

Removal of Estrone, 17 β -Estradiol, and 17 α -Ethinylestradiol from Water by Adsorption onto Chemically Modified Activated Carbon Cloths

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(Received July 16, 2019; Revised January 16, 2020; Accepted February 16, 2020)

Abstract: This paper explores the applicability of unmodified and chemically modified activated carbon cloths (ACCs) for the removal of estrone, 17 β -estradiol, and 17 α -ethinylestradiol from water. In order to examine the influence of surface properties on hormone adsorption, chemical modification of ACCs with HNO₃, HCl, or KOH was employed. Applied treatments increased the specific surface area and changed the content of oxygen functional groups. Increased content of acidic surface oxygen functionalities enhanced adsorption efficiency up to 30 % and had a more dominant influence on adsorption capacity than specific surface area. Adsorption of estrone, 17 β -estradiol, and 17 α -ethinylestradiol followed pseudo-second-order kinetic model, while the equilibrium adsorption data fitted well with the Freundlich isotherm model. Calculated mean sorption energy values of 1.4475, 1.3387, and 1.0541 kJ/mol, for E1, E2, and EE2 respectively, indicated that removal of selected hormones was dominated by physisorption mechanism. Obtained Langmuir adsorption capacities, 12.34, 12.66, and 11.11 mg/g for estrone, 17 β -estradiol, and 17 α -ethinylestradiol, respectively, as well as convenience of manipulation, recommend activated carbon cloth modified with HNO₃ as an efficient adsorbent for removing estrogen hormones from the water.

Keywords: Activated carbon cloth, Surface properties, Adsorption, Estrogenic hormones

Introduction

Some natural and synthetic compounds draw attention due to their adverse impact on the environment and human health. These compounds may interfere with the function of the endocrine system of humans and animals by blocking or imitating the normal function of hormones. Collectively, these compounds are called endocrine-disrupting compounds (EDCs) [1,2]. EDCs are a very heterogeneous group of chemicals and they include wide ranges of substances among which are steroid estrogens, both natural and synthetic. This group of compounds, and particularly the natural hormones estrone (E1), 17 β -estradiol (E2), and the synthetic estrogen 17 α -ethinylestradiol (EE2) are described as very potent estrogenic compounds [3,4]. The presence of these hormones in the environment can have serious negative effects on human and animal health [5]. Some studies reported that elevated concentration of natural and synthetic estrogens may cause feminization of male fish, by means of reduction of testis size [6] and deterioration of reproductive fitness [7]. It was also demonstrated that exposure to elevated concentrations of estrogen hormones could harm the reproductive function of amphibians, for example, affecting vitellogenesis and reproductive behavior [8]. The other studies indicated that there is a potential link between the elevated concentration of EDCs and increased risk of breast cancer in females [9] and prostate cancer in

men [10].

The pathway of the estrogens to the environment is mainly through municipal wastewater [11]. Wastewater treatment plants do not remove them completely, so their effluents contain significant concentrations of hormones [12]. The presence of these compounds in aquatic resources, even at very low concentrations (the order of magnitude ng/l), can lead to a number of functional disorders in aquatic organisms [3,13,14].

A number of water treatment technologies for the removal of different organic pollutants, including hormones, have been used so far, with various degrees of success. Some of these technologies include membrane filtration [15,16], advanced oxidation [17], catalytic degradation [18-31], and different biological processes [32]. Among used methods is adsorption, the process which has many advantages in comparison with the other methods, such as effectiveness, efficiency, economy, simplicity of operation, the possibility of adsorbent reuse and regeneration [33-36]. Within the materials used so far for removal of estrogenic compounds from water are chitin, chitosan, activated carbon [37,38], aliphatic polyamides [39], carbon nanotubes [40-42], bone char [43], hybrid clay materials [44], and molecularly imprinted polymers [45,46]. Different carbon materials are widely used as adsorbents due to their extraordinary physical properties, such as high surface area and wide pore size distribution [47,48]. Surface chemistry, i.e. nature and amount of the functional groups present on carbon material surface is another key factor that affects the adsorption

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efficiency. The carbon surface can be tailored by different treatments in order to promote the adsorption of specific water pollutants. For example, HNO₃ oxidation increased the efficiency of carbon xerogel and activated carbon for adsorption of ciprofloxacin [49], as well as carbon monolith for removal of dimethoate [50], while HCl treatment reduced the amount of multi-walled carbon nanotubes surface oxygen groups, which positively affected adsorption of selected pharmaceuticals [51].

However, most commonly used carbon materials, like activated carbon, possess also some inconveniences, such as the release of fine particles and dust, which can be avoided by the use of activated carbon cloths (ACCs). ACCs gained increasing attention as the potential adsorbents for water treatment purposes, due to advantages in comparison with a traditional AC form, such as rapid adsorption kinetics, high specific surface area (as high as 2500 m²/g), and easy manipulation [52-54]. Adsorption of different types of compounds onto ACCs has been studied so far, e.g. aromatic organic acids [53], phenols [55,56], pharmaceuticals [57], volatile organic compounds [58], pesticides [59], dyes [60], and heavy metals [61].

Although there are numerous studies focusing on adsorption of estrogenic hormones onto different carbon materials, as far as we know, no previous research has investigated the adsorption of these compounds onto ACCs. Therefore, the focal point of this paper was to study the feasibility of ACCs as sorbents for the removal of E1, E2, and EE2 from water. The adsorption performances of ACCs were examined and correlated with their surface composition and morphology in order to identify which material features have the most prominent influence on the adsorption. In the aim to improve the adsorption efficiency, ACCs were chemically treated using various reagents. The influence of applied chemical treatments on adsorption characteristics, primarily specific surface area and surface functionalities, was tested. Consequently, the optimal modification method that promotes the formation of the required porosity and surface chemistry for facilitated adsorption of estrogenic hormones was selected.

Experimental

Chemical Modification of ACCs

The ACCs used in this study were manufactured in the Institute of Nuclear Science Vinča. The viscose rayon cloth (Viskoza Factory, Loznica, Serbia) was used as a carbon precursor. The processes of impregnation, carbonization, and activation are described elsewhere [62].

ACC/HNO₃ and ACC/KOH were obtained by heating of ACC in the solution of 5 M HNO₃ or 4 M KOH for 3 h at temperature ~80 °C, while ACC/HCl was obtained by immersing ACC in the solution of 1 M HCl for 3 h, without heating. After modification, the ACCs were thoroughly

rinsed with distilled water, until a constant pH value of filtrate was achieved, and dried at the temperature of 100 °C.

Sample Characterization

Adsorption and desorption isotherms of nitrogen were measured at -196 °C in order to get textural characteristics of unmodified and chemically modified ACCs samples. Micromeritic ASAP 2020 surface and porosity analyzer (Micromeritics Instrument Corporation, U.S.) was used for this purpose. The specific surface area (S_{BET}) was estimated using the Brunauer, Emmett, Teller (BET) method. The total pore volume (V_{total}), mesopore volume (V_{meso}) and micropore volume (V_{micro}), as well as microporous surface area (S_{micro}), were calculated from the adsorption data using the manufacturer's software ASAP 2020 V3.05 H. External surface area including mesoporous area (S_{exter}) was obtained by the subtraction of S_{micro} from S_{BET} . Pore size distribution and volume of mesopores were estimated using the method which Barrett, Joyner, and Halenda (BJH) proposed from the desorption branch of the isotherms [63].

Characterization of functional groups was carried out by Fourier transform infrared spectroscopy (FTIR). FTIR spectra were measured in the range of 400-4000 cm⁻¹ on a Bomem MB-Series, Hartmann Braun.

Point of Zero Charge Measurements

The point of zero charge (pH_{PZC}) was determined by a modified batch equilibrium method, proposed in the literature [62]. For that purpose, 0.0075 g of ACC sample was immersed in 15 ml of 0.1 M NaCl with adjusted pH value. The initial pH values (pH_i), varying from 2 to 9, were adjusted by 0.1 M NaOH or HCl. The samples were kept under N₂, sealed and stored at room temperature and pH values of filtrated suspensions (pH_f) were measured after 24 h. pH_{PZC} values were determined from the plateau of the pH_f versus pH_i dependence [64].

Adsorption Experiments

Adsorption characteristics of unmodified and chemically modified ACC were examined in a batch system, at room temperature with constant shaking (200 rpm). 0.02 g of ACC samples were immersed in 25 ml of hormone solution mixture of required concentration. After adsorption, all samples were filtered through the PVDF 0.45 μm filters and the concentration of selected hormones was determined by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

Influence of Initial pH Value

Unmodified and chemically modified ACC samples were used in this experiment. Each sample was placed in 25 ml of hormone mixture solution (5 mg/l of each hormone) with pH value previously adjusted to 5, 6, 7, 8, or 10 by the use of diluted CH₃COOH or NH₄OH solutions. The samples were

taken after 3 h of adsorption, filtered, and measured.

Adsorption Kinetics

ACC/HNO₃ was used for adsorption kinetics experiments. The initial concentration of the hormone mixture solution was 5 mg/l. Based on the results of preliminary experiments, the initial pH value was adjusted to 7. The samples were taken after 5, 15, 30, 60, 120, 180 min, 20 h and 24 h of adsorption. For calculation of adsorption kinetic parameters, pseudo-first-order model, introduced by Lagergren, and pseudo-second-order model were used [64,65].

The pseudo-first-order rate equation is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2,303}\right) \cdot t \quad (1)$$

while the pseudo-second-order rate equation is given as:

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

where q_e (mg/g) is the amount of adsorbed hormone per unit mass of the adsorbent at equilibrium, q_t (mg/g) amount of adsorbed hormone per unit mass of the adsorbent at time t , k_1 is the first-order adsorption rate constant (min⁻¹) and k_2 is the second-order adsorption rate constant (g/mg/min).

Adsorption Isotherms

The adsorption isotherm study was carried out at the initial pH value of 7 and various initial concentrations of the hormones mixture (2, 4, 6, 8, 10 and 12 mg/l). ACC/HNO₃ was used as an adsorbent. The samples were taken after 24 h of adsorption. The fitting of the adsorption equilibrium data was conducted using the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin isotherms. The linear forms of Langmuir and Freundlich models are shown in equations (3) and (4), respectively [65,67,68]:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot Q_0} + \frac{1}{Q_0} \cdot C_e \quad (3)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \cdot \ln C_e \quad (4)$$

where C_e is the equilibrium hormone concentration (mg/l), q_e is the amount of adsorbed hormone per unit weight of the adsorbent at equilibrium (mg/g), Q_0 is the maximum adsorption capacity (mg/g), b is the Langmuir isotherm constant and K_f and n are the Freundlich constant and heterogeneity factor, respectively.

Experimental data were modeled by D-R isotherm in order to estimate the nature of the adsorption process, physical or chemical. The linear form of this isotherm is given in the following equation [69]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

where q_m is the monolayer sorption capacity (mg/g), β is the activity coefficient related to sorption energy (mol²/J²), ε is the Polanyi potential, expressed in equation (6) [70]:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (6)$$

where R is gas constant (kJ/mol K) and T is the absolute temperature (K).

The mean sorption energy, E (kJ/mol) is given by equation (7):

$$E = (-2\beta)^{-1/2} \quad (7)$$

The Temkin adsorption isotherm can be expressed by the following equation [65]:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where $B=RT/b$, b is the Temkin constant related to the heat of sorption (J/mol) and A is the Temkin isotherm constant (l/g).

LC-MS/MS Analysis

The separation of hormones was conducted using a Dionex UltiMate 3000[®] LC system (Thermo Fisher Scientific, Waltham, MA, USA). An Agilent Zorbax Eclipse XDB-C18 analytical column (75 mm × 4.6 mm × 3.5 μm) was used for reverse-phase separations. The initial composition of the mobile phase was 25 % formic acid solution (0.1 % water solution) and 75 % methanol at a constant flow rate of 0.5 ml/min, followed by the change in methanol content from 75 % to 100 % in 10 min. For detection and quantification of hormones LTQ XL (Thermo Fisher Scientific, USA) mass spectrometer was used with electrospray ion source and linear ion trap mass analyzer. The measurements were carried out in the positive ionization mode. The optimal source parameters were: source voltage (5.00 kV), sheath gas (8 au), auxiliary gas (12 au), and capillary temperature (350 °C). For quantification purposes, the selected reaction monitoring mode (SRM) was used. The selected precursor

Table 1. LC/MS-MS quantification parameters for selected hormones

Hormone	Retention time (min)	Precursor ion (m/z)	Collision energy (%)	Product ion (m/z)	Isolation width
E1	3.48	271.00	16	253.15	2
E2	3.37	255.00	20	159.05	2
EE2	3.16	279.07	20	133.07	2

ion, the optimal collision energy, the most abundant product ion, as well as its isolation with, for each hormone, are presented in Table 1.

Results and Discussion

Materials Characterization

Textural Properties

Nitrogen adsorption/desorption isotherms of ACCs samples, plotted as the amount of adsorbed/desorbed nitrogen as a function of relative pressure at the temperature of liquid nitrogen, are presented in Figure 1a. The isotherms for all materials have a sharp knee in the low pressure region indicating high adsorption at low relative pressures, and a

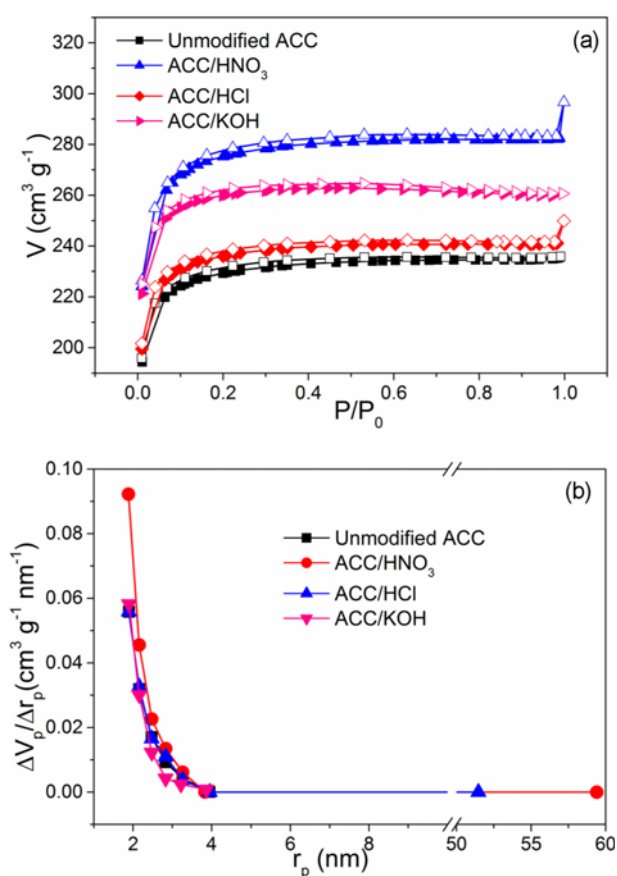


Figure 1. Nitrogen adsorption-desorption isotherms (a) (solid symbols-adsorption, open symbols-desorption) and pore size distribution (b) of the ACCs samples.

very low slope in the high relative pressure region, without hysteresis loop, and are of type I(b), according to IUPAC classification [71]. Type I(b) isotherms are characteristic for microporous materials, having pore size distributions in the range of wider micropores to the narrow mesopores (<2.5 nm). The microporous nature of ACCs is confirmed by pore size distribution (Figure 1b), estimated from the desorption branch of the isotherms using the BJJ method.

The textural characteristics of examined samples are summarized in Table 2. All ACCs samples have a relatively high specific surface area (S_{BET}), ranging from 683 to 820 m²/g. By the comparison of V_{total} and V_{micro} , as well as S_{BET} and S_{micro} , it can be noticed that all ACCs are mostly microporous. BET analysis demonstrated that the specific surface area increased by modification process, from 3 % after HCl treatment up to 20 % after HNO₃ treatment, while mean pore radius (D_{mean}) is slightly reduced on modified samples.

FTIR Spectroscopy

FTIR spectroscopy analysis was conducted in order to explore the changes of the surface functional groups of ACCs after chemical treatment. Figure 2 shows the FTIR spectra of unmodified and chemically treated samples. For all ACC samples, a broad band at approximately 3435 cm⁻¹ is present and it can be assigned to the O-H stretching vibrations of carboxylic or phenolic groups [72-74]. Two distinguished bands at around 2920 and 2850 cm⁻¹ can be attributed to the asymmetric and symmetric C-H stretching vibration of methyl or methylene groups [75,76]. The presence of small bands in the 1660-1430 cm⁻¹ region of the spectra is characteristic of the skeletal C=C vibrations in aromatic rings [77]. The broad band in the 1000-1200 cm⁻¹ region can be assigned to C-O stretching in ether, ester or phenol groups [76,78]. The bands around 1200 cm⁻¹ can originate from the phenolic hydroxyl group, which usually absorbs at that wave number, while the bands in the region from 1024 to 1166 cm⁻¹ can be assigned to C-O vibrations in aromatic ether in pirone and quinine, which belong to functional groups with a basic character [79]. Absorption band below 800 cm⁻¹, which is most prominent in the spectrum of ACC/HCl sample, can be assigned to out-of-plane bending vibrations of C-H groups located at the edges of aromatic planes [72,76].

As shown in Figure 2, there is a change in the content of the surface functional groups after the chemical treatment of ACCs, which are most prominent after HNO₃ treatment and

Table 2. Textural properties and pH_{PZC} of examined samples

Sample	S_{BET} (m ² /g)	S_{micro} (m ² /g)	S_{exter} (m ² /g)	V_{total} , cm ³ /g	V_{meso} (m ³ /g)	V_{micro} (m ³ /g)	D_{mean} (nm)	pH _{PZC}
Unmodified ACC	683	558	125	0.3646	0.0359	0.3460	2.25	4.7
ACC/HNO ₃	820	635	185	0.4383	0.0558	0.4140	2.19	3.6
ACC/HCl	703	578	125	0.3740	0.0355	0.3570	2.20	5.8
ACC/KOH	771	650	121	0.4034	0.0307	0.3950	2.13	6.0

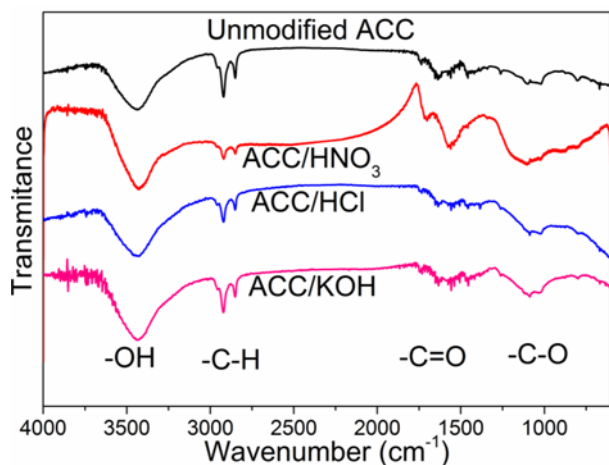


Figure 2. FTIR spectra of ACCs.

least prominent after HCl treatment. The intensity of absorption peaks around 3435 cm^{-1} and in the $1000\text{--}1200\text{ cm}^{-1}$ region is higher in the spectra of the modified ACC (especially in the case of ACC/HNO₃) than in the spectrum of the unmodified sample, which implicates that modified ACCs contain a larger number of OH functional groups in comparison with unmodified. The distinct characteristics of the HNO₃ modified sample spectrum are the appearance of strong adsorption band at 1560 cm^{-1} , which can be attributed to C=O stretching vibrations of carboxylate group [80], and the prominent peak at 1710 cm^{-1} which further suggests the formation of C=O containing surface groups, such as carboxylic, ester or lactone [76,81,82]. It can also be noticed, that the peaks around 2920 and 2850 cm^{-1} have lower signal intensity at modified ACCs (particularly at ACC/HNO₃ sample) in comparison with the same peak of unmodified ACC, which suggest that some of the aliphatic groups were oxidized during the treatment.

Point of Zero Charge

The point of zero charge (PZC) of a material is defined as a point at which its surface charge is equal to zero [43]. The results of PZC experiments are summarized in Figure 3, which presents the plot of the final pH value of the solution after equilibration with AACs (pH_f) versus the initial solution pH value (pH_i). pH_{PZC} value was determined as the pH_f value at which the plateau was obtained, as it is shown in Figure 3. PZC values for all investigated materials are given in Table 2. PZC of unmodified ACC is at pH value 4.7. The modification process with HNO₃ increased the surface acidity of material ($\text{pH}_{\text{PZC}}=3.6$), and that is in accordance with the results of FTIR analysis, which demonstrated the increase of carboxylic functional groups. Based on the obtained pH_{PZC} values (Table 2), it can be observed that surface acidity decreased after modification with HCl and KOH, which implicates the formation of basic surface groups, such as pyrone, quinone, chromene [79], which are

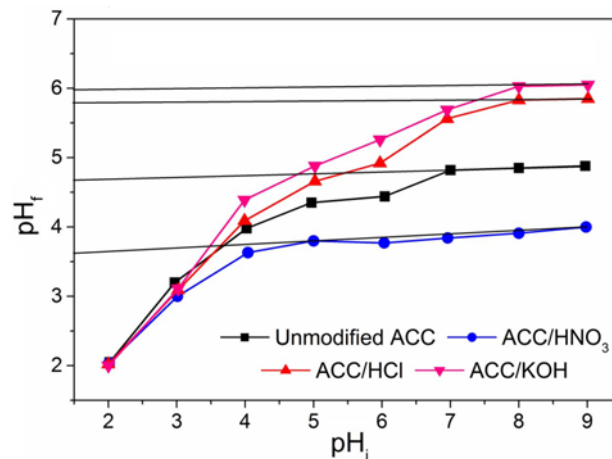


Figure 3. Determination of pH_{PZC} of ACCs.

observed in FTIR spectra of modified ACC samples.

Adsorption Experiments

Influence of Initial pH Value

The effect of initial pH value on the adsorption of selected hormones was examined since it has a significant influence on the adsorption process for ionizable organic chemicals [83] and affects the surface charges of ACCs. Results, presented in Figure 4, showed that pH value is an important parameter in the adsorption process of estrogen hormones onto ACCs. It can be noticed that all examined materials show the highest sorption efficiency in the pH range between 7 and 8. The similar results were obtained for adsorption of these hormones on various materials [84,85]. pK_a values of E1, E2, and EE2 are 10.77, 10.4, and 10.71, respectively [86,87], and in pH range 7–8 all three compounds are in molecular form, while, according to their pH_{PZC} values, ACC surfaces are negatively charged. At higher pH values both ACCs surfaces and hormones are negatively charged, and electrostatic repulsion between them leads to reduced adsorption, as reported in the literature [85,88]. Also, it can be observed that the influence of pH is much more prominent for the adsorption of hormones on unmodified ACC than on modified samples.

Influence of Material Modification

Adsorption efficiency for all tested samples at initial pH value 7 is given in Figure 5. It is notable that modification of ACCs with HNO₃ and KOH increased total uptake capacities, while modification with HCl decreased the adsorption capacities for all tested hormones. The highest adsorption efficiency was observed for sample ACC/HNO₃, which has the highest specific surface area as well as the highest amount of surface oxygen groups. Considering the results obtained by BET analysis for all samples (Table 2), it can be concluded that specific surface area does not have a dominant influence on the adsorption capacity, since the

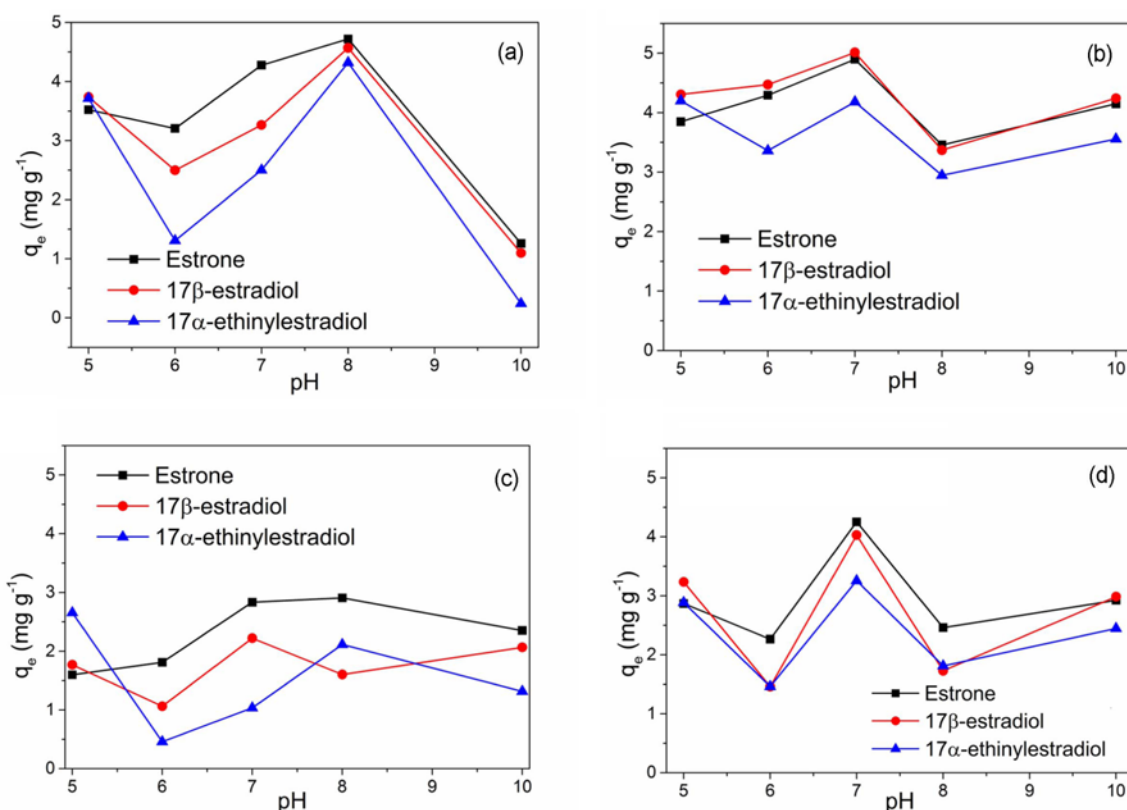


Figure 4. Influence of pH on the adsorption of hormones onto; (a) unmodified ACC and ACCs modified with (b) HNO₃, (c) HCl, and (d) KOH.

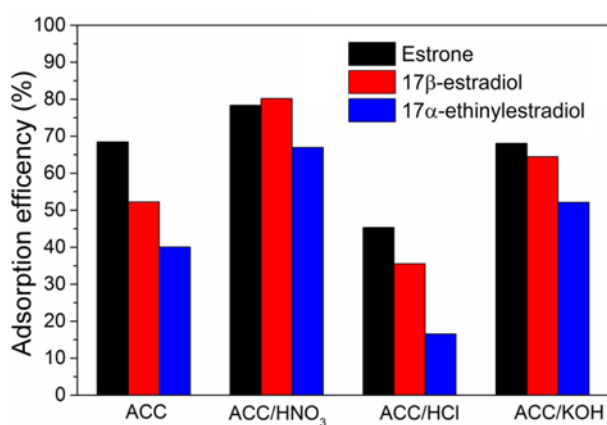


Figure 5. Adsorption efficiency of unmodified and chemically modified ACCs.

sample ACC/HCl, despite its higher surface area in comparison with unmodified ACC, showed lower adsorption capacity. However, it seems that adsorption efficiency follows the same trend as the changes in the content of surface oxygen groups caused by applied chemical treatments. As it was demonstrated by FTIR analysis, HNO₃ treatment caused

most prominent changes in surface chemistry, while the HCl treatment caused the least. Apparently, the increased amount of acidic surface oxygen groups caused by HNO₃ treatment enhanced the adsorption process. All three investigated hormones are characterized by the presence of hydroxyl groups that may form hydrogen bonds with the oxygen-containing functional groups on the adsorbent surface, which is proposed as the main adsorption mechanism [89,90].

Since HNO₃ treatment improved the adsorption capacity of ACC and made it be less pH dependent, the ACC/HNO₃ sample was used as the adsorbent material for kinetics and isotherms studies.

Adsorption Kinetics

The influence of contact time on E1, E2, and EE2 adsorption onto ACC/HNO₃ is presented in Figure 6. It can be noticed that the adsorption of these compounds was faster in the first 3 h, probably due to the availability of the adsorption sites, and then the process slowed down. The equilibrium was reached within 24 h. After 24 h the removal efficiency for E1, E2, and EE2 was 78.2 %, 82 % and 76 %, respectively. The results obtained are much higher than the one obtained on bone char for E2 removal [43] and polymer-

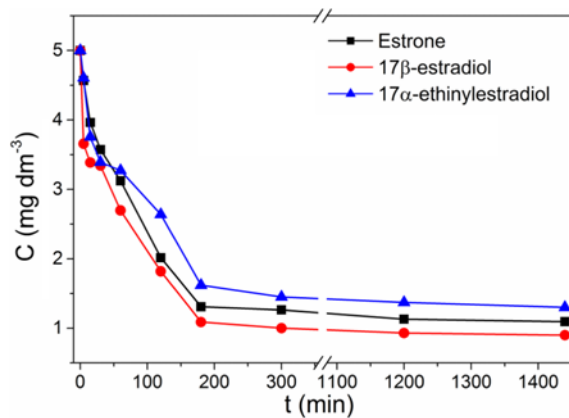


Figure 6. Effect of contact time on the adsorption of E1, E2, and EE2 onto ACCs/HNO₃.

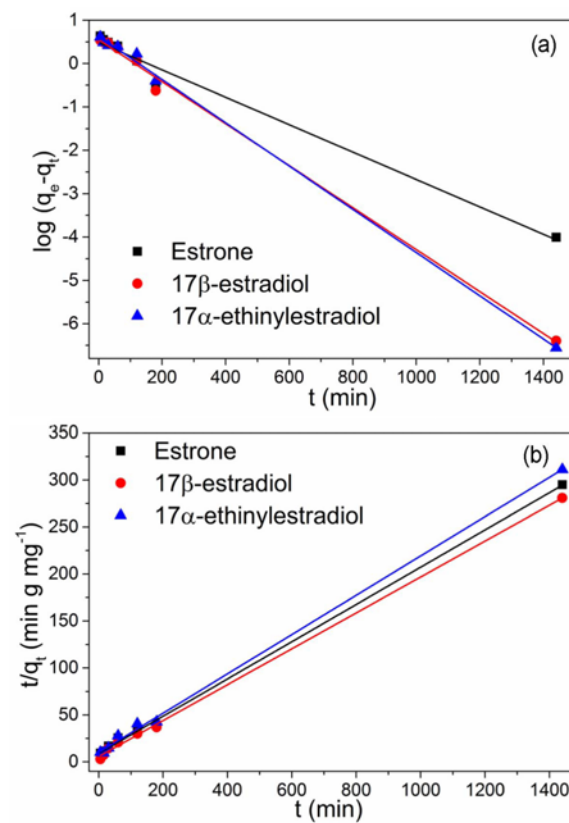


Figure 7. Matching experimental data with linearized kinetics models; (a) pseudo-first and (b) pseudo-second order for adsorption of hormones onto ACC/HNO₃ at pH=7.

based spherical activated carbon for E1 and E2 removal [38], but lower than the one obtained for reduced graphene oxide-magnetic composite for removal of EE2 [89] and few-layered graphene oxide nanosheets for E2 removal [90].

The adsorption kinetic parameters were calculated by fitting the adsorption data with the pseudo-first-order and pseudo-second-order kinetic model (Figure 7).

The adsorption rate constants (k_1 and k_2), correlation coefficients (R^2) and amount of hormones adsorbed at equilibrium calculated from these two models ($q_{e,mod}$), are presented in Table 3. For the purpose of comparison, equilibrium amounts of hormones, obtained experimentally ($q_{e,exp}$), are also given in Table 3.

The R^2 values obtained for the pseudo-second-order model are higher than those obtained for the pseudo-first-order model. The values of $q_{e,exp}$ are closer to theoretical values, $q_{e,mod}$ obtained by the pseudo-second-order model. These observations indicate that the pseudo-second-order kinetic model better describes the adsorption of E1, E2, and EE2 onto ACC/HNO₃, than the pseudo-first-order model.

Adsorption Isotherms

Equilibrium data obtained for E1, E2, and EE2 adsorption onto ACC/HNO₃ are presented in Figure 8. In the examined concentration range adsorption capacities increased with initial hormones concentration. However, the characteristic plateau was not reached, which indicated that the ACC surface was not saturated.

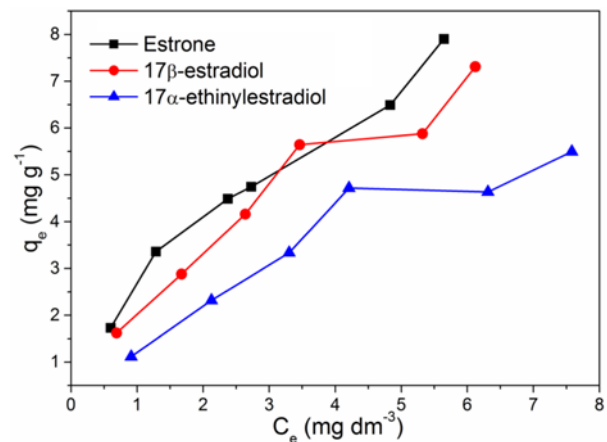


Figure 8. Equilibrium data for E1, E2, and EE2 adsorption onto ACCs/HNO₃.

Table 3. Kinetics parameters and correlation coefficients for adsorption of E1, E2, and EE2 onto ACC/HNO₃

Hormone	Pseudo-first order			Pseudo-second order			$q_{e,exp}$ (mg/g)
	R^2	k_1 (min ⁻¹)	$q_{e,mod}$ (mg/g)	R^2	k_2 (g/mg/min)	$q_{e,mod}$ (mg/g)	
E1	0.9777	0.0073	3.0763	0.9989	0.0044	5.0429	4.8811
E2	0.9964	0.0111	3.5657	0.9990	0.0064	5.2345	5.1256
EE2	0.9980	0.0115	4.2726	0.9984	0.0055	4.7801	4.6259

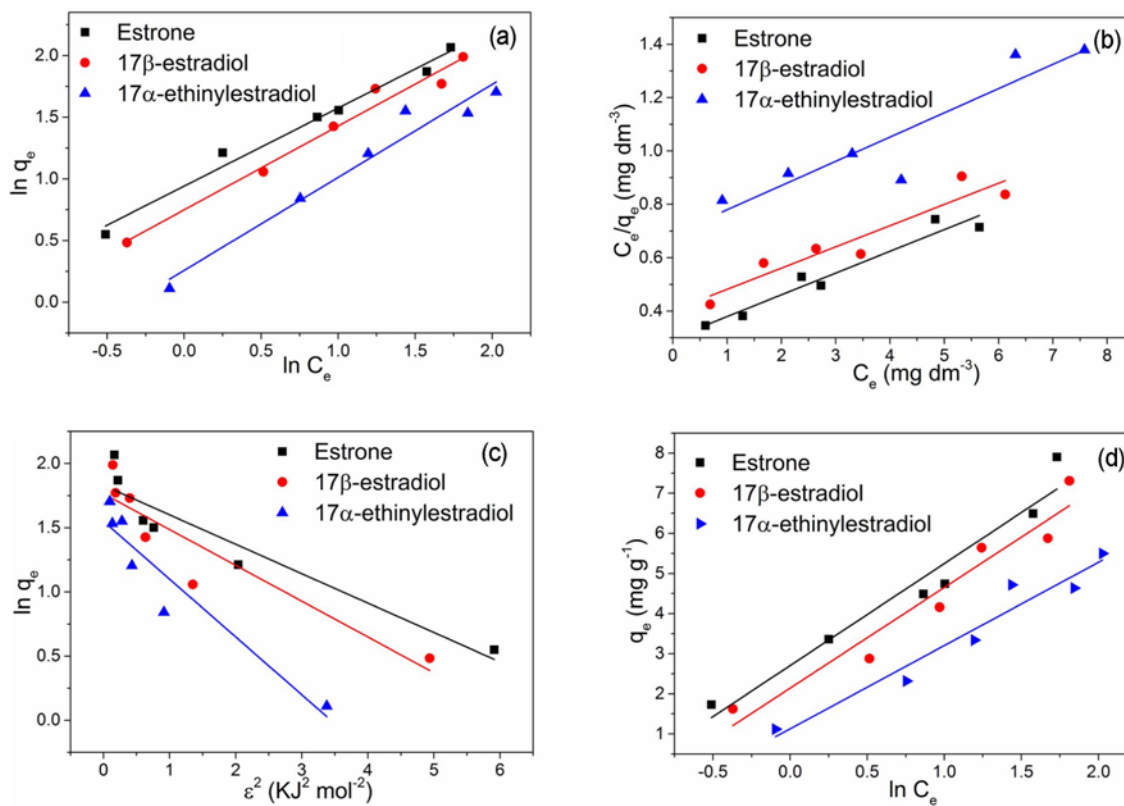


Figure 9. Fitting the experimental data with (a) Freundlich, (b) Langmuir, (c) Dubinin-Radushkevich, and (d) Temkin model.

In order to better understand the adsorption behavior at the equilibrium, different isotherm models were used. Adsorption data were analyzed using Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin isotherm models in order to explore the adsorption process. Equilibrium adsorption data, fitted with different linear isotherm models are presented in Figure 9, while calculated isotherm parameters are given in Table 4.

The Langmuir model is based on assumption of monolayer coverage on a homogenous surface with identical adsorption sites, when there is no interaction between the adsorbate molecules [38,89], while the Temkin isotherm model assumes that the heat of adsorption of all molecules in the layer decreases linearly when the surface of the adsorbent is more covered, and that adsorption include a uniform distribution of binding energies [91]. Both models show the moderate fit with the experimental data, according to the R^2 values (Table 4). The experimental data show the best fit with the Freundlich isotherm model. This model describes multilayer adsorption with the interaction between adsorption molecules and heterogeneous adsorbent surface with different adsorption sites [38,89]. The Dubinin-Radushkevich model, which showed the least agreement with experimental data, also includes heterogeneity of the porous adsorbent and multilayer character of adsorption [41,69]. Since, this

Table 4. Isotherm parameters for adsorption of E1, E2 and EE2 onto ACC/HNO₃

Isotherm parameter	E1	E2	EE2
Langmuir			
Q_0 (mg/g)	12.34	12.66	11.11
b	0.272	0.197	0.131
R^2	0.948	0.892	0.853
Freundlich			
K_f (mg ^{1-1/n} dm ^{3/n} /g)	2.563	2.113	1.294
$1/n$	0.633	0.679	0.754
R^2	0.983	0.978	0.960
D-R			
q_m (mg/g)	6.228	5.842	4.711
E (kJ/mol)	1.447	1.339	1.054
R^2	0.892	0.856	0.902
Temkin			
A (l/g)	13.363	7.213	2.677
B (J/mol)	0.373	0.373	0.455
R^2	0.949	0.936	0.946

theoretical model assumes that the adsorption process follows a pore-filling mechanism, disagreement between

Table 5. Maximum adsorption capacities of different adsorbents for E1, E2 and EE2, from literature data and present work

Hormone	Sorbent	$C_{(\text{solution, mg/l})}$	$C_{(\text{sorbent, g/l})}$	$Q_{\text{max}} (\text{mg/g})$	Ref.
E2	Bone chare	5 and 9	0.5-50	10.12	[43]
E2	Activated charcoal	0.025-0.075	5	7.47×10^{-3}	[94]
EE2	MWCNT	0.025-0.1	0.5	5.59×10^{-3}	[41]
E1	Pyrolyzed coke	0.1×10^{-3} - 1×10^{-3}	0.025-0.25	0.05	[95]
E2				0.033	
E2	Iron nano particles	0.1-1.0	1-9	84.75×10^{-3}	[96]
EE2	Reduced graphene oxide-magnetic composite	0.01-3.0	0.01-0.2	37.33	[89]
E2	Magnetic biochar nanoparticles	0.6-3.0	0.1	24.80-50.24	[97]
E1	Rice husk silica	0.1×10^{-4} - 1×10^{-4}	1.5	0.56×10^{-4}	[98]
E2				0.62×10^{-4}	
E1	Polymer-based spherical activated carbon	0.1×10^{-3}	1	0.94×10^{-4}	[38]
E2				1.04×10^{-4}	
	Montmorillonite			30.27×10^{-3}	
	Kaolin			16.48×10^{-3}	
	Hematite			20.72×10^{-3}	
E2	Montmorillonite-humid acid	0.1-0.8	5	130.64×10^{-3}	[99]
	Kaolin-humid acid			49.32×10^{-3}	
	Hematite-humid acid			25.46×10^{-3}	
E1				12.34	
E2	ACC/HNO ₃	2-12	0.8	12.66	Present work
EE2				11.11	

model and experimental data indicate that hormone diffusion through the porous surface might be suppressed due to hormones dimension.

Freundlich parameter K_f is an indication of the adsorbent capacity, while $1/n$ is a measure of the surface heterogeneity [92]. For all tested hormones, obtained values of $1/n$ are below one, indicating the heterogeneous surface of ACC/HNO₃ and chemical nature of the adsorption process [93].

The value of the mean sorption energy (E), calculated from the slope of the D-R plot, is related to process mechanism. For chemical adsorption, this value is in the range from 8 to 16 kJ/mol and for physical adsorption, the value is smaller than 8 kJ/mol [69]. Obtained values of E for E1, E2, and EE2 were 1.4475, 1.3387, and 1.0541 kJ/mol, respectively, which is in accordance with the energy range of physical adsorption.

Maximum adsorption capacities, calculated from Langmuir isotherm were 12.34, 12.66, and 11.11 mg/g for hormones E1, E2, and EE2, respectively. These results were compared with the maximum adsorption capacities of different adsorbents for E1, E2, and EE2 hormones obtained from some other studies (Table 5).

The experimental conditions, used by Patel *et al.* [43], were the most similar to the conditions used in the present study, which leads to comparable results. The maximum adsorption capacity for hormone E2, reported by Patel *et al.*

[43], was 10.12 mg/g, while for the same hormone ACC/HNO₃ showed the capacity of 12.66 mg/g. Generally, the maximum adsorption capacities presented in Table 5 are significantly lower than the results obtained in this study, which may be explained by the difference in the used hormone concentration range. While the concentration range in this study was 2-12 mg/l, in referred studies concentrations were as low as 0.1 µg/l.

Conclusion

Unmodified and chemically modified activated carbon cloths were used for the adsorption of E1, E2, and EE2 from water. All ACC samples showed the highest adsorption efficiency in the pH range between 7 and 8, and the influence of pH was much more prominent for adsorption on unmodified ACC than on modified samples. The applied chemical modification increased the specific surface area of ACCs and changed the content of the surface functional groups (especially oxygen groups), pH_{PZC} and adsorption properties. For all tested hormones, the highest adsorption capacity was observed for ACC/HNO₃, which has the highest specific surface area and amount of oxygen functional groups. It was found that adsorption efficiency increased with the content of surface oxygen groups, while the specific surface area did not have a dominant influence on the

adsorption capacity. Adsorption of E1, E2, and EE2 onto ACC/HNO₃ followed the pseudo-second order kinetic model, while the Freundlich isotherm model best described the adsorption process. The mean sorption energy indicated that removal of E1, E2, and EE2 was dominated by the physisorption mechanism. Obtained maximum adsorption capacities, which were higher or comparable with the one obtained from literature, indicated that modified activated carbon cloth may be used for removal of selected hormones from water.

Acknowledgements

The authors wish to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support.

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