Adsorption of estrone, 17β-estradiol, and 17α-ethinylestradiol from water onto modified multi-walled carbon nanotubes, carbon cryogel, and carbonized hydrothermal carbon

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Abstract

Carbon materials of different structural and textural properties (multi-walled carbon nanotubes, carbon cryogel, and carbonized hydrothermal carbon) were used as adsorbents for the removal of estrone, 17β-estradiol, and 17α-ethinylestradiol from aqueous solutions. Chemical modification and/or activation were applied to alter surface characteristics and to increase the adsorption and desorption efficiency of carbon materials. Surfaces of treated and untreated carbon materials were characterized through the examination of the textural properties, the nature of surface functional groups, and surface acidity. Although specific surface area and content of surface functional groups did not have a dominant influence on the adsorption process, it was found that a high ratio of surface mesoporosity affected the adsorption process most prominently by increasing adsorption capacity and the rate of the adsorption process. High values of adsorption efficiency (88–100 %) and maximum adsorption capacities (29.45–194.7 mg/g) imply that examined materials, especially mesoporous carbon cryogel and multi-walled carbon nanotubes, can be used as powerful adsorbents for relatively fast removal of estrogen hormones from water.

Introduction

Hormones, both naturally secreted or of synthetic origin, are trace pollutants of major concerns due to their potential of disrupting the endocrine activities of living organisms (Auriol et al. 2006). Steroid estrogens are attracting great attention because of their high estrogenic potential. Although present at very low concentrations (the order of magnitude ng/L) (Auriol et al. 2008), these compounds still can cause serious adverse effects on aquatic organisms (Snyder et al. 2003) and domestic animals (Gao et al. 2019). Many pathological phenomena, such as carcinogenicity, disorders in reproductive function, decreased fertility in fish, infertility, the feminization of male fish, are induced by the presence of steroid estrogens in the environment (Vilela et al. 2018; Khanal et al. 2006; Bilal and Iqbal 2019). The principal way in which these compounds reach the environment is through municipal wastewater. These hormones are not removed from sewage in wastewater-treatment plants completely, so their effluents contain a significant concentration of these substances (Vilela et al. 2018). These substances may also pose a risk to humans and animals indirectly, via food contamination (Hartmann et al. 1998). In this regard, the removal of estrogens from water has become a very important issue worldwide.

Different methods for removing estrogens from water have been used so far, such as adsorption (Wang et al. 2018; Tagliavini et al. 2017), membrane filtration (Akanyeti, et al. 2017; Tagliavini and Schäfer 2018) biodegradation (Fernández et al. 2017), advanced oxidation process (Fonseca et al. 2011), and photodegradation (Sornalingam et al. 2016; Zhang et al. 2007). Adsorption is considered one of the most efficient and economical processes, and the choice of appropriate adsorbent is the key element in the application of this method (Tang et al. 2018; Wang et al. 2018). Different materials were used so far as adsorbents for the removal of steroid estrogens from water such as chitin, chitosan, activated carbon (Zhang and Zhou 2005; Tagliavini et al. 2017), hybrid clay materials (Thanhmingliana et al. 2016),
magnetic graphene oxide (Wang et al. 2018), cyclodextrin polymers (Tang et al. 2018), and iron nanoparticles (Ali et al. 2017).

Carbon materials gained increasing attention as highly efficient adsorbents for both, organic and inorganic substances from the aqueous phase due to their specific surface characteristics, which can easily be tailored or modified (Lalović et al. 2017; Ren et al. 2011). Different types of carbon materials, such as activated carbon (Tagliavini et al. 2017), carbon nanotubes (Kumar and Mohan 2012), pyrolyzed coke (Gökce and Arayici 2016), activated charcoal (Kumar and Mohan 2011), bone char (Patel et al. 2015), reduced graphene oxide-magnetic composite (Luo et al. 2017), magnetic biochar nanoparticles (Dong et al. 2018), were used for estrogen adsorption from water so far. In our previous work (Prokić et al. 2020), it was shown that activated carbon cloth modified with HNO₃, demonstrated high efficiency in removal of estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2) from water.

This paper aimed to examine the efficiency of different carbon materials for adsorption and desorption of estrone, 17β-estradiol, and 17α-ethinylestradiol, and to reveal which features of materials surface affect the adsorption process most prominently. Therefore, carbon materials of different structural and textural properties (carbonized hydrothermal carbon, carbon cryogel, and multi-walled carbon nanotubes) were chosen, while activation or chemical modification was applied to access the influence of surface chemistry on the adsorption process. Material selection was made based on their specific characteristics. The highly porous and hollow structure of multi-walled carbon nanotubes (MWCNTs), as well as developed and controllable porosity of carbon cryogels (CCs), provides strong interaction between material surface and adsorbate molecules. Additionally, the mainly mesoporous structure of these materials allows a fast transfer of adsorbate molecules through the pore network (Celzard et al. 2012; Minović et al. 2015). Due to these textural characteristics, MWCNTs are proven to be a good adsorbent for hormones removal (Dai et al. 2019). Consequently, it is reasonable to expect equally high efficiency of CCs in hormone removal, although, to the best of our knowledge, CCs were not used for hormones removal so far. Following the recent trend in producing carbon materials from different types of biomass waste (Falco et al. 2011), carbonized hydrothermal carbon (CHTC) and activated carbonized hydrothermal carbon (ACHTC), produced from waste beach sawdust, was applied for the first time as an adsorbent for estrone, 17β-estradiol, and 17α-ethinylestradiol removal from water. The process of hormones adsorption onto selected materials was studied by examining the influence of contact time and initial concentration of hormone solution. Based on experimental data, adsorption kinetics was investigated and compared with theoretical models, while the equilibrium data were analyzed with Langmuir and Freundlich isotherms.

**Experimental**

**Materials preparation**

MWNCTs with an average external diameter of 6–9 nm and a length of 5 µm were purchased from Sigma Aldrich, USA. CC was manufactured in the Institute of Nuclear Science Vinča, National Institute of the
Republic of Serbia. CC was obtained by pyrolyzing resorcinol-formaldehyde cryogel in an inert atmosphere (Minović et al. 2015). CHTC and ACHTC were prepared by carbonization and activation of sawdust-based hydrothermal carbon. The hydrothermal synthesis was carried out in an autoclave, at a temperature of 180 °C, under self-generated pressure, for 24 h. The reaction mixture consisted from 6 g of sawdust, 400 mL distilled water, and 0.015 g citric acid (which was used as a catalyst). The solid product obtained by hydrothermal synthesis was filtered and washed with methanol and distilled water. Hydrothermal carbon was carbonized in an inert nitrogen atmosphere, up to a temperature of 900 °C, at a heating rate of 5 °C/min to obtain sample CHTC. Sample ACHTC was obtained by activation of CHTC using KOH as an activating agent. The mass ratio of KOH and CHTC was 2/1. Chemical modification, using HNO₃, HCl, and KOH (Lalović et al. 2017), was applied to alter the surface chemistry of materials, and applied treatment conditions are summarized in Table 1.

| Carbon material | Treatment conditions          |
|-----------------|-------------------------------|
| MWCNT           | -                             |
| MWCNT/HNO₃      | Chemical modification: 4M HNO₃, 4 h, 80°C |
| MWCNT/HCl       | Chemical modification: 1M HCl, 4 h, room temperature |
| MWCNT/KOH       | Chemical modification: 4M KOH, 4 h, 80°C |
| CC              | -                             |
| CC/HNO₃         | Chemical modification: 4M HNO₃, 4 h, 80°C |
| CC/KOH          | Chemical modification: 4M KOH, 4 h, 80°C |
| CHTC            | Carbonization: 900 °C, 5 °C/min, N₂ atmosphere |
| ACHTC           | Activation: KOH:CHTC = 2:1, 900 °C, 5 °C/min, N₂ atmosphere |

**Sample Characterization**

Surface and porosity analyzer Micromeritic ASAP 2020 (Micromeritics Instrument Corporation, U.S.) was used to obtain nitrogen adsorption-desorption isotherms, and to examine textural characteristics of carbon samples. The micropore volume (V\text{\micro}), specific surface area (S\text{BET}), and microporous surface area (S\text{\micro}), were determined from the adsorption data using the manufacturer’s software ASAP 2020 V3.05 H. External surface area, including mesoporous area (S\text{\meso}), is gained by subtracting of S\text{\micro} from S\text{BET}. Pore size distribution was estimated according to Barrett, Joyner, and Halenda (BJH) method (Barrett et al. 1951).
The pH values of aqueous slurries (pH slurry) of the examined materials were measured as follows: 0.2 g of each material was immersed in 2 mL of deionized water. The samples were stored in a plastic tube, under N₂, at room temperature. pH values of the samples were measured after reaching the equilibrium.

Determination of functional groups, present on the surface of examined carbon materials, was performed by Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded in the range from 400 to 4000 cm⁻¹ by applying Bomem MB-Series spectrometer (Hartmann &Braun).

**Adsorption Experiments**

The efficiency of examined materials to adsorb E1, E2, and EE2 from water is presented in Fig. 3a. Most of the examined materials almost completely remove estrogen hormones from water, with adsorption efficiency ranging from 87.22 to 99.76 %, the only exception being CHTC with an efficiency of around 50 % for all hormones. However, the activation of CHTC strongly improved the adsorption efficiency up to 98.2 %. The highest adsorption efficiency, ranging from 99.20 % for E2 to 99.54 % for EE2, was observed for unmodified MWCNT.

The highest desorption efficiency (Fig. 3b), from 91.27 % for E2 to 99.81 % for EE2, was gained for sample MWCNT/KOH, while the lowest results were obtained for CHTC (34.51 % for E2–46.23 % for E1). It can be observed that applied activation and chemical treatments increase desorption efficiency of CHTC and MWCNTs, respectively, while in the case of CC samples modification has negative, or no influence on desorption efficiency.

The influences of contact time on E1, E2, and EE2 adsorption onto different carbon materials are presented in Fig. 4. MWCNT samples exhibited the highest adsorption capacities and fast adsorption process, which reached its equilibrium in approximately 30–60 minutes. CC samples also showed good adsorption capacities in a somewhat slower adsorption process, since the materials were saturated after 180 minutes. Although CHTC showed the fastest adsorption, reaching the equilibrium in less than 30 minutes, its adsorption capacity was the lowest.

In order to investigate the kinetics of hormones adsorption onto examined carbon materials, experimental data were fitted with pseudo-first-order and pseudo-second-order kinetics models (Fig. 4).

The model-fitted parameters of adsorption kinetics, which include correlation coefficients (R²), adsorption rate constants (k₁ and k₂), amount of hormones at equilibrium calculated by these two models (qₑ,cal), are summarized in Tables 3, 4, and 5. Also, the experimentally obtained equilibrium amounts of hormones (qₑ,exp) are given in Tables 3, 4, and 5. Results revealed that all tested samples, except CHTC, showed high adsorption capacities toward examined hormones in the range from 5.34 to 6.16 mg/g.
Table 3
Kinetics parameters and correlation coefficients for adsorption of E1 onto different carbon materials

| Sample      | Pseudo-first order | Pseudo-second order |
|-------------|---------------------|---------------------|
|             | $q_{e, cal}$        | $k_1$, min$^{-1}$   | $R^2$ | $q_{e, cal}$ | $k_2$, g/mg/min | $R^2$ | $q_{e, exp}$ |
|             | mg/g                |                     |       | mg/g         |                     |       | mg/g         |
| MWCNT       | 5.88                | 0.181               | 0.85922 | 6.25         | 0.291               | 0.87939 | 5.99         |
| MWCNT/HNO$_3$ | 5.64                | 0.172               | 0.84849 | 6.06         | 0.261               | 0.94497 | 6.14         |
| MWCNT/HCl   | 5.54                | 0.186               | 0.89108 | 5.89         | 0.299               | 0.92507 | 5.72         |
| MWCNT/KOH   | 5.53                | 0.114               | 0.90328 | 5.98         | 0.167               | 0.91835 | 5.64         |
| CC          | 5.11                | 0.135               | 0.80147 | 5.53         | 0.196               | 0.94949 | 5.49         |
| CC/HNO$_3$  | 5.04                | 0.112               | 0.81767 | 5.48         | 0.160               | 0.94923 | 5.42         |
| CC/KOH      | 5.87                | 0.0404              | 0.99607 | 6.93         | 0.043               | 0.98443 | 5.89         |
| CHTC        | 0.87                | 0.137               | 0.95914 | 0.95         | 0.190               | 0.98818 | 0.95         |
| ACHTC       | 5.40                | 0.0625              | 0.9712  | 6.11         | 0.0757              | 0.99177 | 5.69         |
| Sample          | Pseudo-first order |                        | Pseudo-second order |                        |
|-----------------|--------------------|------------------------|---------------------|-----------------------|
|                 | $q_{e \text{cal}}$ | $k_1$ | $R^2$             | $q_{e \text{cal}}$ | $k_2$ | $R^2$ | $q_{e \text{exp}}$ |
|                 | mg/g               | min$^{-1}$              |                     | mg/g                  | g/mg/min |                     | mg/g                         |
| MWCNT           | 5.86               | 0.186                  | 0.84823             | 6.23                  | 0.303   | 0.90857             | 6.00                         |
| MWCNT/HNO$_3$   | 5.71               | 0.0998                 | 0.79678             | 6.19                  | 0.146   | 0.91329             | 6.16                         |
| MWCNT/HCl       | 5.60               | 0.170                  | 0.87551             | 5.97                  | 0.270   | 0.89545             | 5.74                         |
| MWCNT/KOH       | 5.51               | 0.139                  | 0.90208             | 5.92                  | 0.209   | 0.93677             | 5.66                         |
| CC              | 5.43               | 0.0842                 | 0.93274             | 5.99                  | 0.113   | 0.9578              | 5.66                         |
| CC/HNO$_3$      | 4.94               | 0.0429                 | 0.91715             | 5.69                  | 0.0511  | 0.9644              | 5.40                         |
| CC/KOH          | 5.84               | 0.0412                 | 0.99658             | 6.88                  | 0.0449  | 0.99187             | 5.94                         |
| CHTC            | 0.66               | 0.0369                 | 0.98682             | 0.079                 | 0.0398  | 0.99563             | 0.66                         |
| ACHTC           | 5.33               | 0.0386                 | 0.92163             | 6.19                  | 0.0453  | 0.9633              | 5.73                         |
Table 5
Kinetics parameters and correlation coefficients for adsorption of EE2 onto different carbon materials

| Sample          | Pseudo-first order | Pseudo-second order |
|-----------------|--------------------|---------------------|
|                 | $q_{e\, cal}$ | $k_1$, $R^2$ | $q_{e\, cal}$ | $k_2$, $R^2$ | $q_{e\, exp}$ |
|                 | mg/g | min$^{-1}$ | mg/g | g/mg/min | mg/g |
| MWCNT           | 5.81  | 0.185  | 0.86422 | 6.19  | 0.295  | 0.92962 | 6.01 |
| MWCNT/HNO$_3$  | 5.72  | 0.117  | 0.87257 | 6.21  | 0.168  | 0.94037 | 6.10 |
| MWCNT/HCl      | 5.57  | 0.178  | 0.85838 | 5.92  | 0.285  | 0.91417 | 5.67 |
| MWCNT/KOH      | 5.54  | 0.123  | 0.89992 | 5.97  | 0.183  | 0.93393 | 5.68 |
| CC              | 5.12  | 0.105  | 0.82033 | 5.60  | 0.147  | 0.9473  | 5.68 |
| CC/HNO$_3$     | 4.98  | 0.0442 | 0.9137  | 5.71  | 0.0539 | 0.95869 | 5.34 |
| CC/KOH         | 5.76  | 0.0506 | 0.98826 | 6.61  | 0.0592 | 0.99493 | 5.94 |
| CHTC           | 0.51  | 0.0917 | 0.92216 | 0.56  | 0.122  | 0.98765 | 0.56 |
| ACHTC          | 4.92  | 0.0404 | 0.93807 | 5.71  | 0.0472 | 0.9747  | 5.26 |

According to the values obtained for correlation coefficients ($R^2$), experimental data for almost all tested samples fits better with pseudo-second model kinetics. However, somewhat different finding was obtained by comparing the values of $q_{e\, exp}$ and $q_{e\, cal}$. Although no clear relationship was observed between the type of material and the applied kinetic model, it was noticed that adsorption of hormones onto mesoporous materials (MWCNT and CC) oxidized with HNO$_3$ particularly follows the pseudo-second order kinetic. On the other hand, adsorption of hormones onto CC and MWCNT treated with KOH, preferably follows the pseudo-first order model.

The values of rate constants ($k_1$ and $k_2$) indicate that the adsorption process was faster on materials that have a higher ratio of mesoporosity ($S_{\text{meso}}/S_{\text{micro}}$, Table 2). The fastest adsorption was observed on MWCNTs, which have the highest ratio of mesoporosity, and the estrogen hormones easily access the porous material structure. On the other hand, microporous materials are characterized by slower adsorption, due to the hindered hormone diffusion through the micropores. Taking into consideration surface characteristics of examined materials (Table 2) and values of $q_{e,\, exp}$ (Tables 3, 4, and 5), it can be observed that neither surface acidity, nor specific surface area ($S_{\text{BET}}$), have a decisive influence on the adsorption kinetics of tested materials.
One of each type of material (multi-walled carbon nanotubes, carbon cryogel, and carbonized hydrothermal carbon) was selected for adsorption isotherms study, and to examine the influence of initial hormone concentration on adsorption. MWCNT/KOH, CC/KOH, and ACHTC were selected as samples with high adsorption, and the highest desorption efficiency (Fig. 3). The equilibrium data for adsorption of tested hormones onto MWCNT/KOH, CC/KOH, and ACHTC are fitted with the Langmuir and the Freundlich isotherm models and shown in Fig. 5.

Adsorption capacities of examined materials increase with initial hormones concentration, although the characteristic plateau was not reached in the examined concentration range, especially in the case of MWCNT/KOH and CC/KOH. The calculated parameters of model fittings are given in Table 6. Equilibrium data can be equally well fitted with both isotherm models, although, the Langmuir isotherm model showed a slightly better agreement, indicating that adsorption of the hormones on the surface of MWCNT/KOH, CC/KOH, and ACHTC occurs mostly homogeneously, with no interaction between adsorption molecules (Luo et al. 2017). Obtained maximum adsorption capacities, calculated from the Langmuir isotherm model, were high for all examined hormones, ranging from 29.45 to 194.7 mg/g (Table 6), and the highest value of $Q_0$ was obtained for E2 adsorption onto CC/KOH.

| Material     | Hormone | Freundlich adsorption isotherm | Langmuir adsorption isotherm |
|--------------|---------|---------------------------------|------------------------------|
|              |         | $R^2$  | $K_f$, mg$^{-1/n}$ | $1/n$ | $R^2$ | $Q_0$, mg/g | $b$ |
| MWCNT/KOH    | E1      | 0.95719 | 17.15 | 0.316 | 0.98639 | 50.55 | 0.663 |
|              | E2      | 0.98333 | 17.04 | 0.332 | 0.99038 | 74.31 | 0.331 |
|              | EE2     | 0.91730 | 16.09 | 0.275 | 0.99292 | 39.22 | 1.002 |
| CC/KOH       | E1      | 0.98031 | 18.38 | 0.034 | 0.98505 | 83.78 | 0.314 |
|              | E2      | 0.99547 | 17.26 | 0.342 | 0.99559 | 194.7 | 0.100 |
|              | EE2     | 0.96793 | 16.90 | 0.319 | 0.99653 | 52.90 | 0.576 |
| ACHTC        | E1      | 0.93676 | 12.58 | 0.220 | 0.95144 | 29.45 | 0.972 |
|              | E2      | 0.98475 | 12.06 | 0.249 | 0.99153 | 51.09 | 0.329 |
|              | EE2     | 0.95112 | 9.14  | 0.204 | 0.95210 | 30.75 | 0.450 |

Comparison of values of maximum adsorption capacities of the present and some previous studies are given in Table 7. Based on the results presented in Table 7, it can be concluded that values of $Q_0$ obtained in the present study are comparable or higher than those presented in the literature. Therefore, examined
materials, especially MWCNT/KOH and CC/KOH, can be used as highly efficient adsorbents for removal of estrogen hormones from water.
Table 7
Comparison of maximum adsorption capacities, calculated from Langmuir isotherm model, of different materials as adsorbents for E1, E2 and EE2

| Hormone | Adsorbent | $C_{\text{adsorbate}}$, mg/L | $C_{\text{sorbent}}$, g/L | $Q_0$, mg/g | Ref |
|---------|-----------|----------------------------|--------------------------|-------------|-----|
| E1      | Rice husk | 3–12                       | 4                        | 2.698       | (Honorio et al. 2018) |
| E2      | Bone char | 5 and 9                    | 0.5–50                   | 10.12       | (Patel et al. 2015) |
| E1      | Zeolite/HDTMA | 2–20                 | 1                        | 25.58       | (Zhong et al. 2019) |
| E2      | Zeolite/HDTMA | 2–20                 | 1                        | 25.58       | (zhong et al. 2019) |
| E2      | Zeolite/HDTMA | 2–20                 | 1                        | 25.58       | (zhong et al. 2019) |
| E2      | MWCNTs/FMBO | 0.2-6                 | 0.05                     | 47.25       | (Dai et al. 2019) |
| EE2     | MWCNT     | 0.025–0.1                 | 0.5                      | 5.59×10^{-3} | (Kumar and Mohan 2012) |
| EE2     | MWCNT     | 10–200                    | 1                        | 15.5        | (Silva et al. 2020) |
| E2      | MWCNT-C/C\text{Fe}_2\text{O}_4 | 0.4–2.4              | 0.1                      | 29.1        | (F. Wang et al. 2015) |
| E2      | MWCNT-N/C\text{Fe}_2\text{O}_4 | 31.8                  |                           |             |             |
| EE2     | MWCNT     | 5–70                      | 0.2                      | 26          | (Teixeira et al. 2013) |
| E1      | Pyrolyzed coke | $0.1\times10^{-3}$–$1\times10^{-3}$ | $0.025–0.25$ | 0.05        | (Gökce and Arayici 2016) |
| E2      | Activated charcoal | 0.1–1.5                | 0.5                      | 2.57        | (Huang et al. 2020) |
| E2      | Activated charcoal supported titanate nanotubes | 0.1–1.5                | 0.5                      | 2.78        |             |
| E1      | ACC       | 2–12                      | 0.8                      | 12.34       | (Prokić et al. 2020) |
| E2      | MWCNT/KOH | 2–50                      | 0.8                      | 50.55       | This study |
| E2      | CC/KOH    |                           |                          | 83.78       |             |
### Desorption Experiments

Desorption of hormones from materials was performed using dichloromethane/methanol (1:1, v/v) mixture in a flow system. 5 mL of the solvent mixture was loaded through the column containing examined carbon adsorbent. Prior to the solvent elution, carbon packing was left to soak for 10 min. The obtained eluent was evaporated to the dryness under nitrogen and reconstituted in 25 mL of the mobile phase, which consisted of 75% methanol and 25% formic acid (0.1% water solution).

### LC-ms/ms Analysis

Separation of selected hormones was done using a Surveyor LC system, (Thermo Fisher Scientific, USA). The reverse-phase separation was conducted using an Agilent Zorbax Eclipse XDB-C18 analytical column (75 mm × 4.6 mm × 3.5 µm). The mobile phase composition was 25 % formic acid (0.1 % water solution) and 75 % methanol at a constant flow rate of 0.3 mL/min. The method was isocratic. LCQ Advantage (Thermo Fisher Scientific, USA) mass spectrometer with electrospray ion source and quadrupole ion trap mass analyzer was used for detection and quantification of the hormones. The measurements were recorded in the positive ionization mode.

### Results And Discussion

#### Material characterization

Nitrogen adsorption and desorption isotherms for unmodified samples, multi-walled carbon nanotubes, carbon cryogel, and carbonized hydrothermal carbon, are presented in Fig. 1a, as the function of the adsorbed amount of N$_2$, and relative pressure at -196 °C. According to the IUPAC classification (Sing et al. 1985), isotherms of MWCNT and CC are of type IV with an H$_2$-hysteresis loop. These are characteristics for the pores of undefined shape on the mesoporous materials. Isotherms of CHTC are of type I, related to the microporous materials. At high P/P$_0$, adsorption isotherm obtained for CHTC does not exhibit any limiting adsorption, which is related to the non-rigid aggregates of plate-like particles and slit-shaped pores (Lowell et al. 2004). Pore size distribution (PSD) of MWCNT, CC, and CHTC is shown in Fig. 1b.
Wide PSD, obtained for MWCNT and CC, with an average diameter of 14.98 and 12.14 nm, respectively, confirmed the mesoporous character of these materials. On the other hand, PSD of sample CHTC is very narrow, with an average pore diameter of 1.5 nm, which is characteristic of microporous materials.

The textural characteristics of all, unmodified and modified materials, along with the pH slurry values are summarized in Table 2. Activated carbon material, ACHTC, exhibited the highest specific surface area. From the results obtained for CHTC and ACHTC, it can be observed that activation of CHTC led to a drastic increase in specific surface area from 213 to 1002 m$^2$/g, remaining the microporous character of the surface, with the slight increase in mean pore diameter from 1.5 to 2.9 nm. Applied chemical treatments didn't have a significant influence on the specific surface area of MWCNT, since $S_{BET}$ of modified MWCNTs differs less than 10 %, compared with the unmodified sample. On the other hand, chemical modification more considerably affects the specific surface area of carbon cryogel, decreasing the $S_{BET}$ from 10.8 % (CC/KOH) to 18.42 % (CC/HNO$_3$). As light increase in mean pore diameter was observed for modified MWCNTs and CCs, along with the changes in micropore volume and mesoporous surface.

| Materials     | $S_{BET}$, m$^2$/g | $S_{micro}$, m$^2$/g | $S_{meso}$, m$^2$/g | $S_{meso}/S_{micro}$ | $V_{micro}$ cm$^3$/g | $D_{mean}$ nm | pH slurry |
|---------------|------------------|---------------------|---------------------|----------------------|---------------------|---------------|----------|
| MWCNT        | 252              | 16.3                | 235.8               | 14.47                | 0.0749              | 14.98         | 6.06     |
| MWCNT/HNO$_3$| 258              | 10.0                | 248.1               | 24.81                | 0.0761              | 18.14         | 4.25     |
| MWCNT/KOH    | 246              | 9.8                 | 236.1               | 24.09                | 0.0719              | 17.88         | 8.24     |
| MWCNT/HCl    | 239              | 7.3                 | 231.2               | 31.67                | 0.0692              | 17.16         | 5.96     |
| CC           | 612              | 226.1               | 385.9               | 1.71                 | 0.2347              | 12.14         | 9.68     |
| CC/HNO$_3$   | 499              | 163.1               | 336.1               | 2.06                 | 0.1891              | 13.14         | 5.07     |
| CC/KOH       | 546              | 155.5               | 390.6               | 2.51                 | 0.2075              | 15.38         | 5.44     |
| CHTC         | 213              | 210                 | 3                   | 0.01                 | 0.187               | 1.5           | 7.53     |
| ACHTC        | 1002             | 947                 | 55                  | 0.06                 | 0.479               | 2.9           | 4.71     |

Results given in Table 2 reveal that there are high variations between pH slurry values of the examined materials. These values range from mildly acidic (4.71 of material ACHTC) to basic (9.68 of unmodified CC). Applied chemical treatments altered the surface acidity of tested materials. As it can be seen from pH slurry values, modification with HNO$_3$ and HCl increased surface acidity, while modification with KOH decreased surface acidity of carbon nanotubes, and, unexpectedly, increased the surface acidity of CC.
FTIR spectra of all examined materials are presented in Fig. 2. All spectra exhibit a broad absorption band at approximately 3435 cm\(^{-1}\), which can be attributed to the stretching vibration of OH groups (Biniak et al. 1997), and this peak is the most pronounced in the spectra of CC/HNO\(_3\). Two small peaks in the region 2850–2950 cm\(^{-1}\), present in FTIR spectra of all tested samples, can be assigned to symmetrical and asymmetrical vibrations of C-H in methyl or methylene groups (Lazić et al. 2018). The broad band around 1630 cm\(^{-1}\) at MWCNTs spectra, and two poorly separated bands at 1620 and 1640 cm\(^{-1}\) at CCs, CHTC, and ACHTC spectra can be assigned to the vibrations of the aromatic C = C bond and the bending vibration of the O-H bond, or the stretching vibration of the aliphatic C = C bond (Maletić et al. 2019; Chen et al. 2012; Sevilla and Fuertes 2009; Kalijadis et al. 2015; Rusmirović et al. 2018). The bands observed around 1383 cm\(^{-1}\) for all samples can be attributed to the O-H bond in the carboxyl group (Barroso-Bogeat et al. 2014; Rusmirović et al. 2018). The bands observed in the region 1360 – 1000 cm\(^{-1}\) correspond to C-O stretching and OH banding vibration (Sevilla and Fuertes 2009). The absorption bands in the region below 800 cm\(^{-1}\) probably correspond to out-of-plane bending vibration of C-H groups located at the edges of aromatic planes (Biniak et al. 1997; Goreacioc 2015).

Although, there are no significant differences in the types of surface functionalities, induced by applied chemical treatments, observed differences in the peak intensity imply the alteration in content of surface oxygen groups. Most pronounced changes are visible in the spectra of MWCNTs due to a decrease in intensity of bands located in the region 1300–1000 cm\(^{-1}\) after modification. Changes in this region can be related to the decreased amount of hydroxyl, ester, or ether groups. A decrease in intensity of peaks around 2850–2950 cm\(^{-1}\) observed after HNO\(_3\) and HCl modification of MWCNT and after activation of CHTC, implicate that some of the aliphatic groups were oxidized during the treatments (Prokić et al. 2020). It can be noticed that chemical modification of CC leads to an increase in the intensity of the peaks in 1360 – 1000 cm\(^{-1}\) region, which is more pronounced for HNO\(_3\) treated sample. The spectrum of CC/HNO\(_3\) also displays the low-intensity shoulder peak at 1730 cm\(^{-1}\) which corresponds to C = O stretching vibration in carboxyl groups (Zhang et al. 2015). Applied chemical treatment with HNO\(_3\), as well as activation, brought a significant increase in the intensity of carboxylic C = O peak at 1383 cm\(^{-1}\) for CC/HNO\(_3\), MWCNT/HNO\(_3\), and ACHTC samples, while the peak at 670 cm\(^{-1}\), was most prominently increased in the spectra of MWCNT/KOH and ACHTC. An increased amount of carboxyl groups, observed in the FTIR spectra of CC/HNO\(_3\), MWCNT/HNO\(_3\), and ACHTC (Fig. 2), is consistent with the increased acidity of these samples (Table 2).

**Conclusions**

Chemical modification and activation were applied on different carbon materials to alter their surface characteristics and increase their efficiency in the adsorption and desorption of estrogen hormones. Applied chemical treatments induced a slight increase in pore diameter, followed by changes in microporous and mesoporous surface, while activation in the presence of KOH increased specific surface area almost five times. The nature of surface oxygen groups was not considerably affected by applied
treatments, but these treatments, especially activation and HNO₃ modification, led to the alteration in the amount of hydroxide and carboxyl groups, and surface acidity. It was found that specific surface area and content of surface functional groups did not have a dominant influence on the adsorption process. However, a high ratio of mesoporosity was proved to be the crucial factor for the fast adsorption process, due to unhindered hormone diffusion through the porous matrices of the material. Process of hormones adsorption onto examined materials can be described by pseudo-second order kinetics model, and showed a slightly better agreement with Langmuir adsorption isotherm. Obtained high values of maximum adsorption capacities imply that examined materials, especially mesoporous multi-walled carbon nanotubes and carbon cryogel, can be used as adsorbents for the removal of estrogen hormones from water.

**Declarations**

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**Availability of data and materials** Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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**Consent for publication** Not applicable.

**Competing interests** The authors declare no conflict of interest.

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Figures
Figure 1

Nitrogen adsorption isotherms (a) and pore size distribution (b) for unmodified MWCNT, CC and CHTC

Figure 2

FTIR spectra of examined carbon materials
Figure 3

Adsorption (a) and desorption (b) efficiency of examined materials toward estrogen hormones.

Figure 4

Kinetic data obtained for a) E1, b) E2 and c) EE2 adsorption onto different carbon materials fitted with pseudo-first and pseudo-second order kinetic model.

Figure 5

Equilibrium data of a) E1, b) E2 and c) EE2 adsorption onto CC/KOH, MWCNT/KOH and ACHTC fitted with Freundlich and Langmuir isotherm models.