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Methacrylic acid-ethylene glycol dimethacrylate polymeric sorbent for the removal of estrogens from water

Juan Carlos Bravo*, Alejandrina Gallego, Gema Paniagua, Pilar Fernández, Rosa María Garcinuño

Departamento de Ciencias Analíticas, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, C/Senda del Rey 9, 28040, Madrid, Spain, emails: jbravo@invi.uned.es (J.C. Bravo), agallego@ccia.uned.es (A. Gallego), gpaniagua@ccia.uned.es (G. Paniagua), pfhernando@ccia.uned.es (P. Fernández), rmgarcinuno@ccia.uned.es (R.M. Garcinuño)

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ABSTRACT

The presence of estrogens in environmental waters can cause adverse effects to aquatic organisms. In the last years, diverse researches have been focussed on the development of cost-effective methods for the removal of these compounds in water. In this paper, a series of methacrylic acid-ethylene glycol dimethacrylate polymers with different monomers ratio were synthesised by photochemical (UV irradiation at 365 nm) or thermal (oven at 60°C) initiation. Batch and continuous flow experiments were carried out to evaluate the capacity of these polymers to adsorb estradiol (E2), ethinylestradiol (EE2) and dienestrol (DEN). Adsorption isotherm studies revealed that Langmuir isotherm model was fitted with a better correlation than Freundlich isotherm. Finally, continuous flow experiments were carried out by microcolumn studies to check the suitability of the polymeric sorbent for the removal of estrogens from real water samples. When continuous removal experiments at 8 mL min^{-1} flow rate were carried out, breakthrough adsorption capacities of 28.5, 38 and 69.7 mg g^{-1} for E2, EE2 and DEN, respectively, were achieved.

Keywords: Estrogens; Removal; Polymer; Sorbent; Waters

1. Introduction

The presence in aquatic environment of chemicals that can cause adverse effects on human and wildlife has been widely reported [1–4]. Some of these chemicals are capable of disrupting the endocrine system of fish and wildlife attracting considerable attentions worldwide. Among these endocrine disrupting chemicals, natural and synthetic estrogens have been found [5–10], being of great concern because of their potential to alter the endocrine system of humans and animals [11–14]. These estrogens are widely used in estrogen replacement therapy and as oral contraceptives, and often have been used as growth promoters in cattle [15]. The main way these estrogens enter water environment is through sewage treatment plants receiving industrial and domestic wastewaters, where human and animal waste products are released. The presence of estrogens in the environment could indicate that conventional wastewater treatment processes have limited capacity to remove these compounds. Diverse methods for the removal of estrogens have been investigated. The most widely applied include advanced oxidation processes such as ozonation or manganese oxides application [16–18], adsorption on activated carbon [19–21] and membrane treatment [22–25]. In the last year, removal of estrogens by polymeric sorbents, including molecularly imprinted polymers (MIPs), have been reported [26–32]. However, it is well known that the presence of residual template after extraction can be a serious problem in the practical usage of MIPs, because leakage of this template could cause false results or contamination of samples in the case of removal uses [33–35].

* Corresponding author.

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In this work, a series of methacrylic acid-ethylene glycol dimethacrylate polymers has been synthesised and evaluated for the removal of the estrogens named estradiol (E2), ethinylestradiol (EE2) and dienestrol (DEN), representing natural steroidal estrogen, synthetic steroidal estrogen and synthetic stilbene estrogen, respectively (Fig. 1), from water samples. The separation and quantification of these compounds were carried out by the means of HPLC-DAD. Batch and columns experiments were carried out to evaluate the polymer adsorption, and continuous flow removal of estrogenic compounds from spiked tap and river water was successfully achieved, with the great advantages of simplicity, low cost of polymer synthesis and no possibility of template leakage.

2. Materials and methods

2.1. Chemicals and reagents

Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), b-estradiol (E2), ethinylestradiol (EE) and dienestrol (DEN) were purchased from Sigma-Aldrich (Steinheim, Germany). Azobisisobutyronitrile (AIBN) was obtained from Fluka (Buchs, Switzerland). HPLC grade methanol (MeOH) and acetonitrile (ACN) were purchased from Sigma-Aldrich.

2.2. Instrumentation

A model CN-6T Ultraviolet lamp (Vilber Lourmat, Marne La Vallée, France) and a J.P. Selecta oven (Barcelona, Spain) were used to initiate the polymerisation process. Porosity and surface area were characterised through nitrogen adsorption/desorption analysis using a nitrogen surface analyser (ASAP 2010, Micromeritics, USA). A Minipuls 2 peristaltic pump supplied by Gilson (Villiers-le-Bel, France) connected to a 3 mm i.d. polytetrafluoroethylene (PTFE) microcolumn filled with the synthesised polymer was utilised to develop the continuous flow removal of estrogens from water samples. Chromatographic analyses were performed using an Agilent 1200 series LC system (Agilent Technologies, Waldbronn, Germany) equipped with a quaternary pump (G1311A), a column compartment, a vacuum degasser (G1322A) and a diode-array detector (G1315B). Instrumental parameters were controlled by Agilent ChemStation for LC software. Analyses were performed on an Agilent Eclipse XDB-C18, 150 mm × 4.6 mm, 5 μm particle size. Samples were manually injected through an injection valve (Rheodyne, Model 7725i) fitted with a 20 mL loop.

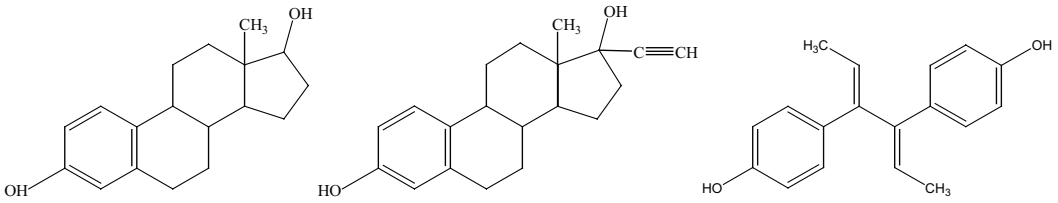
2.3. Preparation of MAA/EGDMA polymers

Polymers were prepared by the radical initiated polymerisation of monomers EGDMA and MAA. Several ratios of EGDMA/MAA were used to carry out the bulk polymerisation. The reactive mixtures, described in Table 1, were prepared by mixing the selected monomers with acetonitrile as porogen in glass tubes. These solutions were homogenised in an ultrasonic bath, and purged with nitrogen to remove the oxygen. The tubes were sealed with parafilm and the polymerisation reaction was initiated by photochemical (UV irradiation at 365 nm) or thermal (oven at 60°C) initiation during 16 h.

The monolithic polymers obtained were crushed, ground in a mortar and wet sieved using methanol. Polymer particles with sizes between 50 and 100 mm were collected, dried and stored until adsorption experiments.

2.4. Textural characterisation

The textural characteristics (surface area, pore size and pore volume) of the optimised polymer were determined by gas adsorption. The adsorption–desorption isotherm for N_2 at –196°C of the polymer previously outgassed at 80°C was



17β-estradiol (E2) Ethynylestradiol (EE2) Dienestrol (DEN)

Fig. 1. Chemical structures of the estrogens studied in this work.

Table 1
Chemical composition and codes of the synthesised polymers

Polymer code	Ratio EGDMA/MAA (mol)	MAA (μL)	EGDMA (μL)	ACN (mL)	Polymerisation
P1	2/1	339	1,510	2.59	60°C
P2	4/1	170	1,510	2.35	60°C
P3	8/1	95	1,700	2.51	60°C
P4	2/1	339	1,510	2.59	UV
P5	4/1	170	1,510	2.35	UV
P6	8/1	95	1,700	2.51	UV

measured with the aid of a Micromeritics ASAP 2010 surface area and porosimetry system. Specific surface area (S_{BET}) was calculated by applying the BET (Brunauer–Emmett–Teller) method [36]. The *t*-plot method [37] was used to obtain external surface area (S_{ext}) and micropore volume (V_{micro}). The micropore surface area (S_{micro}) was calculated by subtracting S_{ext} from S_{BET}. The mesopore cumulative volume and mesopore diameter (D_{meso}) were calculated from BJH (Barrett–Joyner–Halenda) desorption branch [38]. Horvath and Kawazoe (HK) method [39] was applied to micropore size (D_{micro}) analysis.

2.5. Batch adsorption experiments

Batch studies were performed to obtain equilibrium data. To select the optimum synthesised polymer, preliminary studies were carried out with different polymer doses and equilibration times. Adsorption of the analytes on the surfaces of the test vessels and stability of the analytes during the test period were also studied.

Batch adsorption experiments using the six synthesised polymers were conducted at room temperature in parallel for 0.5, 2, 4, 16 and 30 h adsorption times. Different amounts of the polymers were taken in 15 mL amber glass vials containing 4 mL of a solution of 2 μg mL^{-1} concentration of E2, EE2 and DEN to constitute polymer doses of 0.1, 0.2, 0.4, 1 and 2.5 mg mL^{-1}. At the end of the sorption period, the solution was centrifuged and the supernatant was analysed by HPLC. A 20 μL aliquot of supernatant was injected onto the HPLC column at room temperature and a constant flow of 1 mL min^{-1}. The elution program was as follows: from 35% acetonitrile and 65% water to 50% acetonitrile in 5 min and returning to 35% acetonitrile in 5 min. Next, chromatographic column was cleaned with 100% acetonitrile for 5 min and readjusted to the initial conditions. Quantitative measurements of the analytes were carried out by HPLC-DAD detection at 226 nm. The amount of adsorbed estrogens was calculated each time as the difference between the initial concentration and the concentration remained after adsorption. One control sample with only the analytes solution was subjected to the same procedure in order to check the stability of the analytes. A blank sample per polymer with an amount of polymer and free analyte solution was subjected to the same steps. Adsorption isotherms using optimum synthesised polymer were studied with varying concentrations of estrogens at fixed amount of polymer.

2.6. Continuous flow experiments

A fixed amount of selected polymer was slurry-packed with methanol onto PTFE microcolumn (3 mm i.d.). Effects of flow rate and sample pH were studied by passing a volume of 100 mL of 2 μg mL^{-1} spiked Milli-Q water through the microcolumn. Next, behaviour of selected polymer for the removal of estrogens from water samples were tested by passing, at optimised flow rate and pH values, increasing volumes of 2 μg mL^{-1} spiked Milli-Q water through the microcolumn. The effluent solution was then collected and analysed by HPLC following the same procedure described in batch experiments. Breakthrough curves were represented by plotting the effluent concentration remained after removal normalised to influent concentration (C/C_0) vs. the influent volume. In this work, the breakthrough point has been taken as the point at which the analyte concentration in the effluent reaches a maximum allowed value of 5% of its influent value. Breakthrough capacity was taken as the amount of estrogens adsorbed per gram of dry polymer prior the breakthrough point.

2.7. Removal of estrogens from water samples

Tap and river water samples were used to demonstrate the applicability of the polymer to the removal of E2, EE2 and DEN from real samples. In this way, tap water samples obtained in our laboratory and river water samples collected from Manzanares River (Madrid, Spain) were used to carry out the continuous flow procedure. To avoid microcolumn clogging, collected tap and river water samples were filtered through a 0.45-μm membranes (Millipore, Bedford, MA, USA). Then, samples were spiked with the selected estrogens at 2 μg mL^{-1} and used for continuous removal procedure. The measured dissolved organic carbon values of these waters were 0.9 and 5.2 mg L^{-1}, respectively. The polymer microcolumn was conditioned with 25 mL of Milli-Q water and spiked samples were passed through the polymer at a constant flow rate of 8 mL min^{-1} with the aid of a peristaltic pump. Subsequently, the effluent solution was collected and analysed by HPLC-DAD following the previously described method.

3. Results and discussion

3.1. Effect of contact time

The sorption of estrogens was studied as a function of time of contact for the different synthesised polymers. Weighed amounts of the synthesised polymers were taken in test bottles and a volume of estrogen solution of 2 μg mL^{-1} concentration was added to reach 0.1, 0.2, 0.4, 1 and 2.5 polymer doses (mg polymer/mL solution). The test bottles were placed over a mechanical shaker and the adsorption experiments were carried out at 0.5, 2, 4, 16 and 30 h contact time. It was found that adsorption of the three estrogens reached a maximum value after 16 h of shaking and did not change much above this time of contact. Thus a 16-h contact time was adequate to achieve equilibrium. Fig. 2 shows the results of estrogens adsorption onto the different synthesised polymers at the five incubation times, when estrogens concentration of 2 μg mL^{-1} and a polymer dose of 0.2 were used.

It was found that adsorption was slightly lower onto photoinitiated polymers at the five measured adsorption times for the three estrogens. Obtained data showed that the greatest adsorption was achieved for polymers with an EGDMA/MAA ratio of 8/1. Similar results were obtained when the three other polymer doses were used. With these results, polymer P3 was selected for further experiments.

3.2. Effect of polymer dose

The effect of adsorbent dose on the adsorption of E2, EE2 and DEN after 16 h of contact time with selected polymer P3 was studied. From the obtained data (not shown), approximately 2.5 mg of P3 per mL of solution were required

to achieve 95% E2, EE2 and DEN adsorption from spiked Milli-Q water with a 0.5 h contact time, whereas lower polymer doses of 1, 0.4, 0.2 and 0.1 mg mL^{-1} required longer contact times to reach that percentage. Fig. 3 presents the percentages of estrogens adsorbed with variation of polymer P3 dose in a range of 0.1–2.5 mg mL^{-1} after a contact time of 16 h. Adsorption percentages increased with polymer dose due to the increase in sorbent surface area up to optimum dosage of 0.4 mg mL^{-1} (corresponding to 98% adsorption) beyond which the adsorption efficiency is negligible.

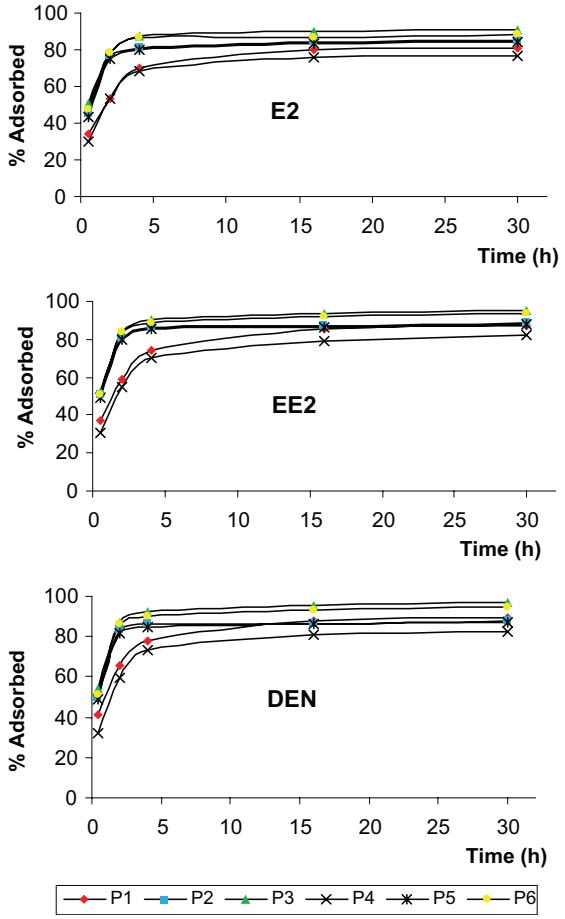


Fig. 2. Estrogen adsorption onto the synthesised polymers at 2 μg mL^{-1} water concentration.

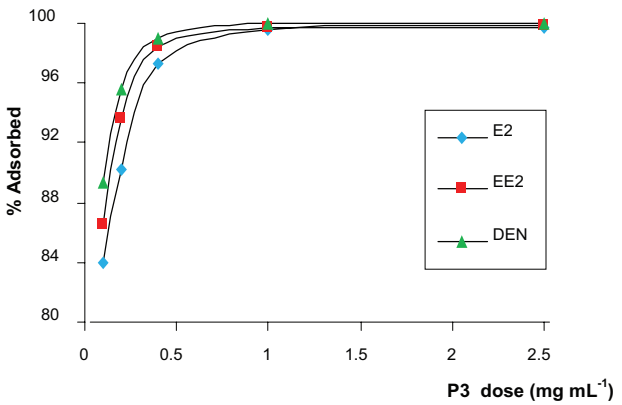


Fig. 3. Effects of polymer P3 dose (mg mL^{-1}) on E2, EE2 and DEN adsorption.

3.3. Porosity of developed polymer

Specific surface area and porosity are important parameters that determine the adsorption properties of porous solids. Obtained BET surface area for the selected polymer was as high as 400 m^2 g^{-1}, a desirable property for a good adsorbent. The pores are usually classified according to their size into three categories: micropores (pore diameter < 2 nm or 20 Å), mesopores (pore diameter 2–50 nm or 20–500 Å) and macropores (pore diameter > 50 nm or 500 Å). Studied polymer shows both micro- (D_{micro} = 9 Å) and mesopores (D_{meso} = 130 Å). Micropore volume (V_{micro}) and mesopore volume (V_{meso}) were found to be 0.156 and 0.998 cm^3 g^{-1} being the adsorbent mainly mesoporous (V_{micro}/V_{meso} = 0.15) which facilitates the access of the estrogen molecules to the interior of the polymer particles and allow to flow throw the adsorbent at a reasonably low pressure.

Porosity and other textural characteristics of P3 polymer are shown in Table 2.

3.4. Adsorption isotherms

Adsorption isotherms for E2, EE2 and DEN removal were carried out varying the estrogens concentration between 0.1 and 10 μg mL^{-1} under previous optimised conditions (16 h equilibrium time and 0.4 P3 polymer dose). Langmuir and Freundlich isotherm models were used to describe the equilibrium data. These models are represented by the following equations:

Langmuir:

$$q_e = q_m \frac{K_l C_e}{1 + K_l C_e} \quad (1)$$

Freundlich:

$$q_e = K_f C_e^{\,n} \quad (2)$$

where q_e is the amount of estrogen adsorbed by the polymer (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}) and C_e is the concentration of the estrogen solution (mg L^{-1}), whereas K_l, K_f and n are constants of the Langmuir and Freundlich isotherms, respectively. Table 3 presents the obtained coefficients of the Langmuir and Freundlich isotherms. It can be seen that isotherm data fit better to Langmuir isotherm model, based on the correlation coefficients. Thus, Langmuir isotherm model is better in describing the adsorption of E2, EE2 and DEN using P3 polymer.

3.5. Adsorption kinetics

In order to better understand the controlling mechanism of adsorption of E2, EE2 and DEN onto P3 polymer, pseudo-first-order [40] and pseudo-second-order [41] kinetic models were used to fit experimental data.

Pseudo-first-order model is based on equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

where q_e and q_t are the amount of estrogen adsorbed by the polymer (mg g^{-1}) at equilibrium and at time t (min) respectively, and k_1 (min^{-1}) is the pseudo-first-order rate constant of the adsorption. Kinetic parameters were calculated from the linear plots of $\log(q_e - q_t)$ vs. t where k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively. The pseudo-first-order kinetic parameters and linear equations are presented in Table 4.

Pseudo-second-order kinetics is described by the following equation:

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

where q_e and q_t are the amount of estrogen adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot of (t/q_t) vs. t gives a linear relationship where values of k_2 and calculated q_e can be obtained from the intercept and slope, respectively. The pseudo-second-order rate constants and linear equations are given in Table 5.

Table 2
Textural characteristics of P3 polymer

S_{BET} [a] (m^2 g^{-1})	S_{ext} [b] (m^2 g^{-1})	S_{micro} [c] (m^2 g^{-1})	V_{micro} [d] (cm^3 g^{-1})	V_{meso} [e] (cm^3 g^{-1})	D_{micro} [f] (Å)	D_{meso} [g] (Å)
400	320	80	0.156	0.998	9	130

[a]BET (Brunauer–Emmett–Teller) specific surface area.
[b]External surface area, calculated by t-plot method.
[c]Micropore specific surface area, estimated by subtracting S_{ext} from S_{BET}.
[d]Micropore volume, derived from the t-method.
[e]Mesopore volume, derived from BJH (Barrett–Joyner–Halenda) method.
[f]Micropore diameter, determined by HK (Horvath-Kawazoe) method.
[g]Mesopore diameter, determined by BJH (Barrett–Joyner–Halenda) method.

Table 3
Isotherm sorption coefficients of estrogens on P3 polymer

Compound	Langmuir			Freundlich		
	q_m	K_l	R^2	K_f	n	R^2
E2	0.0069	0.0300	0.9980	0.0071	0.8788	0.9874
EE2	0.0077	0.0241	0.9986	0.079	0.9036	0.9779
DEN	0.0078	0.0270	0.9978	0.0081	0.9092	0.9859

Table 4
Kinetic parameters and correlation coefficients (R^2) for pseudo-first-order kinetic model

Estrogen	Pseudo-first-order kinetics				
	q_e, exp (mg g^{-1})	Equation	q_e, cal (mg g^{-1})	k_1 (min^{-1})	R^2
E2	4.51	$y = -0.0052x + 0.4314$	2.7002	–0.0119	0.9973
EE2	4.68	$y = -0.0050x + 0.3981$	2.5009	–0.0115	0.9614
DEN	4.78	$y = -0.0054x + 0.4113$	2.5781	–0.1244	0.9689

Table 5
Kinetic parameters and correlation coefficients (R^2) for pseudo-second-order kinetic model

Estrogen	Pseudo-second-order kinetics				
	q_e, exp (mg g^{-1})	Equation	q_e, cal (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
E2	4.51	$y = 0.2066x + 5.6692$	4.8403	0.0075	1
EE2	4.68	$y = 0.1993x + 5.1903$	5.0176	0.0076	0.9994
DEN	4.78	$y = 0.1946x + 4.8762$	5.1387	0.0077	0.9993

The obtained results for calculated values of q_e and R^2 give a better correlation of pseudo-second-order equation with experimental data, which suggest that the adsorption of studied estrogens follows the pseudo-second-order kinetic model.

3.6. Continuous flow experiments

Optimisation of flow rate was carried out by passing 100 mL of 2 μg mL^{-1} spiked Milli-Q water through the P3 microcolumn at increasing rates from 2 mL min^{-1}. E2, EE2 and DEN were fully adsorbed on the polymer at all the flow rates from 2 to 8 mL min^{-1}. When the flow rate used was 9 mL min^{-1} an overpressure was produced on the system and was discarded for further experiments. Therefore, 8 mL min^{-1} was selected as flow rate for continuous removal of estrogens. The effect of sample pH on polymer adsorption was studied by flowing 100 mL of 2 μg mL^{-1} spiked Milli-Q water through the P3 microcolumn at different pH. The flow rate was established at 8 mL min^{-1} and the pH was varied over a 4–9 range. No differences in adsorption behaviour were observed at the studied pH values. For the removal of estrogens, increasing volumes of 2 μg mL^{-1} spiked Milli-Q were passing through the microcolumn at optimised flow rate. Breakthrough curves were represented by plotting the effluent concentration normalised to influent concentration (C/C_0) vs. the influent volume. When effluent concentration reached more than 20% influent concentration for the three estrogens, the polymer microcolumn was washed with methanol to elute the adsorbed analytes. Next, the microcolumn was rinsed with 25 mL Milli-Q water and it was ready for a new removal process. This adsorption–desorption cycle was repeated sequentially for five times with a result of no reduction in the adsorption percentages of the three estrogens, from the first to the 5th cycle, for the selected polymer. Fig. 4 shows the results obtained when increasing volumes of 2 μg mL^{-1} spiked Milli-Q water were passed through P3 microcolumn at 8 mL min^{-1} flow rate. Breakthrough volume increased for the selected estrogens as follows: DEN > EE2 > E2.

3.7. Removal from real water samples

Increasing volumes of 2 μg mL^{-1} spiked tap or river water were passed through P3 microcolumn at 8 mL min^{-1} flow rate, washing the microcolumn when effluent concentration reached more than 20% influent concentration for the three estrogens. Breakthrough curves for the removal of estrogens from spiked tap and river water samples were represented and compared with the previous presented Milli-Q breakthrough curve. Fig. 5 shows that the breakthrough point is reached earlier when the removal of real water samples was carried out, probably due to the presence of competing organic substances present in real waters which can also been adsorbed onto polymeric sorbent, reducing the effective surface area for adsorbing selected estrogens.

Breakthrough capacity (Table 6) decreased for the three estrogens, showing a maximum decrease of 14% in adsorption of DEN from tap water, while a maximum decrease of 27% for DEN was observed when river water samples were used. Despite this reduction on adsorption percentages, P3 polymer shows a high capacity for removing estrogens from real water samples.

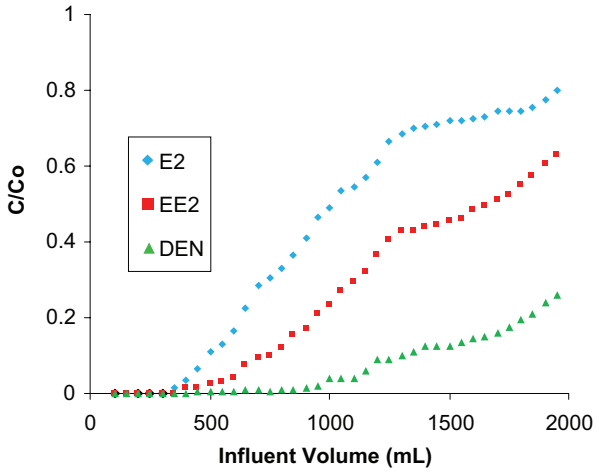


Fig. 4. Breakthrough curves of estrogens removal from spiked Milli-Q water.

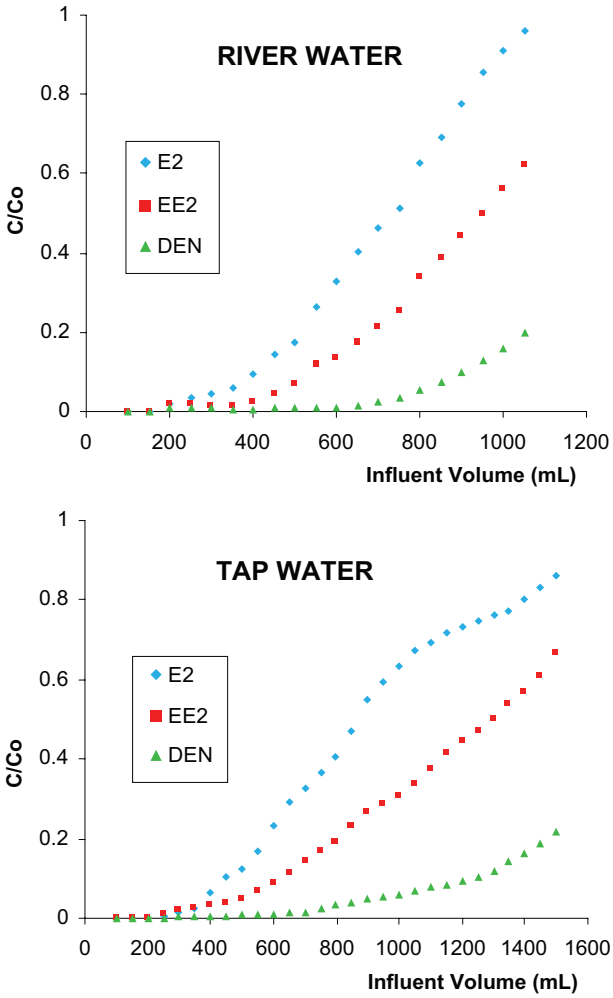


Fig. 5. Breakthrough curves of estrogens removal from spiked real water.

Table 6
Breakthrough capacity of the MAA/EGDMA polymeric sorbent in water samples

Water type	Breakthrough capacity (mg g^{-1})		
	E2	EE2	DEN
Milli-Q	28.5	38	69.7
Tap	25.3	34.8	60.2
River	22.8	31.7	50.7

4. Conclusions

This work demonstrates that estrogens can be successfully removed from water samples by means of a continuous adsorption process based on methacrylic acid-ethylene glycol dimethacrylate polymeric sorbent. Polymer synthesised with 8/1 monomers ratio (EGDMA/MAA) and thermal polymerisation at 60°C showed the best adsorption capacity. When the continuous removal was carried out at 8 mL min^{-1}, the breakthrough volumes were found to be in the following order DEN > EE2 > E2, showing breakthrough capacities of 69.7, 38 and 28.5 mg g^{-1}, respectively. With this simple and low-cost procedure, removal of estrogens from spiked river and tap water samples was successfully applied proving that removal capacity of this sorbent was not highly influenced by the presence of potential competing substances in the sample matrix.

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Conflicts of interest

The authors declare no conflicts of interest.

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