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Removal and destruction of endocrine disrupting contaminants by adsorption with molecularly imprinted polymers followed by simultaneous extraction and phototreatment

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ABSTRACT

This study presents a method to regenerate molecularly imprinted polymers (MIPs) used for the selective removal of endocrine disrupting compounds from aqueous effluents. Regeneration was based on solvent extraction under UV irradiation to regenerate the polymer and the solvent while destroying the contaminants. Acetone was selected as the best solvent for irradiation of estrone (E1), 17β-estradiol (E2) and ethinylestradiol (EE2) using either UVC (254 nm) or UV–vis. A MIP synthesized with E2 as template was then tested for the extraction of this compound from a 2 μg/L loaded aqueous solution. E2 was recovered by 73 ± 11% and 46 ± 13% from the MIPs and a non-imprinted control polymer synthesized under the same conditions, respectively, after a single step elution with acetone. The irradiated polymers and acetone were reused for an additional extraction–regeneration cycle and showed no capacity decrease.

1. Introduction

Endocrine Disrupting Compounds (EDCs) are harmful emerging pollutants commonly found in aquatic environments [1–7]. They are defined as exogenous substances or mixtures that alter functions of the endocrine system and consequently cause adverse health effects in an intact organism, its progeny, or sub-populations [8]. In wildlife, their impacts include reproductive abnormalities, feminisation of males and masculinisation of females [9]. Some of the most potent EDCs are the natural estrogens estrone (E1) and β-estradiol (E2), and the synthetic steroid estrogen ethinylestradiol (EE2), the latter being mainly used in the female contraceptive pill [10,11].

Whereas the fate of EDCs during conventional wastewater treatment is not fully understood yet and only partial pollutant removal is often achieved, the environmental benefit of advanced processes has recently been challenged due to their high energy consumption [12]. Most of the removal capacity of current advanced processes is wasted for the removal of safe compounds present at higher concentration, which impacts treatment costs. Instead, a more cost-efficient strategy consists in selectively removing the target pollutants, which can be achieved by pollutant adsorption with molecularly imprinted polymers (MIPs) as recently demonstrated [13–16]. Here, the adsorbing material is synthesized by template guided polymerization around a hormone-mimicking template molecule, which generates a synthetic analogue to the natural receptors after removal of the template. Thus, pollutant removal is based upon the same mechanisms that make these substances so harmful: their capacity to bind hormone receptors, which should allow the removal of any molecule having a potential estrogenic activity [14].

Adsorption is a non-destructive removal technology and MIPs need to be regenerated and reused to lower treatment costs. The main objective of this work was therefore to develop a method to simultaneously regenerate the polymers and destroy the pollutants. UV irradiation was used for this purpose as photodegradation in organic solvent has proven successful for the destruction of various organic pollutants [17–20] including estrogens [21]. Polymers loaded with pollutants were irradiated directly during solvent extraction in order to (1) improve pollutant transfer from the

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polymers to the solvent by maintaining a low pollutant level in the solvent and (2) regenerate both the solvent and the polymers for reuse. E1, E2 and EE2 were used as model contaminants.

2. Materials and methods

All tests were carried out at room temperature (23 ± 2 °C) in triplicates. Organic solvents were HPLC grade, all other chemicals being reagent grade. Stock solutions of 50 mg/L of E1, E2 and EE2 were prepared in ethanol, methanol, methanol:acetic acid (4:1, v/v), acetone, acetone:acetic acid (4:1, v/v), or acetone:methanol (1:1, v/v), and were diluted in order to carry out the photodegradation tests. Aqueous solutions of E2 were prepared by transferring a volume of acetone stock solution into a volumetric flask, evaporating the acetone, and adding deionised water. The HPLC mobile phase was prepared with ultrapure water.

2.1. Solvent selection

Solutions of 10 mg/L of E1, E2 and EE2 were prepared in ethanol, methanol, methanol:acetic acid (4:1, v/v), acetone, acetone:acetic acid (4:1, v/v) and acetone:methanol (1:1, v/v). UV irradiation tests were performed in 10 mL glass tubes randomly placed under two lamps at a distance of 15 cm and mechanically agitated using a rocking shaker. Aliquots of 5 mL of each solution were irradiated for 72 h under either 2 × 18 W UV–vis blue-lamps (Sylvania Reptistar, Sylvania, USA, ≈30% UVA–5% UVB) or 2 × 15 W UVC germicidal lamps (G15T8, Sankyo Denki, Japan, λ = 254 nm). Light irradiances inside the tubes at 15 cm from the lamps were measured by potassium ferrioxalate actinometry [22] and found equal to 10.7 μEinstein/s and 18.9 μEinstein/s for the UV–vis and UVC lamps, respectively. Samples of 0.75–1 mL were periodically taken from each tube to monitor E1, E2 or EE2 concentration.

2.2. Photodegradation kinetics of E1, E2 and EE2

UV irradiation tests were performed in 10 mL glass tubes as described above. Aliquots of 10 mL of solutions of E1, E2 and EE2 at either 2 mg/L or 10 mg/L in acetone were irradiated for 24 h. Samples of 0.75–1 mL were periodically taken from each tube to determine the concentration of the estrogens by HPLC.

2.3. Polymer synthesis

A MIP with E2 as template was prepared according to Dong et al. [23]: 272.4 mg of E2, 0.68 mL of methacrylic acid, 4.7 mL of ethylene glycol dimethacrylate and 100 mg of α,α′-azoisobutyronitrile were dissolved in 8 mL of acetonitrile in a dried 30 mL glass test tube. The solution was sonicated for 5 min and purged with nitrogen for 5 min. The tube was then sealed and the mixture heated at 43 °C for 20 h. The resulting polymer monolith was recovered, ground in a mortar, sieved (38–106 μm) and washed four times with methanol. The particles of polymers in methanol were kept under the fume hood until complete evaporation of the methanol. The particles were transferred into a Soxhlet extractor for continuous washing with methanol and kept overnight. The washed polymer was finally dried at room temperature. Non-imprinted polymers (NIPs) were synthesized simultaneously under the same conditions but without adding the template.

2.4. Recovery of E2-loaded MIPs using acetone

Six-millilitre glass Solid Phase Extraction (SPE) columns (Supelco) were packed with 100 mg of MIPs or NIPs. The packed columns were washed three times with 4 mL of methanol:acetic acid (4:1, v/v) to remove any traces of E2. Two liters of 2 μg/L E2 aqueous solution was then percolated through each column using a vacuum manifold (Supelco Visiprep™ SPE) and the columns were eluted once with 4 mL of acetone or methanol:acetic acid (4:1, v/v). The concentration of E2 in each extract was determined by HPLC [13]. In order to reuse the polymers after each extraction, these were washed with methanol:acetic acid (4:1, v/v) until the concentration of E2 in the solvent mixture was below detection limit (0.1 mg/L).

2.5. Simultaneous extraction/photodegradation of E2

Two liters of a 3 μg/L E2 aqueous solution was percolated through five SPE columns packed with the MIPs as described above. The loaded polymers were then transferred into glass test tubes and mixed with 6 mL of acetone. Three tubes were irradiated under UV–vis for 10 h, the other two tubes being kept under darkness under agitation to serve as controls. The tubes were then centrifuged at 1500 rpm for 10 min each time and portions of the supernatants were sampled for HPLC analysis. The remaining solvent was removed from each tube and the polymers were extracted again with fresh acetone to determine the remaining quantity of E2 in the polymer. This experiment was repeated twice.

2.6. Acetone regeneration and reuse

MIPs and NIPs were loaded with E2, mixed with 8 mL of acetone and irradiated as described above. After 10 h of irradiation, the acetone was removed from the tubes and saved at 4 °C. The polymers were then dried, transferred into new SPE columns and loaded again with 2 L of a 3 μg/L E2 aqueous solution. The loaded polymers were then transferred to new glass test tubes, extracted with irradiated-acetone previously used and exposed to UV light for 10 h. Controls with loaded MIPs or NIPs were kept in total darkness for the same duration and the acetone was reused in the same manner.

2.7. Analyses

Estrogen concentrations were determined in a Waters 2690 HPLC equipped with a UV photodiode array detector (Waters 996) for E1 detection at 280 nm and a scanning fluorescence detector (Waters 474) for E2 and EE2 detection. Samples were eluted through a C18 column (Ascentis C18, Supelco) using an acetonitrile:water (1:1, v/v) mixture as mobile phase. The injection volume was 20 μL and the flow rate was 1 mL/min. External standards were used to enable quantitative determination of the estrogens. The limit of quantification in organic solvents using HPLC was 2 mg/L for E1 and 0.1 mg/L for E2 and EE2.

3. Results and discussion

Following the selective removal of estrogens from aqueous samples using MIPs, a method was developed to simultaneously regenerate the polymers by solvent extraction and destroy the pollutants by photodegradation. First, the most suitable solvent for the photodestruction of E1, E2, and EE2 was selected and the photodegradation kinetics of these compounds in acetone were further studied. Second, a MIP was synthesized with E2 as template and E2 recovery from loaded polymers using acetone extraction was quantified. Finally, the simultaneous extraction/photodegradation of E2 from loaded polymer using acetone was tested. All kinetics rates are given with a confidence interval at the 95% probability level.

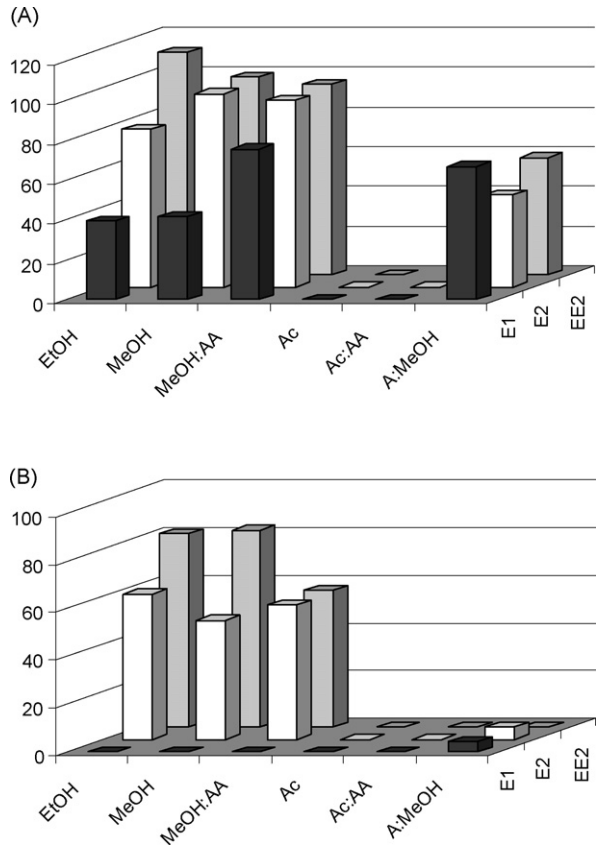

Fig. 1. Remaining concentration (%) of E1, E2, and EE2 initially provided at 10 mg/L in various organic solvents during UV–vis (A) or UVC (B) irradiation. The values plotted represent average on triplicates.

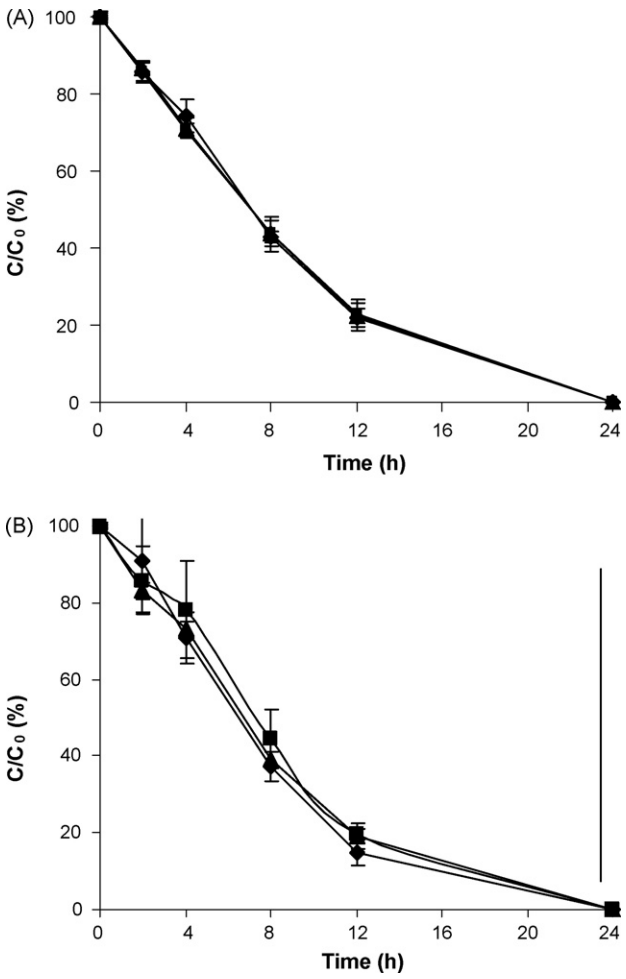

Fig. 2. Remaining concentrations (%) of E1 (triangles), E2 (diamonds), and EE2 (squares) initially provided at 10 mg/L in acetone during (A) UV–vis or (B) UVC irradiation. C_0 is the initial concentration and C is the concentration at time t. The values plotted represent average on triplicates ± S.D.

3.1. Solvent selection

Photodegradation studies in organic solvents are rare and often not optimized with regards to the solvent properties. The type of solvent used can tremendously affect the kinetics of the photodegradation and its pathway as demonstrated by Guieysse and Viklund [18] during the UV–vis of pyrene and phenanthrene in various organic phases. A brief solvent selection was therefore conducted here to compare various economical mixtures. Regardless the light source used, all pollutants were removed after 72 h of irradiation when supplied in acetone or acetone:acetic acid (Fig. 1). The initial removal rates of all estrogens (recorded after 8 h of irradiation) were however faster in acetone than in the acetone:acetic acid mixture and acetone was therefore selected for further testing. Methanol clearly inhibited photodegradation and addition of acetic acid did not have a clear impact. Pollutants disappearance was faster under UVC irradiation in all solvents. The rate at which each compound was removed depended on each solvent or solvent mixture. In acetone, regardless the light source used, EE2 was removed the fastest and E1 and E2 were removed at similar rates.

3.2. Photodegradation kinetics

The UV photodegradation kinetics of E1, E2 and EE2 supplied at 10 mg/L in acetone were of zero-order and similar for all compounds (Fig. 2; $r^2 > 0.99$ in all cases for the first 12 h), suggesting that light supply was limiting at such high pollutant concentration. Photodegradation kinetics of estrogens in aqueous solution are more typical of first-order [9,11] and Liu and Liu [24] reported E1 and E2 pseudo-first-order constants of 0.716 h^{-1} and 1.036 h^{-1}, respectively, at an initial concentration of 10 mg/L using a 30 W UVC disinfection lamp. In our studies, first-order kinetics (with $r^2 > 0.99$ for both light sources) were only observed at lower E2 and EE2 concentration (Fig. 3; this experiment was not conducted for E1 due to its high limit of quantification). The first-order photodegradation rates E2 and E22 were $0.28 \pm 0.04\ h^{-1}$ and $0.29 \pm 0.02\ h^{-1}$, respectively, under UV–vis irradiation; and $0.46 \pm 0.03\ h^{-1}$ and $0.65 \pm 0.08\ h^{-1}$, respectively, under UVC irradiation.

During HPLC analysis of irradiated samples, two peaks (retention times of 2.8 min and 4.2 min) were observed in samples obtained during the UV–vis irradiation of 10 mg E1/L (Fig. 4). Only the peak eluting at 4.2 min was detected during the UVC irradiation of 10 mg E1/L and a new peak appeared after 6.8 min of elution during the UVC photodegradation of 10 mg EE2/L By comparison, E2 and EE2 had retention times of 7.3 min and 6.2 min, respectively. According to the protocol used in this study, analytes should elute in order of decreasing polarity and/or molecular size, suggesting most photoproducts detected were smaller and more oxidized compounds than the parent molecules. All peaks sizes decreased at the end of the experiment, indicating the photoproducts were further transformed. Liu et al. [25] reported that the photolysis of E1 and E2 caused the breakage and oxidation of benzene rings to produce compounds containing carbonyl groups. To the best of our knowledge, only one study on estrogens photodegradation in

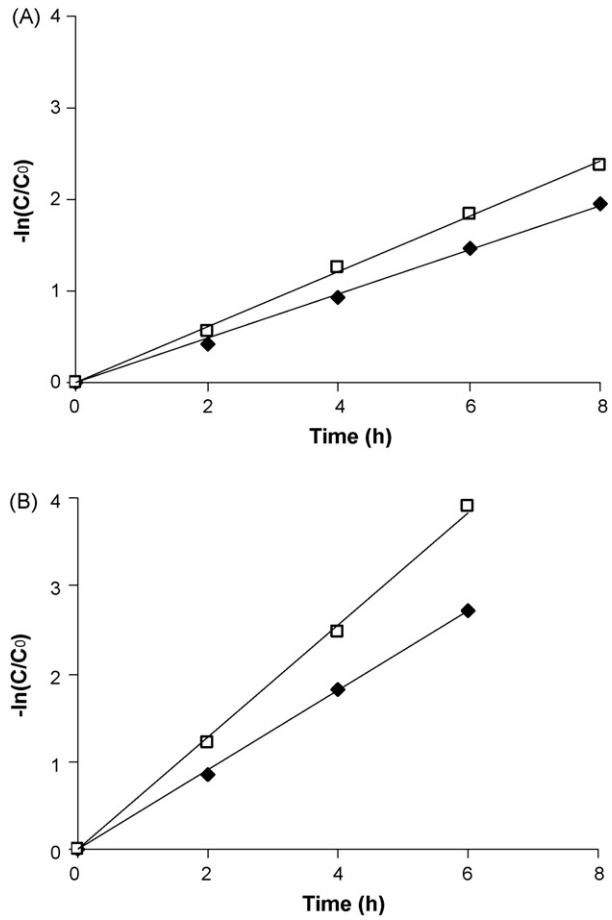

Fig. 3. Remaining concentrations ($-\ln C/C_0$) of E2 (diamonds) and EE2 (squares) initially provided at 2 mg/L in acetone and submitted to (A) UV–vis or (B) UVC irradiation. C_0 and C represent the initial and time t concentrations, respectively. The values plotted represent average on triplicates.

organic solvent has been reported in the literature [21] where 9-hydroperoxide was detected as main products together with other compounds such as dimeric products. No degradation rates were provided.

3.3. Extraction of E2

When acetone was used for extraction, E2 was recovered by $73 \pm 11\%$ and $46 \pm 13\%$ from the MIPs and NIPs, respectively, based on the initial amount of pollutant eluted through the columns (4 μg). The higher recovery recorded in the MIPs confirms the advantage of molecular recognition for the removal of trace contaminants. The results were similar to those reported by [14] in a study achieving E2 recoveries of $100 \pm 0.6\%$ and $77 \pm 5.2\%$ from a 2 μg/L aqueous solution using 4-vinylpyridine-based MIPs and NIPs, respectively, eluted with MeOH:Aa (4:1, v/v). The lower extraction recovery achieved here could be explained by the fact the polymers were only eluted once.

3.4. Simultaneous extraction/phototreatment of E2

UV–vis was preferred because it simulates solar-irradiation (for more cost-efficient treatment) and because UVC might degrade the polymers themselves (this should be investigated in future studies). No E2 removal occurred under darkness (data not shown) whereas only 10% of the estrogen initially extracted remained in the acetone

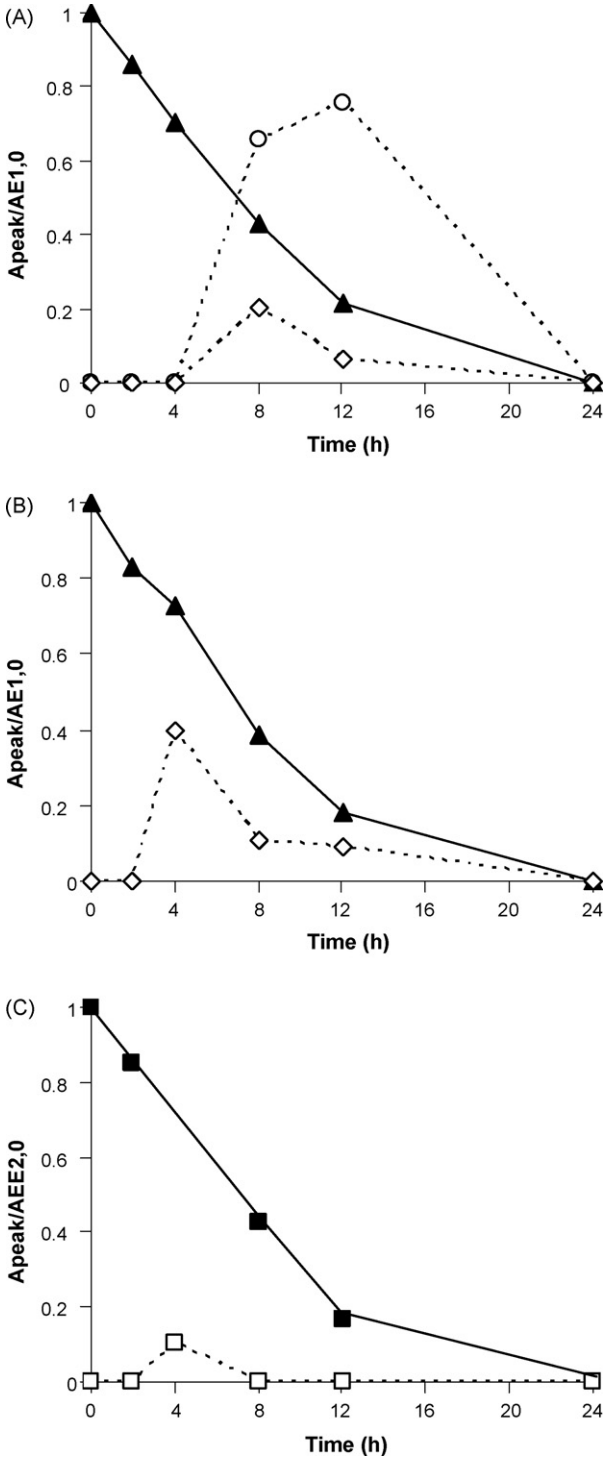

Fig. 4. Normalized chromatographic peak areas ($A_{peak}/A_{Ei,0}$ where A_{peak} = Area of peak detected, and $A_{Ei,0}$ = Area of E1 or EE2 in non-irradiated samples) of detected photodegradation products (open symbols) and remaining parent compounds (closed symbols) during E1 UV–vis irradiation (A), E1 UVC irradiation (B), and EE2 UVC irradiation (C). Open circles, diamonds, and squares represent the peaks eluting after 2.8 min, 4.2 min and 6.8 min, respectively. The values plotted represent average on triplicates. E1, E2, and EE2 were initially supplied at 10 mg/L.

Table 1
Concentration of E2 in the extract during the second simultaneous extraction/phototreatment experiment with acetone

Cycle	Irradiation time (h)	Concentration (mg/L)			
		MIPs		NIPs	
		Irradiated	Control	Irradiated	Control
1	0	0.34 ± 0.04	0.41 ± 0.04	0.28 ± 0.04	0.26 ± 0.05
	10	<0.1[a]	0.48 ± 0.04	<0.1[a]	0.30 ± 0.05
2	0	0.48 ± 0.04	1.17 ± 0.07	0.45 ± 0.04	0.79 ± 0.02
	10	<0.1[a]	1.31 ± 0.09	<0.1[a]	0.95 ± 0.12

[a] Below limit of quantification of 0.1 mg/L.

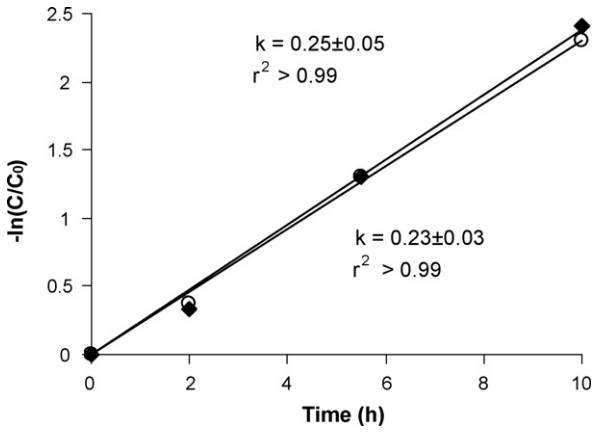

Fig. 5. Remaining concentration ($-\ln C/C_0$) of E2 in the acetone extract during simultaneous extraction/irradiation of polymers preliminary loaded with E2. C_0 and C represent the initial and time t concentrations, respectively. The data presented shows results from duplicated experiments (squares and circles) conducted at one week interval. The values plotted represent average on triplicates; k = first-order kinetics rate.

after 10 h of UV–vis irradiation. E2 removal was well described by a pseudo-first-order kinetics with a rate similar to that determined during the kinetics study at 2 mg E2/L (Fig. 5). No E2 was detected in the extract from the irradiated polymer. This experiment was reproducible.

An additional experiment was carried out to check if the acetone could be used in more than one cycle of extraction/phototreatment (Table 1). E2 accumulated in the control extracts since this compound was not degraded during incubation in darkness. No E2 remained in the irradiated extract after 10 h after both extractions. These results also showed the irradiated acetone and polymers could be reused.

Pollutant degradation occurred in organic phase (the extract) after the estrogens had been removed from water. No photodegradation products were observed to accumulate although this should be confirmed with advanced analysis. The generation of photoproducts is however inherently less risky than when UV irradiation is performed directly on water samples because photoproducts found in the solvent would unlikely bind to the polymers and leach in the water during the next elution and adsorption steps. For the same reason, it was not necessary to monitor changes in endocrine disrupting activity in the solvent extracts. This was earlier done to demonstrate the polymer efficiency to remove toxicity from aqueous samples [14].

4. Conclusions

This study demonstrates a new method for the regeneration of MIPs using solvent extraction under UV irradiation. The efficiency of MIP adsorption followed by solvent elution has already been demonstrated for real samples [14,16] and showed the presence of interferences neither impacts pollutant removal efficiency from water nor reduces pollutant recovery from the polymers. The kinetics of photo-degradation could however be affected by interferences found in the extract. Further studies should therefore focus on optimizing and testing the process under real conditions.

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