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C. Tizaoui, S. Ben Fredj, L. Monser

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Polyamide-6 for the removal and recovery of the estrogenic endocrine disruptors estrone, 17 β -estradiol, 17 α -ethinylestradiol and the oxidation product 2-hydroxyestradiol in water

C. Tizaoui^{a*}, S. Ben Fredj^b, L. Monser^b

^aCentre for Water Advanced Technologies and Environmental Research, Systems and Process Engineering Research Centre, College of Engineering, Bay Campus, Swansea University, Swansea, SA1 8EN, UK;

^bNational Institute of Applied Sciences and Technology, Centre Urbain Nord, Tunis, Tunisia.

***Corresponding author:** Email: c.tizaoui@swansea.ac.uk, Tel: + 44 (0) 1792 606841, Fax: +44 (0) 1792 295676.

Keywords: Endocrine disrupting compounds (EDCs); estrone (E1), 17 β -estradiol (E2), 17 α -ethinylestradiol (EE2); 2-hydroxyestradiol (2OHE2); Polyamide 6 (PA6); secondary treated wastewater.

Abstract

The removal and recovery of highly potent endocrine disrupting chemicals (EDCs) estrone (E1), 17 β -estradiol (E2) and 17 α -ethinylestradiol (EE2) and the oxidation product 2-hydroxyestradiol (2OHE2) in water was achieved on Polyamide 6 (PA6) particles. Hydrogen bonding was the main mechanism driving the adsorption of these EDCs on PA6 at pHs lower than the EDCs pKas (~10.5) and their adsorption was not affected by the water matrix nor by solute-solute interaction. The adsorption isotherms were linear and the values of the linearity constants for E2 and EE2 were almost double those for E1 and 2OHE2. This was correlated to the number of *intermolecular* hydrogen bonds via –OH groups of the EDCs (H-bond donors) available for interaction with PA6's surface via the amide groups (H-bond acceptors). The effect of pH on the adsorption of the EDCs on PA6 was significant only at

pHs > EDCs pKa (~10.5). The breakthrough curves of the EDCs on PA6 particles in a fixed-bed column were successfully modelled using a linearised mass transfer model. This study shows that PA6 appears an effective sorbent for the removal as well as the enrichment and pre-concentration of EDCs in wastewater samples.

1. Introduction

Exposure of humans and aquatic species through water to substances that cause disruption of the endocrine system, called endocrine disrupting chemicals (EDCs), is becoming a serious environmental and health problem [1, 2]. Scientific research studies have for instance linked the intersex in male fish condition to exposure of fish to estrogens in the aquatic environment [3-6]. Other studies have shown that there is potential link between human exposure to EDCs and diseases involving the reproductive, immune and neurological systems [7-9]. Among the EDCs, estrogens (e.g. estrone (E1), 17 β -estradiol (E2) and 17 α -ethinylestradiol (EE2)) and their oxidation products such as 2-hydroxyestradiol (2OHE2) that form during treatment with advanced oxidation processes (AOPs), are important endocrine disruptors because of their high potencies, as shown by *in vitro* and *in vivo* studies [10-12]. These EDCs are also of significant interest because of their wide distribution in almost all water matrices including wastewaters, surface waters, ground waters and even drinking waters [13-18]. The ubiquity of EDCs results mainly from wastewater treatment plants (WWTPs), which were traditionally designed to only remove parameters such as biochemical oxygen demand, suspended solids and nutrients rather than individual organic substances [19]. Typically these estrogens are found at trace level concentrations [20, 21]. Given the concerns regarding the widespread of estrogenic EDCs in water, the European Union has recently introduced a “*watch list*” mechanism to monitor the hormones E2 and EE2, amongst other substances, to support the introduction of future standards for WWTPs effluent discharge of pharmaceuticals and

estrogenic EDCs as part of the European Priority Substances Directive [22]. E1 has also been suggested to be added to this “*watch list*”. Hence there is a need for the development of new highly efficient methods for EDCs removal in water. Besides, efficient recovery of EDCs from water samples is significant for the detection and analysis of these substances.

Several techniques used to remove and recover EDCs in water have extensively been studied [23-26]. For instance, we investigated the removal of estrogenic EDCs in water using liquid-liquid extraction (LLE) and found that, at low pH than their pKa, they preferentially distribute to organic solvents because of their hydrophobicity while ozone-reactive LLE achieved almost instantaneous removal of the EDCs [27, 28]. Ozonation has however produced oxidation products with endocrine disrupting character including 2OHE2 [12, 28]. To this end, the use of adsorption, which is a proven technology in water treatment and purification, could be a viable option for the removal of EDCs and their oxidation products that form during chemical water treatment (e.g. ozonation) [29]. Adsorption has also been used to recover EDCs for purposes such as chromatographic analysis in a technique known as solid phase extraction (SPE). In water treatment, activated carbons are commonly used adsorbents because of their high surface area and pore volume [29] whilst in SPE, adsorbents such as alkyl-bonded silicas (C8 and C18), cross-linked polystyrene divinylbenzene and carbon black have been used to concentrate and recover EDCs [30]. However, activated carbons in water treatment are expensive to regenerate and produce fines due to their brittle nature [31] and despite their popularity, SPE sorbents have limited selectivity and are expensive [32, 33]. It is hence evident that new adsorbents for the removal and recovery of EDCs in waters are needed.

We report in this research paper polyamide 6 (PA6) as an efficient polymeric adsorbent for both the removal and recovery of the estrogenic EDCs E1, E2 and EE2 as well as the oxidation product 2OHE2. The molecular structure and other physico-chemical properties of E1, E2, EE2 and 2OHE2 are summarized in Table S1 (Supplementary data). This is the first time that this adsorbent has been evaluated for the removal and recovery of these EDCs and its choice was inspired from recent studies that have shown that membranes made from industrial-grade aliphatic polyamides (PAs) exhibited specific affinity towards EDCs in water treatment applications [34]. For instance, significant simultaneous sorption capacities were reported for E1 ($0.44 \mu\text{g cm}^{-2}$), E2 ($0.82 \mu\text{g cm}^{-2}$) and EE2 ($1.23 \mu\text{g cm}^{-2}$) using a non-porous $0.2 \mu\text{m}$ PA66 microfiltration membrane ($20 \text{ m}^2 \cdot \text{g}^{-1}$) [34]. The adsorption of EDCs was instantaneous and the regeneration of the PA membrane using alkaline conditions was reported complete. Besides, the sorption capacities of the membranes were not altered after reuse. These characteristics are desirable for efficient adsorption. This study provides a contribution to better understanding the mechanisms that underpin the sorption of E1, E2, EE2 and 2OHE2 onto PA6 particles used as an adsorbent and develops correlations useful for upscaling and optimisation of the adsorption process.

1. Material and methods

2.1. Materials

PA6 was obtained in packed cartridges containing 200 mg of the adsorbent in powder form (Macherey-Nagel, Germany). Analytical standards of E1 (CAS No. 53-16-7), E2 (CAS No. 50-28-2), EE2 (CAS No. 57-63-6) and 2OHE2 (CAS No. 362-05-0) were purchased in powder form from Sigma-Aldrich (Dorset, UK) with purity higher than 99%. Standard stock solutions of EDCs were prepared in methanol at concentrations of 1 g L^{-1} and stored at -21°C . HPLC grade acetonitrile and methanol were purchased from Fisher Scientific (Loughborough, UK). Ultra-pure water was obtained from a Milli-Q water purification

system (Millipore Q system, 18 M Ω .cm, Bedford, MA, USA). Secondary treated urban waste water was sampled from the outfall of the final effluent of the Welsh Water (DŵrCymru) treatment plant at Gowerton (Wales, UK). Upstream the sampling point, the effluent was treated with a conventional activated sludge process followed by UV treatment. The sample used in this study was filtered under vacuum through a 0.22 μ m filter and stored in amber glass bottles at 6 °C.

2.2. Characterization of polyamide 6

PA6 was characterised as follows. The point of zero charge was determined by the batch equilibration method, using KCl (0.1 M) as electrolyte [35]. Briefly, a mass of 0.25 g of fresh dried PA6 was added to the solution of KCl at different initial pH values (pH_i) in the range 2 to 12 set by HCl(0.5M) or NaOH(0.5M). After equilibration (24h), the final pH values (pH_f) were measured. The intersection point between the two curves $\text{pH}_f=f(\text{pH}_i)$ and $\text{pH}_i=f(\text{pH}_f)$ gives the point of zero charge (pzc). The BET surface area, pore volume, and average pore size of PA6 powder were measured using cryogenic nitrogen adsorption-desorption isotherms at 77 K on a Micrometrics ASAP 2000 apparatus. The FTIR spectra of PA6 particles were obtained on a Perkin-Elmer Frontier FTIR spectrometer. Attenuated Total Reflectance (ATR) mode was used and each sample was scanned in the wavenumber range of 400–4000 cm^{-1} . The minimum number of scans was 4 at a resolution of 4 cm^{-1} .

2.3. Adsorption of EDCs on PA6 fixed bed

A down flow fixed-bed of PA6 cartridges (particles size $d_p=58\mu\text{m}$, mass=200 mg, bed height =8.8 mm, column diameter = 8.2 mm, voidage $\epsilon=0.65$) was used. The feed solutions were either Milli-Q water or secondary treated wastewater spiked with EDCs stock solutions at different concentrations up to 20 $\mu\text{g L}^{-1}$ of each EDC. Both single and multicomponent solutions were used in the experiments. The initial pH of water was set to 2, 6 or 12. The feed

solution was fed to the PA6 fixed bed using a bench-scale SPE system (Supelco Vacuum Manifold®, Sigma-Aldrich, Dorset, UK). The feed flow rate was set at 1 or 5 mL min⁻¹. Permeate fractions were collected at given times and analysed with HPLC.

2.4. HPLC Analysis

The HPLC analysis was performed using an Agilent 1200 Series HPLC system equipped with fluorescence (FLD, model G1321A, Agilent, USA) and diode array (DAD, model G2180BA, Agilent, USA) detectors. The DAD was used for the detection of both E2 and EE2 at 200 nm, and the FLD was used for the detection of E1 using λ_{ex} 200 nm and λ_{em} 315 nm. The chromatographic conditions were: mobile phase (50: 50 (v/v) acetonitrile: Milli-Q water) and 1 mL min⁻¹; 6 min run time; 50 μ L injection volume; and Hypersil GOLD C18 column (5 μ m, 150 x 4.6 mm, ThermoScientific, Hertfordshire, UK) thermostatically controlled at 40 °C. Steroids in the aqueous phase were identified and quantified using an external calibration method based on EDCs respective reference standards' retention times. Calibration curves of E1, E2, EE2 and 2OHE2 were linear ($R^2 > 0.99$) for concentrations in the range 0.5 ng L⁻¹ to 1 mg L⁻¹.

3. Results and discussion

3.1. Characterization of PA6 adsorbent

The characteristics of PA6 particles are listed in Table 1.

Table 1

BET measurements show that the PA6 has a surface area of 15.96 m² g⁻¹ which is comparable to that reported for a similar material PA612 (20.1 m² g⁻¹) [36]. The low value of the BET

surface area indicates that PA6 is non porous and based on the particle size and density, the external theoretical surface area of PA6, assumed smooth, is only $6.8 \text{ m}^2 \text{ g}^{-1}$. The difference between the BET and the external theoretical area could be explained by the rough surface morphology of polyamide materials, which exhibit micro-sized pores on their surfaces despite being non-porous internally [36]. Although PA6 has a relatively low surface area and low specific pore volume (Table 1), as compared to activated carbon (500 to $1500 \text{ m}^2 \text{ g}^{-1}$ and 0.7 to $1.8 \text{ cm}^3 \text{ g}^{-1}$ respectively [37]), its structure and amide functional groups warrant merits for EDCs adsorption.

According to Figure 1, the point of zero charge of PA6 corresponds to pH 6.00, which is in agreement with that obtained for PA66 fibre (PZC=6.9) [38]. Consequently, the surface properties of PA6 can change as function of pH on both sides of the point of zero charge leading to positively charged surface for $\text{pH} < 6$ and negatively charged surface for $\text{pH} > 6$.

Figure 1

Figure 2 shows key attributes of the FTIR spectrum of fresh PA6. The medium intensity band at 3295 cm^{-1} is attributable to N-H stretching vibration. The characteristic strong and sharp bands of amide I and amide II of PA6 appear at 1635 cm^{-1} and at 1538 cm^{-1} , which are respectively assigned to C=O stretching vibration (amide I) and to the mixed motion of C-N stretching and N-H in-plane bending vibration (amide II). The C=O dipole and, to a lesser extent, the N-C dipole confer to PA6 the ability to act as H-bond acceptor. The presence of the N-H dipole allows PA6 to also function as H-bond donor.

Figure 2

3.2. Adsorption of EDCs on polyamide 6

3.2.1. Adsorption breakthrough curves

The concentrations of each EDC were determined as function of eluted volume and the ratio (C/C_0) was calculated, where C is the residual concentration in the eluted aliquot and C_0 is the inlet feed concentration. Figure 3 shows the adsorption breakthrough curves for E1, E2, EE2 (a), and the adsorbent uptake normalised by the inlet EDC concentration (b) as function of the cumulative eluted volume. Each EDC was prepared at an initial concentration of approximately $7 \mu\text{g L}^{-1}$ and eluted individually onto the PA6 cartridge.

The breakthrough curves shown on Figure 3(a) are typical to adsorption processes, where initially the fluid emerges from the bed solute-free until reaching the breakpoint at which the concentration of the fluid exiting the bed starts to increase as the un-adsorbed solute begins to appear. Starting from the breakthrough point, the instantaneous mass retained on the adsorbent quickly decreases as the eluting volume increases up to the exhaustion plateau indicating saturation of PA6 (i.e. the equilibrium point). The breakthrough curves of E2 and EE2 superimpose (Figure 3 (a)) indicating that both EDCs have similar adsorption capacity as also shown in Figure 3(b). The values of uptake at equilibrium normalised by the inlet concentration were 0.79 L.g^{-1} for E1, and 1.45 L.g^{-1} for E2 and EE2 respectively.

Figure 3

3.2.2. Adsorption equilibrium lines

The equilibrium mass loading curves were determined at 25°C by integration of the adsorption uptake breakthrough curves using different low inlet EDC concentrations up to $20 \mu\text{g L}^{-1}$ in MQ-water. Linear equilibrium relationships were obtained for all EDCs. At such low concentrations, the molecules adsorbed are extensively spread out over the surface area

of the adsorbent so that molecules do not influence the adsorption of each other. Hence, the adsorbent uptake is proportional to the concentration in the liquid phase. The values of the dimensionless Henry's law adsorption equilibrium constants defined as a concentration ratio based on particle volume, K , are reported in

Table 2. The values of the linear isotherm constants based on adsorbent mass are also reported in

Table 2 (values between brackets). The results indicate that PA6 has almost double affinity towards E2 and EE2 as compared to E1. Given that E2 and EE2 all have phenolic moieties on their respective C3 and C17 and comparable dissociation constant values (pK_a), their hydroxyl moieties are expected to have the same H-bonding donor affinity towards PA6 particles. Duax et al. [39, 40] proposed that the phenol of E2 could act as both an H-bond donor and acceptor in the binding site of an estrogen receptor while Fevig et al.[41] demonstrated that the phenol of E1 acts strictly as H-bond donor. Therefore, differences in H-bonding properties between E1, E2 and EE2 could rationalise the difference between E1 uptake to that of E2 and EE2. E2 and EE2 have higher potential for hydrogen bonding via their respective two -O-H groups, as compared to only one -O-H group in E1 (see Table S1).

Table 2

3.2.3. Effect of pH on EDCs adsorption on PA6

To investigate the effect of pH on the adsorption of EDCs on PA6, three initial pH values (2, 6 and 12) were used. Figure 4 shows that the adsorption of E1, E2 and EE2 was not significantly affected by a change in pH from 2 to 6. However, at pH 12, the adsorption

decreased drastically. Similar effect of pH was also reported in the literature [36]. As weak acids, EDCs ($pK_{as} \sim 10.5$) remain non-ionised at $pH < pK_a$ [27, 42] and dissociate to their base conjugates at aqueous $pH > pK_a$. The deprotonation at high pHs of the EDCs increases their aqueous solubility (Table S2). A speciation set of both PA6 and EDCs, as function of pH, is shown in Table 3. On the basis of its $pzc (=6.00)$, PA6 would be positively charged under acidic environments (i.e. $pH < pzc$) and negatively charged under alkaline conditions (i.e. $pH > pzc$). This implies that at $pHs > pK_a > pzc$, PA6 repels the EDCs via repulsive electrostatic forces preventing them to approach its surface. Overall, at $pH > pK_a (\sim 10.5)$, EDCs are more soluble in water and are electrostatically repelled by PA6, which explains the decrease of their adsorption at pH12.

Figure 4

Table 3

3.2.4. Adsorption mechanism: hydrogen bonding

The adsorption of EDCs on PA6 at neutral pH, lower than the EDCs pK_{as} , was investigated using FTIR to provide information on the interaction between the polymer and the solutes. Hydrogen bonding could potentially lead to significant changes in the FTIR spectrum including frequency shifts and increases of FTIR intensity for bands assigned to vibrational modes of functional groups involved in the hydrogen bonds. FTIRs were performed for PA6-adsorbed-EDCs (after loading 100 mL of $200 \mu\text{gL}^{-1}$ EDCs solution on fresh PA6) and regenerated PA6-adsorbed-EDCs with methanol. The results are shown on Figure 5 as relative ratios of FTIR signal obtained for PA6-adsorbed-EDCs and regenerated PA6-adsorbed-EDCs to fresh PA6. PA6-adsorbed-EDCs spectra show a significant increase of the relative FTIR signal of N—H ($3295, 1538 \text{ cm}^{-1}$) and C=O (1635 cm^{-1}) as compared to fresh PA6. Figure 5

also shows that the regeneration of PA6-adsorbed-EDCs with methanol tends to reinstate the relative intensity of the bands towards the value of one (i.e. fresh PA6). The increase in band intensity after adsorption of EDCs results from intermolecular interaction via hydrogen bonding between the -O-H group of the EDCs as hydrogen-bond donor and the amide group of PA6 as hydrogen-bond acceptor. As the EDCs are released from the surface of PA6 during regeneration with methanol, band intensities evolve to reinstate to their original values of fresh PA6. The strength of hydrogen bonding relevant to this study follows the order $\text{O}-\text{H}\cdots\text{N} > \text{O}-\text{H}\cdots\text{O} > \text{N}-\text{H}\cdots\text{O}$ [43]. This suggests that the interaction between PA6 and the EDCs could be represented, at pH values lower than the EDCs pK_as, as shown in Figure 6.

Figure 5

Figure 6

3.3. Adsorption in multi-component solutions

In real waters, the EDCs co-exist and hence there is potential solute-solute interactions and competition for adsorption sites [44]. Both milli-Q water and secondary treated waste water were spiked with mixtures of the EDCs at $7 \mu\text{g L}^{-1}$ of each EDC and were loaded on PA6. Figure 7 shows similar uptake values for the EDCs either in single-component or multi-component solutions under the same conditions (1 mL min^{-1} , 25°C , pH 6) suggesting that neither intermolecular interactions, nor competition for adsorption sites have taken place. This could be explained by significant abundance of adsorption sites available for the adsorption of the solutes which are found in dilute concentrations. This is also supported by the linearity of the equilibrium isotherms obtained. In addition, Figure 7 shows that the uptake values of EDCs by PA6 remain unchanged despite using different water matrices.

Particularly, the adsorption of the EDCs on PA6 in wastewater effluent, a relatively complex matrix, was not significantly affected, which suggests that PA6 has excellent selectivity for these EDCs. Han et al. have also showed that the adsorption of EE2 into PA612 particles was not affected by the type of water matrices [36].

Figure 7

3.4. Modelling of the breakthrough curves of EDCs adsorption on PA6

The shape (or width) of the breakthrough curve, especially the time point at which the effluent concentration starts to emerge, is an important knowledge for predicting the operation and dynamic response of the adsorption bed. Equally knowledge of the breakthrough curve is crucially important in the design and upscaling of the adsorption column. The shape of the breakthrough curve is determined by the type of the adsorption isotherm and is influenced by the transport processes in the bed and in the particles. For efficient separation, a sharp concentration front is desirable. However, mass dispersion in the axial direction and mass transfer resistances tend to make the breakthrough curves more dispersive (i.e. less sharp). In this study, a linearised rate model equation derived for solute adsorption in packed bed columns (Equation 1) [45] was applied to model the breakthrough curves of the EDCs adsorption on PA6 beds.

$$\frac{C}{C_0} = 0.5 \operatorname{erfc} \left(\frac{7}{8} (\xi^{0.5} - \tau^{0.5}) \right) \quad (\text{Equation 1})$$

where: $\xi = \frac{kKz}{v} \left(\frac{1-\varepsilon}{\varepsilon} \right)$ is dimensionless column length, $\tau = k \left(t - \frac{z}{v} \right)$ is dimensionless time coordinate, erfc is the complementary error function, C is the EDC concentration at the outlet of the bed at time t (mg.L^{-1}), C_0 is the inlet concentration (mg.L^{-1}), k is the overall mass transfer coefficient (s^{-1}), K is dimensionless Henry's law adsorption equilibrium constant defined as a concentration ratio based on particle volume determined experimentally in this study (Table 2), z is the bed length from the inlet (m), v is the interstitial fluid velocity (m.s^{-1}), and ε is the voidage of the bed.

The overall mass transfer coefficient, k , was estimated using established correlations (see Supplementary Material). In addition, k was determined numerically by fitting Equation 1 to the experimental data through minimising the sum of the square error (i.e. $\Sigma[(C/C_0)_{\text{exp}} - (C/C_0)_{\text{model}}]^2$), where k was the independent variable. The numerical calculation was carried out using the Generalised Reduced Gradient Nonlinear Solving method in MS Excel 2010 Solver tool. The model was applied for two flow rates (1 and 5 mL.min^{-1}) and the results (experimental data, model using k determined by Equation S1, and model fitting to experimental data with k being the variable) are shown on Figure 8. Figure 8 (a,b,c) show results for E1, E2 and EE2 at 1 mL.min^{-1} while Figure 8(d) shows an example of results at a flow rate of 5 mL.min^{-1} for E2. As can be observed from Figure 8, the model represented by Equation 1 has excellent agreement with the experimental data for all EDCs. Moreover, the k values determined by fitting the experimental data and those determined directly from established correlations were similar and their values agree well within an error of 1 to 20%. The correlations obtained in this study can hence be used to estimate breakthrough curves of the EDCs uptake on PA6 columns and upscale the adsorption process. The adsorbent usage rate (AUR), a quantity that represents the mass of adsorbent per volume of wastewater treated to breakthrough point, was also estimated at various breakthrough points using an empty bed

contact time (EBCT) of 30 min. As shown in Figure 9, approximately 0.9 kg PA6/m³ for E1 and 0.5 kg PA6/m³ for E2 and EE2 were required. These AUR values are slightly better than those reported for granular activated carbon (GAC) used in wastewater treatment (~ 1 kg/m³) [37]. As the cost per unit mass of PA6 is comparable or relatively cheaper than GAC and based on the AUR values reported above, there is potential that PA6 offers an economic advantage for the removal of EDCs as compared to GAC.

Figure 8

Figure 9

3.5. Adsorption of 2OHE2

Although adsorption could be effective to remove EDCs, advanced oxidation processes (AOPs) are gaining significant attention due to their effectiveness to degrade EDCs rather than transfer them from one phase to another. However, AOPs generate oxidation products that can be more potent than the parent molecules. One of such oxidation products is 2-hydroxyestradiol (2OHE2), a common product resulting from the oxidation of E2 [12, 46]. The adsorption of 2OHE2 on PA6 was also investigated in this study. It was found that the adsorption equilibrium of 2OHE2 followed a linear adsorption isotherm similarly to E1, E2 and EE2 and the dimensionless Henry's law constant, K , was found equal to 1019. This K -value is comparable to that obtained for E1 but significantly lower than E2 ($K_{2OHE2}=0.62K_{E2}$) (Table 2). 2OHE2 has three –O-H groups (see **Error! Reference source not found.** Table S1) which are expected to lead to high uptake capacity (i.e. high K -value) as compared to the other EDCs [47], but as shown experimentally this was not the case. The lower capacity of PA6 towards 2OHE2 could be explained by the diminution of the *intermolecular* hydrogen bonding in 2OHE2 molecule to the expense of the *intramolecular* hydrogen bonding between

the 2 adjacent –O-H groups. As a result, only one –O-H group of the 2OHE2 molecule is likely to interact with PA6 which is reflected in a K-value similar to E1 (E1 has only one –O-H).

The breakthrough curve of 2OHE2 was also determined experimentally and modelled using Equation 1. Figure 10 shows excellent agreement between the experimental data and the model. The *k*-value obtained by calculation agreed to *k*-value obtained by fitting the experimental data to within 15% error margin. The AUR was also calculated for a 30 min EBCT and was found equal to 0.8 kg/m³, which falls within the range of AURs obtained for the other EDCs. Hence, PA6 is an excellent adsorbent for the selective removal of residual EDCs in wastewater as parent components as well as their oxidation products that may result from an oxidation step.

Figure 10

3.6. Recovery of the EDCs on PA6 as a Solid Phase Extraction sorbent

PA6 was used as an SPE sorbent using two eluting solvents methanol and acetonitrile. The recoveries were complete when methanol was used while they were in the range of 57 to 100% when acetonitrile was used. Given that the -OH group of methanol has better affinity towards hydrogen bonding than the ≡N group of acetonitrile, this infers better extraction of the EDCs to methanol. Methanol is hence a preferred eluting solvent of the EDCs from PA6. PA6 was further evaluated for the extraction of EDCs using large volumes of secondary treated wastewater (up to 1L) at initial concentrations in the range 1 to 100 ngL⁻¹. The recoveries of the EDCs with methanol were complete (100%±5%) and an enrichment factor of 2000 (from 1L wastewater to 0.5 mL MeOH) was reached. The method provided high

reproducibility of the results which demonstrate that PA6 could also be used as a suitable sorbent for the enrichment of EDCs and their oxidation products prior to chromatographic analysis.

4. Conclusion

This study presents an investigation on the removal and recovery of potent EDCs namely E1, E2, EE2 and 2OHE2 (an oxidation product of E2) from secondary treated wastewater using polyamide 6 as a sorbent material. The selectivity of the PA6 adsorption process was demonstrated under various water types and the study concludes that:

- PA6 was a selective and effective sorbent material for the removal and recovery of the EDCs from different water matrices. The coexistence of the EDCs in multicomponent solutions did not affect the adsorption capacity of PA6. Hydrogen-bonding appeared as the main interaction mechanism between EDCs and PA6 surface.
- Under typical low EDC concentrations encountered in wastewater, the adsorption equilibria on PA6 particles followed linear isotherms with values of the dimensionless Henry's law adsorption equilibrium constants (pH 6) defined as a concentration ratio based on particle volume, K , of 898, 1655, 1649, and 1019 for E1, E2, EE2, and 2OHE2 respectively.
- The adsorption of EDCs on PA6 was largely unaffected by the water matrix type but drastically decreased for $\text{pH} > \text{pK}_{\text{a}}(\text{EDCs})$ (i.e. ~ 10.5) due to increased ionisation of the molecules at high pH.
- The adsorption breakthrough curves of EDCs on PA6 were modelled using a linearised rate model equation for fixed bed adsorption columns. Excellent agreement between the experimental data and the model was obtained using overall mass transfer

coefficients determined either by fitting the data or calculated directly from established models.

- The characteristic parameters of the model were determined and applied to determine the breakthrough point and the adsorbent usage rate.
- PA6 was also found to be an excellent sorbent material in an SPE operation to fully recover the four EDCs from wastewater achieving enrichment by a factor of 2000 for sample analysis by chromatographic means. Methanol was a more suitable SPE eluting solvent for the EDCs as compared to acetonitrile.

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Appendix A. Supplementary data

Supplementary data associated with this article are attached.

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Figure Caption

Figure 1: pH corresponding to the point of zero charge of PA6.

Figure 2: FT-IR spectrum of fresh PA6 particles.

Figure 3: Adsorption breakthrough curves of individual E1, E2, and EE2 on PA6 cartridge: (a) Non retained fraction of EDCs (C/C_0) as function of eluted volume of aqueous phase, (b) adsorbent uptake normalised by the inlet concentration as function of eluted volume; mass adsorbent = 200 mg, feed flow rate = $1 \text{ mL}\cdot\text{min}^{-1}$, pH 6 and $25 \text{ }^\circ\text{C}$.

Figure 4: Adsorption of EDCs as function of initial pH ($T=25 \text{ }^\circ\text{C}$, initial concentration $C_0=7 \text{ } \mu\text{g L}^{-1}$)

Figure 5: IR signals of PA6 adsorbed EDCs (E1, E2 and EE2) and PA6 regenerated by methanol relative to fresh PA6.

Figure 6: Hydrogen-bonding between EDCs and PA6 ($\text{pH} < \text{pKas} (\sim 10.5)$)

Figure 7: Uptake of EDCs in single and in multi-component spiked Milli-Q and secondary treated waste water solutions ($\text{pH } 6$, 25°C , $C_0=7 \text{ } \mu\text{g L}^{-1}$)

Figure 8: Model fitting of the uptake adsorption breakthrough curves of E1, E2 and EE2 onto PA6 ($C_0=7 \text{ } \mu\text{g L}^{-1}$, a,b,c: 1 mL min^{-1} and d: 5 mL min^{-1})

Figure 9: Adsorbent usage rate at various breakthrough points (EBCT=30 min)

Figure 10: Adsorption breakthrough curve of 2OHE2

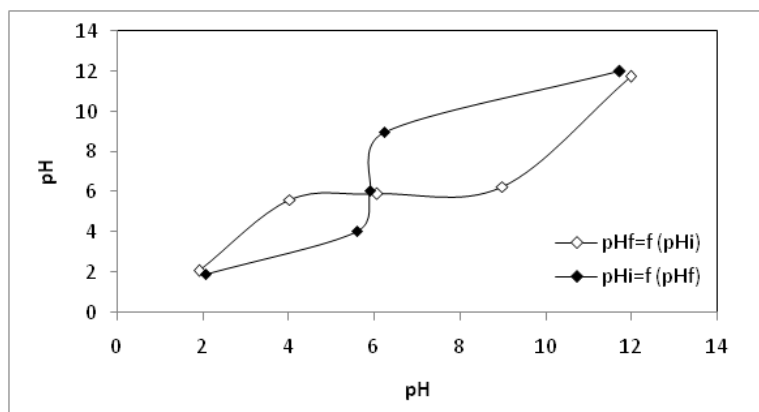


Figure 1

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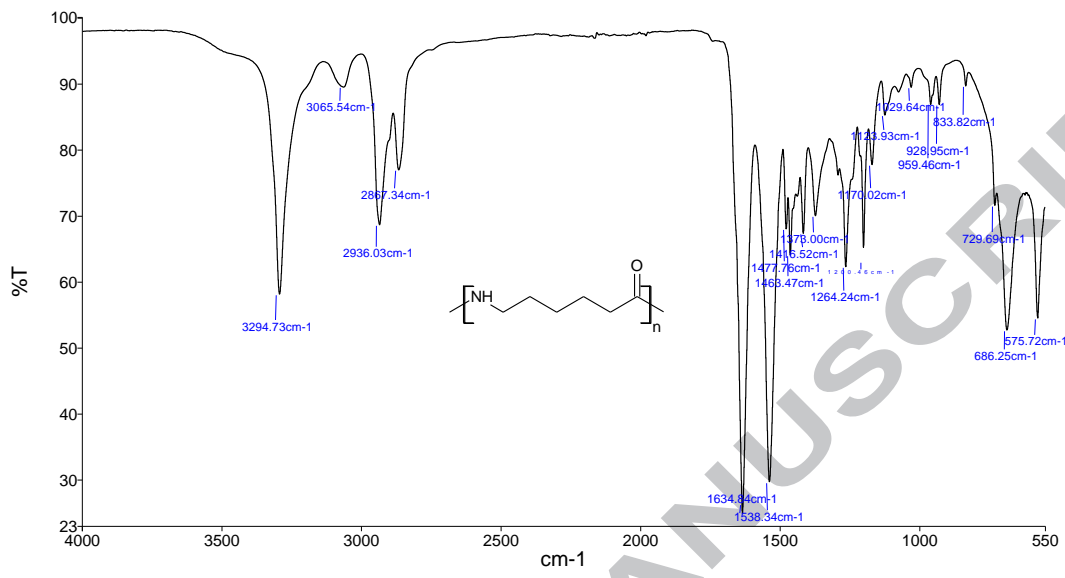


Figure 2

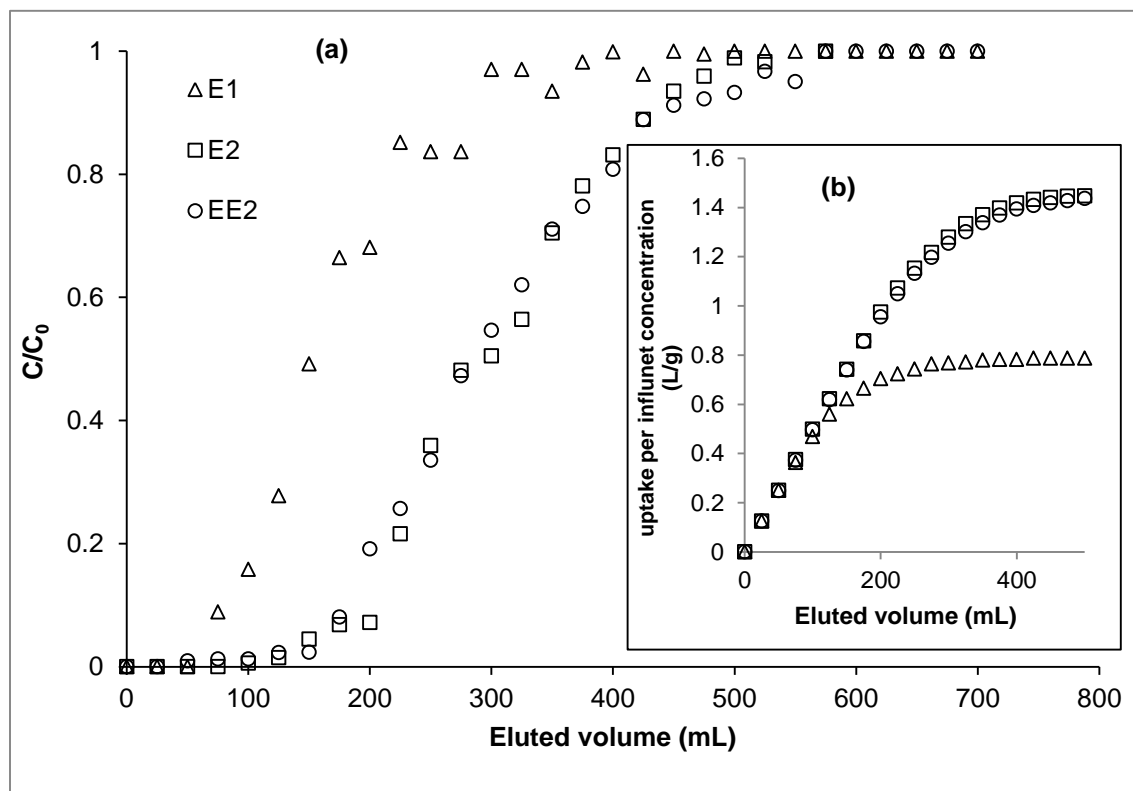


Figure 3

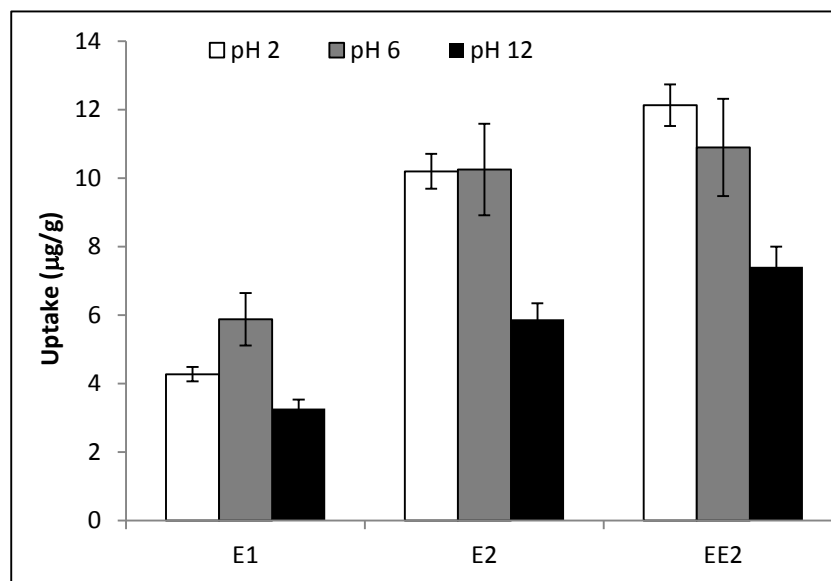


Figure 4

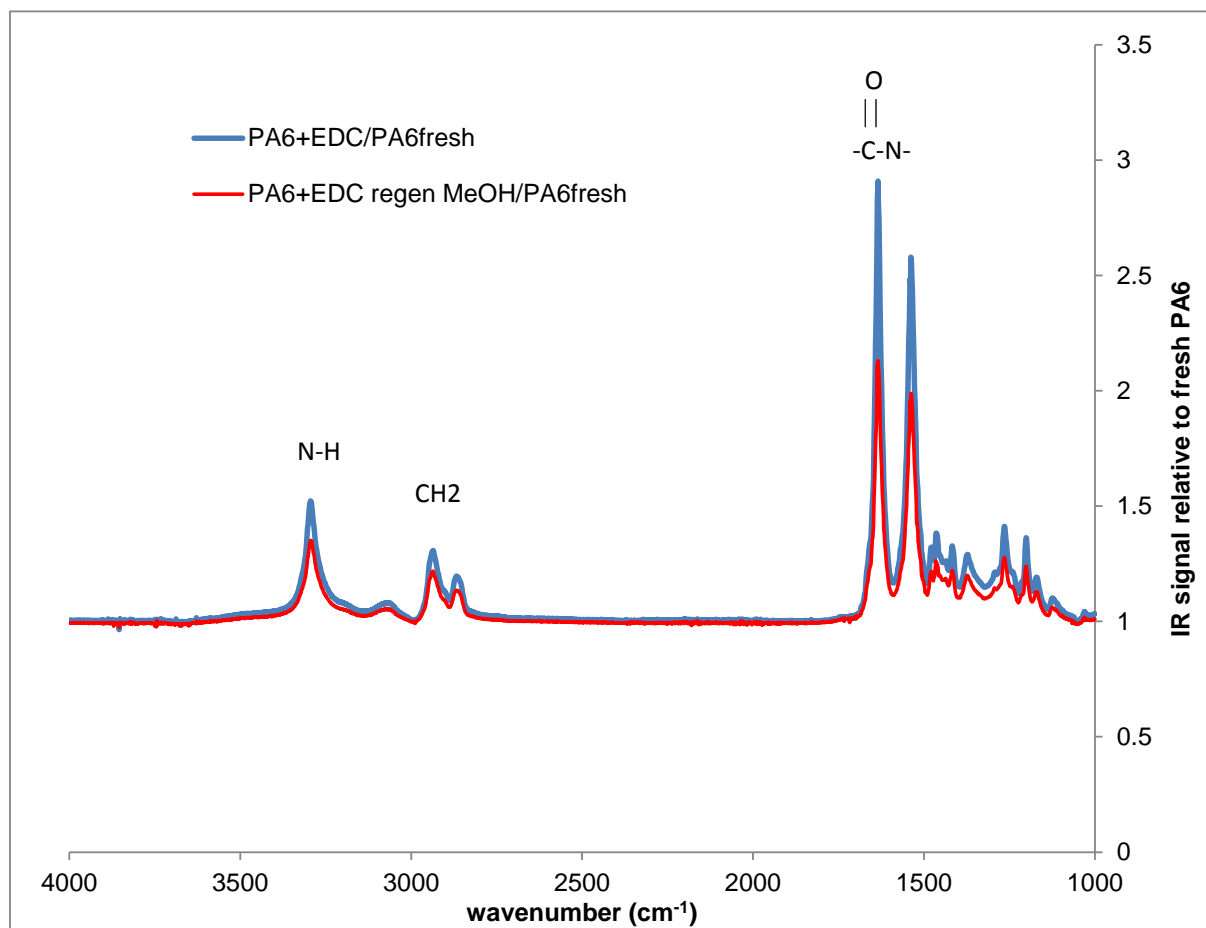


Figure 5

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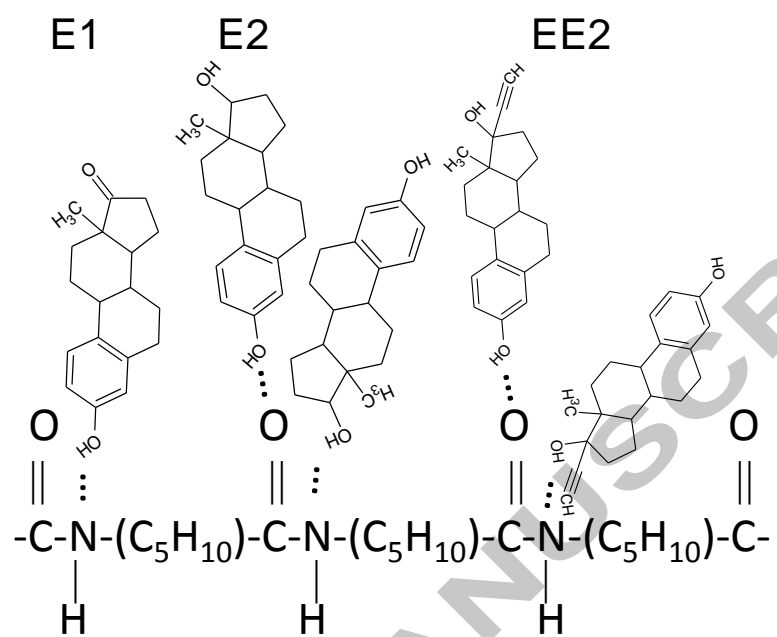


Figure 6

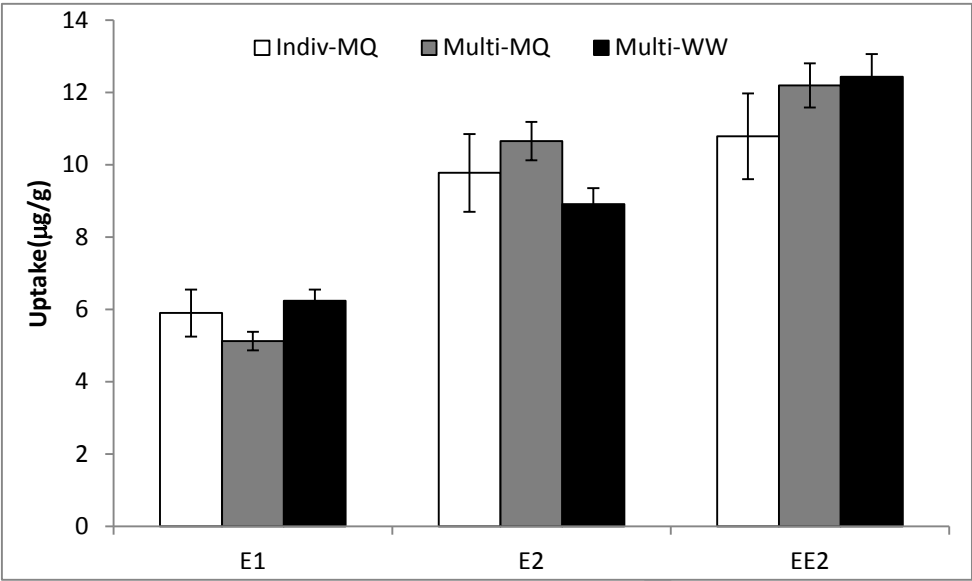


Figure 7

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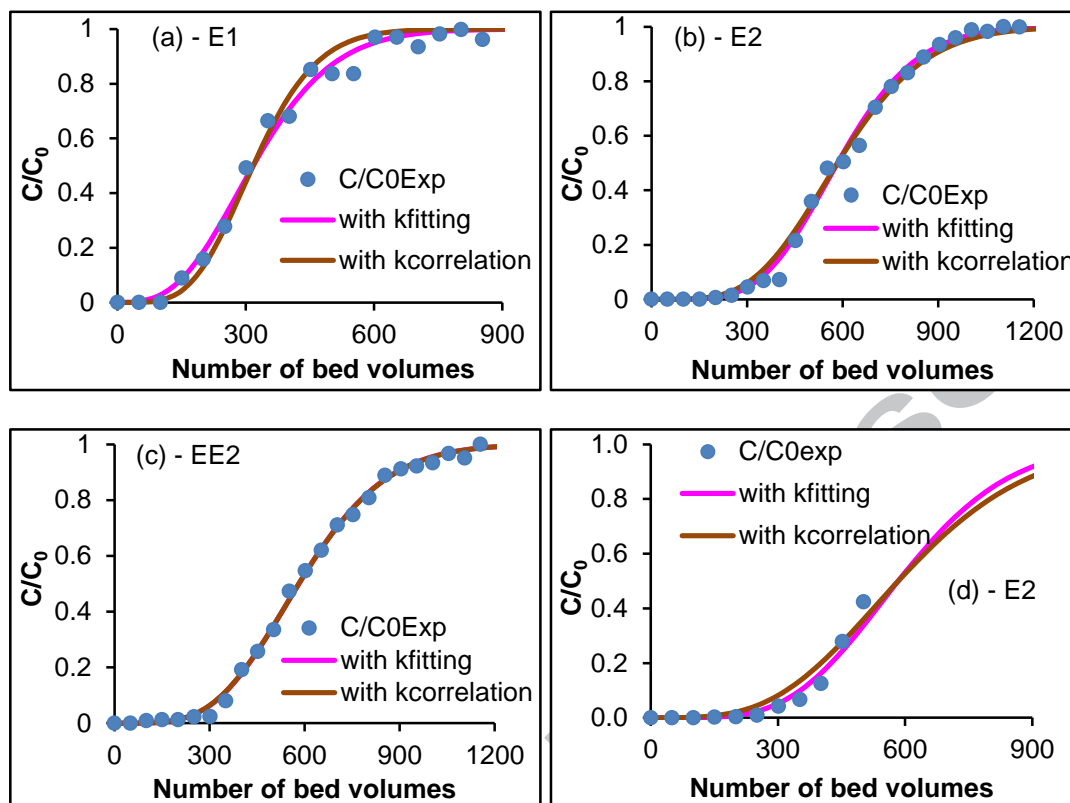


Figure 8

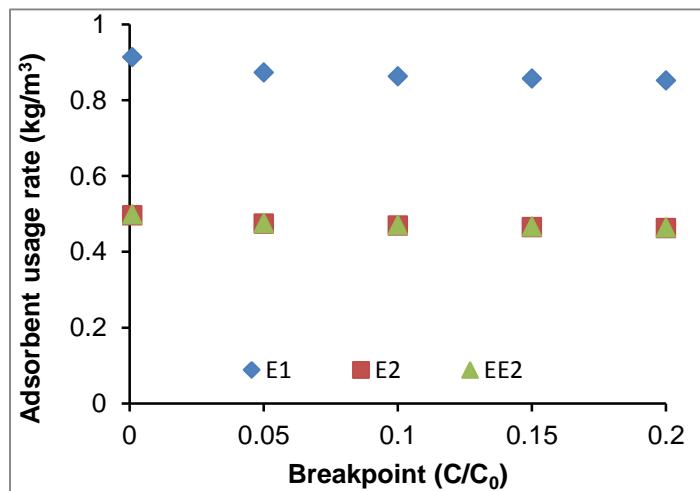


Figure 9

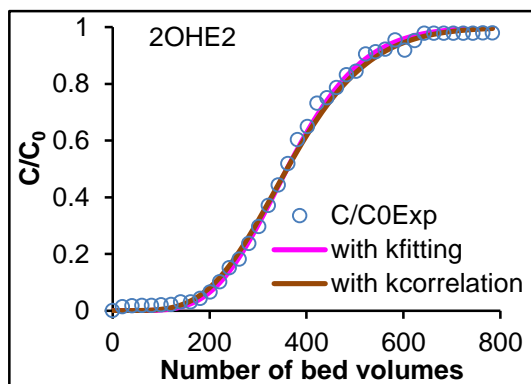


Figure 10

ACCEPTED MANUSCRIPT

Table legends

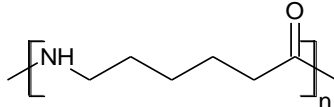
Table 1: Selected characteristics of Polyamide 6 particles.

Table 2: Linear adsorption equilibrium constants (pH = 6).

Table 3: Speciation of PA6 and EDCs (E1, E2 and EE2) molecules as function of pH.

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Table 1

Structure		Particle size (μm)	58
Monomer molecular mass (g mol^{-1})	113.16	BET surface area* (m^2g^{-1})	15.96
Density (g cm^{-3})	1.53	Specific pore volume* (cm^3g^{-1})	0.124

*: determined in this study

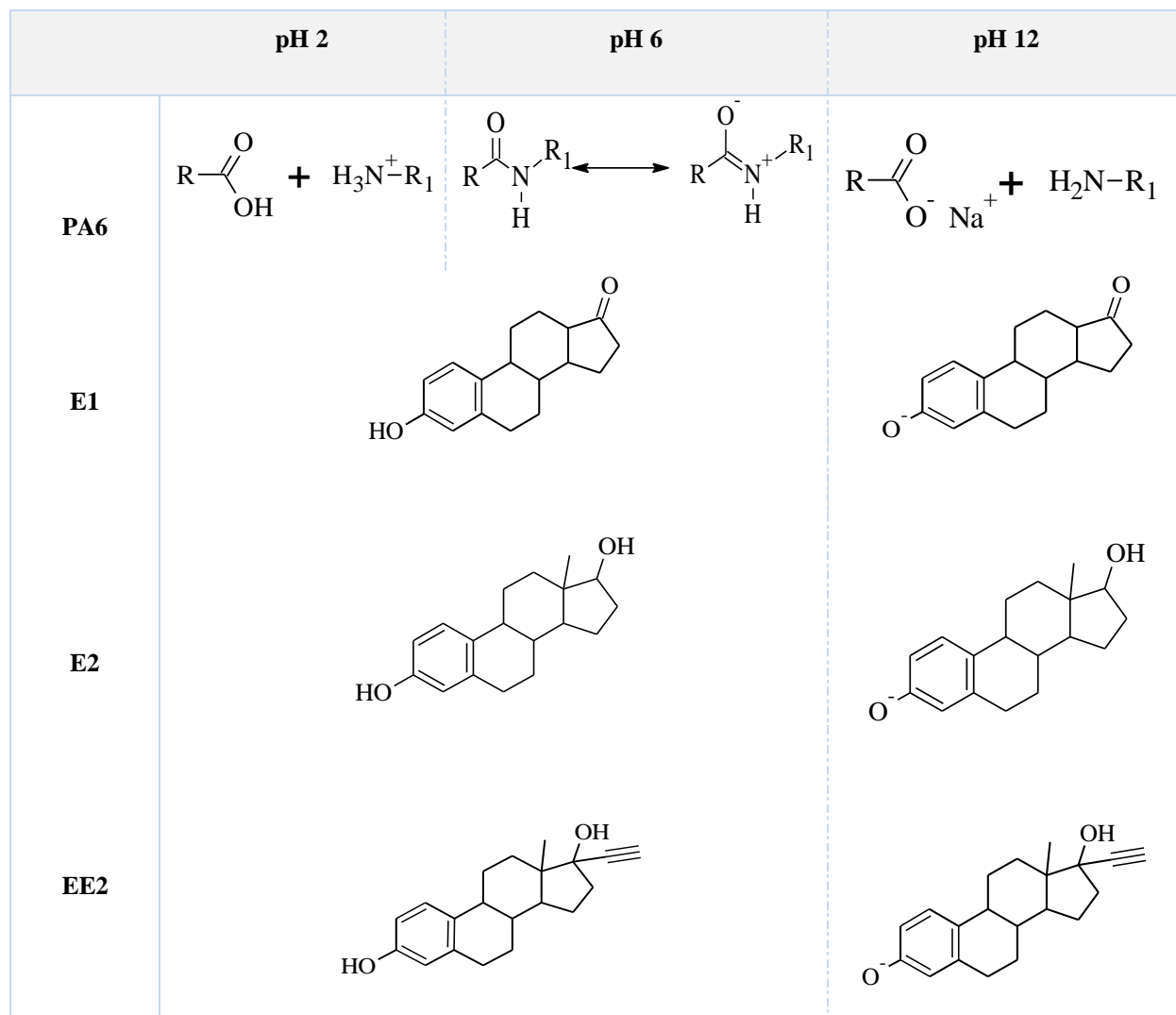
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Table 2

EDC	K
E1	898 (0.787 L/g)*
E2	1655 (1.451 L/g)
EE2	1649 (1.447 L/g)

*: Values between brackets are for the linear isotherm constants based on adsorbent mass

Table 3



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Highlights

- PA6 was effective to selectively remove and recover estrogenic EDCs in wastewater
- H-bonding is largely responsible for EDCs adsorption on PA6 at $\text{pH} < \text{pKas} (\sim 10.5)$
- pHs below pKas have no effect on the uptake of EDCs
- Linear mass transfer model described well the breakthrough curves
- PA6 was also an effective SPE sorbent

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