New Sorbent from Agro-industrial Waste and its Potential Use in 17β-Estradiol and 17α-Ethynylestradiol Removal

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INTRODUCTION

✓ The long-term risks of endocrine disruptors compounds (EDC) still remains unclear for non-target organisms as well as for human health, since EDC can be found in very low concentrations (range of ng L^{-1}) in different environmental compartments.[1,2]

✓ There is a need for developing new reliable analytical methods, which will enable a rapid, sensitive and selective determination of EDC in environmental samples.

✓ Therefore, a sample pretreatment step prior to chromatographic analysis is necessary for pre-concentrating the target analytes.[3]

OBJECTIVE: Develop a new sorbent from agroindustrial waste for removal of 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) from aqueous solution.

EXPERIMENTAL

Sorbent Preparation

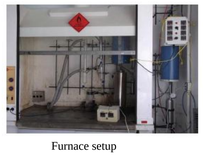
Sorbent preparation by pyrolysis → Mixture of coffee waste, sawdust, calcium oxide (1:1:2) and vegetable oil to form a paste → Paste is carbonized up to 1073.15K (293.15K min^{-1}) under argon atmosphere for 2 h

Template fo preparation of activated carbon in cylinder form

Carbon material cylinder dried at room temperature

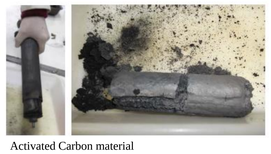
Cylinder introduced into reactor

Finally the material was sieved (< 150 µm)



Furnace setup

Oil extracted from biomass

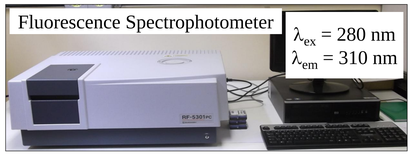


Activated Carbon material

Removal of 17β-estradiol and 17α-ethinylestradiol

Sorbent 30 mg + 20.0 mL solution EE2 or E2 2.00 mg L^{-1} → Suspensions were shaken for 24 h at 298K and 150 rpm

Centrifuged: 3200 rpm t = 5 min → Fluorescence Spectrophotometer (λ_{ex} = 280 nm, λ_{em} = 310 nm)



RESULTS AND DISCUSSION

Analysis of SEM

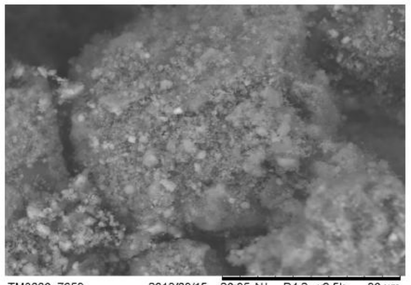


Figure 1: SEM of Activated carbon with magnification 2.500 X. Accelerating voltage 15 keV.

Carbon material lost its fibrous properties after pyrolysis at (1073.15K)

The roughness of material is obvious

Furthermore, the pore size and distribution presented by the adsorbent varied

FTIR Vibrational Spectra

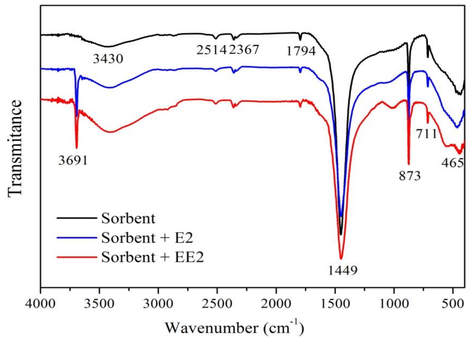


Figure 2: FTIR vibrational spectra. The number indicated for the bands correspond to wavenumbers that are expressed in cm^{-1}.

- ➢ 3691 cm^{-1} OH stretch of "free" (no hydrogen bond) of estrogens
- ➢ ~ 3430 cm^{-1} OH stretching (with hydrogen bond)
- ➢ 1794 cm^{-1} C=O bond of the carbonyl groups or carboxylate esters
- ➢ 1449 cm^{-1} aromatic rings conjugated with the carbonyl group
- ➢ 873 cm^{-1} bending CH

Water Contact Angle (WCA)

➢ Contact Angle (θ) = 115.22° ± 0.026.

➢ (θ) between 90° and 150° is called the hydrophobic surface.[4]

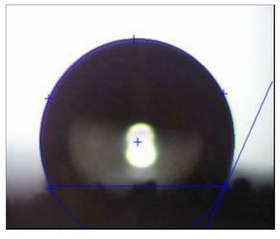


Figure 3: Measure the water contact angle of the activated carbon.

Point of Zero Charge (pH_{PZC}) - Effect of pH

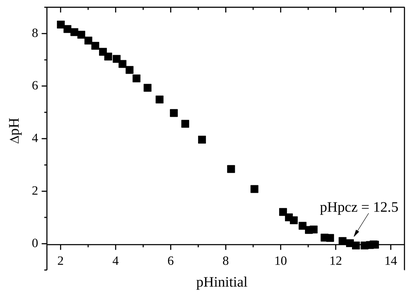


Figure 4: Point of zero charge (pH_{PZC}) of sorbent. Conditions: mass of sorbent 50.0 mg and temperature of 298K.

The pH_{PZC} sorbent was 12.5, which is considered a high value when compared to other materials.[5]

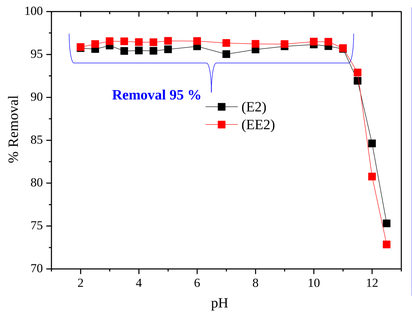


Figure 5: Effect of pH on the E2 and EE2 removal. Conditions: Co= 2.00 mg L^{-1} of E2 or EE2; temperature at 298K; mass of sorbent of 30.0 mg; time of contact 24 h.

✓ Corroborating with the pH_{PZC} data

✓ Removal capacity ↓ at pH values higher than 11 (Removal 75 %)

✓ In order to continue the sorption studies, the initial pH was fixed at 7.0

Effect of Sorbent Dosage

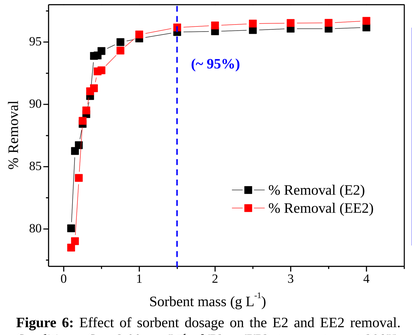


Figure 6: Effect of sorbent dosage on the E2 and EE2 removal. Conditions: Co= 2.00 mg L^{-1} of E2 or EE2; temperature at 298K; time of contact 24 h.

✓ Maximum percentage of removal was achieved with 30 mg of sorbent

✓ Higher values of sorbent did not affect the adsorption curve

Effect of Time

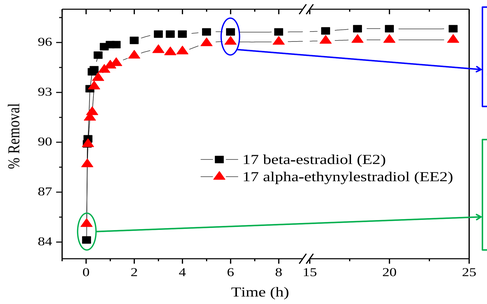


Figure 7: Effect of time on the E2 and EE2 removal. Conditions: Co= 2.00 mg L^{-1} of E2 or EE2; temperature at 298K; mass of sorbent of 30.0 mg; pH = 7.0.

6 h Removal: 96.6% (E2) 96% (EE2)

0.016 h Removal: 84% (E2) 85% (EE2)

Tabela 1: Kinetic parameters for EE2 and E2 removal using activated carbon adsorbent. Conditions: temperature was fixed at 298 K; pH 7.0, mass of adsorbent 30.0 mg, Co = 2.00 mg L^{-1}.

Kinetic Parameters	(EE2)	(E2)
Pseudo-first-order		
q_e (mg g^{-1})	1.260	1.269
k (g mg^{-1} h^{-1})	149.16	132.14
R^2	0.98795	0.98968
Pseudo-second-order		
q_e (mg g^{-1})	1.269	1.278
k (g mg^{-1} h^{-1})	371.55	296.25
R^2	0.99388	0.99659
General order		
q_e (mg g^{-1})	1.319	1.297
k (g mg^{-1} h^{-1})	15036	11090
n	4.911	3.125
R^2	0.99893	0.99895

CONCLUSION

➢ All experiments showed the potential of the agroindustrial sorbent as a new material for adsorption (EDC).

➢ The reuse of the agroindustrial waste for the adsorption of E2 and EE2 has some advantages over the commercial activated carbon as negligible commercial value, due to the fact that it is a waste of production processes.

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