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Adsorption of 17β-estradiol and estrone by activated carbon derived from sewage sludge

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ABSTRACT

Nowadays, the number of treatment plants has been increasing due to advancing technology and industrialization throughout Turkey and the world. This situation brings with it the need to analyse the features of the wastewater of treatment plants and treatment sludge in a more detailed way. In recent years, it has been remarkable to see studies conducted on endocrine disrupting substances (EDCs) in wastewaters and treatment sludge and the effects of these substances on the environment and public health. Being one of the estrogenic hormones, which are EDCs and which are found naturally in organisms, 17β-estradiol and estrone are highly important for the ecological balance. In the adsorption studies for the removal of estrogenic hormones, removal efficiencies, adsorption isotherms, kinetic values and thermodynamic studies have been conducted for 17β-estradiol and estrone. In adsorption studies, isotherm calculations are made with 90% and over removal efficiency and it is seen that the adsorption is in conformity with the Freundlich isotherm. Following the kinetic calculations, it is also seen that the adsorption is in conformity with the second-order rate equations. Following the analysis of the adsorption thermodynamically, ΔG Gibbs free energy is found to be positive and enthalpy and entropy variations are also found to be positive.

Keywords: Adsorption; 17β-Estradiol; Estrone; Endocrine disrupting hormones

1. Introduction

Endocrine disrupting substances (EDCs) significantly perturb scientists because of the imitation of hormones, inhibiting hormonal activity and fatal effects on fertilization systems in humans [1,2]. Natural estrogens, such as 17β-estradiol and estrone, are known to be present in certain wastewater treatment plants as a result of human waste, registering levels considered sufficient to induce estrogenic responses [3–13]. Many researchers have made various investigations for the removal of EDCs. This research is on the methods of adsorption, ozonation, biofiltration, microfiltration and ultrafiltration. Of these methods, adsorption, ozonation, reverse osmosis and nanofiltration are effective in the removal of these substances, whereas the activated sludge and biofiltration methods are inadequate. It is thought that these hormones could not be removed by the conventional treatment methods. It has generally been reported that

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coagulation, flocculation and settling methods are inefficient in the removal of EDCs [14].

1.1. Aim of the study

Most of the endocrine disruptors have been accumulated in biocycle and sediments because of the large and organic structure speciality. Furthermore, endocrine disruptors are transported by various methods into the environment due to their stability and persistance. However, the aquatic environment is the most affected environment of endocrine disruptors. Endocrine disruptors that are accumulated in sediments can have a negative effect on benthic organisms and fishes [15,16]. Also, upper levels of food chain organisms have negative effects by feeding these organisms. Besides, endocrine disruptors in soil also have negative effects to wildlife in forestland. The aim of this study is to decrease the negative effects of 17β-estradiol and estrone on the environment and human health by adsorption technologies using pyrolyzed coke derived from wastewater treatment plant sludge.

1.2. Recent studies

Researches on endocrine disruptive materials showed potential threats on reproductive functions of wildlife, for example, shrinkage of penis size in crocodiles, decrease of sperm quality in panthers, behavioural changes of gulls and pseudohermaphroditism on fish family [17]. In a study, 10 ng/l concentration of 17β-estradiol has a feminization effect on immature carp fish, whereas the 0.1 ng/l of concentration has the same effect on rainbow fish [18]. In a research where rainbow fishes were dosed with 0, 1, 3.2, 10, 32, 100 and 320 ng/l concentrations of 17β-estradiol (E2) for 7–21 d and at the end of time, 17β-estradiol (E2) concentrations were detected to be <5, <5, <5, 9, 23, 72 ve 247 ng/l, respectively. They also observed that gene plasm of fish increased thoroughly with overdose of E2 and time [19]. In another study, researched fathead minnow fish were dosed with 10–32, 100–320 and 1,000 ng/l E2 concentrations for 21 d, and the gene plasm levels were investigated. It was observed that the gene plasm levels increased by over 100 ng/l [20].

Activated carbon can be used for the removal of almost all organic pollutants such as EDCs. However, the efficiency depends on the removal capacity, reaction time, solubility of pollutant and type of activated carbon [21]. It was found in a study that the removal of estrogenic hormones by adsorption was carried out by synthetic 17β-estradiol and estrone by 2 g/l granular activated carbon and equilibrated in 2 h [22]. In another study, which used pyrolyzed coke, adsorption was carried with river water containing EDCs and perfectly fitted the Freundlich isotherm [23].

1.3. Pyrolysis

Pyrolysis is a thermal degradation in an anoxic environment. Pyrolysis is also determined as the degradation of carboneous material in inert environment by heat and nitrogen or hydrogen atmosphere.

Pyrolysis reaction is given below as

$$X(C_6H_{10}O_5) \rightarrow 8H_2O + (C_6H_8O)_x + 2CO + 2CO_2 + CH_4 + H_2 + 7C$$

Products of reaction; $(C_6H_8O)_x$, shows the liquid tar.

For increasing the surface area of the carboneous material, raw material was activated by zinc chloride, phosphoric acid, potassium hydroxide and aluminium chloride.

2. Materials and methods

2.1. Adsorption isotherms

Adsorption equilibrium can be identified by equations as adsorption isotherms. The commonly used isotherms are Langmuir and Freundlich isotherms.

2.1.1. Langmuir isotherm

Langmuir isotherm can be explained by these equations

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \quad (1)$$

$$q_e = \frac{Q_{max} a_L C_e}{1 + a_L C_e} \quad (2)$$

where C_e—concentration of the substance remaining in the solution at equilibrium (mg/l); q_e—amount of material adsorbed onto the adsorbent at equilibrium (mg/g); K_L—constant of adsorbent related to adsorbtivity (l/g); a_L—constant of adsorption energy (l/mg); Q_{max}—maximum adsorption capacity (mg/g) [24].

2.1.2. Freundlich isotherm

This empirical model, such as multilayer adsorption on heterogeneous surfaces, can be applied to non-ideal adsorption and explained by the equation below

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

This equation usually applies in linear form by logarithm on both sides of the equation.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

where C_e—concentration of the residual in the solution at equilibrium time (mg/l); q_e—amount adsorbed onto the adsorbent at equilibrium time (mg/g); K_F—calculated by experimental (adsorption capacity) (l/g); n—adsorption density [25].

2.2. Adsorption kinetics

Several kinetic models are available to calculate the behaviour of the adsorbent and the mechanism of the adsorption process. Generally, two types of kinetic models are used when analysing the adsorption; these are pseudo-first-order model introduced by Lagergren and pseudo-second-order model introduced by Ho.

Lagergren's pseudo-first-order equation can be explained as

$$\log \frac{q_e - q_t}{q_e} = -\frac{k_1}{2,303} \quad (5)$$

where q_e—amount adsorbed at equilibrium (mg/g); q_t—amount adsorbed at any time during the adsorption (mg/g); k_1—Lagergren adsorption constant (min^{-1}).

Ho's pseudo-second-order equation can be explained as

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \frac{1}{q_e}t \quad (6)$$

k_2—pseudo-second-order adsorption constant (g/mg min) [26].

2.3. Thermodynamics of adsorption

In the adsorption mechanism, entropy decreases the order of the amount adsorbed by accumulation. Spontone adsorption occurs by the negative values of ΔH° and ΔG° (exothermic reaction) [26–28].

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

where ΔG°—Gibbs free energy (kJ/mol); ΔH°—enthalpy change (kJ/mol); ΔS°—entropy change (kJ/mol K); T—Kelvin temperature (Kelvin).

At a certain temperature, the Gibbs free energy of the adsorption equilibrium constant is calculated by the constant, K_c [27–29].

$$K_c = \frac{C_a}{C_e} \quad (8)$$

where K_c—equilibrium constant; C_a—amount adsorbed by the adsorbent (ng/l); C_e—residual concentration in the solution (ng/l).

$$\Delta G = -RT \ln K_c^0 \quad (9)$$

R—Gas constant (8,314 J/mol K)

ΔH° and ΔS° can be calculated using the intersection and slope of the line by the graphic of $\ln K_c^0$ and $1/T$ [27]. Positive values of ΔH° show that adsorption is endothermic, whereas negative values were calculated for ΔG°. In other words, the application of adsorption can be understand by enthalpy and negative Gibbs free energy. Positive values of ΔS° show the increase of randomization between solid–solution surfaces.

2.4. Enzyme-linked immunoassay method

DRG-Diagnostics brand 17β-estradiol kit and DiaMetra brand estrone kit were used for reading the values in Perlong DNM-9602 model enzyme-linked immunoassay (ELISA) reader set.

Therefore, the identification and quantification of these EDCs are of major importance. Additionally, it must be noted that urban wastewater effluents are usually a very complex mixture of compounds and only a small part of them have been identified [30]. However, the traditional analytical methods (e.g. GC–MS, LC-MS–(MS) and HPLC) are difficult, expensive and time-consuming and demand the development of specific procedures to measure these compounds in complex environmental samples. Furthermore, large sample volumes are required, besides extensive clean-up procedures to achieve sample purification. Thus, there is a strong need for fast, simple and cost-effective methods for quantitative analysis of EDCs, such as ELISA [31].

The ELISA test is based on a competitive reaction between a specific monoclonal antibody and the analysed compound. Briefly, the EDCs derived from samples and an antigen–enzyme conjugate, i.e. EDCs

labelled with a colouring enzyme, are premixed and added into microplate wells for a competitive assay, vying for a limited number of antibody binding sites. When the EDC concentration is higher than that of the enzyme conjugate, the EDCs will predominantly bind with the antibody and vice versa. Unbound 17β-estradiol or estrone and excess antigen–enzyme conjugates are washed out. Then, the chromogenic substrate is added to develop colour in conjunction with the conjugate's enzyme. The amount of antigen–enzyme conjugate remaining with the antibody will determine the colour intensity. Higher EDCs concentration in the sample, for example, leads to less antigen–enzyme conjugate in a microplate well, generating a lighter colour, i.e. lower absorbance [32]. The standard curve, a dose-response curve from known concentrations of standard EDCs (DRG-Diagnostics standards for 17β-estradiol and DiaMetra standards for estrone), is determined from the absorbance at 450 nm.

2.5. Preparation of hormone solutions

17β-estradiol and estrone hormone solutions were prepared from Cayman commercial brand stock solutions. First they were weighted, then dissolved in methanol and diluted with 1% methanol–distilled water. Solutions were corrected by ELISA kits (Drager) in a microplate reader.

2.6. Preparation of the adsorbent

Activated carbon used in this study was a product of pyrolysis. Raw material of coke was derived from Atakoy Advanced Biological Treatment Plant decantor, sludge was first dried in an oven at 103–105°C temperature, activated with zinc chloride and kept at 50°C for one day. Ten grams of activation chemical was used for 20 g. of sludge. After the activation sludge was pyrolyzed at 600°C temperature, it was subjected to10°C/min. heating rate for one hour. Inert atmosphere was carried out by nitrogen gas. (Fig. 1) Then, with the aim of removing $ZnCl_2$ from the pores of coke, it was kept in 3 M HCl solution for 24 h, washed with distilled water and dried at 103–105°C temperature. Pyrolyzed coke was crushed to 0.5–1 mm size for analysis; Table 1 shows the specifications of pyrolyzed coke [33].

2.7. Adsorption studies

Adsorption studies were carried out with the batch system in a Gallenkamp brand shaker at 20°C temperature, 200 rpm at pH 7.

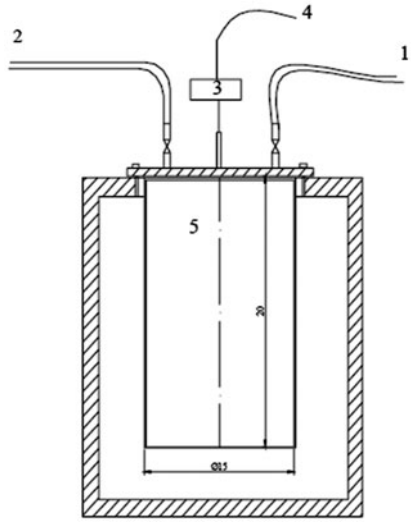

Fig. 1. Scheme of pyrolysis equipment.
Notes: (1) N2 gas input, (2) N2 gas output, (3) PID control device, (4) Thermocouple, and (5) stainless steel reactor.

Table 1
Elemental analysis of raw sludge used for pyrolysis

Parameter	Raw sewage sludge
C (%)	30.86
N (%)	4.21
H (%)	4.36
Ash (%)	60.0

After the equilibrium time was discovered, tests were carried with 100–200, 250–500 and 1,000 ng/l concentrations of 17β-estradiol (E1) and estrone (E2) by the equilibrium time and adsorbent dosage.

3. Results and discussion

Atakoy Biological Treatment Plant sludge was used as the adsorbent in the adsorption tests by pyrolyzing at 600°C temperature and elemental analysis of the sludge is given in Table 1. Table 2 shows the specific surface area of pyrolyzed coke.

Adsorbent dosage was found to be 0.025–0.25 g/l in the adsorption tests. In 90 min, except for 0.025 g/l adsorbent dosage, 88% removal capacity was observed. This situation shows that 0.025 g/l dosage is not adequate for adsorption. On the other hand, high dosages of adsorbent, like 0.2 g/l, have high removal capacities in 120 min.

Fig. 2 shows that in 180 min, adsorption reaches the equilibrium with 0.025 g/l adsorbent dosage. With

Table 2
Specific surface areas of pyrolyzed coke

	Surface area (m^2/g)
BET surface area	683
Micropore area	1,040
Langmuir surface area	1,248

the 0.05 g/l adsorbent dosage, equilibrium time decreases to 60 min. Further study showed that with 0.05 g/l optimum adsorbent dosage and with 60 min shaking time various concentrations of 17β-estradiol were calculated to find out adsorption isotherms. Fig. 3 shows the removal of 1,000 ng/l synthetic estrone concentration for different amounts of the adsorbent dosage. Adsorbent dosage of 0.025 g/l pyrolyzed coke has only 68% removal capacity in 90 min, while with 0.2 g/l, the adsorbent has a removal capacity of 91%.

Data regarding the adsorption of estrone was collected when the adsorbent dosage was 0.05 g/l in 60 min and 88% removal capacity with 1,000 ng/l concentration of estrone.

3.1. Adsorption isotherms

Fig. 4 shows the adsorption of 100–1,000 ng/l concentrations of 17β-estradiol for 0.05 g/l pyrolyzed coke and time.

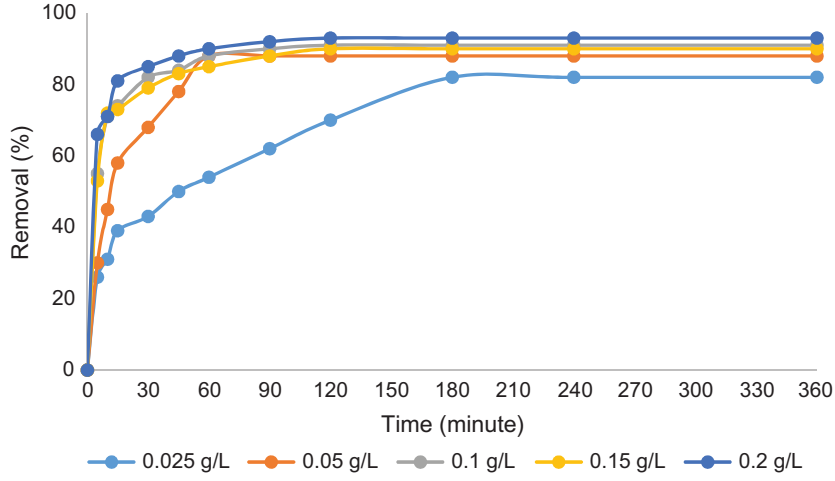

Fig. 2. Adsorption of 1,000 ng/l concentration 17β-estradiol on pyrolyzed coke.

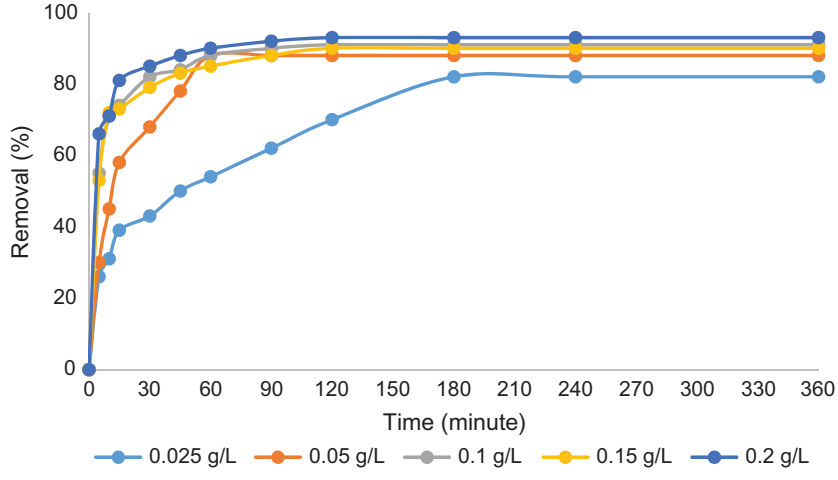

Fig. 3. Adsorption of 1,000 ng/l concentration estrone on pyrolyzed coke.

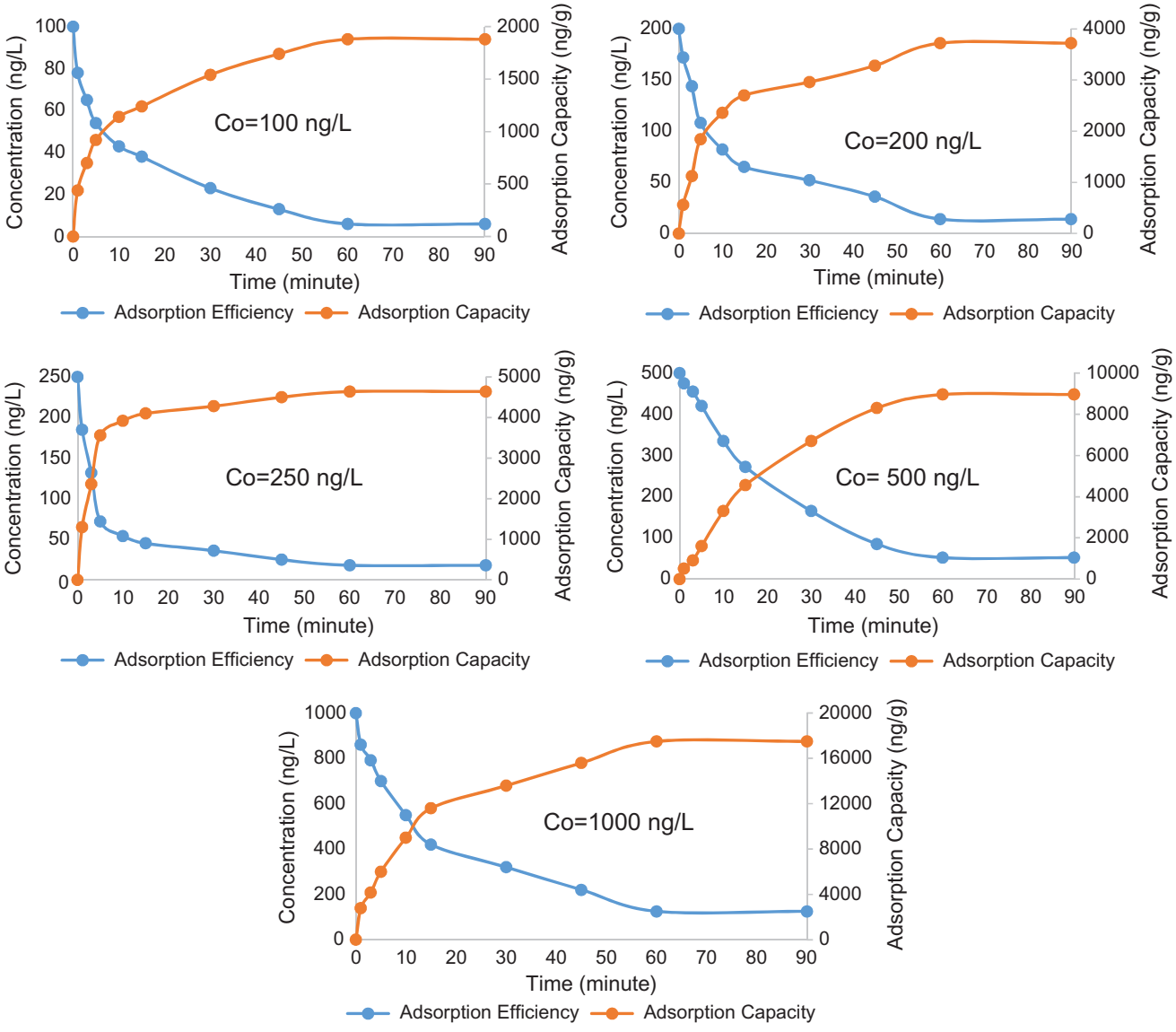

Fig. 4. Adsorption of 100–1,000 ng/l concentration of 17β-estradiol on 0.05 g/l pyrolyzed coke.

After 60 min, concentrations were in equilibrium with 0.05 g/l adsorbent dosage. Fig. 5 shows that in 60 min, estrone adsorption attains equilibrium with 0.05 g/l adsorbent.

Correlation constants (R^2) of Freundlich and Langmuir isotherms were calculated as prior to 1, which shows that the adsorption is feasible.

Figs. 6–9 show the Freundlich and Langmuir isotherms of adsorption, respectively. Parameters of isotherms are given in Table 3.

Correlation coefficients of adsorption $R^2 = 0.997$ for 17β-estradiol and $R^2 = 0.998$ for estrone show the adsorption fits better with the Freundlich isotherm. Also, greater than 1 value of "*n*" constant shows that pyrolyzed coke adsorbed efficiently.

Langmuir isotherm coefficients of 17β-estradiol and estrone adsorption were calculated as positive, despite this correlation coefficient is not close to 1, which shows that adsorption is not feasible for Langmuir isotherm.

3.2. Kinetic models

Kinetics of 17β-estradiol and estrone adsorption on sludge pyrolyzed coke were calculated for Lagergren pseudo-first-order and pseudo-second-order

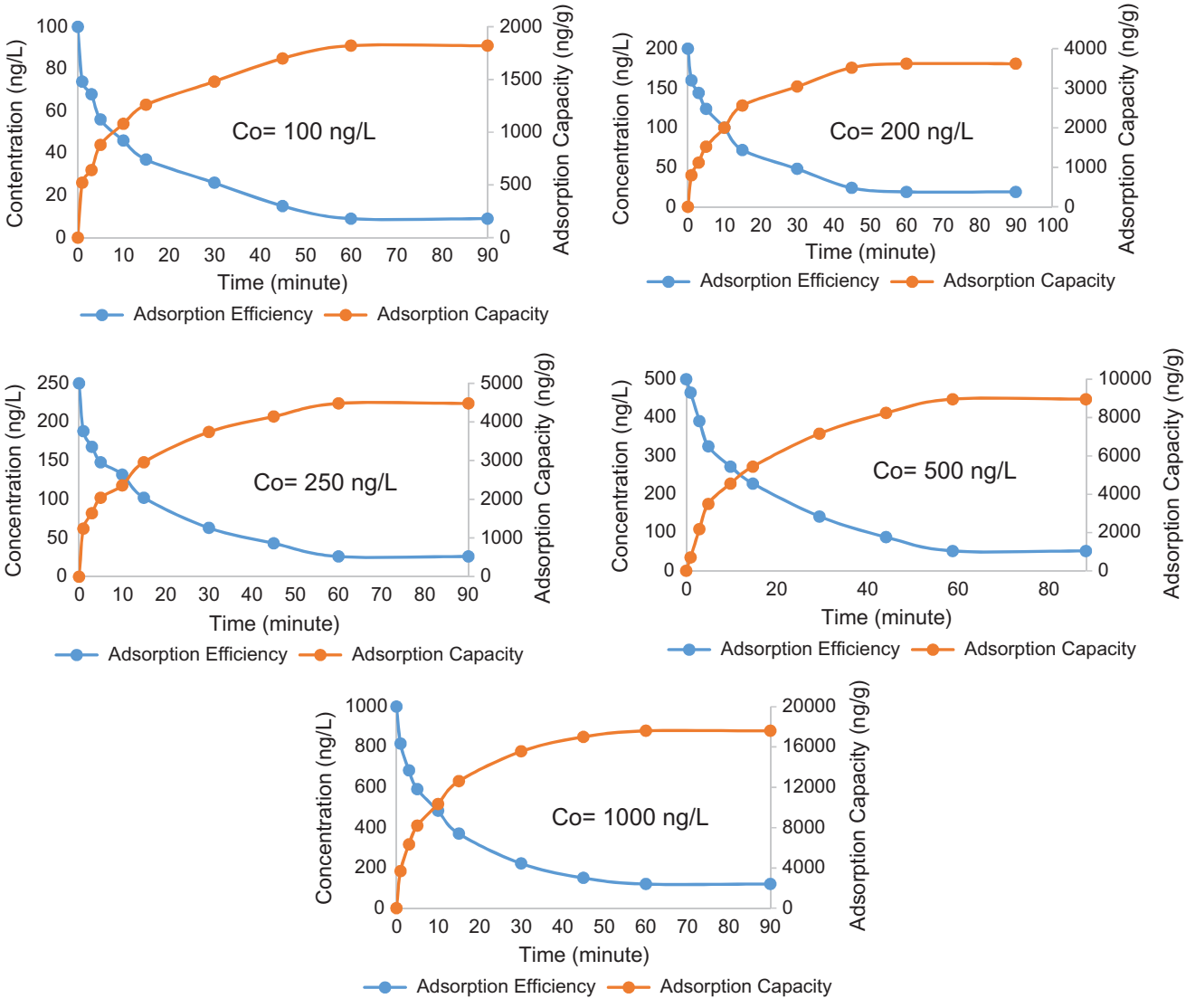

Fig. 5. Adsorption of 100–1,000 ng/l concentration of estrone on 0.05 g/l pyrolyzed coke.

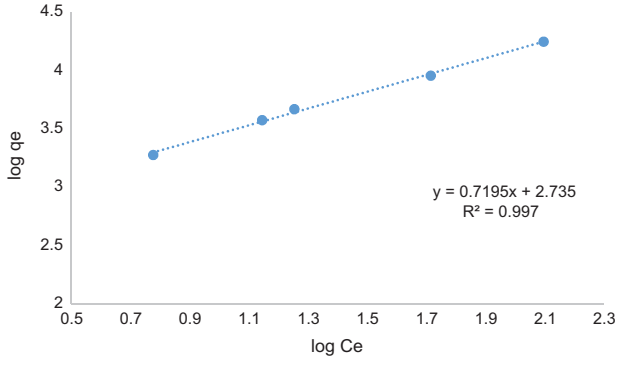

Fig. 6. Freundlich isotherm for 17β-estradiol adsorption.

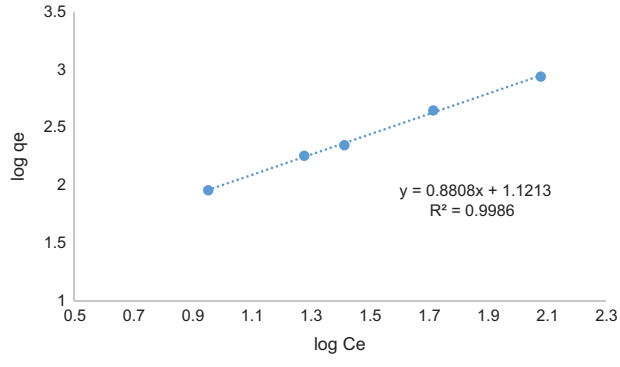

Fig. 7. Freundlich isotherm for estrone adsorption.

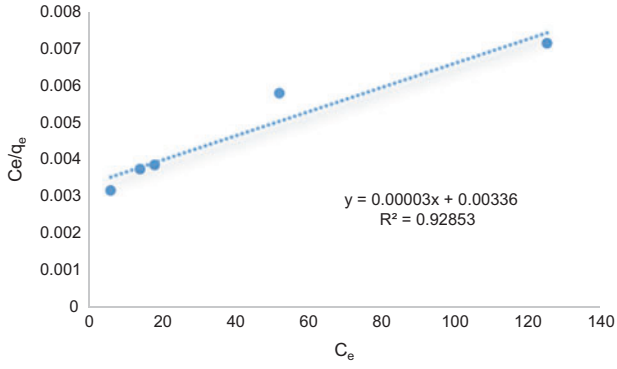

Fig. 8. Langmuir isotherm for 17β-estradiol adsorption.

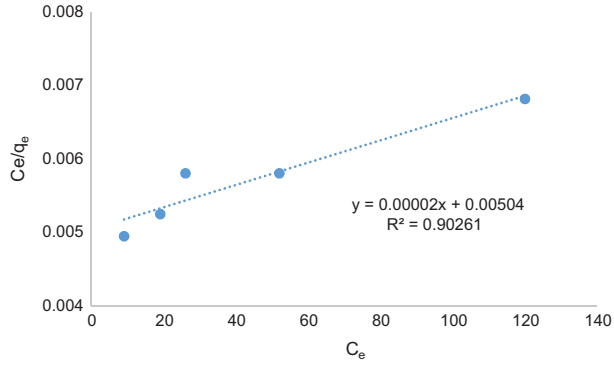

Fig. 9. Langmuir isotherm for estrone adsorption.

Table 3
Freundlich and Langmuir isotherm coefficients

	Freundlich isotherm			Langmuir isotherm		
Endocrine disruptor hormone	K_f (L/g)	n	R^2	Q_{max} (mg/g)	K_L (l/g)	R^2
17β-Estradiol	543	1.39	0.997	0.033	294	0.9286
Estrone	13.22	1.13	0.9986	0.05	200	0.9028

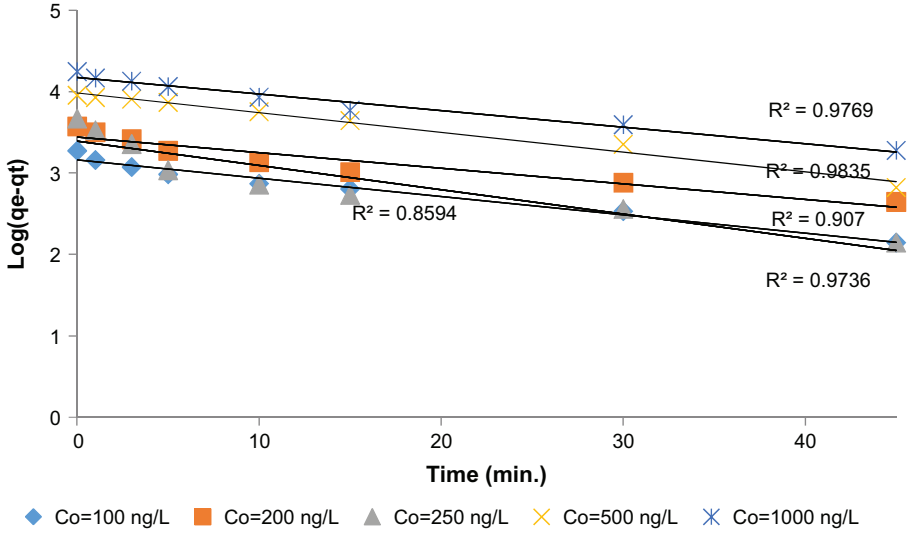

Fig. 10. Lagergren first-order kinetic model curves for 17β-estradiol.

models. Kinetic graphics for 17β-estradiol and estrone were carried at 20°C temperature with various initial concentrations.

3.2.1. Lagergren pseudo-first-order kinetic model

Lagergren pseudo-first-order kinetic model was applied to pyrolyzed coke estrogenic hormone adsorption and teoric values were calculated by drawing $\log(q_e - q_t)$ graphics against time (Figs. 10 and 11) (Table 4). Kinetic coefficients of the model can be seen in Table 4, correlation coefficient fits better for the estrone adsorption than the 17β-estradiol adsorption.

As seen in Table 4, "k" coefficient is positive for 17β-estradiol and estrone adsorption. Adsorption data of 17β-estradiol and estrone by pyrolyzed coke

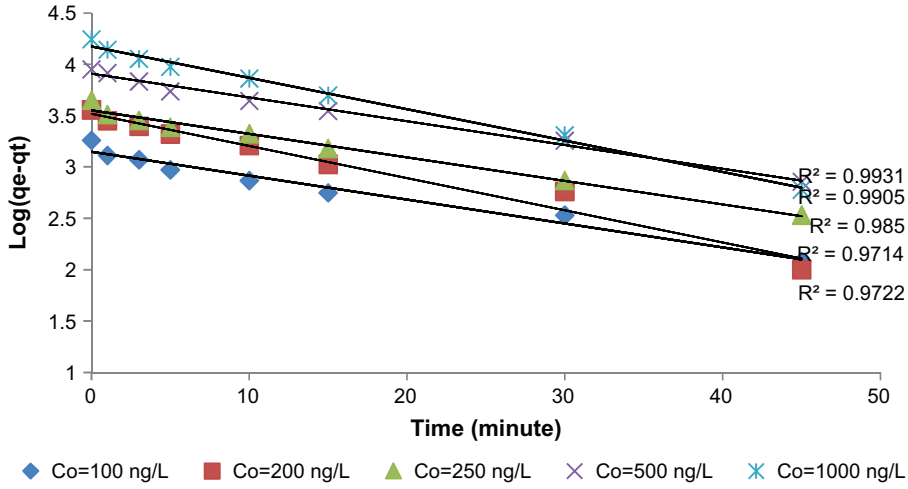

Fig. 11. Lagergren first-order kinetic model curves for estrone.

Table 4
Theoretical and experimental data of Lagergren pseudo-first-order for estrogenic hormones

Estrogenic hormone	Initial concentration (ng/l)	$q_{e(cal)}$	$q_{e(exp)}$	k_1 (min^{-1})	R^2
17β-Estradiol	100	1,453	1880	0.052	0.9736
	200	2,749	3,720	0.044	0.907
	250	2,459	4,640	0.069	0.8594
	500	9,596	8,960	0.56	0.9835
	1,000	15,041	17,500	0.047	0.9769
Estrone	100	1,407	1820	0.054	0.9722
	200	3,288	3,620	0.072	0.9714
	250	3,558	4,480	0.053	0.985
	500	8,084	8,960	0.053	0.9905
	1,000	14,949	17,600	0.070	0.9931

Table 5
Theoretical and experimental data of Lagergren pseudo-second-order for estrogenic hormones

Estrogenic hormone	Initial concentration	$q_{e(cal)}$	$q_{e(exp)}$	k_2 (g/mg.min)	R^2
17β-Estradiol	100	2,000	1,880	9.26×10^{-5}	0.9922
	200	3,333	3,720	6×10^{-5}	0.9916
	250	5,000	4,640	10^{-4}	0.9991
	500	11,111	8,960	4.26×10^{-6}	0.9107
	1,000	20,000	17,500	6.25×10^{-6}	0.9855
Estrone	100	2,000	1820	9.26×10^{-5}	0.9922
	200	3,333	3,620	6×10^{-5}	0.9916
	250	5,000	4,480	3.33×10^{-5}	0.9901
	500	10,000	8,960	10^{-5}	0.9842
	1,000	20,000	17,600	8.33×10^{-6}	0.9945

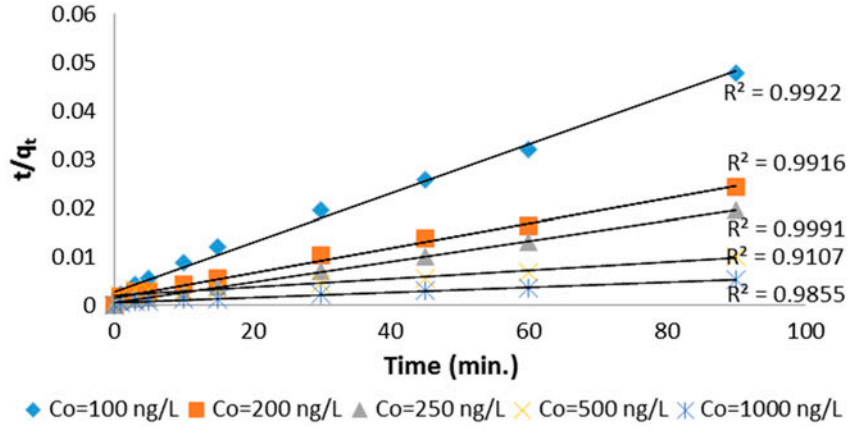

Fig. 12. Pseudo-second-order kinetic model curves for 17β-estradiol.

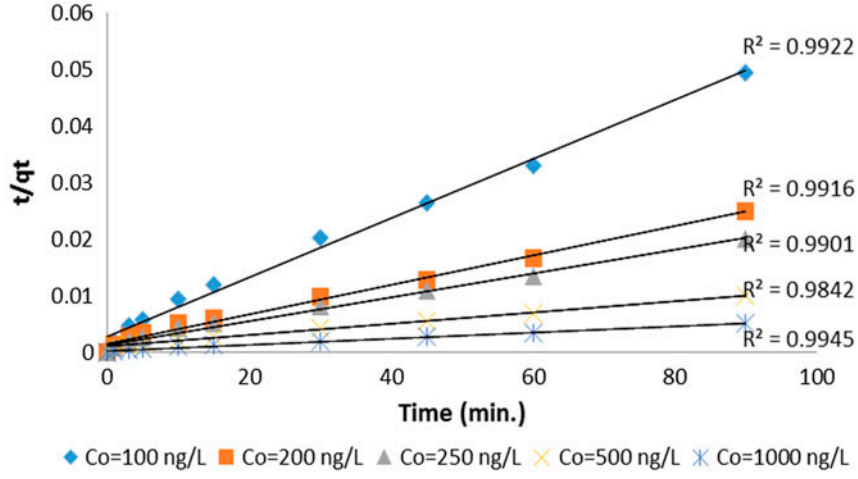

Fig. 13. Pseudo-second-order kinetic model curves for estrone.

Table 6
Gibbs free energies of estrogenic hormones

Estrogenic hormone	Temperature (K)	Equilibrium concentration (ng/l)	K_c	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)
17β-Estradiol	288	20	11.5	−5,848.03	15,313	73.524
	293	18	12.889	−6,227.33		
	298	16	14.625	−6,646.66		
	303	15	15.667	−6,931.56		
Estrone	288	27	8.26	−5,055.66	13,316	63.57
	293	26	8.615	−5,245.94		
	298	24	9.42	−5,556.79		
	303	21	10.9	−6,017.63		

derived from waste sludge from graphics proved that it fitted the pseudo-first-order kinetic model. Also, correlation coefficients show that estrone adsorption is feasible by this kinetic model, pseudo-second-order kinetic model has to be calculated.

3.2.2. Pseudo-second-order kinetic model

Table 5 shows the pseudo-second-order kinetic model coefficients of pyrolyzed coke–estrogenic hormone adsorption were calculated from the data $t/q_{t,}$ against time graphics (Figs. 11 and 12). Correlation coefficients of estrogenic hormones were close to "1" meaning that they fitted the kinetic model better (see Fig. 13).

3.2.3. Thermodynamic studies

For the thermodynamic investigation of estrogenic hormone adsorption, 250 ng/l synthetic samples were studied with 0.01 g adsorbent, 200 rpm shaker in 60 min with various temperatures. Experiments were carried out at a temperature of 288–303 K and enthalpy (ΔH°) and entropy (ΔS°) data were calculated from K_c—Gibbs free energy change (ΔG) and $1/T - \ln K_c$ graphics.

Gibbs free energy data were calculated as negative, whereas the enthalpy and entropy were calculated as positive of estrogenic hormone adsorption.

4. Conclusion

One of the methods of disposal of sewage sludge, known as land spreading, as an alternative to pyrolyzing it in order to make an adsorbent is a feature of studies in recent years. By this method, waste minimization has been realized in an economical way. In this study, waste sludge was pyrolyzed to make an adsorbent which has a 683 m^2/g BET surface area. 100–1,000 ng/l concentrations of synthetic estrogenic hormone samples were adsorbed with 0.05 g/l adsorbent and 88–94% removal capacities were evaluated for 17β-estradiol and estrone, respectively. A similar study was carried with 1–100 ng/l synthetic estrogen concentrations on 0.2 g/l, 1,000 m^2/g surface area adsorbent dosage and 49–81% removal capacities were calculated [34].

In the future, pyrolyzed coke will be more effective in adsorption studies with the waste minimization importance.

Freundich isotherm constants of 17β-estradiol and estrone adsorption data were calculated at 1.39 and 1.13, respectively. Greater than 1 values of "n" constant shows that adsorption is effective and multilayered (Table 3).

After investigating the adsorption isotherms, Lagergren pseudo-first-order and pseudo-second-order rates were calculated. As seen from Table 4, up to 1 of value R^2 and different values of theoretical and experimental equilibrium adsorbed amounts proved they did not fit the Lagergren pseudo-first-order model.

Pseudo-second-order data were investigated for 17β-estradiol and estrone adsorption and the values were calculated as positive constants and close to "1" correlation constants. $q_{e(cal)}$ and $q_{e(exp)}$ data for 17β-estradiol and estrone adsorption were close to each other (Table 5).

The adsorption of estrogenic hormones onto pyrolyzed coke appears to fit the pseudo-second-order kinetic model. This indicates the adsorption rate, concentration of adsorbent, regardless of the solid phase adsorption capacity and timed indicate.

Adsorption was also investigated thermodynamically; temperature effect on Gibbs free energy (ΔG); and equilibrium constant (K_c). K_c value was found to increase with the increase in temperature. Increase in temperature makes adsorption a little better by moving the molecules. On the other hand, positive enthalpy value indicates that adsorption is endothermic (Table 6).

Positive and high results, increased and ongoing irregularities in the process of adsorption of the hormone, illustrates an interactive relationship. Negative Gibbs free energy change and spontaneity show the feasibility of the process.

Entropy (ΔS); affinity of adsorbent to adsorbed and until a positive result is a value that indicates interest in the solid–liquid interface during the reaction shows that an increase in the disorder. This situation means that important changes can occur inside the adsorbent during adsorption.

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