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Removal of 17β-oestradiol and 17α-ethinyl oestradiol from water by activated carbons and hypercrosslinked polymeric phases

B. Saha *, E. Karounou, M. Streat

Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

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ABSTRACT

There has been growing concern about man-made and naturally occurring chemicals in the environment in recent years. These chemicals interfere with the hormone (or endocrine) system, suggesting far-reaching effects on reproduction and development in current and future man and wildlife generations. Recent research has highlighted the existence of these substances in sewage and industrial effluents and their potential for recycling back into the environment, including drinking water, through point and non-point sources. 17β-Oestradiol (E2) and 17α-ethinyl oestradiol (EE2) are amongst the compounds of concern since they were found to cause adverse effects to fish even at low concentration levels.

In this work, the adsorption of E2 and EE2 onto several granular activated carbons and Macronet polymers was investigated by batch experiments after a low level detection system was developed using Gas Chromatography Mass Spectrometry (GC/MS). Equilibrium experiments were carried out for all adsorbents to quantify the sorption capacity for E2 and EE2 and the data were correlated using conventional theoretical treatments. For better assessment of the sorbents, their physical properties including surface area, average pore diameter and micropore volume and chemical structure were characterised by N_2 adsorption experiments. Further characterisation was performed with scanning electron microscopy (SEM), FTIR spectroscopy, sodium capacity determination, pH titration, development of proton-binding curves and zeta potential measurements. Kinetic experiments were performed at different size ranges of adsorbents and the results were analysed by applying a particle diffusion model. This study demonstrates the potential of these adsorbents for the removal of endocrine-disrupting compounds from aqueous solution.

1. Introduction

Environmental science is presently concerned with the existence of a large number of chemicals in the environment classified as endocrine-disrupting compounds (EDCs), which can cause adverse effects to wildlife through bioaccumulation at very low concentrations (ng/L). EDCs can affect the physiological processes that are under hormonal control such as reproductive system development and function. Significant research work is being undertaken worldwide by various organisations e.g. United States Environmental Protection Agency (USEPA), United Kingdom Environment Agency (UKEA), Oslo and Paris Commission (OSPAR), Japan Environment Agency (JEA) and World Wildlife Fund (WWF), to characterise the levels of suspected EDCs to which human and wildlife are exposed and to determine their fate in the environment and their possible effects on ecosystems and human health. The probability of future European legislation to eliminate hormonally active compounds from wastewaters suggests that new and alternative methods should be developed for their removal.

The natural steroid hormones, 17β-oestradiol and oestrone and the synthetic oestrogen, 17α-ethinyl oestradiol are amongst the EDC list. They have been identified from a range of investigations, from laboratory in vitro culture experiments, standard in vivo toxicological evaluations or field observations [1–3]. Tests performed in vivo [1] have shown that male fish exposed to oestrogens also produce a yolk protein, vitellogenin. Research has revealed that the production of the yolk protein and the difference in its rate of production are indicators of presence of environmental pollutants with oestrogenic activity [2,3]. This activity exists in effluents from sewage treatment works (STWs) suggesting that it is predominantly of domestic origin.

Prior to excretion, natural oestrogens, e.g. 17β-oestradiol, oestrone and oestriol are metabolised by hydroxylation and conjugation to glucuronide and sulphate conjugates, which are compounds that are biologically inactive [4,5]. However, the action of some microorganisms during sewage treatment hydrolyses the inactive compounds back to the biologically active oestrogens. Furthermore, the synthetic compound EE2 always appears to be in the biologically

* Corresponding author. Tel.: +44 (0)1509222505; fax: +44 (0)1509223923.
E-mail address: B.Saha@lboro.ac.uk (B. Saha).

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active form and is not present in the conjugated form, bound to glucuronides or sulphate molecules [6,7].

The presence of oestrogenic substances in effluents in their active form and their effects on wildlife has alerted water companies running STWs throughout the world. The issue needs to be addressed and methods of resolving the problem need to be implemented. Conventional sewage treatment processes adopt primary settlement followed by secondary settlement, percolating filters and sand filters and/or secondary and activated sludge treatment [8,9]. Alternative treatment processes such as ozonation, chlorination and carbon, polymer or membrane filtration may be more efficient for steroid reduction [10,11]. Removal of endocrine-disrupting compounds from water has been reported by molecularly imprinted polymers [12,13], using macroporous molecularly imprinted cryogels in a moving-bed reactor [14] by nanofiltration [15] and ultrafiltration membranes [16] and using membrane processes [17,18]. Kanda and Churchley [19] reported the removal of endocrine-disrupting compounds during conventional wastewater treatment from Nuneaton sewage treatment works (Warwickshire, England). Gane et al. [20] invented a process that relates to the removal of endocrine-disrupting compounds from an aqueous medium by adding surface-reacted natural calcium carbonate or an aqueous suspension comprising surface-reacted calcium carbonate. Darton et al. [21] have suggested improving the performance of activated sludge treatment plants. The process involves placing supported biofilms in the aeration tanks. Tests on their set-up were reported to remove 90–95% of 100 μg/L EE2 after 20 days of continuous contact of both synthetic and actual sewage with the biofilm.

Levels of pesticides have been reduced by the use of activated carbon in water treatment [22]. Activated carbon is an adsorbent that has been extensively used for water purification since it has the ability to effectively remove various inorganic and organic substances and is also cost effective [23]. Activated carbon possesses a high internal surface area and controlled pore-size distribution while displaying interesting adsorptive characteristics due to the presence of various surface functional groups. By investigating the use of conventional activated carbons as adsorbents for oestrogen removal, it will be possible to assess their performance and their potential in STWs.

Hypersol-Macronet polymers are a special type of adsorbent possessing high surface area (>1000 $m^2 g^{-1}$) and controlled pore-size distribution. These novel adsorbents were developed by Davankov et al. [24] and are now produced by Purolite International Limited with a wide variety of pore sizes and chemical functionalities [25]. Hypersol-Macronet polymers are based on a spherical styrene-divinyl benzene copolymer that is crosslinked while the polymer is in the swollen state. These adsorbents have demonstrated effective removal of moderately polar pesticides such as atrazine from water [22]. It was established that moderately polar substances can interact with the hydrophobic surface of these adsorbents [26]. Hypersol-Macronet polymers are also believed to be potentially efficient adsorbents for the removal of specific EDCs, e.g. E2 and EE2, from water.

The aim of this work is to evaluate particulate adsorbents (activated carbons and Hypersol-Macronet polymers) for the specific removal of EDCs particularly E2 and EE2 from water. The activated carbons used in this work are produced from different precursors and obtained from various manufacturers as shown in Table 1, while the polymeric materials were supplied by Purolite International Limited, UK (Table 2). In the present work, adsorption experiments using relatively low concentrations (4 μg/L) of single solute oestrogens in aqueous solutions were performed in order to study and compare the adsorption capacities. Kinetics studies of the conventional activated carbons and polymeric resins were also performed to assess the time that adsorption can occur.

Table 1
Activated granular carbons specifications.

Carbon	Carbon manufacturer	Precursor
WV-A 1100	Westvaco Corporation	Wood
Brimac 216	Tate & Lyle Process Technology	Bone charcoal
SAC6	Eurocarb	Coconut shell
YAO	Eurocarb	Coconut shell

Table 2
Hypersol-Macronet polymers specifications.

Polymer	Surface area ($m^2 g^{-1}$)	Pore volume (mL/g)	D_{50} Å (meso and macropores)	Functionality
MN 100	800–1000	1–1.1	850–950	WBA[a]
MN 200	800–1000	1–1.1	850–950	None
MN 250	800–1000	0.6–0.8	300–400	None
MN 500	800–1000	1–1.1	850–950	SAC[b]

[a] WBA: Weak base anion exchanger.
[b] SAC: Strong acid cation exchanger.

2. Methods and materials

2.1. Materials

The adsorption experiments were carried out with E2 and EE2 (see Fig. 1), supplied by Sigma–Aldrich Ltd., UK. All solvents used, i.e. dichloromethane, acetone, hexane, methanol and ethyl acetate were of Distrol grade and were supplied by Fisher Scientific, UK, along with 0.1 M sulphuric acid, 0.1 M sodium hydroxide and 0.1 M hydrogen chloride. Mirex was purchased from Qmx Laboratories Limited, UK. The derivatisation reagents, *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) and trimethylsilylimidazole (TMSI) were obtained from Sigma–Aldrich. The C_{18} solid phase extraction (SPE) columns (1000 mg, 6 mL) were supplied by Fisher Scientific, UK. The specifications of the activated carbons and polymeric materials used in this work are presented in Tables 1 and 2, respectively.

2.2. Oestrogen determination

2.2.1. Preparation of standards

Individual stock solutions of 100 mg/L of all oestrogens (E2 and EE2) were prepared in Distrol grade acetone. A 10 mg/L working solution of each oestrogen was prepared by dilution from the stock solutions for use in the experiments.

Calibration was conducted using several concentrations of the individual oestrogens ranging from 0 to 2.5 mg/L. The standard concentrations were prepared from dilution of the working solution. Aliquots of 0.7 mL of the individual standard concentrations were transferred to 1 mL reaction vials (Wheaton derivatisation vials). The vials were placed in a heating block and the solvent was evaporated to dryness at 333 K by a stream of nitrogen before commencing the derivatisation procedure.

2.2.2. Oestrogen pre-concentration

Solid Phase Extraction (SPE) was employed for the pre-concentration of the aqueous solutions used in the batch adsorption studies prior to their GC/MS analysis. A filtration step was carried out prior to extraction using glass fibre to remove adsorbent particles. The pH was adjusted to 4 using 0.1 M sulphuric acid. A 16 port manifold with PTFE valves was used for SPE, which was connected to a peristaltic pump. Flow rate of 3 mL/min was used. Cartridges were placed on a vacuum manifold and were conditioned by 10 mL Distrol grade methanol followed by 10 mL of 2% methanol