for greater reliability of the results, the concentrations of EE2 in the prepared solutions and after the adsorption process were determined by the chromatographic method. Solutions were stored in a polyethylene bottle at 277 K.

Instrumentation

EE2 identification and quantification analyses were performed in a high-performance liquid chromatograph (Infinity 1260 – Agilent Technologies[®], Germany) composed of a quaternary pump, an automatic injector, a column heating module, and a molecular fluorescence detector. An Eclipse Plus C8 chromatographic column (4.6 mm \times 150 mm – 5 μ m) from Agilent Technologies was used. Chromatographic condition used for the analysis was mobile phase (MP) in isocratic mode – ACN:water (3:2), MP flow – 0.5 mL min⁻¹, injection volume – 10 μ L, chromatographic column temperature – 318 K, wavelength of the fluorescence detector (FLD) – 230 nm (excitation) and 310 nm (emission). The MP was previously filtered through cellulose ester (Millipore[®]) and nylon membranes (Supelco Analytical) with 0.45 μ m porosity and deaerated in an ultrasonic bath (SoniClean 2 Model – Sanders Medical). The quality control and quality assurance of the chromatographic method can be consulted in our other study (Procópio *et al.* 2020), however, in summary, the evaluated parameters were selectivity, linearity, precision, accuracy, limit of detection, limit of quantification, and robustness.

Adsorbent

To save disposal costs and possible environmental problems, in this work an agro-industrial residue or by-product agricultural abundant, cheap and renewable was used as a natural adsorbent for the adsorption tests in the EE2 removal. Raw peanut shells, free from washing, drying, grinding, sieving and chemical treatments, were used. The materials were collected at the local market in the city of Itajubá, Minas Gerais, Brazil. A lignocellulosic compound, peanut shells are potential adsorbents in the pollutant removal due to their physical-chemical characteristics. According to Brown *et al.* (2000), raw peanut shells have 8–10% humidity, 6–7% protein, 60–70% fiber, 34–45% cellulose, 27–33% lignin, 2–3 ash and 61% porosity. Also due to their chemical

composition and complex structures, lignocellulosic materials can be used to adsorb pollutants with no modification or physical and chemical treatment (Ossman *et al.* 2014).

Adsorption experiments

Adsorption experiments were performed at room temperature (approximately 293 K). Beakers of 150 mL were used containing the mass of peanut shells and 100 mL of the solution of EE2 contraceptive Cycle 21. Experiments were carried out at a constant agitation for 6 h. The parameters used and evaluated in the adsorption process were adsorbent mass (0.5, 1 and 2 g), pH (4, 6 and 8) and stirring speed (300, 400 and 500 rpm). For calculation purposes, the possible errors arising from the changes in the volume of the solution due to the water absorption by the different mass of peanut shell were disregarded.

1.0 mL of aliquots of the solution were collected at time intervals of 1, 2, 3, 4, 5 and 6 h. All aliquots were filtered using qualitative paper to remove larger particles and impurities. Furthermore, for the removal of smaller particles, a syringe (10 mL – Art Glass) coupled to a filter (Allcrom) with 0.45- μm porosity was used.

The EE2 removal rate in aqueous solutions by the adsorbent was determined according to Equation (1) (Cardoso *et al.* 2011):

$$\% \text{Removal} = 100 \times \frac{C_0 - C_t}{C_0} \quad (1)$$

where C_0 is the EE2 initial concentration placed in solution ($\mu\text{g L}^{-1}$) and C_t is the EE2 remaining concentration in solution after the adsorption process ($\mu\text{g L}^{-1}$).

The amount of EE2 adsorbed by the adsorbent was determined from Equation (2) (Guerreiro *et al.* 2020):

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (2)$$

where q_t is the amount of EE2 adsorbed by the adsorbent at time t ($\mu\text{g g}^{-1}$), C_t is the remaining concentration of EE2 in the solution at time t ($\mu\text{g L}^{-1}$), V is the volume of the solution (L), and m is the adsorbent mass (g).

Kinetic study

Experimental conditions of the EE2 adsorption process for the kinetic study were as follows: 2 g (adsorbent mass), 6 (pH) and 500 rpm (stirring speed). The experiments were performed in triplicate and its preparation follows the adsorption experiments step mentioned above. However, aliquots were collected at times 0, 1, 2, 3, 4, 5, 6 and 24 h. The temperatures used for the experiments were 309, 329 and 339 K.

Isothermal study

Isothermal study was performed under the same experimental conditions as the kinetic study, but varying the EE2 concentration in the solution. For this, 500 mL of solution containing 15 EE2 contraceptive Cycle 21 pills was prepared. Aliquots of 5, 10, 20, 30, 40 and 50 mL were transferred to 100-mL volumetric flasks, completing the volume with deionized water. Subsequently, the solutions were transferred to beakers for the adsorption process. 1 mL of aliquots were collected at time 0 and 24 h and the EE2 remaining concentrations in the solutions were determined by Equation (2). The temperatures used for the experiments were 306, 326 and 333 K.

RESULTS AND DISCUSSION

Adsorption experiments

A multivariate optimization technique using the Box–Behnken model was used for the adsorption experiments as in our other study (Procópio *et al.* 2020) with the aid of Statistica[®] software, and an Excel spreadsheet or Origin[®] software for the treatment of the data. The parameters (stirring speed – 300, 400 and 500 rpm; adsorbent mass – 0.5, 1 and 2 g and pH – 4, 6 and 8) were varied in three levels, totaling 15 experiments (Table 1).

From Table 1 it was observed that experiment 8 (stirring speed = 500 rpm, mass = 1 g and pH = 8), experiment 12 (stirring speed = 400 rpm, mass = 2 g and pH = 8), and experiment 4 (stirring speed = 500 rpm, mass = 2 g and pH = 6) showed the best results, with 60, 63 and 64% of EE2 removal, respectively. It is noted that the adsorbent mass and the stirring speed were the main factors that affected the results in a more pronounced way.

Table 1 | Parameters and conditions in three levels and the removal rate for the 15 adsorption experiments

Experiments	Parameters ^a /Condition ^b	%Removal
1	I(a),II(a),III(b)	40.5
2	I(c),II(a),III(b)	51.8
3	I(a),II(c),III(b)	48.2
4	I(c),II(c),III(b)	64.6
5	I(a),II(b),III(a)	47.5
6	I(c),II(b),III(a)	55.8
7	I(a),II(b),III(c)	56.0
8	I(c),II(b),III(c)	60.2
9	I(b),II(a),III(a)	43.4
10	I(b),II(c),III(a)	57.7
11	I(b),II(a),III(c)	39.5
12	I(b),II(c),III(c)	63.5
13	I(b),II(b),III(b)	53.1
14	I(b),II(b),III(b)	54.3
15	I(b),II(b),III(b)	52.1

^aParameters: I = Stirring speed (rpm), II = Mass (g), III = pH.

^bConditions: Stirring speed (a = 300; b = 400; c = 500).

Mass (a = 0.5; b = 1; c = 2).

pH (a = 4; b = 6; c = 8).

The stirring speed had great influence on the removal process because it is directly linked to the distribution of the analyte in the solution and the contact of the adsorbent mass (Esmaeli *et al.* 2013; Fontana *et al.* 2016a). However, the adsorbent mass was the most important parameter in EE2 removal, as it was the determinant factor in the adsorbent/adsorbate equilibrium. This phenomenon can be related to the increase in available sites for EE2 adsorption as the adsorbent mass in the aqueous medium increases, which in this case was 0.5–2 g of peanut shells (Fontana *et al.* 2016b). The pH of the solution had little significance in the EE2 removal process, although it showed better results varying the values from 6 to 8 (Wang *et al.* 2015).

Therefore, according to the preliminary data in our other study (Procópio *et al.* 2020) and the results of Table 1, the best experimental condition found for EE2 adsorption and removal by peanut shells was 500 rpm of stirring speed, 2 g of adsorbent mass and pH of 6. In this optimum condition, a new experiment was carried out in triplicate (100 mL EE2 263 $\mu\text{g L}^{-1}$), whose stirring period was 24 h, obtaining a total EE2 removal by the peanut shells close to 90%.

The EE2 removal rate found in this study was considered significant, when compared to other studies involving EE2 adsorption and removal. Researches involving peanut shells in EE2 adsorption have not been found, but it is possible to find some interesting studies about EE2 removal by other materials, for example Fernandes *et al.* (2011). In this work, the authors evaluated the EE2 removal rate from aqueous solutions using decomposed peat as adsorbent and, as a result, obtained approximately 55% of removal using an EE2 initial concentration of 0.1 mg L^{-1} and varying the adsorbent mass from 50 to 200 mg and with the adsorption process operating through magnetic stirring for 36 h. Wang *et al.* (2018) reported EE2 removal using magnetic ion exchange resins and, as a result, obtained a maximum removal of 75% for EE2 at the initial concentration of 20 $\mu\text{g L}^{-1}$. On the other hand, Clara *et al.* (2004) evaluated EE2 adsorption in activated and inactivated sludge, EE2 at 1 mg L^{-1} and adsorbents at concentrations of 1–7 g L^{-1} , stirred over a period of 24 h. Even at very high initial concentrations, a great adsorption affinity to the adsorbent could be observed by the results obtained from the parameters of partition or distribution coefficient, organic matter, and the organic carbon content of the sorbent. Rudder *et al.* (2004) studied the removal of EE2 from water by an advanced treatment using three upstream bio-reactors with a capacity of 2 L that were filled through sand, granulated activated carbon and MnO_2 granules, obtaining respectively, 17.3, 99.8 and 81.7% of EE2 removal by varying the initial concentration of EE2 from 5 to 20 $\mu\text{g L}^{-1}$. Cheng *et al.* (2018) investigated microalgae mutant *Chlorella PY-ZU1* under 15% CO_2 in the EE2 removal in wastewater. The authors used EE2 concentrations in the range of 0.01–5 mg L^{-1} to stimulate

microalgae growth, obtaining a 94% removal rate by *Chlorella* PY-ZU1 at an EE2 concentration of 5 mg L^{-1} . Finally, Almeida *et al.* (2022) synthesized a nanocomposite based on graphene oxide, magnetic chitosan and organoclay (GO/mCS/OC) for EE2 adsorption. They evaluated the effects of dosage, sonication time and pH on the process, resulting in a material with a maximum adsorption capacity of 50.5 mg g^{-1} at 30°C .

In this sense, comparing the rate of adsorption and/or removal of this contaminant with other studies, there is a great alternative for the peanut shells used in this work for applications in processes of EE2 adsorption, a natural adsorbent of residues from agro-industrial activities, biodegradable, available in large quantities and ecologically correct.

Kinetic study

Kinetic study was evaluated to verify and describe the phenomenon of mass transfer, removal speed and equilibrium time during the adsorption process between EE2 (adsorbate) and peanut shells (adsorbent) (Coelho *et al.* 2014; Haro *et al.* 2017). Figure 1 illustrates the kinetic behavior of the EE2 hormone adsorption process in peanut shells for 24 h. There is a high adsorption affinity between the EE2 hormone and the adsorbent, as there is a sharp drop in the EE2 concentration in solution in the first 6 h of the experiment for both temperatures. From 6 to 24 h, the adsorption kinetics showed a less accentuated and slow behavior, until reaching the equilibrium time in 24 h.

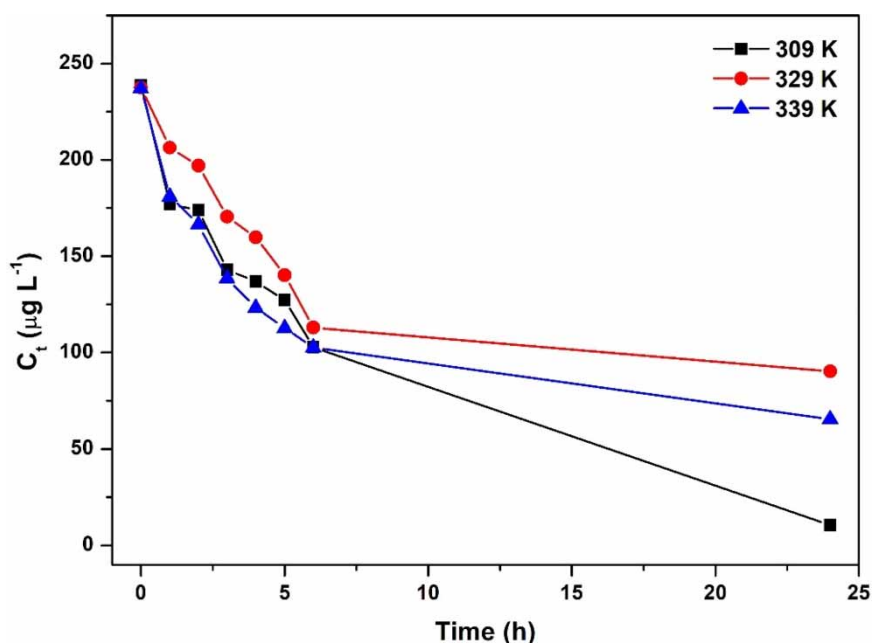


Figure 1 | Effects of adsorption contact time at temperatures 309, 329 and 339 K (C_t – EE2 concentration at time t), C_0 (309 K) = $238 \mu\text{g L}^{-1}$; C_0 (329 K) = $237 \mu\text{g L}^{-1}$; C_0 (339 K) = $237 \mu\text{g L}^{-1}$ (C_0 – EE2 concentration at time zero).

Therefore, the sharp start of the adsorption kinetics may be related to the phenomena of diffusion and convection, external mass transfer and internal diffusion. These phenomena are directly linked to the transport of EE2 molecules within the solution to the adsorbent external surface, known as the hydrodynamic limit layer, and the transport of the solute by diffusion through the limit layer to the pores of the adsorbent referring to external diffusion. After 6 h, the adsorption kinetics may be related mainly to the internal diffusion of EE2 molecules in the adsorbent, in which the adsorption process occurs on the surface and internal pores of the adsorbent, a region with low availability of active sites and mass transfer (Balsamo & Montagnaro 2019; Baup *et al.* 2000; Dabrowski 2001; Fernandes *et al.* 2011). According to Balsamo & Montagnaro (2019) the kinetics of the process does not depend on the stage in which the adsorbate (contaminant) is adsorbed on the external surface of the adsorbent, however, the internal and external diffusion step of the adsorbate on the surface and internal pores of the adsorbent is determinant in the kinetics. Therefore, the kinetics is dependent on the intrinsic characteristics of the adsorbate (molecule size) and adsorbent (porosity) that affect the total rate of adsorption, beyond to the surface area, pore size distribution and the chemical nature of the adsorbent, for example, greater than the pore size of the adsorbent cause its inactivation, reducing the useful surface of adsorption (Carolin *et al.* 2017).

Another important factor observed in the adsorption kinetics was the temperature. The increase in temperature reduced the adsorption capacity of the adsorbent and favored the desorption process of the EE2 molecules. This phenomenon may be related to the kinetic or thermal energies acquired by the EE2 molecules, which gained greater molecular mobility in the internal and external pores of peanut shells. Consequently, it favored the breakdown of chemical interactions (Van der Waals and electrostatic forces) between the adsorbate and the adsorbent, and an increase in the residual concentration of solute in the solution (Jimenez *et al.* 2004; Moreno-Castilla 2004; Guerreiro *et al.* 2020). Like all plant biomass, peanut shells are lignocellulosic materials with cellulose, hemicellulose and lignin in their chemical composition. Cellulose is a polymer formed by glucose monomers (C₆H₁₀O₅)_n joined by glycosidic bonds, each glucose unit has three alcoholic hydroxyl groups that can establish hydrogen bonds. Hemicellulose is a mixture of polymers of hexoses, pentoses and uronic acids, a class of polysaccharides that are hydrogen bonded to cellulose. Lignin is a polymer with a complex chemical structure derived from phenylpropanoid units. EE2 is a synthetic estrogen derived from steroid hormones with a structure formed by cyclo[a]phenanthrene with additions of double bonds, hydroxyl, methyl and ethynyl groups. Therefore, using peanut shell as an adsorbent is an alternative as a natural adsorbent due to its chemical composition (polysaccharides, proteins and lipids) that have many polar functional groups (carboxyl, carbonyl, hydroxyl and amino) that may be involved in interactions or bonds with EE2 (Hon 1994; Saliba *et al.* 2001; Ngah & Hanafiah 2008; Tanyildizi 2011; Bilal & Iqbal 2019; García-Fuentevilla *et al.* 2022). As an example, Reaction 1 reports the elements of the adsorption process, where the adsorbent is peanut shell, the solute is EE2 in the fluid phase and the adsorbate is the EE2 adsorbed on the solid phase of the adsorbent.



It was observed that 227.5 µg L⁻¹ of EE2 was adsorbed at an equilibrium of 309 K. When the temperature is increased from 309 to 329 K, only 147 µg L⁻¹ of EE2 was adsorbed by the peanut shells, a decrease in the percentage of EE2 removal from 95.6 to 62.0%. The increase in temperature favored the inverse reaction, that is, in the direction of the reactants formation and the solute (EE2) residual concentration increased in solution, as seen in Figure 1. At 309 K, the EE2 concentration in solution was 10.5 µg L⁻¹, while at temperatures of 329 and 339 K, the concentrations were 90.2 and 65.4 µg L⁻¹, respectively, in 24 h of process. However, an experimental anomaly was observed in the efficiency of the process, which may be related to the temperature variation and the agitation of the solution by the heating plate used for the process. Also a more appropriate way to minimize this experimental error would be to use a thermostatic bath with agitator in a controlled manner.

To evaluate the performance and obtain more information about the EE2 adsorption process on peanut shells, the experimental data were adequate to theoretical and mathematical models to explain the possible mechanisms and characteristics of adsorption. Pseudo-first-order, pseudo-second-order and Elovich kinetic models were tested on the experimental data (Lagergren 1898; Tanyildizi 2011; Tran *et al.* 2017; Seyedvakili & Samipoorgiri 2018) and Figure 2 shows the curves resulted from the nonlinear adjustments of the experimental data for the studied kinetic models using OriginPro[®] 8.5 software. The results of kinetic information are shown in Table 2.

The pseudo-first-order kinetic model is represented by Equation (3) (Liu & Liu 2008; Seyedvakili & Samipoorgiri 2018; Silva *et al.* 2018):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e is the amount of EE2 adsorbed at equilibrium (µg g⁻¹), q_t is the amount of EE2 adsorbed at time t (µg g⁻¹), and k_1 is equilibrium rate constant of pseudo-first-order adsorption (h⁻¹). Assuming that $q_t = 0$ at $t = 0$, the integrated form of Equation (3) becomes:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

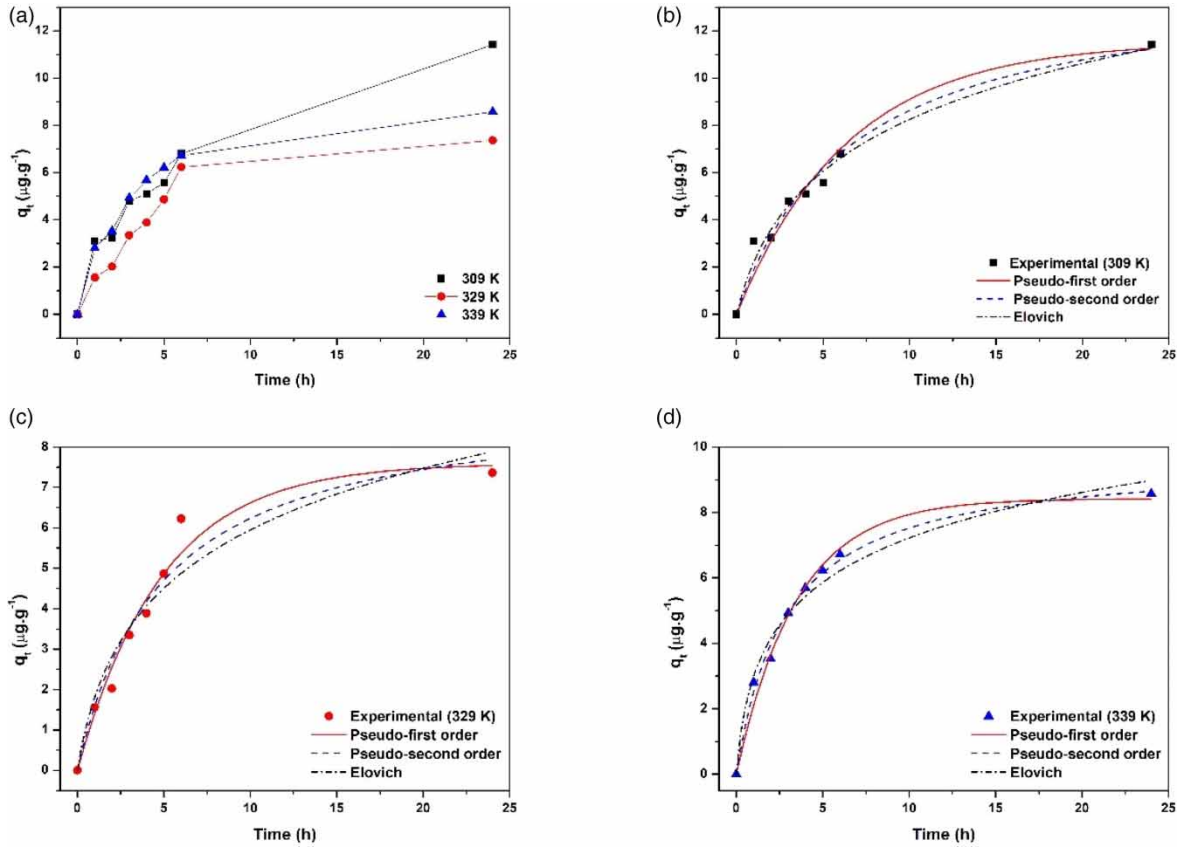


Figure 2 | Kinetic adsorption curves for EE2 in peanut shells for 24 h: (a) evaluation of adsorption capacity at temperatures of 309, 329 and 339 K. Adequacy of experimental data to kinetic models of pseudo-first-order, pseudo-second-order, and Elovich at (b) 309 K, (c) 329 K and (d) 339 K.

Table 2 | Parameters obtained of nonlinear adjustments of experimental data to pseudo-first-order, pseudo-second-order and Elovich kinetic models at different temperatures

Kinetic models	Parameters	Temperature (K)		
		309	329	339
Pseudo-first-order	q_e (exp) ($\mu\text{g g}^{-1}$)	11.41	7.359	8.575
	q_e ($\mu\text{g g}^{-1}$)	11.53	7.597	8.419
	k_1 (h^{-1})	0.1555	0.2049	0.2858
	R^2	0.9560	0.9665	0.9849
Pseudo-second-order	q_e ($\mu\text{g g}^{-1}$)	14.32	9.239	9.681
	k_2 ($\text{g } \mu\text{g}^{-1} \text{h}^{-1}$)	0.01058	0.02243	0.03602
	R^2	0.9686	0.9461	0.9920
Elovich	α ($\mu\text{g g}^{-1} \text{h}^{-1}$)	3.034	2.741	6.764
	β ($\mu\text{g g}^{-1}$)	0.2683	0.4276	0.4886
	R^2	0.9802	0.9171	0.9756

The pseudo-second-order kinetic model is represented by Equation (5) (Ho & Mckay 2004; Seyedvakili & Samipoorgiri 2018; Silva *et al.* 2018):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is equilibrium rate constant of pseudo-second-order adsorption ($\text{g } \mu\text{g}^{-1} \text{ h}^{-1}$). Assuming that $q_t = 0$ at $t = 0$, the integrated form of Equation (5) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

Equation (6) can be rearranged to obtain:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (7)$$

The Elovich kinetic model is represented expressed by Equation (8) (Ho & Mckay 2004; Seyedvakili & Samipoorgiri 2018; Silva *et al.* 2018):

$$\frac{dq_t}{dt} = \alpha e^{(-\beta q_t)} \quad (8)$$

where q_t is the amount of EE2 adsorbed at time t , α is the initial adsorption rate ($\mu\text{g g}^{-1} \text{ h}^{-1}$) and β is the desorption constant ($\mu\text{g g}^{-1}$). Integration of Equation (8) assuming $q_t = 0$ at $t = 0$ gives:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \quad (9)$$

Table 2 presents the kinetic parameters and correlation coefficients (R^2) for the kinetic models applied at the different temperatures studied. The experimental data obtained from the EE2 adsorption process on peanut shells were better adjusted to the Elovich kinetic model at 309 K ($R^2 = 0.9802$) (Figure 2(b)), pseudo-first-order at 329 K ($R^2 = 0.9665$) (Figure 2(c)), and pseudo-second-order at 339 K ($R^2 = 0.9920$) (Figure 2(d)), which presented the highest R^2 at the respective temperatures. However, the values of q_e calculated from the nonlinear adjustment of the pseudo-first-order kinetic model for the temperatures 309, 329 and 339 K were concordant to the experimental q_e values. The pseudo-second-order model showed good R^2 values, however, the q_e values of calculated were relatively different from the experimental q_e values. Based on these results, it is suggested that the adsorption system between EE2/peanut shells is more a first-order reaction than a second-order one. Therefore, from the experimental data (Figure 1) and what was said earlier, it is assumed that the adsorption process does not occur by a single mechanism, but rather by a mixture of mechanisms. The adsorption kinetics of EE2 molecules occurs mainly by the mechanism of external diffusion, observed by the abrupt onset of kinetics up to 6 h of reaction, a region with high availability of active sites and mass transfer. Such a mechanism is dependent on the amount of adsorbate adsorbed and on the active sites on the adsorbent surface (Krishnan & Anirudhan 2002; Yang & Al-Duri 2005; Fontana *et al.* 2016a, 2016b; Haro *et al.* 2017; Silva *et al.* 2018).

By adjusting the experimental data to the pseudo-first-order and pseudo-second-order kinetic models, it was possible to determine another important parameter for the study of adsorption kinetics the activation energy (E_a) of the adsorption process from the Arrhenius equation (Equation (10)) (Guerreiro *et al.* 2020; Fang *et al.* 2021). E_a is described as the minimum kinetic energy required for a reaction to occur, that is, it is related to the energy barrier that the adsorbate needs to overcome for the adsorption to be effective (Fontana *et al.* 2016a).

$$k = A e^{-\frac{E_a}{RT}} \quad (10)$$

The linear form of the Arrhenius equation is expressed by Equation (11):

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (11)$$

where k is the adsorption kinetic constant obtained from the kinetic adjustment, E_a is the adsorption activation energy (J mol^{-1}), A is the temperature independent factor (h^{-1} or $\text{g } \mu\text{g}^{-1} \text{ h}^{-1}$), R is the gas

constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the solution temperature (K). Arrhenius parameters (A and E_a) were obtained from angular (slope $-E_a/R$) and linear (intercept $-\ln A$) coefficients of the line after graphing $\ln k \times 1/T$.

The E_a was evaluated by the Arrhenius plot of $\ln k$ versus $1/T$ shown in Figure 3. The magnitude of E_a gives an idea about the speed of adsorption kinetics, where high E_a values lead to slow kinetics and low E_a values lead to faster kinetics (Guerreiro *et al.* 2020). According to Equation (11) and Figure 2, the activation energy for the adsorption process of EE2 on peanut shells was 16.69 and 34.95 kJ mol^{-1} for a pseudo-first-order and pseudo-second-order kinetic behavior, respectively. E_a values indicated that the adsorption system between EE2/peanut shells has a lower potential barrier for a first-order reaction and a higher potential barrier for a second-order reaction.

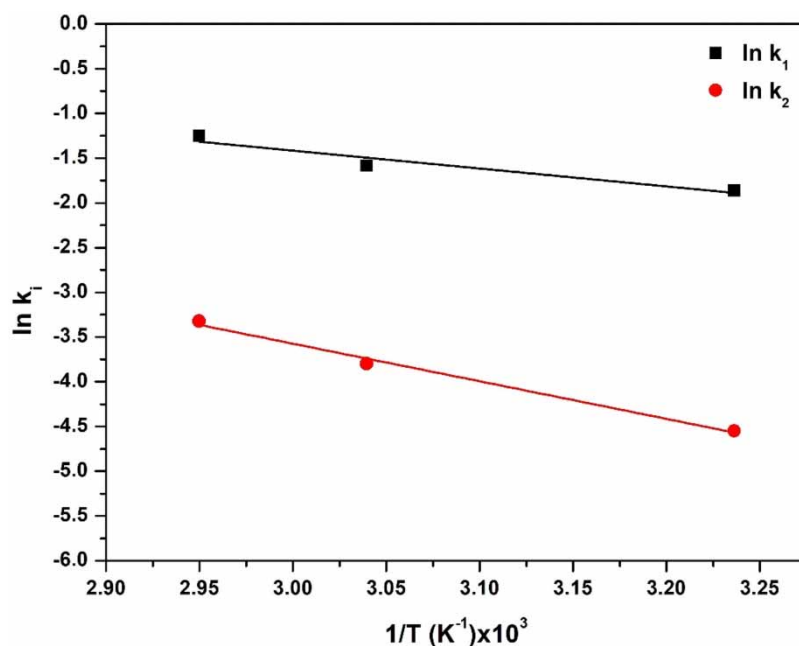


Figure 3 | Arrhenius plot for adsorption of EE2 on peanut shells for pseudo-first-order and pseudo-second-order kinetic behaviors.

Isothermal study

Adsorption isotherms were analyzed to describe the equilibrium phenomena between the residual concentration of EE2 in solution and the amount of EE2 adsorbed per unit mass of the adsorbent at a certain temperature. This analysis was also used to reveal information about the peanut maximum adsorption capacity, as previously reported in the literature (Armagan & Toprak 2013; Coelho *et al.* 2014). The experimental equilibrium data were adjusted to the isothermal models of Langmuir, Freundlich and Sips (Janos *et al.* 2009; Foo & Hameed 2010; Han *et al.* 2013; Almeida *et al.* 2022; Brahma & Saikia 2022) by nonlinear regression using OriginPro[®] 8.5 software. Figure 4 shows the curves resulted from the nonlinear adjustments of the experimental data for the studied isothermal models and the results of isothermal information (parameters and R^2) are shown in Table 3. It is observed in Figure 4(a) that the temperature directly affects the adsorption isotherm process. Although none of the isotherm data showed a defined saturation plateau, it can be said that the adsorbent and EE2 showed good affinity due to the concave behavior of the experimental curves (Cabrera-Lafaurie *et al.* 2014). However, for high residual concentrations (C_e), the interactions between EE2 and adsorbent were weak with increasing temperature, but increased considerably with low C_e of the EE2 at 306 K, which can be seen by the slope of the curve and the maximum amount adsorbed at saturation. Therefore, peanut shells will adsorb higher amounts of EE2 at concentrations lower than $25 \mu\text{g L}^{-1}$.

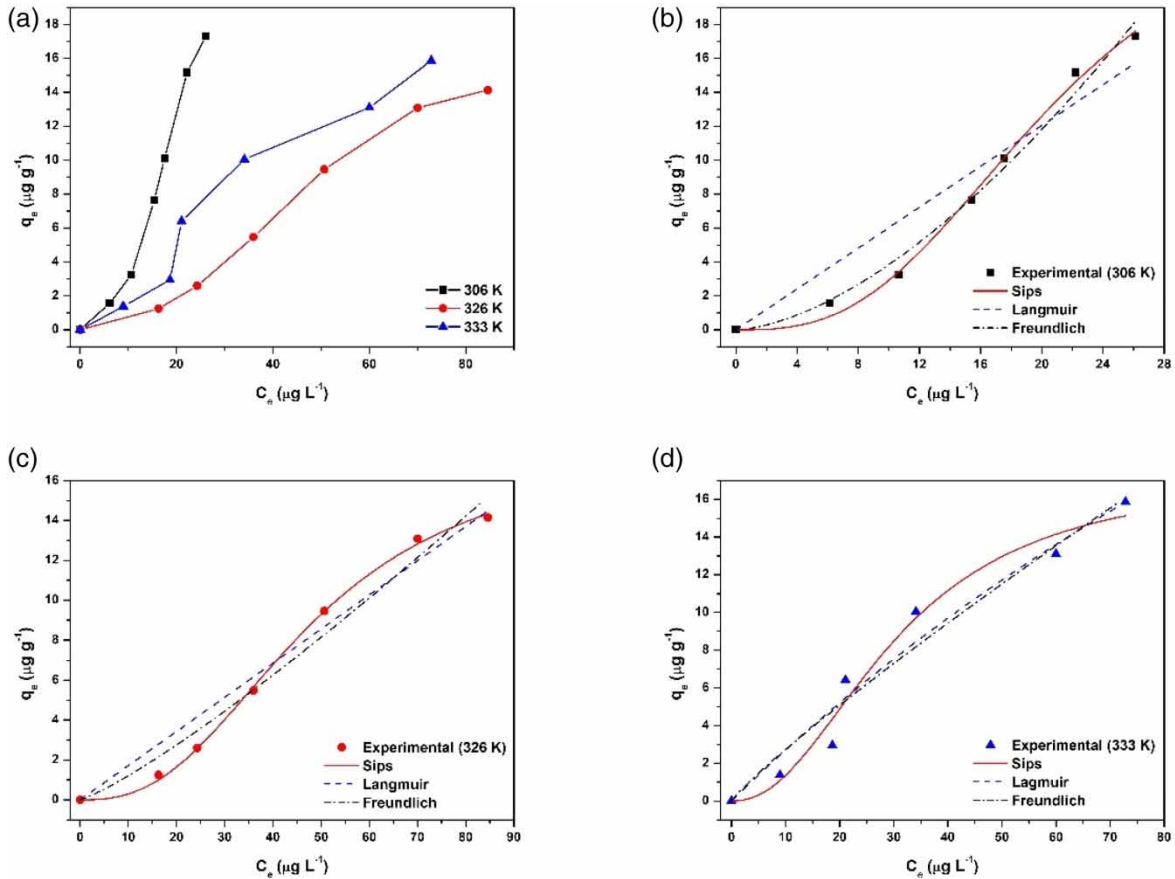


Figure 4 | Isothermal adsorption curves for EE2 in peanut shells for 24 h: (a) evaluation of the behavior of the maximum adsorption capacity and of the adsorbate concentration in the solution at 306, 326 and 333 K. Adequacy of experimental data to isothermal models of Langmuir, Freundlich and Sips at (b) 306 K, (c) 326 K and (d) 333 K.

Table 3 | Langmuir, Freundlich and Sips isothermal model parameters for EE2 adsorption by peanut shells, at temperatures 306, 326 and 333 K

Isothermal models	Parameters	Temperature (K)		
		306	326	333
Langmuir	q_{\max} (exp) ($\mu\text{g g}^{-1}$)	17.30	14.14	15.87
	q_{\max} ($\mu\text{g g}^{-1}$)	69.2×10^5	23.2×10^5	69.98
	K_L ($\text{L } \mu\text{g}^{-1}$)	8.710×10^{-6}	7.353×10^{-6}	4.020×10^{-3}
	R^2	0.8969	0.9555	0.9537
Freundlich	K_F ($\mu\text{g g}^{-1}$) ($\text{L } \mu\text{g}^{-1}$) ^{1/n}	9.272×10^{-2}	7.866×10^{-2}	0.3504
	n	0.6181	0.8431	1.120
	R^2	0.9840	0.9694	0.9490
Sips	q_{\max} ($\mu\text{g g}^{-1}$)	27.04	17.59	17.38
	K_S ($\mu\text{g L}^{-1}$) ^{-1/n}	1.725×10^{-6}	4.240×10^{-5}	5.350×10^{-4}
	n	2.847	2.603	2.201
	R^2	0.9936	0.9984	0.9656

In the literature, the study of isotherms is focused on gas/solid and liquid/solid systems, in this case, for a gas/solid system, the experimental data showed a V-type isotherm behavior, in which the adsorbent–adsorbate interactions are weak, but they are obtained with certain porous adsorbents of mesoporous structure with pores from 2 to 50 nm (Brunauer *et al.* 1938; Sing *et al.* 1985); however, for a liquid/solid system it has characteristics of a

sigmoidal isotherm, in which there is a moderate attraction between adsorbate and adsorbent, and competition of solvent and solute molecules for the active sites of the adsorbent (Moreno-Castilla 2004).

The Langmuir model is represented by Equation (12) (Langmuir 1918; Kinniburgh 1986):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (12)$$

where C_e is the equilibrium concentration of solute in solution ($\mu\text{g L}^{-1}$), q_e is the adsorption capacity at equilibrium ($\mu\text{g g}^{-1}$), q_{\max} is the maximum adsorption capacity ($\mu\text{g g}^{-1}$) and K_L is the constant of Langmuir ($\text{L } \mu\text{g}^{-1}$).

The Freundlich model is represented by Equation (13) (Freundlich 1906; Kinniburgh 1986):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (13)$$

where K_F is the constant of Freundlich ($\mu\text{g g}^{-1}$) ($\text{L } \mu\text{g}^{-1}$) $^{1/n}$ and n is the Freundlich exponent (dimensionless).

The Sips model is a combination of the Langmuir–Freundlich model and is represented by Equation (14) (Sips 1948; Kinniburgh 1986):

$$q_e = \frac{q_{\max} K_S C_e^{\frac{1}{n}}}{1 + K_S C_e^{\frac{1}{n}}} \quad (14)$$

where K_S is the constant of Sips ($\mu\text{g L}^{-1}$) $^{-1/n}$ and n is the Sips exponent (dimensionless).

From Table 3 and Figure 4, the experimental data of the adsorption process were better adjusted to the Sips isothermal model for the respective temperatures of 306 K ($R^2 = 0.9936$) (Figure 4(b)), 326 K ($R^2 = 0.9984$) (Figure 4(c)) and 333 K ($R^2 = 0.9656$) (Figure 4(d)) however, it presented n values greater than 1, a parameter that predicts the heterogeneity of the adsorbent surface and indicates whether the adsorption process can occur in monolayers or multilayers. Langmuir model presented calculated q_{\max} values totally inconsistent with the experimental values and unfavorable R^2 values. However, the EE2 adsorption on peanut shells adjusted the Freundlich model at 306 K ($R^2 = 0.9840$, $n = 0.6181$) and the increase in temperature disfavors the model, as the R^2 values decrease and the n values increase, but the adsorption is still favorable in the interval $1 < n < 10$, and for $1/n > 1$ the isotherms present upward or concave curvature where the marginal sorption energy is proportional with the surface concentration (Delle Site 2001; Febrianto *et al.* 2009; Eren *et al.* 2010). Therefore, the adsorption phenomenon can be described by the Freundlich isotherm, an indicating that the EE2 adsorption on peanut shells can occur in multilayers and present a heterogeneous surface of the active sites of the adsorbent, which can be caused by the presence of different functional groups and the various interactions between adsorbent–adsorbate. However, as the Sips isotherm is the combination of the Langmuir and Freundlich model, and based on the results of R^2 , it can't be disregarded, even with $n > 1$, the adsorption can also occur in a set of monolayers and the adsorbent presents characteristics of a homogeneous surface (Baláz *et al.* 2005; Deng *et al.* 2009; Eren *et al.* 2010).

Fei *et al.* (2017), in a study of the characterization of EE2 adsorption behavior in marine sediments, obtained better EE2 adsorption isotherms adjusted by Freundlich model. In the tested concentration range, a K_F from 15.8 to 39.8 L kg^{-1} and a $1/n$ value from 0.5 to 0.8 were found, suggesting that EE2 adsorption would become saturated when EE2 residual concentration in aqueous medium increased. However, Han *et al.* (2013), used polyamide particles 612 (PA612) of industrial grade as adsorbents for EE2 removal obtaining values for q_{\max} , K_F and $1/n$ equals to 25.4 mg g^{-1} , 16.1 (mg g^{-1}) ($\text{L } \text{mg}^{-1}$) $^{1/n}$ and 0.87, respectively, indicating that the PA 612 particles have affinity for EE2 solutes in water. Joseph *et al.* (2013), studying the EE2 removal by coagulation and combined adsorption using single/multiple-walled carbon nanomaterials and powdered active charcoal in landfill leachate matrices, obtained excellent results. EE2 adsorption capacity was in the $\log K_F$ range from 3.41 to 1.38 and $1/n$ value from 0.32 to 1.36, representing over a 90% removal, which the mechanism is mainly related to the hydrophobic interactions and donor /receptor electron interactions π - π . Besides, studies on the adsorptive capacity and use of peanut shells in solution to remove contaminants such as metals were found in the literature, but not for EE2 (Brown *et al.* 2000; Johnson *et al.* 2002; Romero *et al.* 2004; Zhu *et al.* 2009; Al-Othman *et al.* 2012; Ossman *et al.* 2014).

Thermodynamic study

Thermodynamic parameters are investigated and determined to reveal the viability, spontaneity, temperature influence and energy changes that occur in an adsorption process. Three thermodynamic parameters were evaluated, ΔH° , ΔS° and ΔG° , and the van't Hoff equation has been widely used to determine these parameters. The values can be calculated by using the following Equation (15) (Liu & Liu 2008; Ghosal & Gupta 2017; Lima *et al.* 2019):

$$\ln K_{\text{eq}}^\circ = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (15)$$

where K_{eq}° is the adsorption equilibrium constant (dimensionless), ΔS° is the standard entropy change (kJ/mol/K), R is the universal gas constant (0.008314 kJ mol⁻¹ K⁻¹); ΔH° is the standard enthalpy change (kJ mol⁻¹); T is the temperature (K). The parameters ΔH° and ΔS° were obtained from angular (slope $-\Delta H^\circ/R$) and linear (intercept $-\Delta S^\circ/R$) coefficients of the line after graphical de $\ln K_{\text{eq}} \times 1/T$.

However, according to Lima *et al.* 2019, the correct way to calculate the thermodynamic equilibrium constant for the adsorption system is by Equation (18):

$$K_{\text{eq}}^\circ = \frac{10^6 \cdot K_S \cdot MW_{\text{adsorbate}} \cdot [\text{adsorbate}]^\circ}{\gamma} \quad (16)$$

where K_S is the Sips isotherm model equilibrium constant (L μg^{-1}), MW is the adsorbate molecular weight (g mol⁻¹), γ is the coefficient of activity (dimensionless), $[\text{Adsorbate}]^\circ$ is the standard concentration of the adsorbate (1 mol L⁻¹), however, for this calculation, it is considered that the adsorbate solution is very diluted to consider that the γ is unitary. The K_S obtained in the Sips isotherm must become dimensionless for being applied in the van't Hoff Equation (15), it is recommended to use this Equation (16) described for the calculation of thermodynamic parameters. The standard Gibbs free energy change (ΔG°) can be obtained from either of Equations (17) or (18):

$$\Delta G^\circ = -RT \ln K_{\text{eq}}^\circ \quad (17)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

Table 4 presents the thermodynamic parameter values obtained for the adsorption process at the studied temperatures.

Table 4 | Thermodynamic parameters (ΔG° , ΔH° , ΔS°) obtained for EE2 adsorption by peanut shells at 306, 326 and 333 K

T (K)	K_S	K_{eq}	R^2	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ K ⁻¹ mol ⁻¹)
306	1.725×10^{-6}	511.3		-15.87		
326	4.240×10^{-5}	12,567	0.9528	-25.59	168.9	0.6022
333	5.350×10^{-4}	158,575		-33.16		

According to the results in Table 4, the ΔG° negative values indicate that the EE2 adsorption on peanut shells is a spontaneous process, that is, the process was thermodynamically favorable and directly proportional to the temperature. ΔH° positive value indicates the endothermic nature of the adsorption process, where energy is absorbed by the EE2/adsorbent system. The value of 168.9 kJ mol⁻¹ (ΔH°) is characteristic of the existence of strong intermolecular interactions between EE2/adsorbent and a high probability of the process occurring by chemisorption. The positive value of ΔS° (0.6022 kJ K⁻¹ mol⁻¹) suggests a small increase in randomness at the adsorbate-adsorbent interface (system) and solution, a greater affinity of the adsorbent for the adsorbate and the adsorbate is less hydrated on the surface of the adsorbent than in solution (Liu & Xu 2007; Ghosal & Gupta 2017; Fang *et al.* 2021; Tang *et al.* 2021).

CONCLUSION

In this study, raw peanut shells as adsorbents showed performance in removing EE2 from the aqueous medium. The high removal and adsorption capacity even with a small amount of adsorbent and low concentration of adsorbate, suggests peanut shells as a promising adsorbent for application in wastewater treatment. From the best adsorption condition (agitation speed = 500 rpm, adsorbent mass = 2 g and pH = 6), 90% removal was obtained and an adsorptive capacity of $17.3 \mu\text{g g}^{-1}$ at 306 K. Kinetic data adjusted the pseudo-first-order model, however, it indicated that adsorption can occur by a mixture of mechanisms, in which the mechanism of external mass transfer and external diffusion were the main steps of the adsorption process, directly related to the abrupt drop in kinetics after 6 h of the process. The system presented an E_a of $16.69 \text{ kJ mol}^{-1}$, indicative of a slow adsorption kinetics because of the high reaction potential barrier. The Sips isothermal model was able to describe the sorption behavior for the adsorbent and the EE2 as it presented a better fit to the experimental data, suggesting that peanut shells have heterogeneous characteristics and that there is formation of monolayers and multilayers by chemisorption. ΔG° negative values indicated that the EE2 adsorption process was a favorable and spontaneous process. ΔH° positive value ($168.9 \text{ kJ mol}^{-1}$) indicated the endothermic and chemical nature of the adsorption process. ΔS° positive value ($0.6022 \text{ kJ K}^{-1} \text{ mol}^{-1}$) indicated a small increase in the degree of disorganization and affinity of the EE2/adsorbent system. Therefore, the compilation of results points to peanut shells as a promising adsorbent alternative for the removal of endocrine interferents, with impactful benefits for nature and suggests an evaluation of this adsorbent in real aqueous matrices for possible wastewater treatment.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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