Modeling 17α-ethinylestradiol removal in membrane bioreactors

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Abstract
The aim of this work was to develop a model that describes the fate of the synthetic hormone 17α-ethinylestradiol (EE2) in a membrane bioreactor (MBR) process. Results from the modeled experimental data show that sorption is the main removal mechanism during the first 10 days of exposure to EE2, but the removal efficiency drops from 97% to 28% as sorptive capacity saturates. Then, as the biomass slowly (over a period of 10 days) adapts to the presence of EE2, the removal increases again to 68%. The proposed model considers co-metabolism on soluble EE2 during the aerobic growth of nitrifying bacteria with a logistic function to describe the adaptation period. This structure is able to represent the observed behaviour of EE2 in the studied MBR process.

Keywords
Acclimation; Activated Sludge Model; Co-metabolism; MBR; Modeling, Emerging contaminants, Endocrine disruptors

INTRODUCTION

Conventional activated sludge (CAS) is a widely used bioprocess to treat municipal wastewaters. With the addition of membrane filtration, membrane bioreactors (MBRs) offer the benefit of constant effluent quality in terms of total suspended solids (TSS) and the high sludge retention time (SRT) characteristic of MBRs leads to a more diversified and efficient biomass. Activated sludge models (ASM) are well established for the engineering design practice of the wastewater industry. While these models were originally developed for CAS systems they are now more and more applied to MBR processes (Fenu et al., 2010). However, key factors still need further investigation.

Literature indicates that wastewater discharges in receiving waters contribute significantly to the presence of contaminants of emerging interest in sources of drinking water (Benotti et al., 2009). For this purpose, dynamic models of the fate of micropollutants in wastewater systems were developed during the SCORE-PP project (*Source Control Options for Reducing Emissions of Priority Pollutants,* www.scorepp.eu). Although the CAS process was included in the SCORE-PP project, nothing was proposed for MBR systems. A dedicated literature review revealed various studies on removal of micropollutants in MBR (e.g. Sipma et al., 2010, Paetkau et al., 2011) but no paper has been found on modeling their fate. Therefore, the wastewater industry would benefit from the development of new models for the removal of these particular pollutants in MBR. The objective of the work was thus to develop an MBR model for emerging contaminants.

The synthetic hormone 17α-ethinylestradiol (EE2), widely used in human contraceptives, is an emerging contaminant of great concern (Clouzot et al., 2008). EE2 was chosen because it is one of

the most potent endocrine disrupters and its environmental concentration is known to impact endocrine system and reproductive functions of aquatic organisms, amphibians, birds and mammals. EE2 was shown to be primarily removed by sorption in CAS system (Andersen et al., 2005) because this synthetic hormone has a low biodegradability and a high hydrophobicity. EE2 biodegradation has been mainly attributed to co-metabolism through the key enzyme of nitrification, the ammonium monooxygenase (AMO) (Yi and Harper, 2007). The long SRT applied in the MBR process supports the development of nitrifying biomass and thus, is expected to improve EE2 removal.

The first step of the study was to collect an extensive experimental data set on EE2 removal in a pilot-scale MBR operated under various conditions. Then, the experimental data were used to develop and calibrate the MBR model. The final objective was to apply the academic knowledge acquired for EE2 to the optimization of wastewater treatment plant (WWTP) design and operation.

METHODS

17α-ethinylestradiol

The values of the partition coefficient of EE2, K_D, in the literature range from 0.28 l/g (Gomes et al., 2011) to 1.0 l/g (Clara et al., 2004). Its octanol-water partition coefficient, K_{OW}, varies between 4677 l/g and 14125 l/g while its Henry's law constant is $7.94 * 10^{-12}$ atm.m³/mol (de Mes et al., 2005). Therefore, EE2 is assumed to be non-volatile and susceptible to sorption. Moreover, studies have shown that EE2 is slowly biodegradable under aerobic conditions when nitrifying bacteria are present (Shi et al., 2004).

Experimental data

Activated sludge sampled from a full-scale CAS system was grown on a synthetic substrate (C/N/P: 100/10/2) during 83 days in a membrane bioreactor (MBR) consisting of a reactor followed by an external membrane (Clouzot et al., 2010). Afterwards, EE2 was added in the influent at a constant concentration of 0.5 $mg.L^{-1}$ during 16 days. The hormone was quantified in the permeate to calculate its removal.

The MBR was operated under different conditions to evaluate the effect on EE2 removal (Table 1). A hydraulic retention time (HRT) of 20h was first tested and then, a 7h-HRT was applied to simulate an overload of pollution. EE2 was removed from the influent between the two HRT-experiments. Dissolved oxygen was provided on a cyclic period to allow two hours of aerobic conditions followed by one hour of anoxic conditions.

Table 1. Operating conditions of the different experimental phases

	Phase 1 (2.4 days)	Phase 2 (4 days)	Phase 3 (8 days)
HRT	20 h	20 h	7 h
EE2	YES	NO	YES
Substrate	YES	YES	YES
Oxygen	YES	YES	YES

Modeling approach

Modeling was performed using the software WEST (www.mikebydhi.com). The pilot plant was represented by a single MBR unit without any backwashing system since no membrane cleanup was performed during the experiment. Moreover, no fouling was observed during the experiment, and thus, a simple MBR model that does not consider fouling was chosen. A controller and a timer were used to simulate the cyclic aeration of the reactor and to maintain the dissolved oxygen concentration between 0 and 3 mg/l.

The fate of the traditional activated sludge components was described using the ASM1 model (Henze et al., 1987) (Table 2). The decay rates of autotrophic biomass (b_A) and heterotrophic biomass (b_H), the fraction of biomass converted to inert matter (f_P) and the yield for autotrophic biomass (Y_A) determined in the MBR experiments of Jiang et al. (2005) were selected. The default value of the maximum specific growth rates of autotrophic biomass (μ_A) and heterotrophic biomass (μ_H) at 20°C were chosen since they allowed near-complete removal of soluble substrate and ammonia, as was observed during the experiment. The yield for heterotrophic biomass (Y_H) was calibrated in order to obtain a suspended solids concentration of 13 g/l at steady state, a value that was rather constant throughout the experiment. The higher value selected for Y_H can be explained by the use of glucose as a carbon source, which has a higher yield than acetate and wastewater due to an enhanced storage metabolism (Dircks et al. 1999).

Table 2. Calibrated values of the ASM1 kinetics parameters.

Parameters	ASM1 values (20°C)	Calibrated values	Units	References
b_A	0.04	0.08	d^{-1}	Jiang et al. (2005)
b_H	0.62	0.25	d^{-1}	Jiang et al. (2005)
f_P	0.08	0.06	-	Jiang et al. (2005)
μ_A	0.8	0.8	d^{-1}	Henze et al. (1987)
μ_H	6.0	6.0	d^{-1}	Henze et al. (1987)
Y_A	0.24	0.25	g_{COD}/g_N	Jiang et al. (2005)
Y_H	0.67	0.7	g_{COD}/g_{COD}	-

RESULTS AND DISCUSSION

The proposed add-in to the ASM1 (Henze et al, 1987) includes two additional components, soluble concentration of EE2, S_{EE2} (mg/l) and sorbed concentration of EE2, X_{EE2} (mg/l), and three additional processes, sorption/desorption of EE2 on TSS (mg TSS/l) and co-metabolic degradation of soluble EE2 by nitrifying bacteria, X_{BA} (mg COD/l) (Table 3).

Sorption model

The structure of the sorption/desorption processes mimics the one used by Lindblom et al. (2009) where sorption is described by a pseudo-first order reaction with a sorption rate k_{sor} (l/mg.d), the TSS concentration and the concentration of soluble EE2. Desorption is proportional to the concentration of sorbed EE2 in a first order manner with a desorption rate k_{des} (d^{-1}). At steady-state, the ratio between the sorption rate and the desorption rate equals K_D (l/mg), the partition coefficient. The data showed that sorption became limited as time went by and this was modeled by a saturation function similar to the one used in the hydrolysis kinetic function, but with a

modification similar to the Hill kinetics, i.e. a power-law on the concentration. The parameter K_{EE2} represents the maximum number of sorption sites that are available for sorption.

Table 3. Gujer matrix of the add-in model describing EE2's sorption and co-metabolic degradation

Process	S_O	S_{EE2}	X_{EE2}	X_{BA}	Process rate (g/m³.d)
Sorption		−1	1		$k_{sor} * X_{TSS} * S_{EE2} * \left(\frac{K_{EE2}^{n_{EE2}}}{K_{EE2}^{n_{EE2}} + \left(X_{EE2} / X_{TSS} \right)^{n_{EE2}}} \right)$
Desorption		1	−1		$\frac{k_{sor} \cdot X_{EE2}}{K_D}$
Co-metabolic degradation by growing nitrifiers	−1	−1			$\eta_{EE2}(t) * \mu_A * \frac{S_{NH}}{K_{NH} + S_{NH}} * \frac{S_O}{K_{OA} + S_O} * \frac{S_{EE2}}{K_{NEE2} + S_{EE2}} * X_{BA}$

Biodegradation model

The degradation of EE2 is assumed to be achieved by co-metabolism on soluble EE2 during the aerobic growth of nitrifying bacteria, X_{BA} (mg/l) (Table 3). Hence, a new process rate similar to the one used for the aerobic growth of autotrophic biomass in ASM1 was created for co-metabolic degradation of EE2. The difference is an additional kinetic limitation term, i.e. it stops when no more EE2 is present. As the results below show, the biodegradation of EE2 is not instantaneous, some adaptation seems required. To this end a Verhulst-type logistic function (η_{EE2}) was added to the biodegradation kinetics (Verhulst, 1845). It is basically a differential equation describing how the fraction of the maximum rate that can be obtained, η_{EE2}, evolves in function of time, t (d):

$$\frac{d\eta_{EE2}}{dt} = k_{ACC}\eta_{EE2}\left(1 - \frac{\eta_{EE2}}{\eta_{EE2,max}}\right)$$; which solves into:

$$\eta_{EE2}(t) = \frac{\eta_{EE2,max} * \eta_{EE2,ini}}{\eta_{EE2,ini} + \left(\eta_{EE2,max} - \eta_{EE2,ini}\right) e^{-k_{ACC} * t}}$$; where:

$\eta_{EE2,max}$, can be viewed as the maximum sustainable fraction of the process rate;
$\eta_{EE2,ini}$, represents an initial fraction of the process rate;
k_{acc} is the rate at which the fraction of the process rate evolves (d^{-1}).

Calibration

A partition coefficient was calculated using the log(K_{OW}) values found in literature and the empirical formula (Karickhoff, 1981) shown below:

$$K_D = 0.41 * f_{OC} * K_{OW},$$

where f_{OC} is the fraction of organic carbon in the biomass. A f_{OC} value of 0.41 was calculated according to the ratio of VSS/TSS of 0.78 that was measured during the experiment with a ratio of

the mass of carbon in pure biomass ($C_5H_7O_2N$) of 0.53. The K_D value obtained was 2.374 l/g, somewhat higher than what is found in literature. Calibration was performed on the sorption rate (k_{sor}), a value of 0.5 l/mg.d was applied in the model. Parameter values for the co-metabolic degradation of EE2 were calibrated in order to get the best fit during phase 3 of the experiment. Table 4 shows all kinetic parameters used in the add-in model.

Table 4. Calibrated values of the add-in model's kinetic parameters.

Parameters	Calibrated values	Units
k_{sor}	0.5	l/mg.d
k_{des}	210	d^{-1}
K_{EE2}	0.00022	-
n_{EE2}	2	-
k_{ACC}	0.95	d^{-1}
$\eta_{EE2,ini}$	$9*10^{-6}$	-
$\eta_{EE2,max}$	0.25	-
K_{NEE2}	0.6	mg/l

The percentage of EE2 removal was measured during the last 14 days of the MBR experiment (Figure 1). When EE2 was first added at a 20h-HRT, the removal gradually decreased from 100% to 90% over a period of three days. Sorption was characterized as the main removal mechanism (Clouzot et., 2010) and the model successfully described the experimental data for this phase.

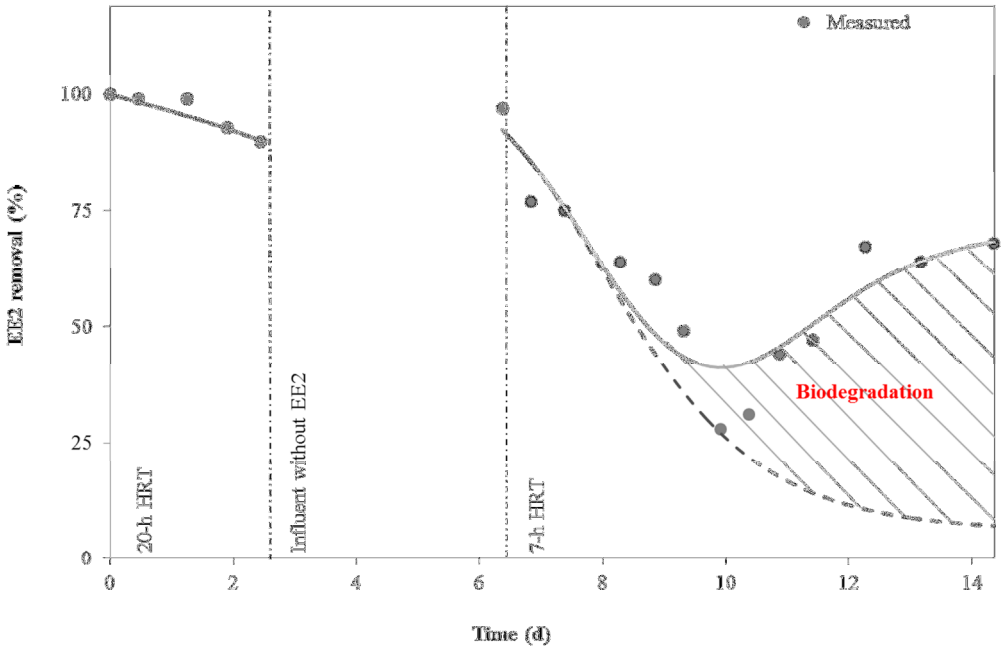

Figure 1. Experimental and modeled removal efficiencies of EE2 in the pilot-scale MBR.

A simulation performed without the co-metabolism kinetic shows that long-term removal of EE2 by sorption stabilizes at 5%. This rather low value can be explained by the long SRT applied to the model, which retains most of the sorbed EE2 and therefore saturates the sorption sites available in the Hill kinetics, and by the high influent load of EE2 applied to the MBR.

The same trend was observed at the beginning of the 7h-HRT phase. The removal decreased from 97% to 28% due to the saturation of the sorption sites and then, biodegradation increased the removal efficiency to 68%. Results from this experiment showed that biomass required an adaptation phase of about 10 days before it could biodegrade EE2. The proposed model is rather good at describing the beginning of phase 3, where only sorption is a factor in the removal of EE2. Then, the model results show that the Verhulst adaptation kinetics was quite successful in integrating EE2 co-metabolism in the model.

Model application

Several simulations were performed in order to evaluate the removal efficiency of EE2 in different operating conditions. The removal efficiencies reported in Table 5 were obtained after a steady-state was achieved for HRT values of 20h and 7h. The results show that the MBR remains efficient at removing EE2 when the HRT is 20h, even at low temperature (Exp. 2), with a lower aerobic/anoxic ratio (Exp. 3), and at an SRT of 5 days (Exp. 4). However, when the SRT is lowered to 2 days (Exp. 5), the complete absence of nitrification has a significant effect on the removal of EE2. Moreover, in that specific scenario, the TSS concentration in the wasted sludge is less than 1.5 g/l, therefore, nearly 30% of the influent EE2 is discharged with the sludge as soluble EE2. When the HRT was set to 7h, the operating conditions had a greater impact on the removal efficiencies. The lower temperature altered nitrification, but it increased the TSS concentration in the reactor, which allowed more sorption to occur. At a SRT of 2 days, no nitrification and co-metabolism was observed, which means that EE2 was only removed by sorption.

Table 5. Removal percentages at steady-state under various operating conditions.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
SRT (d)	50	50	50	5	2
Temperature (°C)	20	5	20	20	20
Aeration	2h/1h (no)	2h/1h (no)	1h/2h (no)	2h/1h (no)	2h/1h (no)
Removal % @ HRT 7h	71	65	71	60	26
Removal % @ HRT 20h	90	88	89	86	61

CONCLUSION

In this paper, an add-in model to ASM1 that describes the fate of the synthetic hormone 17α-ethinylestradiol in a MBR pilot was presented. The proposed model was able to adequately represent the different removal phases, such as the dynamically faster sorption process in the first 10 days and the co-metabolic mechanism that required an adaptation period modeled with a Verhulst kinetic. Various scenarios were analyzed and showed that the low SRT values had a significant impact on the removal of EE2 because it alters both nitrification and co-metabolism.

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