REMOVAL OF 17β-ESTRADIOL BY NYLON FILTER MEMBRANE: ADSORPTION KINETICS AND THERMODYNAMICS

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ABSTRACT

The natural estrogen 17β-estradiol (E2) is one of the known endocrine disrupting chemicals (EDCs) that have been entering water systems via human and animal waste products. The adsorption kinetics and thermodynamics of nylon membranes used in a filter for the removal of 17β-estradiol (E2) in water were studied. Experimental results showed that a linear adsorption isotherm was applicable over the E2 concentration range from 0.5 mg L^{-1} to 3.0 mg L^{-1}. The adsorption obeyed pseudo-first-order kinetics and diffusion-limited model. The rate of adsorption was fast, as controlled by surface adsorption rather than diffusive transport into surface sites. Thermodynamic parameters such as standard change in free energy, enthalpy and entropy indicated that adsorption of E2 on a nylon membrane was exothermic.

Key words: *17β-estradiol, nylon membrane, adsorption, isotherm, kinetics, thermodynamics*

1.   INTRODUCTION

The natural estrogen 17β-estradiol (E2) (Figure 1) is one of the known endocrine disrupting chemicals (EDCs) that have been entering water systems via human and animal waste products (Liu et al. 2004; Meng et al. 2005). Even when present at trace concentrations of ng L^{-1}, EDCs can interfere with the regulatory network in humans and wildlife (Le Noir et al. 2007). A study by Lahnsteiner et al., with male rainbow trout exposed to E2 during the spawning season, showed that concentrations ≥ 1 ng L^{-1} were significantly reducing the semen volume obtained per male (Lahnsteiner et al. 2006). It is very important, for ecosystem health, to develop a technique that can clean up wastewater from contamination by EDCs.

The conventional techniques for removal of EDCs include membrane bioreactors (Comerton et al. 2007),(McCallum et al. 2008), ozonation and sand filtration (Nakada et al. 2007), potassium ferrate treatment (Li et al. 2008), reverse osmosis (Hashimoto et al. 2007), ultrasound destruction (Suri et al. 2007), adsorption (Kumar et al. 2009), and aerobic/anaerobic microbial degradation (Lee and Liu 2002). Since estrogens are hydrophobic organic compounds of low volatility, adsorption could play an important role in determining the fate of these compounds during the wastewater treatment process. Activated carbon is the most widely used adsorbent in industrial applications(Lee et al. 2009) Westerhof et al. used activated carbon powder and oxidation (via chlorination and ozonation) to treat natural waters spiked with different EDCs (Westerhoff et al. 2005). Suzuki et al. reported that E2 concentration in the digestion liquid from livestock waste was reduced (by 80%) after treatment with activated carbon adsorption (Suzuki et al. 2009). Ultrafiltration and microfiltration membranes are also used widely in water treatment (Song et al. 2009). Waite et al. observed the accumulation of E1 on hydrophobic hollow fiber membrane surfaces even in the presence of various other compounds (Chang et al. 2003). However, none of these conventional water treatment processes is totally efficient in removing EDCs and E2(Bolong et al. 2009; Jones et al. 2005).
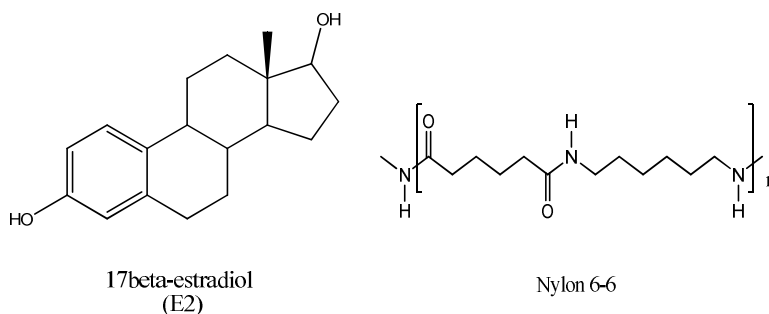

17beta-estradiol
(E2)

Nylon 6-6

Figure 1. Chemical structures of E2 and nylon membranes

Nylon (Figure 1.) membranes have long been recognized for their intrinsically hydrophilic nature that results in easy wetting across the membrane (Pall-corperation 2010). High capillarity and rapid absorbent wicking are obtainable without the necessity of pre-wetting prior to contact with water. Their stability and durability are often showcased as these membranes will not crack, shrink, or tear. The binding mechanism for Nylon 6.6 membranes is through hydrophobic and electrostatic interactions. Their microporous structure provides an available area of up to 300 cm^2 for each cm^2 of planar membrane. From our previous experience, nylon was a good adsorbent for the removal of E2 from water. In this study, we focused on the thermodynamics and kinetics of E2 adsorption onto nylon membrane in water. The equilibrium isotherm was assessed, and kinetic models were developed for batch adsorption. The objective was to determine whether nylon membrane filtration would be a simple, low-cost and time-efficient technology for the removal of E2 from water.

2.   EXPERIMENTAL

2.1. Materials
17β-Estradiol (E2) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Syringe filters with a 25-mm-diameter, 0.45-μm-porosity nylon membrane inside were obtained from Sati International Scientific (Montreal, Quebec, CA). The filter provides a total effective filtration area of 4.9 cm^2 with a membrane mass of 33 ± 1 mg. An enzyme linked immuno sorbent assay (ELISA) kit for E2 determination was purchased from Abraxis (Warminster, PA, USA). Distilled deionized water (DDW), 18-MΩ.cm, was obtained from a Millipore Milli-Q water system (Bedford, MD, USA).

2.2. Instruments
The high performance liquid chromatography (HPLC) system consisted of a solvent pump (Shimadzu LC-6A, Kyoto, Japan), an injector valve (Valco Cheminert VIGI C2XL, Houston, TX, USA) equipped with a 20-μL sample loop, a column (150 x 2 mm, Spherisorb, C8, 3 μm, pore size 120Å, Thermo Scientific, Waltham, MA, USA), a fluorescence detector (PerkinElmer LC240, Waltham, MA, USA), and a data acquisition system (Baseline N2000, Hangzhou, Zhejiang, China). Determination of E2 in water by HPLC used DDW/MeOH/acetonitrile (2:1:1) as the mobile phase. Fluorescence detection (FD) was optimal at excitation and emission wavelengths of 220 nm and 310 nm [(Yu et al. 2007)], with a detection limit of 10 μg L^{-1}. Trace E2 was determined by ELISA using the Abraxis kit and a spectrometer (Thermo Spectronic, USA). With an absorption wavelength of 450 nm, a detection limit of 1.5 ng L^{-1} was attained.

2.3. Adsorption Experiments
For dead-end filtration tests to study the adsorption characteristics of E2, a syringe filter (with nylon membrane inside) was used. Water containing E2 was driven through the filter by a syringe pump (PHYSIO 22, Harvard Apparatus, Holliston, MA, USA), at a flow rate of 5.4 mL min^{-1}.

For batch adsorption tests, nylon membranes were first soaked in Milli-Q water for 24 h. Various process parameters like initial E2 concentration, pH, water temperature, and size of nylon membrane were investigated. Nylon membranes (8.2-67.0 mg) of varying size (1.20-10.2 cm^2) were placed in 20-mL vials, containing 20 mL of E2 aqueous solutions ranging from 20 ng L^{-1} to 3.5 mg L^{-1}. The samples were placed in a water bath (274K - 326K) on top of a magnetic stirrer (1000 rpm) for a specific time period. At the end of batch adsorption, samples were taken from the vials to determine the equilibrium E2 concentrations by HPLC-FD. The amount of E2 adsorbed to the membrane (q_e) was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{A_M}$$
$$(1)$$

where C_0 (μg L^{-1}) is the initial concentration of E2, C_e (μg L^{-1}) is the equilibrium concentration of E2, V is the volume of the aqueous solution (L), and A_M (cm^2) is the area of nylon membrane.

3.   RESULTS AND DISCUSSION

3.1. Kinetics of Adsorption
Pseudo-first-order and pseudo-second-order models have been widely used in understanding adsorption kinetics. These two models were tested for the adsorption of E2 onto a nylon membrane, and the better model was selected on the basis of linear regression coefficient (r^2) values. The pseudo-first-order model can be described by Lagergren's Eq. (2) (Hall et al. 1966; Lagergren 1898).

$$\log (q_e - q_t) = \log q_e - \frac{k_{ad}\, t}{2.303} \tag{2}$$

where q_e and q_t are the amounts of E2 adsorbed (μg cm^{-2}) at equilibrium and at time t (min), and k_{ad} is the pseudo-first-order rate constant (min^{-1}). When log (q$_e$ – q$_t$) is plotted against t, the slope of the straight line yields a value for the rate constant.

Pseudo-second-order kinetics is best described by Ho's Eq. (3) (Ho and McKay 1998):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{3}$$

where k is the rate constant of pseudo-second-order adsorption (cm^2 μg^{-1}min^{-1}) and kq_e^2 is the initial adsorption rate constant (h).
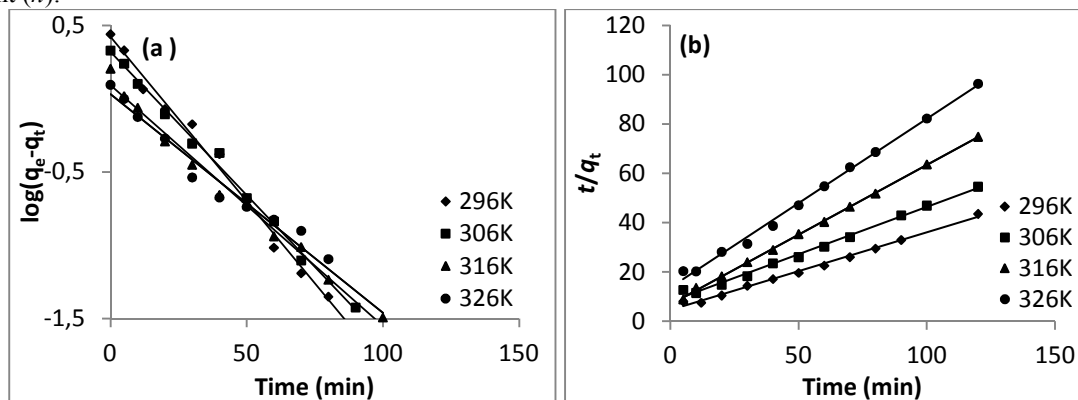

Figure 2. (a) Pseudo-first-order model and (b) pseudo-second-order model for adsorption of E2 onto nylon membrane at different temperatures. Concentration of E2: 1.0 mg L^{-1}; nylon membrane size: 4.9 cm^2.

Table 1. Effect of temperature on rate constants for E2 adsorption onto nylon membrane

	Experimental	Pseudo-first-order model			Pseudo-second-order model				Diffusion-limited model		
T (K)	q_e experimental (μg cm^{-2})	q_e calculated (μg cm^{-2})	r^2	k_{ad} (min^{-1})	q_e calculated (μg cm^{-2})	r^2	k (cm^2 μg^{-1}min^{-1})	h (μg cm^{-2} min^{-1})	q_e calculated (μg cm^{-2})	r^2	A
296	2.754	2.708	0.994	0.051	3.174	0.993	0.0062	0.7716	3.166	0.992	0.035
306	2.128	2.165	0.997	0.044	2.621	0.993	0.0052	0.4392	2.165	0.976	0.022
316	1.602	1.534	0.993	0.037	1.785	0.999	0.0130	0.5092	1.933	0.982	0.012
326	1.242	1.211	0.997	0.032	1.466	0.995	0.0097	0.2554	1.812	0.897	0.008

We applied the pseudo-first-order and pseudo-second-order models for four different temperatures, and the results are presented in Table 1. Both models basically include all steps of adsorption such as external film diffusion, adsorption, and diffusion adsorption (Hall et al. 1966; Ho and McKay 1998; Lagergren 1898). Figure 2 shows the linearized plots of the pseudo-first-order and pseudo-second-order models. As we can see, the correlation coefficients obtained for the two models were similar. When the temperature was changed from 296K to 326K, the adsorption rate constant for pseudo-first-order decreased from 0.051 to 0.032 min^{-1}; the initial adsorption rate for pseudo-second-order model, h, decreased from 0.77 to 0.25 μg cm^{-2} min^{-1}. In addition to the r^2 values, the amount of E2 adsorbed at equilibrium, q_e, calculated from the pseudo-first-order model is more comparable with the experimental data. This suggests that adsorption of E2 molecules to nylon membrane can be interpreted by the formation of 1:1 surface complexes, the rate of which depends on the E2 concentration in solution to a first order.

3.2. Diffusion-limited Model
Adsorption is generally regarded as a process involving both solution-phase transport and surface processes. Transport from the bulk solution to the solution layer next to the membrane surface can be neglected because vigorous magnetic stirring is employed (as done in this study). After entering the pores, each E2 molecule must diffuse to an available binding site, where an adsorption "bond" between E2 and the membrane is formed. The adsorption can be considered diffusion controlled if diffusion is much slower than adsorption, or reaction controlled if the opposite is true (Bornzin and Miller 1982). On the basis of the one-dimensional diffusion equation and the

Smoluchowski boundary condition (an assumption that the solute concentration adjacent to the membrane surface is zero), the following expression can describe E2 diffusion to the membrane surface (Jones and O'Melia 2000):

$$q_t = q_e \left\{ 1 - \exp\left[\left(\frac{2AC_0}{q_e}\right)\left(\frac{Dt}{\pi}\right)^{1/2} \right] \right\} \tag{4}$$

where D is the Stokes diffusion coefficient (dm^2/min); q_t and q_e are surface concentrations ($\mu g\ cm^{-2}$) at time t (min) and at equilibrium, respectively; C_0 is the initial E2 concentration (ng/L); and A is a parameter with a value between 0 and 1, When $A \to 1$, the adsorption rate can be considered to be limited by diffusion(Chang et al. 2003).

When our experimental data were fitted into the kinetic behavior described by Eq. 4 for batch adsorption, the correlation coefficients obtained were between 0.897-0.992 (see Table 1). In the simulation, A was used as a fitting parameter which turned out to be 0.008-0.035. Although there was a linear match between the experimental data and the kinetic behavior described by the diffusion limitation model, the small value of A that the adsorption rate was much lower than the diffusion rate. In other words, processes other than diffusion controlled the rate of E2 adsorption onto the membrane surface under the given experimental conditions. This finding indicates that the solute concentration adjacent to membrane surface was not zero. Hence, surface adsorption was the principal limitation rather than diffusive transport to binding sites (located both on the surface and inside the pores of nylon membrane).

3.3. Adsorption Isotherms

Isotherms are useful in understanding the adsorption interaction and estimating some design parameters. Our equilibrium adsorption data were analyzed using both the Freundlich's and Langmuir's isotherm models. The Freundlich's isotherm model is commonly used to study non-ideal adsorption involving heterogeneous phenomena:

$$C_{se} = K_f C_e^{1/n} \tag{5}$$

where K_f and n are constants for the capacity and intensity of adsorption, respectively, incorporating all influencing factors. Linear Freundlich plots of log C_{se} versus log C_e were constructed, where C_e (mg L^{-1}) is the equilibrium concentration of E2 and C_{se} (mg g^{-1}) is the amount of E2 adsorbed at equilibrium. Based on our adsorption data, E2 partitioning between the nylon membrane and the aqueous solution at equilibrium could be described by a Freundlich equation of $C_{se} = 1.10\ C_e^{1/1.06}$ for 296K. The straight line fit produced a correlation coefficient (R^2) > 0.994, indicating a high acceptability of the Freundlich's model (see Fig. 3b).
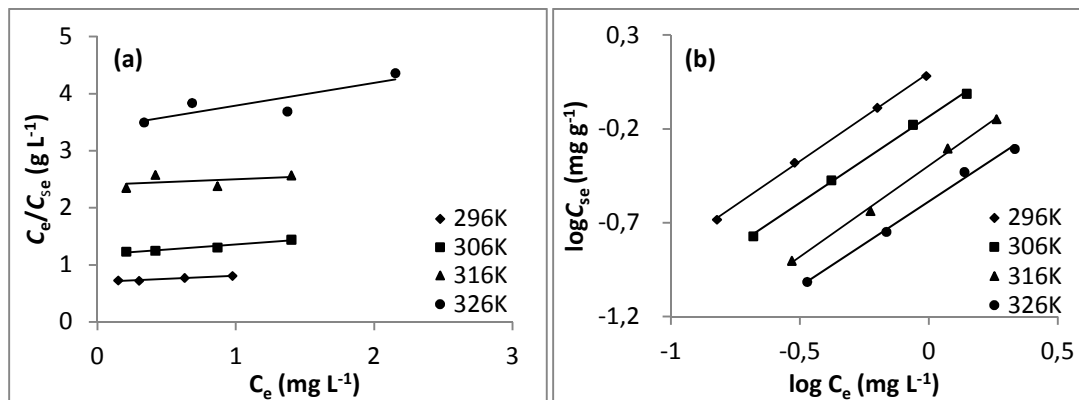

Figure 3. (a) Langmuir plot and (b) Freundlich plot for adsorption of E2 by nylon membrane at different temperatures. Nylon membrane size: 4.9 cm^2.

The Langmuir's isotherm model for evaluating monolayer adsorption phenomena is described by the general equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{6}$$

where C_e (mg L^{-1}) is the equilibrium concentration of E2, C_{se} (mg g^{-1}) is the amount of E2 adsorbed at equilibrium, and Q_0 and b are the Langmuir constants related to the capacity and energy of adsorption, respectively. Fitting of our experimental data to the Langmuir's adsorption isotherm (see Fig. 3 a) showed significantly less linearization (R^2 ranging from 0.189 to 0.954) than the Freundlich's isotherm model, thus indicating its non-acceptability.

3.4. Thermodynamic Parameters

Thermodynamic properties, such as the Gibbs free energy change (ΔG^0, J mol^{-1}), enthalpy change (ΔH^0, J mol^{-1}) and

entropy change (ΔS^0, J mol^{-1} K^{-1}) were obtained from analysis of experimental data at different temperatures using the following equations

$$\Delta G^0 = -RTlnK$$
(6)

$$lnK = -\frac{\Delta G}{RT} = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{RT}\right)$$
(7)

where K is the thermodynamic equilibrium constant, i.e., ratio of the equilibrium E2 concentration on the adsorbent (membrane) to that in the solution. This constant is determined using the method of Wu and Yu (Wu and Yu 2006) by plotting $ln(q_e/C_e)$ versus q_e and extrapolating to zero (see Fig. 4).
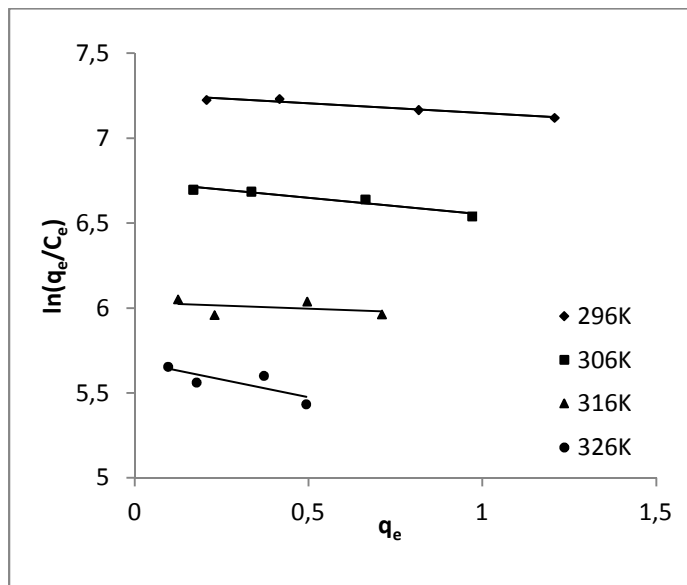

Figure 4. Plots of ln(q$_e$/C$_e$) as a function of q$_e$ for adsorption of E2 on nylon membrane

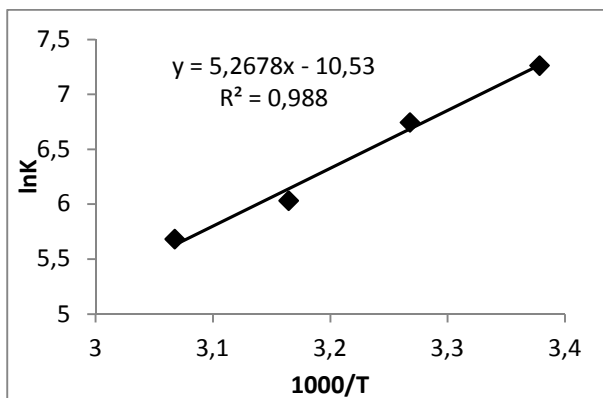*Figure 5.   Van't Hoff plot for adsorption of E2 on nylon membrane*

A plot of lnK versus 1000/T yielded a straight line in the Van't Hoff plot (see Fig. 5). The values of ΔH^0 and ΔS^0 obtained from the slope and intercept of the plot are summarized in Table 2. The negative value of ΔH^0 (-43.8 ± 0.1 kJ mol^{-1}) indicates the exothermic nature of adsorption. Figure 2 above showed that adsorption capability decreased with increasing temperature, which is now confirmed by the negative value of ΔH^0. The negative value of ΔS^0 (-87.5 ± 0.1 J mol^{-1} K^{-1}) can be explained by E2 adsorption to the nylon membrane, which resulted in a decrease in freedom. The negative value of ΔG^0 indicates a decrease in Gibbs free energy, which verifies the feasibility and spontaneity of the adsorption process with a high affinity of E2 towards nylon membrane.

Table 2. Thermodynamic parameters for the adsorption of E2 on nylon membrane

T (K)	ΔG^0 (J mol^{-1})	ΔH^0 (J mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
296	-17,878		
306	-17,003	-43,792	−87.5
316	-16,129		
326	-15,252		

3.5. Dead End Filtration

Filtration of E2 aqueous solutions through a nylon membrane exhibited a high retention of E2 due to adsorption. Assuming that partitioning of E2 onto the membrane walls attained equilibrium quickly when the E2 solution was passing through the porous membrane, the concentration of E2 in the filtrate and the amount of E2 accumulated on the membrane walls (q_s) can be described by an isotherm relationship. From the discussion in Section 3.3, the Freundlich's isotherm model can be written as:

$$C_{\text{filtrate}} = 0.904\, q_s^{1.06} \quad \text{(at 296K)} \tag{8}$$

and the membrane retention (R) due to adsorption can be expressed as:

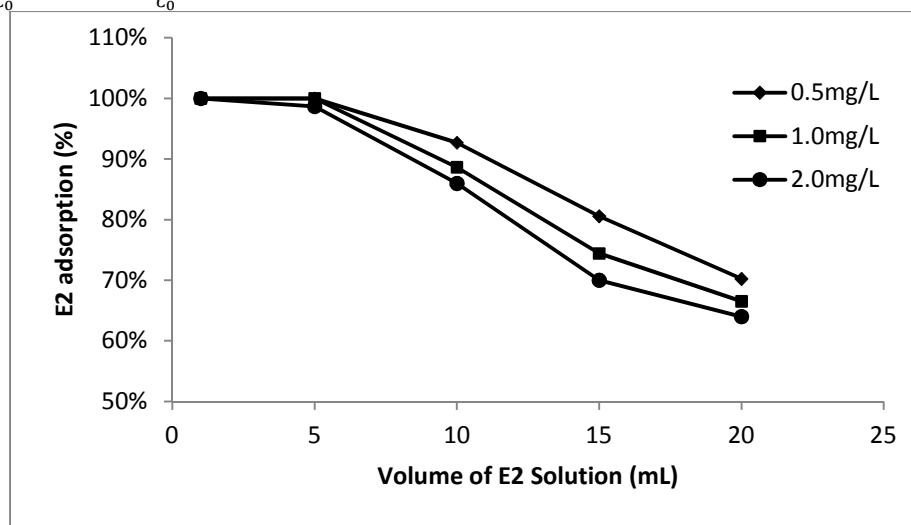$$R = 1 - \frac{C_{\text{filtrate}}}{C_0} = 1 - \frac{0.904 q_s^{1.06}}{C_0} \tag{9}$$

Figure 6. Decrease in membrane retention (or E2 adsorption) with E2 solution volume during dead-end filtration.
Flow rate: 5.4 mL min^{-1}; nylon membrane size: 4.9 cm^2.

Figure 6 shows the changes in membrane retention during dead-end filtration of E2 solution. It can be seen that E2 adsorption (representing R) by the nylon membrane inside a syringe filter decreased with increasing solution volume. This trend agrees with the prediction from Eq.(9) that the retention of E2 will decrease with increasing amount of E2 (q_s) accumulated on the membrane walls. When the surface concentration accumulated up to the equilibrium value dictated by the E2 concentration in the influent, membrane retention would become zero and no further adsorption of E2 would occur. The time taken for the membrane walls to become saturated depends on the rate of adsorption. Finally, a comparison of the 0.904 for dead-end filtration (in Eq. 8) with the 1.10 for batch adsorption (under Eq. 5) suggests that filtration is not as efficient as batch adsorption, albeit faster, for removing E2 from the aqueous solution.

4. CONCLUSION

E2 adsorption onto nylon membrane was found to be pseudo-first-order in batch binding kinetics, and the experimental results fitted well into the linear Freundlich's adsorption isotherm. The adsorption equilibrium constants at various temperatures were used to determine the thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0. The ΔG^0 value was negative, signifying the spontaneous nature of adsorption. The negative value of ΔH^0 showed that adsorption was favored at low temperatures. The retention of E2 during dead-end filtration decreased gradually with time, due to an increasing amount of E2 accumulated on the membrane walls.

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