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Adsorption of 17*β*-estradiol onto two polymeric adsorbents and activated carbon

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Removal of 17*β*-estradiol from aqueous streams by two polymeric resins XAD-7 and XAD-16, and by Granulated Activated Carbon (GAC) was investigated. Adsorption equilibrium isotherms were measured at various ionic strengths (0.1, 20 and 100 mM NaCl) and pH (4, 5.7, 10). The adsorption equilibrium isotherms were correlated with the Langmuir and Freundlich isotherm models. It was found that the adsorption capacity was strongly dependent on the ionic strength and pH of the external phase in the case of GAC. There are no serious influences of salt concentration and pH were observed in the case of polymeric adsorbents. Higher sorption capacity was obtained in the case of the XAD-16 polymer and GAC.
Thermodynamic parameters for the adsorption process were determined using adsorption equilibrium parameters calculated at three temperatures (23, 37, 50 ^{o}C). The negative values of Gibbs energy about –10 kJ/mol for XAD-7, –14 kJ/mol for XAD-16, and –18 kJ/mol for GAC indicate that adsorption has spontaneous nature. For the polymeric adsorbents the enthalpy of adsorption was found to be negative and relatively low –11 and –26 kJ/mol for XAD-7 and XAD-16, respectively, that indicates physical character of adsorption. The adsorption on GAC was chemical in nature according to calculated value of enthalpy (58 kJ/mol). The negative values of entropy for the polymers indicate decreased randomness at the solid/solution interface, while the positive entropy for GAC indicates an increased randomness during estradiol adsorption.

1. Introduction

Among the other endocrine disrupting chemicals EDCs steroidal estrogens (SEs) are the most potent endocrine disrupters even at ng/L range. They are continuously released by humans and animals into the environment (Ternes et al., 1999, Khanal et al., 2006). Considering the potential impact of SEs, it is highly important to removal them from water and wastewater. Adsorption is most common method in the cleaning technology. Choosing the adsorbent depends on the adsorption capacity as well as on the cost of the regeneration of spent adsorbent. Activated carbon is widely used as adsorbent, but it is well known that regeneration of activated carbon is difficult. On the other hand, synthetic adsorbents can be easily regenerated by suitable solvent rinsing.

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The purpose of this work is to study the adsorption of 17β-estradiol from aqueous solution using two types of polymeric adsorbents and GAC. 17β-stradiol is one of the basic natural estrogens, exhibiting high estrogenic activity and persistence in waters. The macroporous acrylic (XAD-7) and styrenic (XAD-16) polymer adsorbent have uniform surface chemistry and pore structure, and large surface area. GAC is more popular than powdered activated carbon (PAC) in the treatment process because of easier operation.

2. Experimental

The equilibrium experiments were determined by contacting a mass of adsorbent, 0.02 g, with different concentrations of estradiol. Volume of liquid phase was 100 mL. Ionic strength was adjusted using NaCl. The pH was adjusted using 0.1 M NaOH or 0.1 M HCl. The flasks were shaken at 200 rpm on the orbital shaker. Concentration of liquid phase was determined by HPLC, using 150-mm ZORBAX Eclipse XDB-C18 column (Agilent), UV-detector at the 278 nm, and mobile phase acetonitrile:water as 1:1. For estimation of thermodynamic parameters, the equilibrium experiments were conducted at three temperatures 23, 37, and 50 ^{o}C.

3. Theory

3.1 Adsorption equilibrium

Adsorption isotherms were obtained to evaluate contaminant distribution between solid and liquid phases as a function of concentration. The adsorption equilibrium was described using Langmuir and Freundlich models.

The amount of estradiol at equilibrium, q_{eq}, (mg/L), was calculated from experimental data by equation:

$$q_{\mathrm{eq}} = (C_0 - C_{\mathrm{eq}})V / \frac{m}{\rho}\ , \tag{1}$$

where C_0 is initial liquid–phase solute concentration, (mg/L), C_{eq} is equilibrium liquid–phase solute concentration, (mg/L), m is the dose of wet adsorbent, (g), V is the liquid volume, (L), and ρ is the density wet adsorbent, (g/L).

The general Freundlich equation is expressed by:

$$q_{\mathrm{eq}} = k_{\mathrm{f}} C_{\mathrm{eq}}^{\mathrm{n}}\ , \tag{2}$$

where k_{f} is the Freundlich coefficient, (mg/L), n is the Freundlich exponent.

Langmuir's model is expressed by equation:

$$q_{\mathrm{eq}} = \frac{b q_{\mathrm{m}} C_{\mathrm{eq}}}{1 + b C_{eq}}\ , \tag{3}$$

where b is Langmuir constant, (L/mg) , and q_{m} is adsorption capacity, (mg/L).

3.2 Estimation of thermodynamic parameters

For estimation of thermodynamic parameters, such as equilibrium constant K_{ads}, Gibbs free energy $\Delta_{\mathrm{ads}}G$, enthalpy $\Delta_{\mathrm{ads}}H$, and entropy $\Delta_{\mathrm{ads}}S$, the equilibrium adsorption experiments were conducted at three temperatures: 23, 37, and 50 ^oC. The equilibrium constant was taken as the initial slope of the isotherm:

$$K_{ads} = \lim_{c_{eq}\to 0}\left(\frac{q}{C_{eq}}\right) \tag{4}$$

The K_{ads} value was obtained from the linearized form of Langmuir equation, there the adsorption capacity q_m was regarded independent of temperature.

The Gibbs free energy was calculated at each temperature from Eq. (5), where R is the universal gas constant (J/mol K), and T is absolute temperature, (K). The other thermodynamic parameters were calculated using van't Hoff equation (Eq. (6)).

$$\Delta_{ads}G = -RT\ln K_{ads} \tag{5}$$

$$\ln K_{ads} = \frac{\Delta_{ads}S}{R} - \frac{\Delta_{ads}H}{RT} \tag{6}$$

4. Results and discussions

4.1 Effect of pH on the adsorption

The effect of the pH on estradiol adsorption onto adsorbents is illustrated in Fig. 1. No significant effect of pH on the adsorption estradiol onto polymers was observed. Estradiol is neutral at ambient drinking water pH levels with pK_a=10.4. For GAC the highest adsorption was at pH 4. At this condition activated carbon is neutral (i.p. of GAC at pH = 4) as well as estradiol molecule. The lowest of adsorption was at pH 10. At this point carbon particles have negative charge as well as estradiol molecules become to be negative. As the result electrostatic interaction is repulsive.

The adsorption equilibrium data was fitted to Freundlich and Langmuir models. The adsorption constants computed from Eqs. (2) and (3) are presented in the Table 1.

4.2 Influence of ionic strength on adsorption

The adsorption isotherms of estradiol onto adsorbents at the 0.1, 20, and 100 mM NaCl concentrations are plotted in Fig. 2. In the case of polymeric adsorbents, the addition of electrolyte was found to have no remarkable influence on adsorption amount. In the case of AC, adsorption increases with increasing ionic strength. Similar results were described by Zhang and Zhou (2005). Since the double layer thickness at the adsorbent surface is oppositely related to the solution ionic strength,

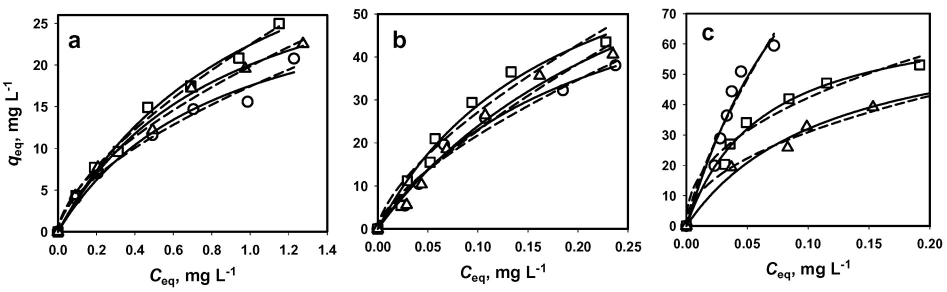

Figure 1. Effect of pH on estradiol adsorption on: (a) XAD-7, (b) XAD-16, (c) AC. Symbols: experimental data at pH = 4 (○), pH = 5.7 (□), and pH = 10(Δ). Lines: solid line – Langmuir model, dashed line – Freundlich model.

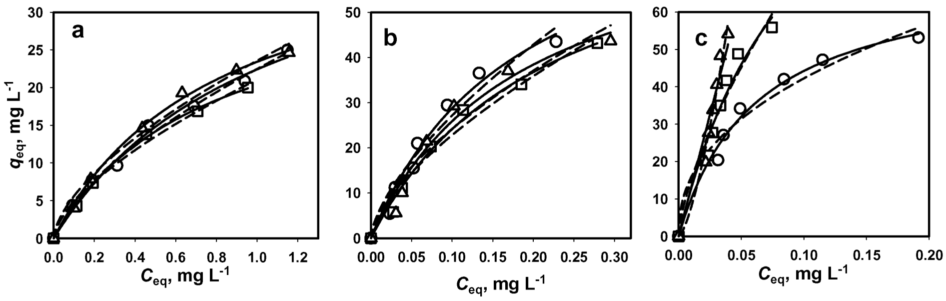

Figure 2. Effect of external solution ionic strength on estradiol adsorption on:(a) XAD-7,(b) XAD-16,(c) AC. Symbols: experimental data at 0.1 M (○), 20 M (□), and 100 mM (Δ). Lines: solid line – Langmuir model, dashed line – Freundlich model.

the range of charges influence of the carbon surface decays with the increase of the salt concentration. Neutral estradiol molecules are adsorbed more strongly onto the less charged surface of GAC. Other possible explanation can be related to the decreasing of aqueous solubility due to presence of salt. As result, E2 molecules being more attracted to the adsorbent particles (Means, 1995). This phenomenon usually referred as "salting out" effect. But, "salting out" effect seems to be not significant because weak effect with other adsorbents.

4.3 Influence of temperature on the adsorption

The effect of temperature on the adsorption of estradiol onto adsorbents at 296–313 K is shown in Fig. 3. In the case of polymeric adsorbents, adsorption capacity decreases with increasing temperature, suggesting that adsorption is exothermic. On the other hand, adsorption of estradiol on the GAC increases with the increasing temperature that indicates endothermic character of adsorption.

The negative values of Gibbs energy about –10 kJ/mol for XAD-7, –14 kJ/mol for XAD-16, and –18 kJ/mol for GAC. Increasing of values in the direction GAC>XAD-16>XAD-7 suggests increase in the strength of the adsorption in the same order. The small negative values of enthalpy for polymeric adsorbents –11 kJ/mol and –26 kJ/mol for XAD-7 and XAD-16, respectively, indicate that the adsorption process has physical nature. The value of enthalpy of the adsorption 58 kJ/mol in the case of GAC indicates rather chemical character of the adsorption. Positive value of enthalpy is not common, but same results have been observed for the adsorption of dyes onto activated carbon (Al-Degs el al., 2008, Namasivayam and Kavitha, 2002).

The adsorption entropy was –0.3 and –4.6 J/mol K for XAD-7 and XAD-16, respectively. The negative value of entropy indicates that degree of freedom decreases at solid/liquid interface during the adsorption. For GAC positive adsorption entropy 33 J/mol K indicates an increased randomness after adsorption. The negative entropy is typical for adsorption of small molecules, whereas positive value is not common. The total entropy of the system is the sum of the entropy of the solutes and that of the solvent molecules. The entropy change of the solute due to adsorption is always negative. However, the solvent molecules, which are surrounding the solute molecules in the liquid phase, are restructured during adsorption. The positive $\Delta_{ads}S$, observed for

GAC, actually originate from increasing entropy of the solvent. The cause of the negative $\Delta_{ads}S$ for adsorption on the XAD polymers is that the entropy of the solutes decreases more than the entropy of the solvent increases.

Table 1. Comparison of the Langmuir and Freundlich parameters of estradiol adsorption onto XAD-16, XAD-7, and GAC adsorbents

Parameter values	Langmuir		R^2	Freundlich		R^2
	q_m, mg/L	b, L/ mg		k_f, (mg/L)	n	
XAD-16						
Temperature (K)						
296	81.7	0.18	0.979	123.4	0.66	0.957
310	66.0	0.16	0.968	106.3	0.65	0.942
323	59.0	0.28	0.999	61.6	0.62	0.987
Ionic strength (M)						
0.0001	81.7	0.18	0.979	123.4	0.66	0.939
0.02	76.9	0.22	0.990	102.6	0.65	0.977
0.1	74.5	0.19	0.970	100.0	0.62	0.938
pH						
4.0	70.6	0.21	0.983	101.9	0.67	0.970
5.6	81.7	0.18	0.979	123.4	0.66	0.957
10.0	97.2	0.30	0.986	127.6	0.74	0.973
XAD-7						
Temperature (K)						
296	44.8	1.1	0.991	22.5	0.66	0.994
310	34.3	0.75	0.998	19.4	0.58	0.993
323	21.0	0.47	0.994	14.5	0.49	0.980
Ionic strength (M)						
0.0001	46.3	1.1	0.991	22.5	0.66	0.994
0.02	35.7	0.75	0.999	21.1	0.64	0.993
0.1	42.5	0.82	0.998	23.6	0.63	0.987
pH						
4	32.2	0.84	0.977	17.4	0.60	0.986
5.6	46.3	1.1	0.991	22.5	0.66	0.994
10	37.8	0.88	0.992	19.9	0.61	0.994
GAC						
Temperature (K)						
296	67.6	0.06	0.986	113.4	0.43	0.970
310	70.7	0.04	0.989	184.6	0.45	0.986
323	88.2	0.02	0.994	143.6	0.25	0.998
Ionic strength (M)						
0.0001	71.7	0.06	0.988	113.4	0.43	0.970
0.02	133.1	0.09	0.968	351.0	0.68	0.956
0.1	-	-	-	6443.5	1.46	0.979
pH						
4	168.4	0.12	0.950	451.6	0.75	0.939
5.6	71.7	0.06	0.968	113.4	0.43	0.970
10	69.2	0.12	0.989	91.7	0.47	0.993

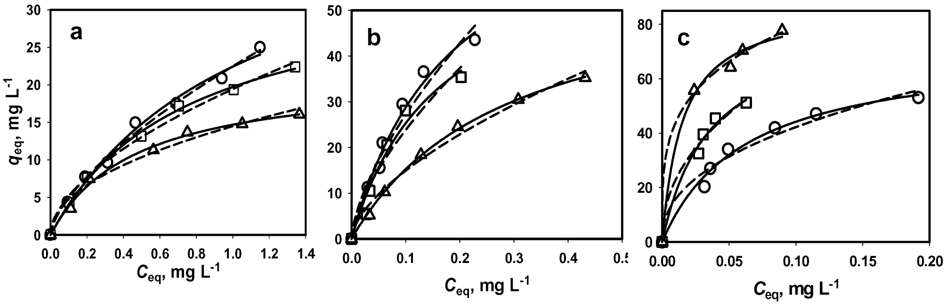

Figure 3. Effect of temperature on estradiol adsorption on: (a) XAD-7, (b) XAD-16, (c) AC. Symbols: experimental data at 296 K (○), 310 K (□), and 323 K (Δ). Lines: solid line – Langmuir model, dashed line – Freundlich model.

5. Conclusions

Adsorption equilibrium of estradiol at different pH, salt concentration, and temperature were measured for the two kinds of polymeric adsorbents and GAC. It was found that better adsorbents for the estradiol removal were styrenic XAD-16 adsorbent and GAC with almost equal capacity values. Results show that adsorption characteristics of activated carbon in the aqueous solution depended on the ambient conditions. High salt concentration as well as low pH facilitates adsorption of estradiol onto GAC. But there are no strong influences of salt concentration and pH were detected in the case of polymeric adsorbents. For all tested adsorbents both Langmuir and Freundlich isotherm models fit very well to experimental data points.

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