

KINETIC STUDY OF THE ADSORPTION OF 17 α -ETHYNYLESTRADIOL (EE2) BY COMMERCIALY AVAILABLE ACTIVATED CARBON

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ABSTRACT

In recent years, scientists show great concern about the presence of endocrine disrupting compounds (EDCs) in the aquatic environment. EDCs include a family of emerging microcontaminants that have the ability to interact with the endocrine system of the organisms, causing various developmental and reproductive disorders. The occurrence of these substances in aquatic ecosystems may affect the endocrine system of humans and wildlife. EDCs enter the aquatic environment due to their insufficient removal by conventional wastewater treatment plants (WWTPs). The present study demonstrates the potential of activated carbon as adsorbent in removing synthetic estrogen 17 α -ethynylestradiol (EE2) from aqueous phase. The adsorption kinetics data were analysed by two commonly used empirical kinetic models, namely the pseudo-first order (PFO) and pseudo-second order (PSO) kinetic adsorption model, using linear and nonlinear regression methods. It was found that PSO kinetic model fitted the adsorption of EE2 on activated carbon much better than PFO model.

Keywords: adsorption, EE2, activated carbon, kinetic study

1. Introduction

Recently, the occurrence of EDCs in the aquatic environment has caused concern for researchers since they comprise one of the main focuses of the current environmental research. EDCs are chemicals that mimic or block the activity of natural hormones in humans and aquatic wildlife, thus disrupting their reproductive systems (Snyder *et al.*, 2003). The majority of EDCs that have entered the environment are pharmaceuticals excreted from humans at low concentrations, which are subsequently discharged into water bodies due to their partial removal from WWTPs (Kolpin *et al.*, 2002). Among the EDCs that are prevalent in the aquatic environment, 17 α -ethynylestradiol (EE2), a synthetic estrogen, has been most frequently found in wastewater. In order to avoid the potential risks caused by estrogens in aquatic environments, their removal from water is considered significantly important. There are many possible techniques for water treatments. The adsorption process by solid adsorbents is one of the most efficient methods for the treatment and removal of organic contaminants from water and wastewater. Activated carbon can be used as adsorbent for water and wastewater treatment since it has been shown to remove a wide variety of dissolved organic and inorganic contaminants from water. The advantages of using activated carbon include its large surface area, pore structure, and thermostability, which improve its ability to remove contaminants from various aqueous media. In this work, the adsorption of EE2 from aqueous solution by activated carbon was investigated. Two commonly used empirical kinetic models were applied, namely the PFO and PSO kinetic adsorption models. In addition, linear and non-linear regression of the PFO and PSO kinetic models was performed in order to analyse the experimental data.

2. Experimental

2.1. Materials and reagents

17 α -ethynylestradiol (EE2: C₂₀H₂₄O₂) was obtained from Sigma-Aldrich and used as received. Activated carbon samples (GAC1240W, GAC 1240EN, SAUF 8008-2, W35, GAC 830W and GAC

830EN) were kindly supplied by Norit. Acetonitrile used for high performance liquid chromatography (HPLC) was Chromasolv gradient grade and was purchased from Sigma-Aldrich. Ultrapure water (UPW, pH = 5.5 and resistivity 18.2 MΩ·cm at 25 °C), employed for solution preparation and as HPLC eluent, was prepared from a water purification system (Simplicity UV) purchased from Merck Millipore.

2.2. Batch adsorption experiments

Batch adsorption experiments were performed in 500 mL capacity glass beakers, under continuous stirring using a magnetic stir bar and a stirrer. In a typical adsorption experiment, 300 mL of the aqueous solution of EE2 were loaded in the glass beaker, and then the appropriate amount of activated carbon was added into the solution. At given time intervals, aliquots of the suspension were withdrawn and immediately centrifuged at 13200 rpm for 15 min on an Eppendorf Microcentrifuge 5415D in order to remove activated carbon particles. Then, the concentration of EE2 in the supernatant was determined by HPLC (Waters Alliance 2695 HPLC system) employing a Luna C-18(2) column (5µm, 250 mm × 4.6 mm) and a security guard column (4 mm × 3 mm), both purchased from Phenomenex. The mobile phase consisting of 35:65 ultrapure water:acetonitrile eluted isocratically at 1 mL/min and 30 °C, while the injection volume was 100µL. Detection was achieved through a fluorescence detector (Waters 474 Scanning Fluorescence Detector) in which the excitation and emission wavelengths were set at 280 nm and 305 nm, respectively. The adsorption kinetic study was carried out at 25 °C, at inherent solution pH, with initial EE2 concentration 3.7·µmol·L⁻¹ and activated carbon concentration 100 mg·L⁻¹.

3. Results and discussion

The effect of contact time on the adsorption of EE2 onto six commercially available activated carbons was studied and the results are shown in Figure 1. The adsorption capacity of activated carbon for EE2 was calculated according to the following equation:

$$q(t) = \frac{(C_0 - C(t))V}{m} \quad (1)$$

where $q(t)$ are the adsorbed amounts of EE2 onto activated carbon at various times t per unit mass of adsorbent, expressed in µmol·g⁻¹; C_0 is the initial concentration of EE2, while $C(t)$ represents the concentration of EE2 at various times t , both expressed in µmol·L⁻¹; V is the volume of the solution in L; and m is the mass of the adsorbent in g. As can be seen in Figure 1, the adsorption capacity increased very quickly from the first minute and the adsorption equilibrium was reached within 0.5 hours for the activated carbons W35 and SA UF 8008-2. The adsorption capacity of the activated carbons 1240EN, 1240W, 830W and 830EN, increased slower and the adsorption equilibrium was reached within 30 hours. The experimental equilibrium adsorption capacity of the five activated carbons was almost similar (W35: 37.15µmol·g⁻¹, SA UF 8008-2: 36.16 µmol·g⁻¹, 1240EN: 34.69 µmol·g⁻¹, 1240W: 37.16 µmol·g⁻¹ and 830EN: 33.58 µmol·g⁻¹). The sample 830W exhibited lower equilibrium adsorption capacity (19.96 µmol·g⁻¹).

The experimental adsorption data were analysed with the pseudo-first order (PFO) and the pseudo-second order (PSO) kinetic adsorption models (Tseng *et al.*, 2014).

The linear form of the PFO adsorption model can be written as:

$$\ln(q_e - q(t)) = \ln q_e - k_1 t \quad (2)$$

The nonlinear form of Eq. (2) can be written as:

$$q(t) = q_e(1 - e^{-k_1 t}) \quad (3)$$

On the other hand, the most commonly applied linear form of the PSO adsorption model has the following formulation:

$$\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where $q(t)$ and q_e have been defined previously and k_2 is the rate constant of the pseudo-second order model of adsorption, expressed in $\text{g} \cdot \mu\text{mol}^{-1} \cdot \text{min}^{-1}$.

The non-linear form of PSO adsorption model can be written as:

$$q(t) = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

The determination of values of q_e , k_1 and k_2 was carried out by the linear and nonlinear form of PFO and PSO kinetic models. For the linear form of PFO and the PSO kinetic model, Eq. (2) and Eq. (4) were used. The determination of q_e and k_1 of PFO kinetic model was accomplished by linear regression from the intercept and slope of the linear plot of $\ln(q_e - q(t))$ versus t . In addition, the determination of q_e and k_2 of the PSO kinetic model was accomplished by linear regression from the intercept and slope of the linear plot of $t/q(t)$ versus t . On the other hand, for the nonlinear equations of the PFO and the PSO kinetic models, the commercially available software SigmaPlotTM was used (Tseng *et al.*, 2014). For the nonlinear equation of the PFO kinetic model (i.e. Eq. (3)), the “Exponential Rise to Maximum equation, Single, 2 Parameter” equation of SigmaPlotTM, was employed, which is given by the following equation:

$$y = a(1 - e^{-bx}) \quad (6)$$

where the corresponding parameters are $y = q(t)$, $a = q_e$, $b = k_1$, $x = t$.

In the case of the nonlinear equation of PSO kinetic model, the equation “Hyperbola equation, Single Rectangular, 2 Parameter” of SigmaPlotTM was used, which is given by:

$$y = \frac{ax}{b + x} \quad (7)$$

where the corresponding parameters are $y = q(t)$, $a = q_e$, $b = 1/(q_e k_2)$, $x = t$.

Based on the above analysis, both linear and nonlinear regression for the PFO and PSO kinetic adsorption models was performed and the results are presented in Figure 1, Table 2 and Table 3. As can be seen in Figure 1 and Table 1, the linear form of the PFO kinetic model largely fails to describe the experimental results. Especially, in the case of W35 and SA UF 8008-2 activated carbon, the equilibrium adsorption capacity obtained from the linear PFO kinetic model was calculated as $2.058 \mu\text{mol} \cdot \text{g}^{-1}$ and $3.43 \mu\text{mol} \cdot \text{g}^{-1}$, respectively, while the corresponding experimental values were $37.15 \mu\text{mol} \cdot \text{g}^{-1}$ and $36.16 \mu\text{mol} \cdot \text{g}^{-1}$ for W35 and SA UF 8008-2, respectively. In addition, the value of the coefficient of determination, r^2 , was very low (i.e. 0.5268 and 0.6084 for W35 and SA UF 8008-2, respectively), thus indicating that the linear equation of PFO kinetic model fails to describe the experimental results. Regarding the nonlinear PFO kinetic model, the equilibrium adsorption capacity was calculated as $37.10 \mu\text{mol} \cdot \text{g}^{-1}$ and $35.60 \mu\text{mol} \cdot \text{g}^{-1}$ for W35 and SA UF 8008-2, respectively, while the coefficient of determination was 0.9999 and 0.9979, respectively. The above results indicating that the nonlinear form of the PFO kinetic model gives values of equilibrium adsorption capacity which are closer to the experimental ones, and fits better the experimental results. On the other hand, as can be seen in Table 2, the values of the coefficient of determination (r^2) for the linear and the nonlinear form of PSO kinetic model were higher than 0.96. The equilibrium adsorption capacities obtained from the linear and nonlinear PSO kinetic model were calculated and presented in Table 2 and were in very good agreement with the corresponding experimental values. As can be seen in Table 2, the coefficients of determination for the linear form of the PSO kinetic model were, in some cases, higher than the corresponding values of the nonlinear form. However, it has been reported that the fitting of the experimental values to the linear form of PSO kinetic model generally gives higher coefficients of determination compared to those obtained by the nonlinear form of the model

(Tseng *et al.* 2014). Therefore there is an ongoing disagreement regarding the misleading conclusion that the linear form of PSO model is more effective than the non linear form (Tseng *et al.*, 2014).

Table 1: Parameters of the pseudo-first order kinetic model for the adsorption of EE2

Activated Carbon	BET (m ² /g)	k ₁ , min ⁻¹		q _{e,cal} , μmol·g ⁻¹		r ²	
		linear	nonlinear	linear	nonlinear	linear	nonlinear
1240EN	1150	0.0024	0.0037	23.11	35.09	0.9112	0.9856
1240W	1100	0.0015	0.0022	31.55	36.40	0.9869	0.9825
830W	1100	0.0008	0.0020	16.06	18.11	0.9503	0.9794
830EN	1150	0.0022	0.0017	37.77	34.10	0.9814	0.9986
W35	875	0.0762	0.8534	2.058	37.10	0.5268	0.9999
SA UF	1200	0.0485	0.8711	3.43	35.60	0.6084	0.9979

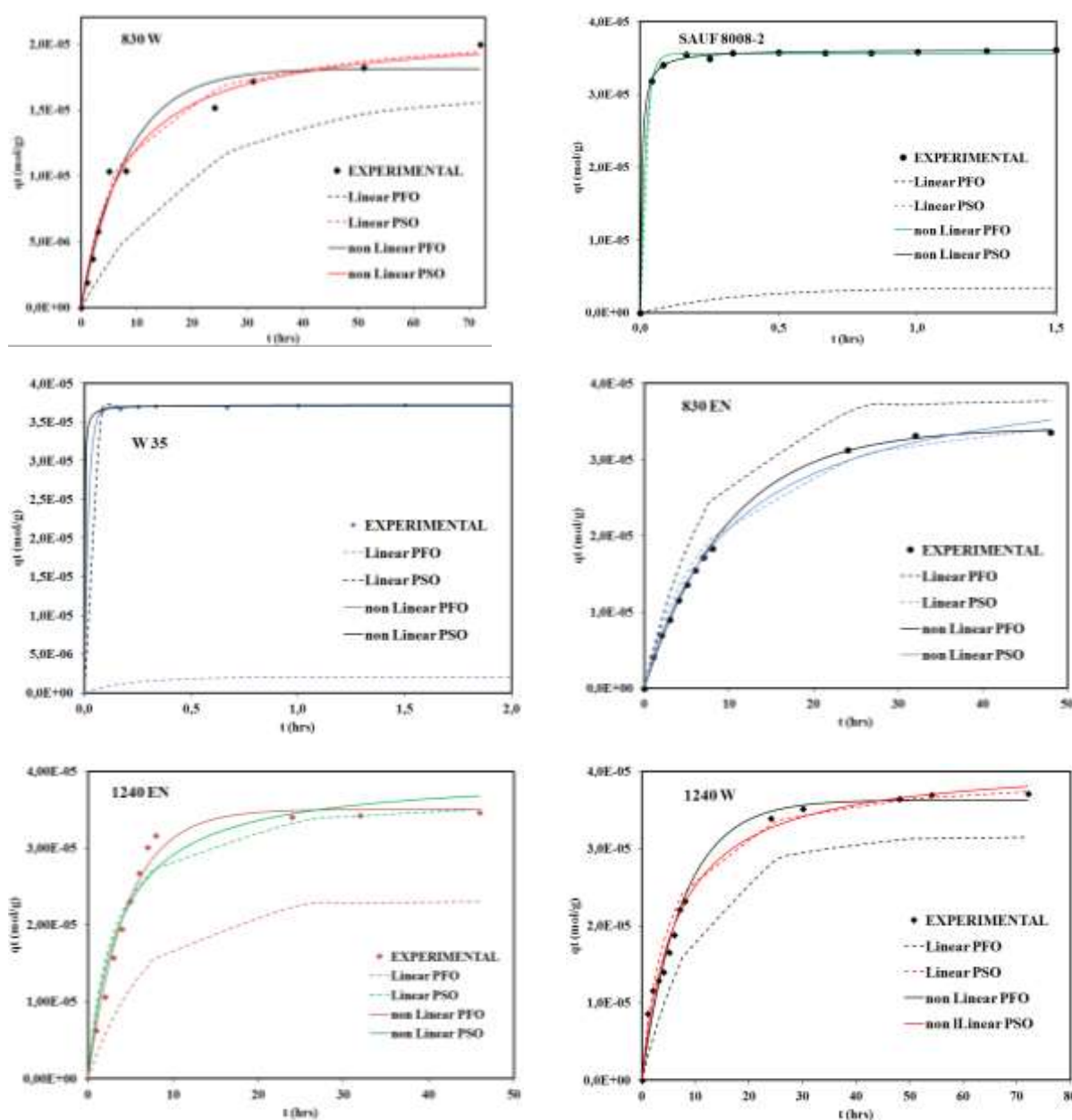


Figure 1: Effect of contact time on the adsorption of EE2 onto six commercially available activated carbons. Dotted lines are linear models and solid lines are nonlinear models.

Table 2: Parameters of the pseudo-second order kinetic model for the adsorption of EE2

Activated Carbon	BET m ² /g	k ₂ , g·μmol ⁻¹ ·min ⁻¹		q _{e,cal} , μmol·g ⁻¹		r ²	
		linear	nonlinear	linear	nonlinear	linear	nonlinear
1240EN	1150	1.54×10 ⁻⁴	1.15×10 ⁻⁴	37.32	39.8	0.9899	0.9551
1240W	1100	8.15×10 ⁻⁵	6.22×10 ⁻⁵	40.12	41.5	0.9937	0.9877
830W	1100	1.08×10 ⁻⁴	1.03×10 ⁻⁴	21.36	21.3	0.9850	0.9724
830EN	1150	5.11×10 ⁻⁵	3.72×10 ⁻⁵	39.91	42.9	0.9656	0.9956
W35	875	3.97×10 ⁻¹	2.96×10 ⁻¹	37.21	37.2	1	1
SA UF	1200	9.01×10 ⁻²	8.47×10 ⁻²	36.16	36.2	1	0.9995

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