Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1075161

57 (2016) 15570–15579
July

Taylor & Francis
Taylor & Francis Group

Evaluation of the effectiveness of microparticle-embedded cryogel system in removal of 17*β*-estradiol from aqueous solution

Aslı Göçenoğlu Sarıkaya, Bilgen Osman*, Ali Kara

Department of Chemistry, Uludag University, Gorukle Campus, Bursa 16059, Nilufer, Turkey, Tel./Fax: +90 224 2942863; email: agocenoglu@uludag.edu.tr (A. Göçenoğlu Sarıkaya), Tel./Fax: +90 224 2941735; email: bilgeno@uludag.edu.tr (B. Osman), Tel./Fax: +90 224 2941733; email: akara@uludag.edu.tr (A. Kara)

Received 22 April 2015; Accepted 11 July 2015

ABSTRACT

In this study, we have synthesized microparticle-embedded cryogel system for removal of 17*β*-estradiol (E2). Firstly, the poly(hydroxyethyl methacrylate-N-methacryloyl-L-tryptophan methyl ester) poly(HEMA-MATrp) microparticles were produced by emulsion polymerization. And then, poly(HEMA-MATrp) microparticles were embedded in poly(hydroxyethyl methacrylate) cryogel and [PHEMA/MATrp] cryogel system was prepared. [PHEMA/MATrp] cryogel system was used for the removal of E2. The characterization studies of the poly(HEMA-MATrp) microparticles and cryogel system were conducted by infrared spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and swelling studies. The effects of initial concentration, temperature, and contact time on adsorption of E2 were investigated. Maximum adsorption capacity of PHEMA/MATrp cryogel was determined as 2.75 mg E2/g cryogel at 25°C. The adsorption process obeyed both pseudo-second-order and intraparticle diffusion kinetic models. All the isotherm data can be fitted Langmuir isotherm model with high correlation coefficients for all studied temperatures. Thermodynamic parameters $\Delta H^\circ = 654.9$ J/mol, $\Delta S^\circ = 85.90$ J/K/mol, and $\Delta G^\circ = -23.14$ to −26.23 kJ/mol with the rise in temperature from 4 to 40°C indicated that the adsorption process was endothermic and spontaneous. The E2 adsorption capacity did not change after five batch successive adsorption–desorption cycles, demonstrating the usefulness of the microparticle-embedded cryogel system in applications.

Keywords: Endocrine disrupting; Cryogel; Estradiol; Removal; Particle-embedded

1. Introduction

Endocrine-disrupting contaminants (EDCs) cause many defects on human and wild life such as reproductive system deformities on humans [1], cancer risk [2], human infertility [3], feminization of male fish [4], or masculinization of females [5]. EDCs which are mostly natural female hormones like 17*β*-estradiol (E2) [5] or consumer products such as pharmaceuticals and personal care products [4], pollute the environment [6] and diffuse the water resources at low concentrations [4]. Due to this, water-treatment methods become more important to remove EDCs from surface and drinking water [1]. Even though the common methods like oxidation processes [7], ozonation [8], sand filtration [9], chlorination [10], nanofiltration, and reverse

*Corresponding author.

1944-3994/1944-3986 © 2015 Balaban Desalination Publications. All rights reserved.

osmosis systems [11,12] are traditional but are not specific and expensive for constant removing.

As a result of the importance of EDCs such as estrone and 17β-estradiol, their occurrence and environmental behavior has been widely studied. In comparison to traditional contaminants such as pesticides, the concentrations of the most potent EDCs (e.g. steroidal hormones) are low, generally within ng/L range. In a study of several sewage treatment works (STW) in the UK, STW effluents contained 17β-estradiol at a concentration of 1–50 ng/L. In 16 German municipal STW effluents, estrogens were measured at concentrations up to 80 ng/L estrone, 3 ng/L 17β-estradiol, and 15 ng/L 17α-ethynylestradiol, and in 10 Canadian STW effluents corresponding values of 48 ng/L estrone, 64 ng/L 17β-estradiol, and 42 ng/L 17α-ethynylestradiol were reported [13]. In addition, EDCs have been detected in drinking water supplies in pg/L range [14]. All these results would suggest that the current sewage treatment processes have limited capacity in removing certain EDCs.

Due to the high porosity, high permeability, soft, flexibility, and high flow velocity cryogels are widely used as new chromatographic materials for separation and purification of biomolecules, such as proteins, plasmid DNA, and viruses, from crude feedstocks [15–17] and also different applications as immobilization matrices in biotechnology [18–21], as scaffolds in tissue engineering [22–26], and as drug-delivery carriers in pharmaceutical fields [27]. Cryogels permit the free passage of microparticles, nanoparticles, or bioparticles without blockage because of the pore size within the range of 10–100 μm. Cryogels have many advantages like large pores, short diffusion path, low pressure drop, and very short residence time but due to the large pores, the adsorption capacity of biomolecules is low. For increasing the surface area particle embedding will become a new approach in bioseparation prosesses [28].

Considering the potential impacts of EDCs, it is highly important to remove them from wastewater before discharge. The objectives of this study were therefore to study the kinetics and equilibria of E2 removal from water by adsorption, and to evaluate the effects of various parameters on adsorption performance. Firstly, poly(hydroxyethyl methacrylate) (PHEMA) cryogel embedded with poly(hydroxyethyl methacrylate-N-methacryloyl-L-tryptophan methyl ester) poly(HEMA-MATrp) microparticles and [PHEMA/MATrp] cryogel system was prepared. PHEMA/MATrp cryogel was characterized by swelling tests, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and infrared spectroscopy (IR). To evaluate the efficiency of PHEMA/MATrp cryogel to separate E2 from aqueous solution, the effect of various experimental parameters such as initial concentration, contact time, and temperature to E2 adsorption were determined. In order to clarify the adsorption process, adsorption isotherms and kinetic studies were conducted and thermodynamic parameters were also calculated.

2. Experimental

2.1. Materials

17β-estradiol (E2) (≥98%) was supplied by Sigma (St. Louis, USA). Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 4°C until used. L-tryptophan methyl ester and methacryloyl chloride were purchased from Sigma Chemical Co. (St. Louis, USA). The polyvinyl alcohol (PVAL; Mw: 100.000, 98% hydrolyzed) was supplied by Aldrich Chem. Co. (USA). N,N´-Methylene-bis(acrylamide) (MBAAm) and ammonium persulfate (APS) were purchased from Sigma (St. Louis, USA). All other chemicals were of reagent grade and were purchased from Sigma–Aldrich and Merck AG (Darmstadt, Germany). All water used in the binding experiments was purified using a Barnstead (Dubuque, IA) ROpure LPw reverse osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731), followed by a Barnstead D3804 NANOpurew organic/colloid removal and ion-exchange packed-bed system.

2.2. Synthesis of N-methacryloyl-L-tryptophan methyl ester (MATrp) monomer

The synthesis and characterization of functional monomer MATrp were reported previously [29]. In the synthesis reaction, L-tryptophan methyl ester (5.0 g) and hydroquinone (0.2 g) were dissolved in 100 mL of dichloromethane solution. This solution was cooled to 0°C. Triethylamine (12.7 g) was added to the solution. Methacryloyl chloride (5.0 mL) was poured slowly into this solution and then stirred magnetically at room temperature for 2 h. At the end of the chemical reaction, hydroquinone and unreacted methacryloyl chloride were extracted with a 10% NaOH solution. The aqueous phase was evaporated in a rotary evaporator. The residue (i.e. MATrp) was recrystallized in ethanol. The NMR spectrum of MATrp was given in our previous paper [29].

2.3. Preparation of poly(HEMA–MATrp) microparticles

Poly(HEMA–MATrp) microparticles were produced by surfactant-free emulsion polymerization. For

synthesis, the following experimental procedure was applied: 0.5 g of poly(vinyl alcohol) was dissolved in 100 mL of deionized water and added to the polymerization reactor. Then, 0.65 mmol of HEMA, 5.82 mmol of EGDMA, and 100 μL of MATrp monomer were added to this solution and slowly stirred for 30 min. 0.063 g of potassium persulphate was added in the reactor as an initiator and was conducted at 40˚C for 24 h. After the polymerization, microparticles were cleaned by washing with ethanol and water several times to remove the unreacted monomers at room temperature. For this purpose, the microparticles were precipitated and collected with the help of a centrifuge (Beckman Coulter, Allegra-64R Centrifuge) at 18 000 *g* for 1 h and resuspended in ethanol and water several times. After that poly(HEMA–MATrp) microparticles were further washed with deionized water.

2.4. Preparation of PHEMA/MATrp cryogel

Water and MBAAm were added in the polymerization recipe as the pore-former and cross-linker, respectively. Preparation procedure is as follows: HEMA (1.3 mL) and poly(HEMA-MATrp) microparticle solution (3.7 mL) were dissolved in deionized water (5.0 mL). Poly(HEMA-MATrp) microparticle solution contains 1.2 mg microparticle per mL. MBAAm (0.283 g) was dissolved in deionized water (10 mL). Second solution was mixed with the previous one. The cryogel was then prepared by free radical polymerization initiated by TEMED (25 μL) and APS (20 mg). After adding APS (0.1% (w/v) of the total monomers), the solution was cooled in an ice bath for 2–3 min. TEMED (0.1% (w/v) of the total monomers) was added and the reaction mixture was stirred for 1 min. The reaction mixture was poured immediately into plastic syringe (total volume: 5 mL, internal diameter: 0.8 cm) with closed outlet at the bottom. The polymerization solution in the syringe was frozen at −12˚C for 24 h and then thawed at room temperature. In order to remove unreacted monomers and initiator, the cryogel was washed with 200 mL of water, cut into circular disks (1.0 cm in diameter), and stored in buffer containing 0.02% sodium azide at 4˚C [30]. The optical photograph of poly(HEMA-MATrp) microparticle-embedded PHEMA/MATrp cryogel disks was given in Fig. 1.

2.5. Characterization of PHEMA/MATrp cryogel

FTIR spectrum of poly(HEMA–MATrp) microparticles was obtained using a (FTIR spectrophotometer Perkin Elmer, Spectrum 100, USA).

Fig. 1. Optical photograph of PHEMA/MATrp cryogel.

The surface morphology and internal structure of PHEMA/MATrp cryogel were observed via a scanning electron microscope (Jeol, JEM 1200EX, Tokyo, Japan).

The swelling degree of the cryogel disk (*S*) was determined as follows: cryogel disk was washed on porous filter until washing was clear. Then it was sucked dry and then transferred to pre-weighed vial and weighed ($m_{\text{wet gel}}$). After drying to constant mass in the oven at 60˚C, the mass of dried cryogel disk was determined ($m_{\text{dry gel}}$). The swelling degree was calculated as:

$$S = (m_{\text{wet gel}} - m_{\text{dry gel}})/m_{\text{dry gel}} \quad (1)$$

The chemical composition of the poly(HEMA-MATrp) microparticle surface was analyzed using XPS Apparatus (PHI-5000) from PHI, USA. The experimental conditions are as follows: the energy of excitation source monochromatic Al K_α radiation is 1,486.6 eV, and survey scan range is 0–1,100 eV. The electron take-off angle was fixed at 45˚. After scanning the overall spectrum for 2–3 min, peaks over narrow ranges were recorded for 4–5 min.

2.6. Batch adsorption experiments

Batch analysis was used for the determination of adsorption isotherms. Cryogel disks were put into a

100 mL Erlenmeyer containing a solution of E2 at desired temperatures. The equilibrium was allowed in 100 mL erlenmayer flasks kept in a Heidolph Unimax 1010 incubator at a constant shaking speed of 140 rpm, at 3 h. The concentrations of E2 were determined spectrophotometrically (272 nm). The amount of adsorbed E2 was calculated as:

$$Q = \frac{[(C_0 - C)]V}{m} \quad (2)$$

where Q is the amount of adsorbed E2 on a unit mass of the beads (mg/g); C_0 and C are the concentrations of E2 in the initial solution and final solution after treatment for a certain period of time, respectively (mg/L); V is the volume of the aqueous phase (mL); and m is the mass of the cryogel disk used (g).

The initial concentration of E2 was determined using calibration plot obtained with pure E2 solutions at different concentrations. The measurements were performed spectrophotometrically at 272 nm.

In order to investigate the effect of initial E2 concentration to adsorption capacity of PHEMA/MATrp cryogel at different temperatures (4, 25, and 40°C), the concentration of E2 in the medium varied in the range of 10–100 mg/L at pH 7.0. The solutions were prepared using methanol:water mixture (1:1 v/v) as solvent because of low solubility of E2 in water.

Adsorption kinetics was determined by analyzing uptake of the E2 from the solution at different time intervals for 180 min at 50 mg/L initial E2 concentration.

2.7. Desorption of E2 from PHEMA/MATrp cryogel

In order to determine the reusability of PHEMA/MATrp cryogel, the E2 adsorption and desorption cycle were repeated five times using the same cryogel (initial E2 concentration: 50 mg/L). The E2 desorption from the PHEMA/MATrp cryogel was carried out using acetonitrile:methanol (v:v; 7:3), by stirring magnetically at 140 rpm at room temperature for 3 h. The final concentration of E2 in the aqueous phase was determined by spectrophotometric method.

3. Results and discussion

3.1. Properties of PHEMA/MATrp cryogel

FTIR spectra of poly(HEMA–MATrp) microparticles and poly(HEMA) cryogel were recorded to determine the existence MATrp monomer in the polymeric structure of poly(HEMA-MATrp) microparticles (Fig. 2). The broad peak in the range of 3,200–3,500 cm^{-1} is due to the stretching of –OH groups of HEMA. The intensive peak at 1,719 cm^{-1} corresponds to the stretching vibration band of C=O group and C–H stretching at 2,942 cm^{-1}. In addition, the characteristic adsorption band regarding the stretching vibration of carbonyl group belongs to amide bond at

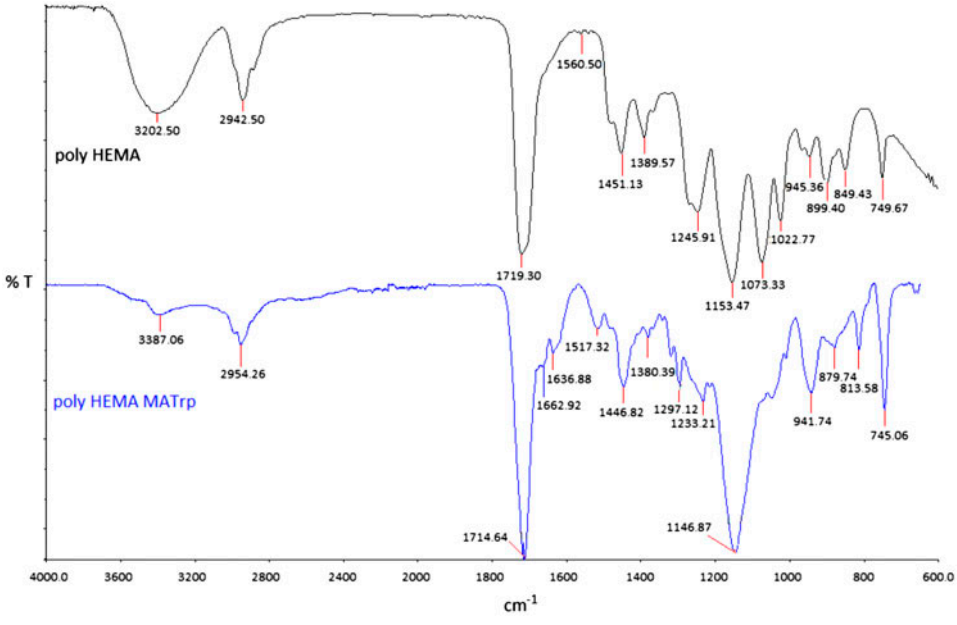

Fig. 2. FTIR spectra of poly(HEMA–MATrp) microparticles and poly(HEMA) cryogel.

1,662 cm^{-1} in the FTIR spectrum of poly(HEMA-MATrp) microparticles supports that MATrp monomer was successfully incorporated into polymeric structure.

The SEM images of the internal structure of PHEMA/MATrp cryogel disks are shown in Fig. 3. The microparticles are in spherical form. The average diameter of poly(HEMA-MATrp) microparticles is approximately 2.5 μm. The PHEMA/MATrp cryogel disks produced in such a way have porous and thin polymer walls, large continuous interconnected pores that provide channels for the mobile phase to flow through. Pore size of the matrix allows E2 to enter easily through the pores. The swelling degree was found as 6.37 g H_2O/g for PHEMA/MATrp cryogel disk. Polymeric cryogel disk is elastic, white, opaque, and sponge like. This cryogel disk can be easily compressed by hand to remove the water accumulated inside the pores. When the compressed piece of cryogel was submerged in water, soaked in water, and within 1–2 s restored its original size and shape due to its shape memory.

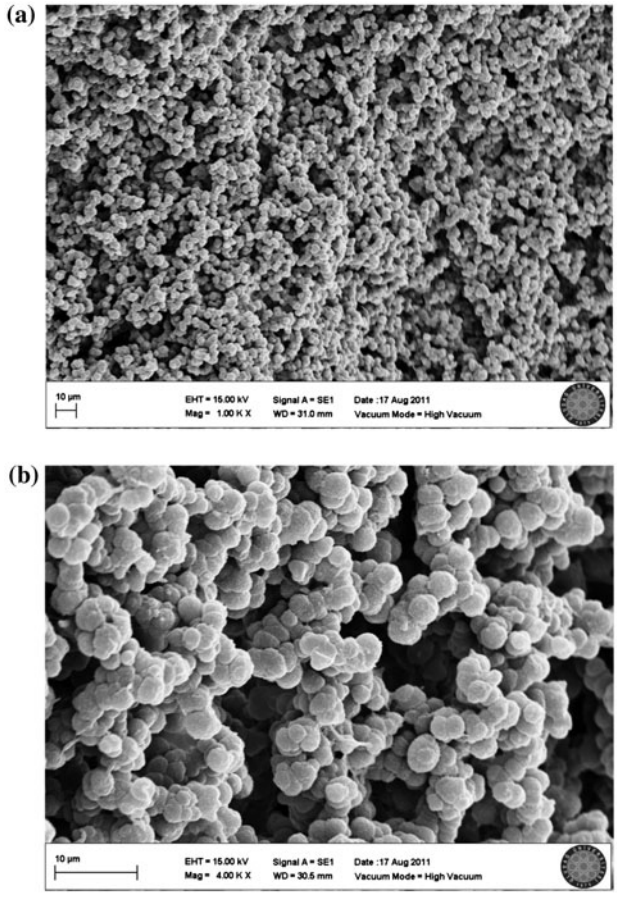

Fig. 3. The SEM images of the PHEMA/MATrp cryogel at different magnifications (a) 1000X and (b) 4000X.

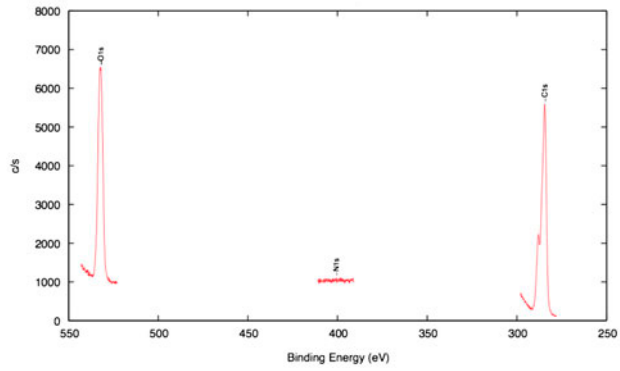

Fig. 4. The XPS spectrum of the poly(HEMA-MATrp) microparticles.

The XPS spectrum of the poly(HEMA-MATrp) microparticles was shown in Fig. 4. The element ratio % for C1s (287 eV), O1s (534 eV), and N1s (400 eV) was determined as 69.9% C1s, 29.8% O1s, and 0.2% N1s, respectively (data not shown). The existence of N atoms in the surface elemental composition certified that MATp monomer added to chemical structure of microparticles.

3.2. Kinetic, isotherm, and thermodynamic analyses of E2 adsorption on PHEMA/MATrp cryogel disks

3.2.1. Kinetic studies

Kinetic studies were perfomed at three different temperatures at 50 mg/L initial concentration of E2. The increasing E2 adsorption with the rise in temperature from 277 to 313 K shows that the adsorption is endothermic (Fig. 5). For all tested temperatures, adsorption rates were extremely fast in the first 60 min. This result shows that the PHEMA/MATrp cryogel disks can be effectively used to separate E2 from aqueous phase. For testing the dynamic experimental data, pseudo-first-order kinetic model [31], pseudo-second-order kinetic model [32], and intraparticle diffusion model [33] were used at the initial concentration, 50 mg/L E2, and three temperatures (277, 298, and 313 K) for 180 min (Fig. 5).

The linear form of the applied model can be given as:

$$\text{Pseudo-first-order}: \ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\text{Pseudo-second-order}: \ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$\text{Intraparticle diffusion}: \ q_t = k_i t^{1/2} \quad (5)$$

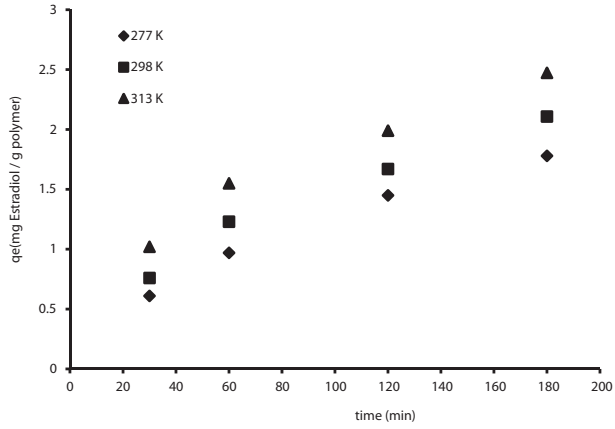

Fig. 5. Effect of temperature on adsorption of E2 onto the PHEMA/MATrp cryogel disks.

where k_1 (1/min) and k_2 ((g/mg)/min) are kinetic constants for pseudo-first-order and pseudo-second-order kinetic models, respectively. k_i ((mg/g)/min$^{1/2}$) is the intraparticle diffusion rate constant, and C (mmol/g) is the constant proportional to the extent of boundary layer thickness. The values of constants in Eqs. (3)–(5) can be obtained from the slopes and intercepts of the fitted curves.

The validities of these three kinetic models for all temperatures were checked and the values of the parameters and correlation coefficients obtained from these three kinetic models are all listed in Table 1. The adsorption kinetics of E2 for all tested kinetic models was also given in Fig. 6. The highest correlation coefficient values of pseudo-second-order model for all temperatures and the closest q_e (experimental) to q_e (calculated) indicated the second-order nature of the present adsorption process. In addition, the intraparticle diffusion model has high correlation coefficients for all studied temperatures due to high porosity of poly(HEMA-MATrp) microparticle-embedded poly (HEMA) cryogel.

The adsorption rate constant of pseudo-second-order of adsorption, k_2, is a function of solution temperature by the following Arrhenius-type relationship;

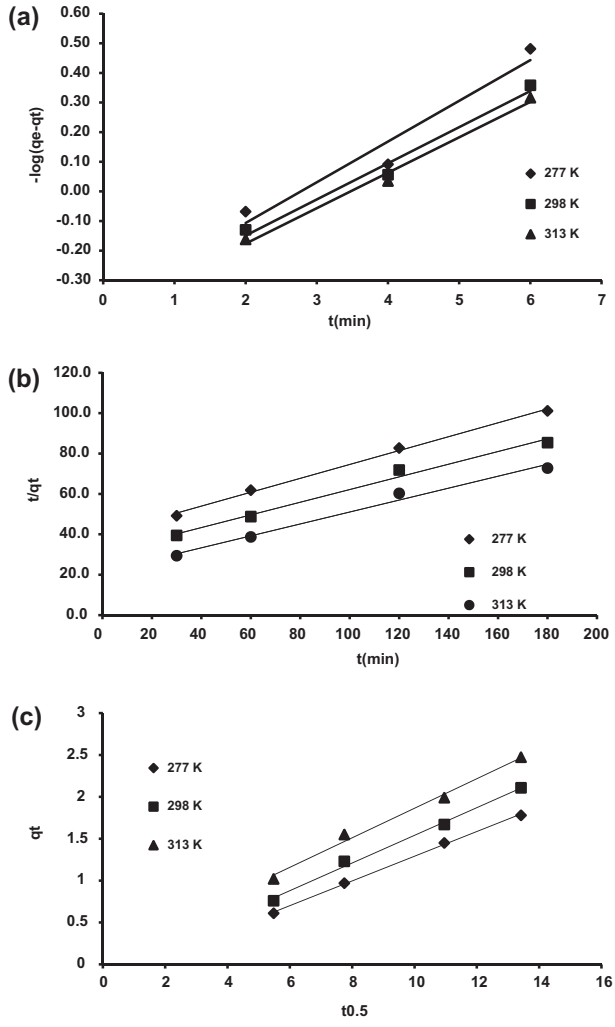

Fig. 6. Adsorption kinetics of adsorption of E2 onto the PHEMA/MATrp cryogel disks at different temperatures: (a) pseudo-first-order, (b) pseudo-second-order, and (c) intraparticle diffusion.

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \tag{6}$$

Table 1
Kinetic parameters for the adsorption of estradiol onto the PHEMA/MATrp cryogel disks

Parameters		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model	
Temperature (K)	Experimental q_e (mg/g)	$k_1 \times 10^{-2}$ (1/min)	q_{eq} (mg/g)	R^2	$k_2 \times 10^{-3}$ ((g/mg)/min)	q_{eq} (mg/g)	R^2	$k_1 \times 10^{-2}$ ((mg/g)/min$^{0.5}$)	R^2
277	1.780	31.64	2.407	0.9447	2.942	2.908	0.9965	14.76	0.9989
298	2.108	28.09	2.472	0.9816	3.202	3.186	0.9876	16.51	0.9943
313	2.473	27.54	2.603	0.9898	4.072	3.382	0.9865	17.64	0.9905

where k_0 is the independent temperature factor (g/(mg min)), R is the gas constant (8.314 J/mol/K), and T is the solution temperature (K). The values of the k_2 increased from 2.942×10^{-3} to 4.072×10^{-3} g/mg min, for an increase in the solution temperature of 277–313 K.

From Arrhenius equation, the activation energy (E_a) for E2 adsorption was calculated as 6.171 kJ/mol. The calculated activation energy value was within the typical activation energy range for physical adsorption. If the activation energy is less than 25–30 kJ/mol, the adsorption occurs by diffusion-controlled process [34,35]. The calculated activation energy value was below 25 kJ/mol, which provides the evidence that the adsorption rate of E2 is controlled by diffusion.

3.2.2. Isothermal studies

Adsorption isotherm data of E2 were derived at 277, 298, and 313 K temperatures. As shown in Fig. 7, the adsorption amount increased for all temperatures with increasing initial concentration of E2. The maximum E2 adsorption capacity of the PHEMA/MATrp cryogel disks was determined as 2.75 mg/g cryogel at 298 K.

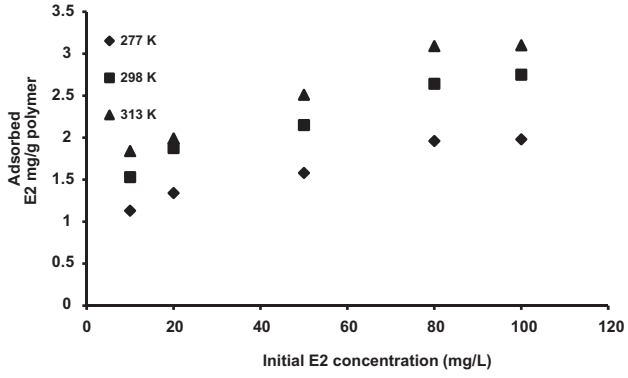

Fig. 7. Effect of initial concentration of estradiol onto the PHEMA/MATrp cryogel disks.

The isotherm data were treated according to Langmuir and Freundlich isotherm models. The linear forms of the applied models can be given as:

$$\text{Langmuir}: \frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \tag{7}$$

$$\text{Freundlich}: \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{8}$$

where Q_L (mg/g) is the maximum amount of E2 per unit weight of the PHEMA/MATrp cryogel disks to form complete monolayer coverage on the surface bound at high equilibrium E2 concentration C_e (mg/L), and K_L is Langmuir constant related to the affinity of binding sites (L/mg). q_e is the amount of adsorbate adsorbed at equilibrium time (mg/g), K_f (mg/g) $(L/mg)^{1/n}$ and n are isotherm constants that indicate capacity and intensity of the adsorption, respectively.

All isotherm parameters were obtained from the slopes and intercepts of the fitted straight lines and were summarized in Table 2. Langmuir isotherm fits well with the experimental data correlation coefficient ($0.9871 \le R^2 \le 0.9983$). Calculated maximum capacities are close to maximum capacities obtained at equilibrium (Table 2). The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of binding sites on the PHEMA/MATrp cryogel surface since the Langmuir equation assumes that the surface is homogeneous.

$$R_L = \frac{1}{1 + K C_e} \tag{9}$$

where K is the Langmuir constant (L/mg) and C_e is the adsorbate concentration (mg/L). Parameter R_L indicates the shape of isotherm and the R_L value between 0 and 1 indicates a favorable adsorption. The fact that all the R_L values for the adsorption of E2 onto the PHEMA/MATrp cryogel are in the range

Table 2
Parameters of Langmuir and Freundlich isotherm models for the adsorption of E2 onto the PHEMA/MATrp cryogel disks

	Langmuir isotherm constants				Freundlich isotherm constants		
Parameters Temperature (K)	$K_L \times 10^{-3}$ (L/mg)	Q_L (mg/g)	R^2	R_L range	$K_F \times 10^{-2}$ (mg/g) $(L/mg)^{1/n}$	n	R^2
277	84.09	2.194	0.9882	0.1063–0.5432	66.58	4.2159	0.9770
298	86.61	3.005	0.9871	0.1035–0.5359	92.84	4.2699	0.9750
338	87.55	3.439	0.9883	0.1025–0.5332	107.8	4.3380	0.9590

0.1025–0.5432, which shows that the adsorption process is favorable.

3.2.3. Thermodynamic analysis

The enthalpy (ΔH°), the entropy (ΔS°), and the Gibbs free energy (ΔG°) changes of adsorption were calculated for thermodynamic analysis of E2 adsorption. The enthalpy (ΔH°) and entropy (ΔS°) changes of the process can be determined from the van't Hoff equation, which is used to evaluate the variation of equilibrium constant with temperature. The integrated form of this equation is given as:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) \quad (10)$$

The equation free energy for each temperature is then obtained as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

From Eq. (11), Gibbs free energy change of adsorption (ΔG°) was calculated as −23.14, −24.95, and −26.23 kJ/mol for the adsorption of E2 onto the PHEMA/MATrp cryogel disks at 277, 298, and 313 K, respectively. The negative ΔG° values indicated that the adsorption of E2 onto the PHEMA/MATrp cryogel disks was thermodynamically feasible and spontaneous. The enthalpy (ΔH°) and entropy (ΔS°) changes were determined as 654.9 J/mol and 85.90 J/mol K, respectively. The positive value of ΔH° confirmed the endothermic character of the adsorption process. The positive values of ΔS° also revealed the increase in randomness at the solid–solute interface during the adsorption of E2 onto the PHEMA/MATrp cryogel disks.

3.3. Desorption from PHEMA/MATrp cryogel disks

Desorption studies were studied at 50 mg/L initial E2 concentration in a batch system. The E2 adsorption capacity was slightly decreased during the five successive adsorption–desorption cycles (2.10, 2.10, 2.08, 2.09, 2.09 mg E2/g cryogel). These results showed that PHEMA/MATrp cryogel disks can be repeatedly used in E2 adsorption without excessive losses in their initial adsorption capacities.

4. Conclusions

In this study, PHEMA/MATrp cryogel disks were synthesized for the removal of E2 from aqueous phase. Firstly, poly(HEMA-MATrp) microparticles were synthesized, afterward microparticle-embedded PHEMA/MATrp cryogel disks were prepared. To evaluate the efficiency of microparticle-embedded cryogel disks to remove E2 from the aqueous phase, the effect of various experimental parameters such as initial concentration, contact time, and temperature to E2 adsorption was investigated. The adsorption process was clarified with kinetic and isothermal studies. The pseudo-second-order kinetic model fits the experimental data with high correlation coefficients for all temperatures. All the isotherm data can be fitted with the Langmuir isotherm model. Kinetic and thermodynamic studies suggested that the adsorption process was fast, endothermic, and spontaneous. The total capacity of PHEMA/MATrp cryogel disks was determined as 2.75 mg E2 per gram cryogel at 25°C. The disks were regenerated easily and the regenerated disks can be reused for E2 adsorption. The high capacity of poly(HEMA/MATrp) cryogel disks for E2 adsorption has a potential applicability for industrial processes.

Acknowledgement

This work was funded by the Research Foundation of Uludag University (Project No. KUAP-2015/19).

Nomenclature

C	—	constant proportional to the extent of boundary layer thickness (mmol/g)
C_e	—	concentration of E2 at equilibrium (mg/L)
C_0	—	initial concentration of E2 in solution (mg/L)
ΔG°	—	Gibbs free energy of adsorption (J/mol)
ΔH°	—	isosteric enthalpy of adsorption (J/mol)
ΔS°	—	entropy change of the adsorption process (J/K/mol)
E_a	—	activation energy of adsorption (kJ/mol)
K	—	the Langmuir constant (L/mg)
K_f	—	the Freundlich constant ((mg/g) (L/mg)$^{1/n}$)
k_1	—	the rate constant of pseudo-first-order adsorption (min^{-1})
k_2	—	the rate constant of pseudo-second-order adsorption ((g/mg)/min)
k_i	—	the intraparticle diffusion rate constant ((mg/g)/min$^{1/2}$)
K_L	—	the Langmuir constant related to the affinity of binding sites (L/mg)
m	—	the mass of the cryogel disk used (g)
$m_{dry\ gel}$	—	the mass of dried cryogel disk
$m_{wet\ gel}$	—	the mass of wet cryogel disk
n	—	intensity of the adsorption
Q	—	the amount of E2 adsorbed on a unit mass of the beads (mg/g)
q_e	—	the amount of E2 adsorbed on the adsorbent at equilibrium (mg/g)

q_t — the amount of E2 adsorbed on the adsorbent at any time (mg/g)
q_m — the maximum amount of E2 adsorbed per unit mass adsorbent (mg/g)
Q_L — the maximum amount of E2 adsorbed per unit mass adsorbent (mg/g)
R — the gas constant (8.314 J/mol/K)
R^2 — linear regression coefficient
S — the swelling degree of the cryogel disk
t — time (min)
T — temperature (K)
V — the volume of the aqueous phase (mL)

References

[1] İ. Koç, G. Baydemir, E. Bayram, H. Yavuz, A. Denizli, Selective removal of 17-estradiol with molecularly imprinted particle-embedded cryogel systems, J. Hazard. Mater. 192 (2011) 1819–1826.
[2] R.H. Kaufman, E. Adam, E.E. Hatch, K. Noller, A.L. Herbst, J.R. Palmer, R.N. Hoover, Continued follow-up of pregnancy outcomes in diethylstilbestrol-exposed offspring, Obstet. Gynecol. 96(4) (2000) 483–489.
[3] R.J. Golden, K.L. Noller, L. Titus-Ernstoff, R.H. Kaufman, R. Mittendorf, R. Stillman, E.A. Reese, Environmental endocrine modulators and human health: An assessment of the biological evidence, Crit. Rev. Toxicol. 28 (1998) 109–227.
[4] M. Le Noir, A.S. Lepeuple, B. Guieysse, B. Mattiasson, Selective removal of 17β-estradiol at trace concentration using a molecularly imprinted polymer, Water Res. 41 (2007) 2825–2831.
[5] P. Fernández-Álvarez, M. Le Noir, B. Guieysse, Removal and destruction of endocrine disrupting contaminants by adsorption with molecularly imprinted polymers followed by simultaneous extraction and phototreatment, J. Hazard. Mater. 163 (2009) 1107–1112.
[6] M. Le Noir, F. Plieva, T. Hey, B. Guieysse, B. Mattiasson, Macroporous molecularly imprinted polymer/cryogel composite systems for the removal of endocrine disrupting trace contaminants, J. Chromatogr. A 1154 (2007) 158–164.
[7] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: Hybrid methods, Adv. Environ. Res. 8(3–4) (2004) 553–597.
[8] M. Petrovic, S. Gonzalez, D. Barcelo, Analysis and removal of emerging contaminants in wastewater and drinking water, TrAC, Trends Anal. Chem. 22 (2003) 685–696.
[9] C.H. Huang, D.L. Sedlak, Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectrometry, Environ. Toxicol. Chem. 20(1) (2001) 133–139.
[10] J. Hu, S. Cheng, T. Aizawa, Y. Terao, S. Kunikane, Products of aqueous chlorination of 17β-estradiol and their estrogenic activities, Environ. Sci. Technol. 37(24) (2003) 5665–5670.
[11] A. Coors, P.D. Jones, J.P. Giesy, H.T. Ratte, Removal of estrogenic activity from municipal waste landfill leachate assessed with a bioassay based on reporter gene expression, Environ. Sci. Technol. 37(15) (2003) 3430–3434.
[12] S. Khan, T. Wintgens, P. Sherman, J. Zaricky, A. Schäfer, A performance comparison of individual and combined treatment modules for water recycling, Environ. Prog. 24(4) (2005) 383–391.
[13] H.M. Kuch, K. Ballschmiter, Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC−(NCI)−MS in the picogram per liter range, Environ. Sci. Technol. 35 (2001) 3201–3206.
[14] Y. Zhang, J.L. Zhou, Removal of estrone and 17β-estradiol from water by adsorption, Water Res. 39(16) (2005) 3991–4003.
[15] V.I. Lozinsky, I.Y. Galaev, F.M. Plieva, I.N. Savina, H. Jungvid, B. Mattiasson, Polymeric cryogels as promising materials of biotechnological interest, Trends Biotechnol. 21 (2003) 445–451.
[16] F.M. Plieva, I.Y. Galaev, B. Mattiasson, Macroporous gels prepared at subzero temperatures as novel materials for chromatography of particulate-containing fluids and cell culture applications, J. Sep. Sci. 30 (2007) 1657–1671.
[17] F.M. Plieva, B. Mattiasson, Macroporous gel particles as novel sorbent materials: Rational design, Ind. Eng. Chem. Res. 47 (2008) 4131–4141.
[18] N.S. Bibi, P.R. Gavara, S.L.S. Espinosa, M. Grasselli, M. Fernández-Lahore, Synthesis and performance of 3D-Megaporous structures for enzyme immobilization and protein capture, Biotechnol. Progr. 27 (2011) 1329–1338.
[19] A. Hanora, F.M. Plieva, M. Hedström, I.Y. Galaev, B. Mattiasson, Capture of bacterial endotoxins using a supermacroporous monolithic matrix with immobilized polyethyleneimine, lysozyme or polymyxin B, J. Biotechnol. 118 (2005) 421.
[20] E. Jain, A.A. Karande, A. Kumar, Supermacroporous polymer-based cryogel bioreactor for monoclonal antibody production in continuous culture using hybridoma cells, Biotechnol. Prog. 27 (2011) 170–180.
[21] E. Velickova, E. Winkelhausen, S. Kuzmanova, M. Cvetkovska, C. Tsvetanov, Hydroxyethylcellulose cryogels used for entrapment of *Saccharomyces cerevisiae* cells, React. Funct. Polym. 69(9) (2009) 688–693.
[22] S. Bhat, A. Tripathi, A. Kumar, Supermacroprous chitosan-agarose-gelatin cryogels: *In vitro* characterization and *in vivo* assessment for cartilage tissue engineering, J. R. Soc. Interface 8(57) (2011) 540–554.
[23] K. Bloch, A. Vanichkin, L.G. Damshkaln, V.I. Lozinsky, P. Vardi, Vascularization of wide pore agarose-gelatin cryogel scaffolds implanted subcutaneously in diabetic and non-diabetic mice, Acta Biomater. 6 (2010) 1200–1205.
[24] M.B. Dainiak, I.U. Allan, I.N. Savina, L. Cornelio, E.S. James, S.L. James, S.V. Mikhalovsky, H. Jungvid, I.Y. Galaev, Gelatin–fibrinogen cryogel dermal matrices for wound repair: Preparation, optimisation and *in vitro* study, Biomaterials 31(1) (2010) 67–76.
[25] M. Jurga, M.B. Dainiak, A. Sarnowska, A. Jablonska, A. Tripathi, F.M. Plieva, I.N. Savina, L. Strojek, H. Jungvid, A. Kumar, B. Lukomska, K. Domanska-Janik, N. Forraz, C.P. McGuckin, The performance of laminin-containing cryogel scaffolds in neural tissue regeneration, Biomaterials 32(13) (2011) 3423–3434.

[26] N. Kathuria, A. Tripathi, K.K. Kar, A. Kumar, Synthesis and characterization of elastic and macroporous chitosan-gelatin cryogels for tissue engineering, Acta Biomater. 5(1) (2009) 406–418.
[27] B. Kostova, D. Momekova, P. Petrov, G. Momekov, N. Toncheva-Moncheva, C.B. Tsvetanov, N. Lambov, Poly(ethoxytriethyleneglycol acrylate) cryogels as novel sustained drug release systems for oral application, Polymer 52(5) (2011) 1217–1222.
[28] Ö. Biçen Ünlüer, A. Ersöz, A. Denizli, R. Demirel, R. Say, Separation and purification of hyaluronic acid by embedded glucuronic acid imprinted polymers into cryogel, J. Chromatogr. B 934 (2013) 46– 52.
[29] B. Osman, E.T. Özer, A. Kara, E. Yeşilova, N. Beşirli, Properties of magnetic microbeads in removing bisphenol-A from aqueous phase, J. Porous Mater. 22 (1) (2015) 37–46.
[30] N. Bereli, D. Türkmen, K. Köse, A. Denizli, Glutamic acid containing supermacroporous poly(hydroxyethyl methacrylate) cryogel disks for UO_2^{2+} removal, Mater. Sci. Eng., C 32 (2012) 2052–2059.
[31] S. Lagergren, Zurtheorie der sogenannten adsorption gel osterstoffe, Handlingar 25 (1898) 1–39.
[32] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater. 136 (2006) 681–689.
[33] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solutions, J. Sanitary Eng. Div. ASCE 89 (1963) 31–60.
[34] F.N. Arslanoğlu, F. Kar, N. Arslan, Adsorption of dark coloured compounds from peach pulp by using granular activated carbon, J. Food Eng. (2004) 1–9.
[35] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollution sorption by biosorbents: Review, Sep. Purif. Methods 29(2) (2000) 189–232.