



Hybrid polystyrene nanoparticle-ultrafiltration system for hormone removal from water



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ABSTRACT

Occurrence of hormones in water resources even at low concentrations of ng/L is a potential risk for both environmental and public health. Hybrid sorbent-ultrafiltration (UF) systems are among the technologies under investigation for their potential as a sustainable and energy-efficient process for the removal of hormones from water. In this study polystyrene (PS) nanoparticles were explored as sorbent in a hybrid system. Estrone adsorption capacity of 52 nm PS nanoparticles was found to be 79.6 ng/g at equilibrium estrone concentration of 5.9 ng/L. The performance of the hybrid PS nanoparticle-UF system was studied in terms of adsorption and membrane permeability under varying solution pH, particle size and particle concentration. The results indicated that neutral pH range is optimal for operation of the system and estrone removal with nanoparticles above 465 nm is negligible. The highest estrone removal (40%) was achieved by the hybrid system using a 100 kDa UF membrane and 84 mg/L PS (52 nm) nanoparticle concentration. The capacity of the system to remove estrone was found to be lower than most nanofiltration/reverse osmosis (NF/RO) systems but with a final permeability of 75 L/m² h bar, at least five times higher than most of the NF/RO systems.

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1. Introduction

Hormones, both naturally secreted by human and animal bodies and synthetic, are known to be one of the most dangerous trace contaminant groups as they have high potential to disrupt the endocrine activities of living organisms [1]. The excreted or disposed hormones end up either in wastewater treatment plants (WWTPs) or directly in surface waters [2]. Current WWTPs are not able to remove hormones from water adequately [3] resulting in detected concentrations up to 275 ng/L in WWTP effluents [3–10], 195 ng/L in surface waters [11–13] and 120 ng/L in ground waters [14].

Even at such low concentrations, hormones can interfere with the endocrine regulatory systems of many living organisms causing disorders such as feminization of male fish [15–18] and increased risk of cancer in humans [19,20]. A recent rise in public awareness resulted in more studies conducted to explore efficient treatment processes for removing endocrine disrupting compounds from water [21].

While evaluating effective technologies, low energy requirement should be kept as one of the criteria considering that energy resources are becoming scarcer every day. The technologies showing promising results for the removal of hormones are advanced oxidation/ozonation processes (AOPs) [21,22] and nanofiltration/reverse osmosis (NF/RO) [23–25]. Nevertheless, NF/RO systems have high energy requirement ~ 1 kWh/m³ [26] whereas AOPs are susceptible to formation of toxic by-products [27–30] which contribute to residual estrogenic activity in the treated water [31,32].

Recently, hybrid activated carbon-low pressure membrane systems were investigated as an alternative technology [33–35]. The energy requirement of looser membrane systems such as ultrafiltration is 0.1–0.2 kWh/m³ [36,37], an order of magnitude less than the ~ 1 kWh/m³ required for NF/RO systems [26]. Although activated carbon seems to be an efficient sorbent for hormones [38–41] the thermal regeneration required can be highly energy consuming [42]. Due to the relatively easy regeneration characteristics and the availability of functionalisation methods, polymeric sorbents are often indicated as potentially better candidates than activated carbon [43]. High sorption of hormones on non-polymeric nanomaterials has been reported recently [44–46] showing high potential for water treatment applications [47] and has been attributed

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Table 1
Characterization of the PS nanoparticles.

Diameter ^a (nm)	43 ± 5.9 (fluorescent)	52 ± 7.9	81 ± 10	465 ± 11	3000 ± 65
Diameter ^b (nm)	49.1 ± 2.5	49.0 ± 2.5	71.8 ± 3.7	469.8 ± 23.9	–
Diameter ^c (nm)	–	49.4 ± 9.8	73.3 ± 17.7	476.1 ± 17.9	–
Zeta Potential ^b (mV)	–62.7 ± 8.0	–52.2 ± 6.7	–64.1 ± 8.2	–106.7 ± 13.7	–92.9 ± 11.9

^a According to the manufacturer.

^b Measured in 20 mM NaCl and 1 mM NaHCO₃ with size analyser.

^c Size obtained from SEM images.

Table 2
UF membrane characteristics and operational conditions.

MWCO	Pore Diameter ^a	Pore Diameter ^b	Operating Pressure	Average Pure Water Flux	Pure Water Permeability	Clean Membrane Resistance ^c
kDa	Nm	Nm	Bar	L/m ² h	L/m ² h bar	1/m
1	1.59	2.64	5	22 ± 4	4	8.27E + 13
3	2.84	4.37	5	39 ± 5	8	4.69E + 13
5	3.72	5.53	5	56 ± 9	11	3.24E + 13
10	5.37	7.61	5	109 ± 9	22	1.68E + 13
30	9.62	12.6	1	326 ± 19	326	1.07E + 12
100	18.2	21.9	0.5	433 ± 55	865	4.30E + 11

^a Estimated after Worch [52,53].

^b Estimated after Crittenden et al. [54].

^c Calculated with Eq. (4) using average operation temperature (21 °C).

to their large surface area. Nano size polymer sorbents can be a promising compromise for hormone removal combining high surface area with functionalisation and easy regeneration. Effective sorption of steroid hormones on resins made of cross-linked polystyrene divinylbenzene (PS-DVB) has been reported [48].

In this study, a hybrid polystyrene (PS) nanoparticle-UF system was studied for the removal of hormones from water. PS nanoparticles were employed, firstly because they provide a large surface area due to their nano-size and, secondly, because they can easily be manufactured in different sizes and functionalized. Moreover, non-porous and chemically resistant PS particles would enable easy regeneration of the materials. Treatment with organic solvents, bases or acids, steam, supercritical fluids or microwave radiation are among the methods used for the regeneration of the spent polymeric sorbents [43]. Hormone sorption capacity of the plain PS nanoparticles at environmental hormone concentrations has not been studied before and such a study can give an indication on the mechanisms underlying sorption on nanoparticles and where to act to improve the system performance.

This work aims to investigate the fundamental design parameters of the hybrid PS nanoparticle-UF system and evaluate the performance in comparison to NF/RO technologies in terms of hormone removal and membrane permeability. One of the major limitations in UF is fouling which results in deterioration in membrane performance. The system performance was studied with changing: particle size, particle concentration, solution pH and molecular weight cut off (MWCO) of the UF membrane. All of these parameters can potentially influence both hormone adsorption onto the particles and membrane permeability.

2. Materials and methodology

2.1. Solution chemistry and hormones

Analytical grade chemicals and ultra-pure water (conductivity: 18.2 mS/cm) obtained by PuraLab Ultra (Elga LabWater, UK) were used to prepare the solutions. The pH of the solutions was adjusted with 1 M HCl and 1 M NaOH (Fisher, UK). Nanoparticle characterisation and experiments were conducted in background electrolyte solution of 1 mM NaHCO₃ and 20 mM NaCl (Fisher, UK).

Estrone (E1) solutions were prepared using tritium labelled [2,4,6,7-³H] estrone (2.449 TBq/mmol) with a radioactive activity of 37

MBq/mL (Perkin Elmer, UK). Non-labelled estrone (≥98% purity) (Sigma Aldrich, UK) was used together with the tritium labelled estrone where needed for preparing the solutions with concentrations ≥500 ng/L. The radioactivity of estrone was measured in disintegration per minute (dpm) with a Beckman LS 6500 scintillation counter (Fullerton, USA) after mixing 0.5 mL of sample with 3.5 mL of Ultima Gold LLT (Perkin Elmer, UK) in 20 mL scintillation vials (Perkin Elmer, UK). Each sample was measured three times, each for a duration of 10 min, and the average value was reported. The instrument was calibrated each time a new hormone stock solution was prepared.

2.2. Nanoparticle characterization

Plain (52, 81, 465 and 3000 nm) and fluorescent (43 nm) PS nanoparticles (Polysciences Inc., Germany) were used. Prior to experiments and instrumental analysis, the nanoparticle solutions were sonicated for 5–10 s with 150 W ultrasonic cleaner (Sonic Wave, UK) to break any possible aggregates.

The effective diameter and zeta potential measurement of the nanoparticles were determined by 90Plus/BI-MAS Particle Size and Zeta Plus (Brookhaven Instruments, New York, USA), respectively, by taking the mean of 10 measurements. Prior to the measurements, the samples were allowed to equilibrate at the temperature of the sample holder in the instrument for at least five minutes. Concentrations of ~0.60% v/v for 43 nm, 52 and 81 nm and 0.15% v/v for 465 and 3000 nm size were used for the zeta potential measurements of PS nanoparticles.

The size and the surface charge of the particles are presented in Table 1. Particle sizes provided by the manufacturer were used in the analysis as the values were confirmed by the measurement conducted with particle size analyser and scanning electron microscopy (SEM). The microscope images of 52, 81 and 465 nm particles confirm that the particles are spherical, uniform and have a narrow size distribution as can be seen in the Supporting Information Fig. S-1. Zeta potential values show that the absolute surface charge of the particles with larger size (465 and 3000 nm) is higher compared to 43, 52 and 81 nm particles. Higher zeta potential for larger PS particles was also reported by Elimelech [49] and was attributed to the higher surface charge density [50].

Constant zeta potential values for 52 nm particles, presented in Supporting Information Fig. S-2, imply that solution pH between

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