



Application of biochar from agro-industrial waste in solid-phase extraction for the determination of 17 β -estradiol from aqueous solution

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Abstract

In this study, the biochar produced from coffee wastes and eucalyptus sawdust was employed as an adsorbent in solid-phase extraction devices for the determination of 17 β -estradiol from aqueous solution. Parameters such as adsorbent mass, solvent type, eluent volume, ionic strength, breakthrough volume, and the cartridge reuse were evaluated. The best experimental conditions for solid-phase extraction concerning adsorbent mass, elution solvent, eluent volume, ionic strength, breakthrough volume, and cartridge reuse were established. The most suitable conditions for 1.0-mL cartridge were: mass of 50 mg, elution solvent 5.0 mL of acetonitrile/water 90:10 (v:v), 0.003 mol L⁻¹ NaCl concentration, and 17 β -estradiol solution volume 50.0 mL. The solid-phase extraction results showed that, although 17 β -estradiol recovery was about 60%, the removal efficiency was 100% and the cartridges of 200 and 500 mg can be reused eight and four times, respectively, without any decrease in adsorption capacity. The results demonstrate the potential use of biochar as new adsorbent in solid-phase extraction devices for the removal of estrogens in aqueous solution.

Keywords Cartridge · Charcoal · Estrogen · Solid waste

Introduction

With the evolution of agriculture in Brazil, due to the development of new technologies in seeds, plant changes, planting and harvesting processes, an increase in agricultural production of grains and fruits was obtained (Wolfert et al. 2017; Pivoto et al. 2018). Consequently, these factors led to the generation of agro-industrial residues such as rice husk, peach seed, coffee residues, forest residues such as pine and

eucalyptus, among others. Among their problems, we highlight those of coffee wastes and eucalyptus residues: The former is because it is one of the most consumed beverages in Brazil (Sousa et al. 2016), and the latter is because it is one of the most common regarding reforestation, and because it has a short growing time, from 5 to 7 years.

In the last decades (Pereira et al. 2008), the interest in the application of these residues has increased, since both the discarding in the soil and the burning of these materials can generate a series of environmental problems. Some of these problems are changes in soil pH, contamination of river waters, and changes in air quality (Marion et al. 2017), which can be caused by the presence of phenolic compounds in these wastes (Kosmala et al. 2011; Anirudhan et al. 2009). Another factor that has attracted attention is why not taking advantage of this insignificant value-added waste to produce adsorbents for the removal of contaminants present in water (Zhang et al. 2014; Cheraghi et al. 2015; Shang et al. 2016; Ebadati et al. 2019).

A class of contaminants that deserves attention is the endocrine disrupting compounds (EDC), which are chemicals that can alter one or several functions in the natural endocrine system performance of animals and humans

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(Tijani et al. 2013). Increasing evidence also suggests that they can affect not only exposed individuals but also their children and subsequent generations as a consequence of the cumulative effect. These contaminants have been found in environmental samples in extremely low concentrations (ng L^{-1}). However, several studies with animals, such as fish, mollusks, among others, show that exposure to EDC even at low concentrations can cause reproductive disorders, dysplasia, among others (Xi et al. 2013).

Among the endocrine disruptors are natural estrogens [17 β -estradiol (E2), estrone (E1), and estriol (E3)] and synthetic estrogens [17 α -ethynylestradiol (EE2)], which are the main cause of estrogenic activities found in bodies aquatic and sewage waste (Mompelat et al. 2009). Humans and animals produce natural estrogens, and estriol is a metabolite of estrone and is produced in greater amounts during pregnancy. Due to the participation of the fetus in the formation of estriol, this is a sensitive indicator of placental and/or fetal well-being. The estrogen 17 α -ethynylestradiol, in turn, is one of the components of the contraceptive pill, with each pill containing 30–50 μg of this estrogen (Aerni et al. 2004; Oguz and Kankaya 2013).

Although these compounds are very important and essential for life, a part of them (excess) is excreted by humans and animals in the form of urine and feces, and this may be one of the reasons for the presence of EDC in river waters (Rocha et al. 2013), springs supply, and even drinking water. Besides that, the presence of contaminant caffeine in these samples is an indicator of water quality, i.e., if caffeine is present in the treated water; it is likely that other chemical compounds with similar chemical structure have not been eliminated during water treatment, such as the endocrine disrupting compounds (Machado et al. 2016).

In view of these aspects, the motivation of this study is related to two factors: (1) the fact that there is no effective treatment for estrogen removal in environmental matrices, mainly in developing countries; and (2) concern with the disposal/treatment of the large volume of agro-industrial waste generated daily (Oliveira et al. 2018). According to the literature (Nartey and Zhao 2014), the biochar can be prepared with any material that has carbon in its structure, and the higher the carbon content, the better the yield of your preparation process. To address environmental issues, precursors for the manufacture of biochar must be abundant in the region and/or country in which they will be used (Cao et al. 2017; Bispo et al. 2018; Ariyanto et al. 2018; Inaniyan and Raychoudhury 2018). Considering these aspects, the objective of this study was to apply the biochar produced from coffee wastes and eucalyptus sawdust as adsorbent in solid-phase extraction (SPE) devices for the determination of 17 β -estradiol (E2) from aqueous solution. Parameters such as adsorbent mass, solvent type, eluent volume, ionic strength, breakthrough volume, and the cartridge reuse were

evaluated. This research work was carried out at the Institute of Chemistry of Universidade Federal do Rio Grande do Sul (UFRGS, Brazil) in the period from March 1, 2012, to August 31, 2015.

Materials and methods

Chemicals and materials

The estrogen 17 β -estradiol (E2) ($\geq 98\%$ pure) was supplied purchased from Sigma-Aldrich (St. Louis, USA), and it was used as the standard. Methanol and acetonitrile (HPLC grade) were purchased by J.T. Baker (Phillipsburg, NJ). Sodium chloride (analytical grade) was purchased from Merck (Darmstadt, Germany). Commercial cartridge OASIS[®] (HLB 60 μm) with 500 mg solid phase was obtained from Waters (Milford, USA). A stock solution of 150 mg L^{-1} of E2 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} E2 was prepared from serial dilution of the stock solution. Working aqueous solution was prepared daily by diluting the 13.0 mg L^{-1} solution with water, to attain the required concentration for calibration measurement. The water used in this work was ultrapure (resistivity 18.2 $\text{M}\Omega\text{ cm}$) obtained with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Biochar adsorbent preparation

The biochar employed in this work was prepared and characterized according to the methodology described by Rovani and collaborators (2014, 2016).

Solid-phase extraction cartridges preparation

Solid-phase extraction (SPE) cartridges were prepared by packaging an appropriate amount of biochar into a syringe of 1.0 mL (5 mm diameter) containing glass wool (previously washed) in the lower part to avoid losses of adsorbent during the adsorption process of E2. The white containing only the glass wool was also made (Fig. S1). Cartridge conditioning was performed with 1.0 mL of acetonitrile and equilibrated with 5.0 mL of deionized water. Then, 5.0 mL of E2 solution [1.0 mg L^{-1} with 0.5% acetonitrile/water (v: v)] was passed through SPE cartridges under vacuum. The estrogen 17 β -estradiol was eluted with 5.0 mL of a suitable solvent and quantified by spectrofluorimetry. SPE procedures were performed using a Supelco Visiprep-DL system purchased from Sigma-Aldrich (São Paulo, Brazil), coupled to a 406 mBar vacuum pump of the Edwards (São Paulo, Brazil) (Fig. S2).

Determination of 17 β -estradiol concentration

Quantification of 17 β -estradiol (E2) in the solution was performed by molecular fluorescence spectroscopy using a Shimadzu spectrofluorimeter; model RF-5301 PC (Columbia, USA). Fluorescence emission spectra were recorded employing an excitation wavelength (λ_{ex}) of 280 nm, by scanning from 295 to 350 nm of emission wavelength (λ_{em}) (Lima et al. 2011). The following merit parameters were determined: linearity, linear determination coefficient (R^2), limit of detection (LOD), and limit of quantification (LOQ). The LOD and LOQ values for 17 β -estradiol were calculated based on the IUPAC definition (Thompson et al. 2002), using calibration curve parameters obtained through fluorescence spectra.

Results and discussion

Optimization of SPE parameters

Numerous factors may influence the efficiency of solid-phase extraction (SPE) making its evaluation indispensable during the development of the method. Thus, SPE technique was optimized by adjusting the critical parameters that affect the efficiency of the adsorption or elution of the analyte. The parameters evaluated were: E2 solution flow through the cartridge (extraction time), solution pH, adsorbent mass, elution solvent ratio, ionic strength, eluent volume, E2 solution volume, and reuse of the prepared cartridge.

Effect of biochar mass

The results of the solid-phase extraction tests employing different biochar mass are shown in Fig. S3. According to the data presented, 50 mg of adsorbent was sufficient to efficiently remove E2, with removal percentage close to 100%. Also, it has been observed that by increasing the amount of biochar mass the removal percentage remains practically constant. Thus, 50 mg of adsorbent was satisfactory to remove/concentrate 17 β -estradiol efficiently. According to the literature (Moreno-Castilla 2004; Guillarduci et al. 2006; Pan et al. 2008; Azzouz et al. 2018), the interactions between biochar and aromatic compounds can occur in different ways: formation of donor–receptor complex, hydrogen bonds, Van der Waals force, and π – π stacking. All these interactions must be taken into account to explain the experimental adsorption data presented.

Effect of elution solvent

The choice of an organic solvent as the eluent in the SPE technique plays an important role in the elution of analytes

from adsorbent (Guillette et al. 1994; Dean et al. 1998; Azzouz et al. 2018). Most of the interactions involved in the E2 adsorption are intermolecular forces such as Van der Waals interactions, so the organic molecules should be easily eluted from the solid phase by a solvent such as methanol or acetonitrile (Liu et al. 2018). In this context, E2 recovery tests were performed with methanol and acetonitrile, where it was observed that the acetonitrile presented higher estrogen recovery, so the experiments were performed with acetonitrile.

The effect of the elution solvent was evaluated for the best adsorbent mass, with different proportions of acetonitrile/water [20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10, and 100:0 (v: v)]. As shown in Fig. 1, the best results were obtained with a mixture of acetonitrile/water 90:10 (v:v), where the E2 recovery percentage was about 65%. For reasons of preferred solubility of E2 in 90% acetonitrile, the effects of Van der Waals forces were decreased with increasing elution solvent (Liu et al. 2013). This may be the reason why the 90:10 mixture of acetonitrile/water was the most effective elution solvent studied.

Effect of ionic strength

Figure S4 shows the effect of ionic strength, which was modified by the addition of NaCl (0.003, 0.005, 0.010, and 0.020 mol L⁻¹), in the 17 β -estradiol removal by SPE. As can be seen, the E2 removal was efficient for all salt concentrations. In general, the presence of NaCl increases the solubility of the analytes in water, making the hydrophobic interaction between E2 and biochar occur more easily.

The effect of ionic strength (NaCl concentration) on E2 recovery is presented in Fig. 2a: adsorbent mass 50 mg; flow 1.0 mL min⁻¹; E2 initial concentration 1.0 mg L⁻¹; E2

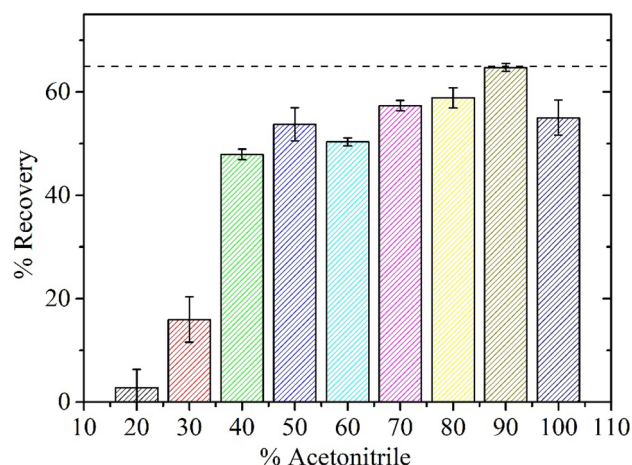


Fig. 1 Effect of elution solvent on the E2 recovery percentage for the adsorbent mass 50 mg. Conditions: flow 1.0 mL min⁻¹; E2 [initial] 1.0 mg L⁻¹; E2 solution 5 mL; and elution solvent 5 mL



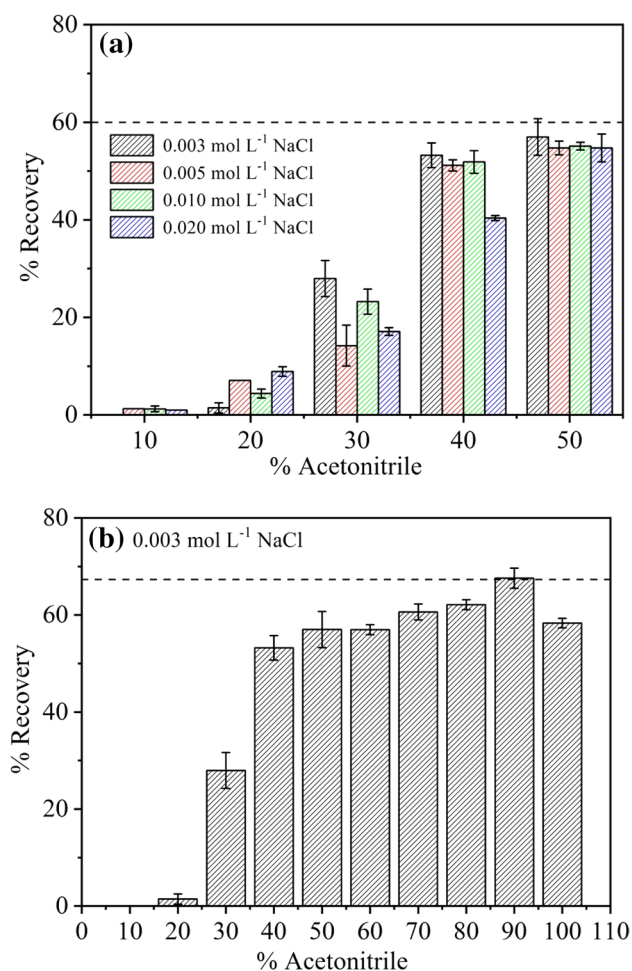


Fig. 2 Effect of the acetonitrile ratio as eluting solvent on the E2 recovery for different NaCl concentrations (a) and for 0.003 mol L⁻¹ NaCl concentration (b)

solution volume 5.0 mL; and elution solvent volume 5.0 mL (acetonitrile/water v:v) (Fig. 2). According to the results, it was possible to observe that, above 30% acetonitrile, the highest E2 recovery/elution percentages were obtained for the salt concentration of 0.003 mol L⁻¹. With increasing amount of NaCl, a decrease in the percentage of E2 recovery was observed. According to the literature (Liu et al. 2013), when a larger amount of salt is added to the solution, the complexing of π electron subunits of biochar with cations can be formed by cation interaction π and partial active centers can be occupied, leading to a lower extraction of the analyte. Thus, as the 0.003 mol L⁻¹ NaCl concentration shows the highest E2 elution percentages, the effect of the elution solvent with a higher amount of acetonitrile was evaluated for this salt concentration; Fig. 2b shows this effect.

According to Fig. 2b, the best result was for the acetonitrile/water mixture 90:10, where the E2 elution percentage was around 67%, corroborating with previous results (Fig. 1). However, with the presence of 0.003 mol L⁻¹

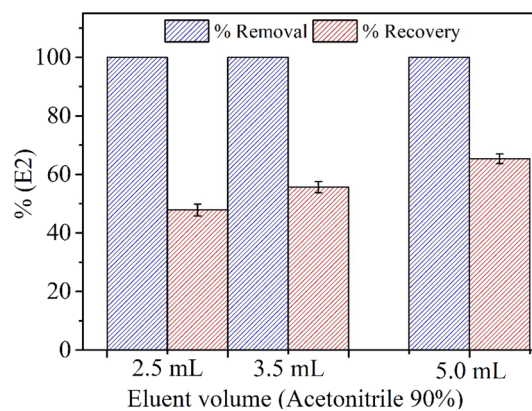


Fig. 3 Effect of eluent volume [acetonitrile/water 90:10 (v:v)] in function of the E2 recovery percentage (red) and E2 removal percentage (blue)

NaCl there was a slight increase in the elution percentage of E2. Considering these aspects, further experiments were carried out with 0.003 mol L⁻¹ NaCl.

Effect of eluent volume and breakthrough volume

Figure 3 shows the effect of the eluent volume [acetonitrile/water 90:10 (v:v)] in function of the E2 recovery percentage: adsorbent mass 50 mg; flow 1.0 mL min⁻¹; E2 initial concentration 0.5 mg L⁻¹; 0.003 mol L⁻¹ NaCl concentration; and E2 solution volume 5.0 mL. From the result obtained, it can be concluded that 5.0 mL of acetonitrile/water 90:10 (v:v) was the eluent volume which presented the highest recovery percentage of E2 (~66%), which is by the above results. In this manner, a solvent volume of elution of 5.0 mL was continued.

The determination of the breakthrough volume is a very important parameter that must be evaluated. This is defined as the volume of sample that can be percolated through the SPE cartridge without the loss of analyte (Pessoa et al. 2012, 2014). The breakthrough volumes assessed for E2 are presented in Fig. S5, where the E2 solution volumes were 25.0, 50.0, and 75.0 mL: adsorbent mass 50 mg; flow 1.0 mL min⁻¹; 0.003 mol L⁻¹ NaCl concentration; E2 initial concentration 0.10 mg L⁻¹ (blue) and 0.05 mg L⁻¹ (red); and elution solvent volume 5.0 mL [acetonitrile/water 90:10 (v:v)]. According to the results, the E2 extraction capacity decreases with increasing volume, corroborating with data from the literature (Pessoa et al. 2012; Liu et al. 2013). In general, the E2 recovery percentages (approximately 60%) show slight variation for volumes of 17 β -estradiol solution up to 50.0 mL. The sample volume of 50.0 mL was selected for the reuse of cartridge experiments.



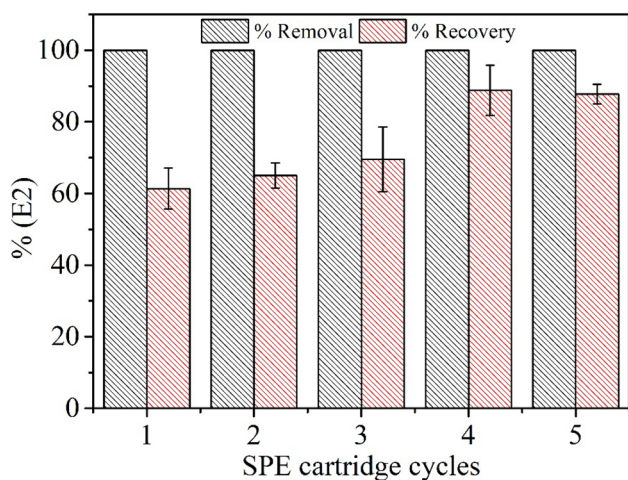


Fig. 4 Effect of reuse cycles for three SPE cartridges. Conditions: adsorbent 50 mg; flow 1.0 mL min⁻¹; [E2 initial] 0.05 mg L⁻¹; 0.003 mol L⁻¹ [NaCl]; E2 solution 50.0 mL; elution solvent 5.0 mL

Reuse cycles

The reuse of the SPE cartridges (Fig. 4), with 50 mg of adsorbent mass, was evaluated for three devices under the same conditions, where five cycles of E2 removal and recovery were performed for each of them. The E2 removal percentage was 100%, and the results for E2 recovery are expressed by the mean and standard deviation of the three cartridges. The initial conditioning of the cartridges was performed with 1.0 mL of acetonitrile and equilibrated with 5.0 mL of deionized water. Subsequently, 50.0 mL of 0.05 mg L⁻¹ 17 β -estradiol solution and 0.003 mol L⁻¹ of NaCl were added to each cartridge. Then, E2 elution was performed with 5.0 mL of acetonitrile/water 90:10 (v:v). After each elution, a new conditioning was performed with 1.0 mL of acetonitrile and equilibrated with 5.0 mL of deionized water.

According to Fig. 4, it was observed that the E2 recovery percentage remains practically constant in the first two cycles and from the third cycle the occurrence of a memory effect is observed, with coelution of the adsorbed E2 molecules in the solid phase in the first cycles of reuse. This means that the devices can be used up to two cycles. Although the E2 recovery capacity is only around 60%, the E2 removal percentage (100%) is efficient at all cycles, probably due to some higher force interactions involved. In general, the eluted E2 molecules are those that exhibit weaker interactions with coal, such as Van der Waals interactions.

Comparison with commercial cartridge

For a better comparison with the commercial cartridge, new device was prepared, from the optimized conditions

previously, in larger syringes (6 mL) with 200 and 500 mg of biochar. As the adsorbent mass is higher, after several tests it was determined that the best initial conditioning would be with 4.0 mL of acetonitrile and equilibrated with 20.0 mL of ultrapure water. Subsequently, 50.0 mL of 0.05 mg L⁻¹ E2 solution and 0.003 mol L⁻¹ NaCl were added to each cartridge. Then, E2 elution was performed with 5.0 mL of acetonitrile/water 90:10 (v:v). After each elution, a new conditioning was performed with 1.0 mL of acetonitrile and equilibrated with 5.0 mL of deionized water.

Reuse cycles of 6-mL SPE cartridge

Figure 5 shows the reuse cycles of SPE cartridge prepared with 200 and 500 mg of biochar as a function of the E2 removal and E2 recovery percentage: 50.0 mL of 0.05 mg L⁻¹ E2 solution and 0.003 mol L⁻¹ NaCl were added to each cartridge, and

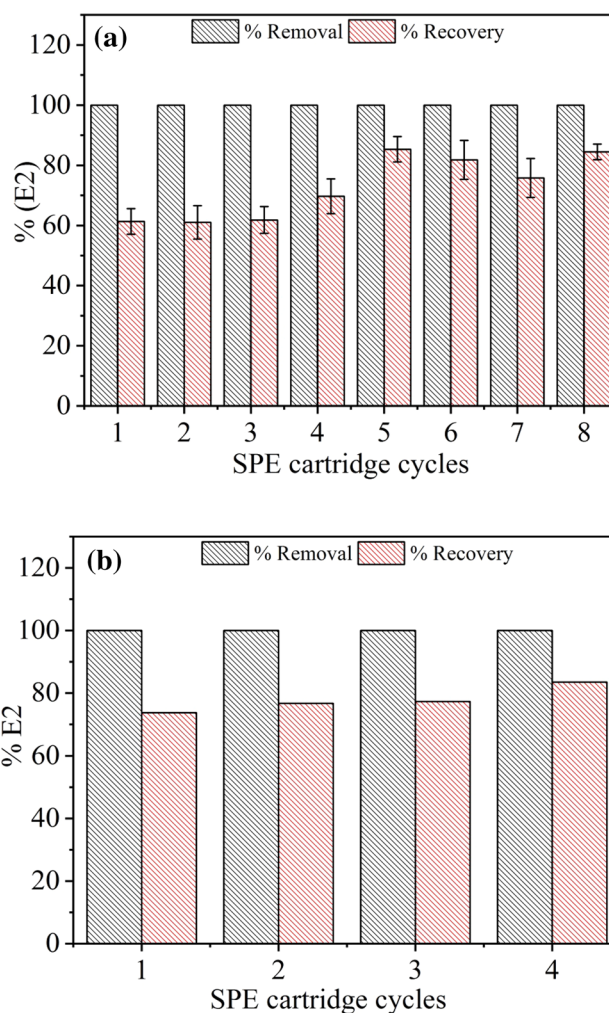


Fig. 5 Effect of reuse cycles for three SPE cartridges. Conditions: adsorbent 200 mg (a) and 500 mg (b); flow 1.0 mL min⁻¹; [E2 initial] 0.05 mg L⁻¹; 0.003 mol L⁻¹ [NaCl]; E2 solution 50.0 mL



E2 elution was performed with 5.0 mL of acetonitrile/water 90:10 (v:v). It was observed that the E2 recovery percentage remains practically constant in the first three cycles and from the fourth cycle a memory effect was observed with coelution of the E2 molecules adsorbed in the solid phase. Corroborating with the result of the reuse of 50-mg cartridges, however, with the increase in the cartridge volume and the mass of biochar, it was possible to have one more cycle with E2 recovery percentage constant. It is important to note that in eight cycles, to cartridge prepared with 200 mg of biochar, the percentage of E2 removal was efficient. SPE cartridge of this study was more efficient than the literature study “modified activated carbon prepared from acorn shells as a solid-phase extraction sorbent for the preconcentration and determination of trace amounts of nickel in food samples” (Ebrahimi 2017).

Reuse cycles of commercial SPE cartridge

The commercial cartridge used was OASIS[®] (HLB 60 μm) with 500 mg solid phase obtained from Waters (Milford, USA). The characteristics of this cartridge according to the certificate of analysis of the company are: specific area 801 $\text{m}^2 \text{g}^{-1}$; mean pore diameter 8.7 nm; total pore volume 1.36 $\text{cm}^3 \text{g}^{-1}$; and mean particle diameter 52.6 μm . The solid phase is hydrophilic–lipophilic and reverse phase equilibrium, which can be used for all components (for example drugs and their polar metabolites).

Initial cartridge conditioning was performed in amounts proportional to the increase in solid-phase mass, 4.0 mL of acetonitrile, and equilibrated with 20.0 mL of ultrapure water. Subsequently, 50.0 mL of 0.05 mg L^{-1} E2 solution and 0.003 mol L^{-1} of NaCl were added to the cartridge. Then, E2 elution was performed with 5.0 mL of acetonitrile/water 90:10 (v:v). After each elution, a new conditioning was performed with 1.0 mL of acetonitrile and equilibrated with 5.0 mL of deionized water. Figure S6 shows the effect of the reuse cycles for the 500-mg commercial cartridge, where ten cycles were performed. According to the results, it is observed that in the first two reuse cycles the cartridge was efficient for both E2 concentration and E2 recovery. From the third to the sixth cycle of E2 recovery, percentage is observed around 90%. In the seventh cycle, there was coelution of the adsorbed E2 molecules in the solid phase between the third and sixth cycles of reuse. As expected for a commercial cartridge, the 17 β -estradiol recovery/elution was effective for two cycles.

Conclusion

The best experimental conditions for solid-phase extraction concerning adsorbent mass, elution solvent, eluent volume, ionic strength, breakthrough volume, and cartridge

reuse were established. The most suitable conditions for 17 β -estradiol efficiently removing and recovering a constant percentage of this estrogen in 1.0 mL cartridge are: mass of 50 mg, elution solvent 5.0 mL of acetonitrile/water 90:10 (v:v), 0.003 mol L^{-1} NaCl concentration, E2 solution volume 50.0 mL, and two cycles of reuse. By increasing the cartridge volume to 6.0 mL and adsorbent mass to 200 mg, E2 recovery was constant for three cycles of reuse. The experiments demonstrated that although the E2 recovery percentage was only around 60%, E2 removal percentages were effective in all experiments and all cartridge reuse cycles.

When the tests were performed with a commercial 500-mg cartridge, the E2 recovery percentage was fully effective for up to two cycles. As commercial cartridges are usually used only once and discarded, the prepared cartridge can also be used, provided they are new optimizations which have been made to increase E2 elution. As prospects for other studies, we test other methods of analyte elution, such as performing elution by centrifugation, by ultrasound or at higher temperatures. On the other hand, the characteristics of the prepared material are suitable for the use of this material as a filter in water treatment plants.

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