Micropollutants Removal in MBR Reactors: A comperative study

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ABSTRACT

Currently over 1 billion people is estimated short of adequate potable water and this is expected to rise to 2.5 billion in the year 2025. Membrane Bioreactors (MBR) facilitate reuse of wastewaters and provide an additional water resource. The removals of selected endocrine disrupter compounds (EDCs), namely, diltiazem (Dtz), progesterone, estrone and carbamazepine (Cbz), as model micropollutants, were comparatively investigated in two full scale and one pilot scale MBR plant. Aeration tank samples were decanted for 30 mins. and supernatants were analyzed for the EDCs to simulate an equivalent activated sludge process. Three SRTs, i.e. 10, 15, 20 days, and six different flux rates ranging between 13 and 30 L/m^2-h were tested for MBR plants in METU campus. It has been observed that there was little noticeable effect of flux rates and sludge retention times on the removals of selected EDCs in the membrane plants. Progesterone, estrone and acetaminophen were completely removed from wastewater by way of biodegradation while CBZ was not removed at all. However, diltiazem, which was not removed in two of the static MBR plants, was totally removed in the rotating MBR.

Keywords: membrane bioreactor, transmembrane pressure, flux, endocrine disrupter compounds, suction time

Introduction

Following urbanization and rapid industrialization over 100 000 synthetic chemicals have been introduced to the environment since 1930s (Snyder et al., 2003). Most of these chemicals are finally disposed into rivers, lakes and seas via sewage receiving or not-receiving proper treatment. Desbrow et al. (1998), and Song et al. (2009) pointed out the sewage treatment work (STW) effluents as the major source of EDCs in the ecosystem due to their presumed incapability of reducing these compounds to levels below the no-effect concentrations to fish. Of the discharged chemicals those that are reported to interfere with the functioning of the hormone systems of animals and man are referred with the generic name 'endocrine disrupters' (EDCs). EDCs can be natural or synthetic in origin but their effects on the endocrine system are similar (Snyder et al., 2003). As a result of interference with the endocrine system noticeable negative effects on fish, bird, reptile and mammal populations have been implicated (Bowden, 2009; Fossi and Marsili 2003; Colborn, 1996, Snyder and Benonti, 2010; Desbrow et al. 1998; Routledge et al. 1998). For example, sexual abnormalities and decline in the male fish population living at the proximity of a wastewater treatment plant outfalls have been reported (Purdon et. al.1994). The current concept in combating micro-pollutants in the environment is the 'multiple barrier' approach. This calls for elimination of contaminants during wastewater, as well as drinking water treatment. The membrane bioreactor (MBR) systems, which are considered new generation treatment technologies, are claimed superior over conventional treatment in EDCs removal, probably owing to the excellent quality effluents that they produce. The studies on removal of EDCs in WWTPs are summarized in Table 1.

Table 1. Studies on removal of EDCs in WWTPs.

Compound	Location of Study	Removal %	Type of treatment	Reference
Diltiazem	TanCheon, Korea (FS)	-	CAS	Choi et al., 2008.
	JungRang, Korea (FS)	-	CAS	Choi et al., 2008.
	NanJi, Korea (FS)	-	CAS	Choi et al., 2008.
	SeoNam, Korea (FS)	-	CAS	Choi et al., 2008.
Prog.	USA (PS)	99	CAS	Esperanza et al., 2007
E_1	Kristianstad, Sweden (FS)	78	CAS+ CT	Zorita et al. 2009
	U.K.	88	CAS	Ternes et al. 1999
	USA	64	CAS	Snyder, 2002
	WWTPs, Korea	87.1	CAS+BNR+UV	Behera et al., 2011

	USA (PS)	99.9	CAS	Esperanza et al., 2007
CBZ	Netherlands	9	CAS	Heberer 2002
	Austria	-	CAS	Clara et al., 2005
	Terrassa, Spain (FS)	-	CAS	Radjenovic et al., 2009
	Terrassa, Spain (PS)	-	FSh-MBR	Radjenovic et al., 2009
	Terrassa, Spain (PS)	-	HF-MBR	Radjenovic et al., 2009
	Alcala´de Henares, Spain (FS)	9.5	CAS	Rosal et al., 2010
	Korea	23.1	CAS+BNR+UV	Behera et al., 2011
	TanCheon, Korea (FS)	50	CAS	Choi et al., 2008
	JungRang, Korea (FS)	50	CAS	Choi et al., 2008
	NanJi, Korea (FS)	-	CAS	Choi et al., 2008
	SeoNam, Korea (FS)	50	CAS	Choi et al., 2008
	Galicia, Spain (PS)	99	SBR+AC+MBR	Serrano et al., 2011
Acetamino-phen	Belgium (LS)	99.9	MBR	Gusseme et al.,2011
	Spain (FS)	99	CAS	Gomez et al.,2007
	Terrassa, Spain (FS)	99	CAS	Radjenovic et al., 2009
	Terrassa, Spain (PS)	99.9	FSh-MBR	Radjenovic et al., 2009
	Terrassa, Spain (PS)	99.9	HF-MBR	Radjenovic et al., 2009
	Alcala´de Henares, Spain (FS)	100	CAS	Rosal et al., 2010
	WWTPs, Korea (FS)	99.9	CAS+UV	Behera et al., 2011
	TanCheon, Korea (FS)	99	CAS	Choi et al., 2008.
	JungRang, Korea (FS)	99	CAS	Choi et al., 2008.
	NanJi, Korea (FS)	99	CAS	Choi et al., 2008.
	SeoNam, Korea (FS)	99	CAS	Choi et al., 2008.

FS= Full Scale, PS= Pilot Scale, HF= Hollow fiber, FSh= Ftale Sheet, CAS=conventional activated sludge, MBR= membrane bioreactor, UV=ultraviolet, AC=Activated carbon, BNR= biological nutrient removal, CT= chemical treatment, LS=laboratory scale

As can be seen from Table 1, diltiazem (DTZ) and carbamezapine (CBZ), the two commonly prescribed medications, are not at all removed in CAS systems, with the exception of SBR+AC+MBR systems, as reported by Serrano et al., 2011; where 99 % CBZ removal was recorded. However mode of removal, whether biodegradation or adsorption, is unclear. The removal of EDCs in effluents are largely dictated by the physicochemical characteristics of the compounds and their bio-degradability. For example all the compounds in Table 1, other than CBZ or DTZ, were successfully removed by CAS or other systems, as these are biodegradable. Yet, effect of MBR operating parameters on the removal of EDCs have not been fully resolved. The two parameters, i.e. flux rate and SRT, need to be investigated further in order to determine the capacity limits of MBRs. Former is important in that higher flux rates should lead to larger cake layers over the membrane surfaces; or concentration polarization as it is sometimes referred, thereby affecting increased pressure and contact between the solute and the biofilm. A long SRT may also affect removals simply by giving more time to biomass to acclimatize to a particular compound. In this study, removal of five different EDCs including natural hormones and pharmaceuticals, was investigated in two full-scale and one pilot scale MBR plants. Effect of flux rate and SRT on EDCs removal were also studied within this context.

Material and Methods

Chemicals

Analytical reagent grade chemicals used during the study. The selected Endocrine Disrupting Compounds, EDCs, diltiazem (>99%), progesterone (>99%), estrone (>99%) were obtained from Sigma, carbamazepine (>99%) and acetaminophen (>99%) were purchased from Sigma-Aldrich.

Laboratory analysis

All the liquid samples were 24 h composite obtained by using a pump and timer system. Composite samples were kept at refrigeration at 4 ^{o}C. Sludge samples were obtained from the waste sludge, WAS, stream and dried to constant weight. Supernatant samples were obtained from the aeration tank by decanting the mixed liquor for 30 minutes and analyzing supernatants for the desired parameters. As is, these samples were somewhat identical to effluents from activated sludge settlers.

All parameters were analyzed in parallel. Analytic methods were performed according to Standards Methods. The COD, ammonium nitrogen, and nitrate were measured using Hach Dr 2000 Model Spectrophotometer. The Hach COD reagent (Cat No.21259-51) was used for COD analysis, Ammonia Salicylate (Cat No.23953-66)

reagent powders and Ammonia Cyanurate (Cat No.23955-66) for ammonium nitrogen and The Hach Nitriver reagent (Cat No.14065-99) and Hach nitraver reagents (Cat No.14119-99) for nitrate determination. Dissolved oxygen was determined in-situ by Jumo dTrans O_2-01 model DO-meter. An Agilent 1200 type HPLC fitted with 6410A type quadrupole MS detector, consisting of autosampler and electrospray ionization, was used for the detection of the selected endocrine disrupting compounds, diltiazem (DTZ), carbamazepine (CBZ), acetaminophen (ATP), Estrone and Progesterone. Details of the instrumental analysis for sludge and wastewater samples are already published (Komesli et al., 2012; Muz et al 2012; Sönmez et al., 2012).

Description of the MBR Systems

MBR Pants at METU

During the study, one full scale MBR plant, described as vacuum rotating membrane, VRM, with a capacity of 150 to 200 m^3/d; one pilot scale MBR plant with a capacity of 600 to 1500 L/d were used to study the effect of flux rate on the removal of EDCs at short SRTs. The full scale VRM plant unit was consist of two tanks arranged in series. The first tank is the aeration tank used for biological treatment and the second one is the so called filter chamber where the rotating membrane filter is housed (Figure 1). After filtration through the membranes, treated wastewater passes through a UV unit for further disinfection.

Figure 1 Pictures of the full-scale VRM (left) and pilot scale MBR units at METU Campus, Turkey.

Pilot MBR plant at METU

The pilot MBR plant is also situated close to the VRM plant and shares the same influent as with the actual VRM plant. The incoming domestic effluent from the academic village and dormitories is first filtered through a 3 mm fine screen before entering the aeration tanks. The screened wastewater for the pilot plant is stored in a 350 L tank and pumped at a steady rate to the MBR plant by a submerged pump (Figure 1).The relationship between TMP and flux rates in the VRM and pilot plants are presented in fig. 2. Details of both plants are summarized in Table 2.

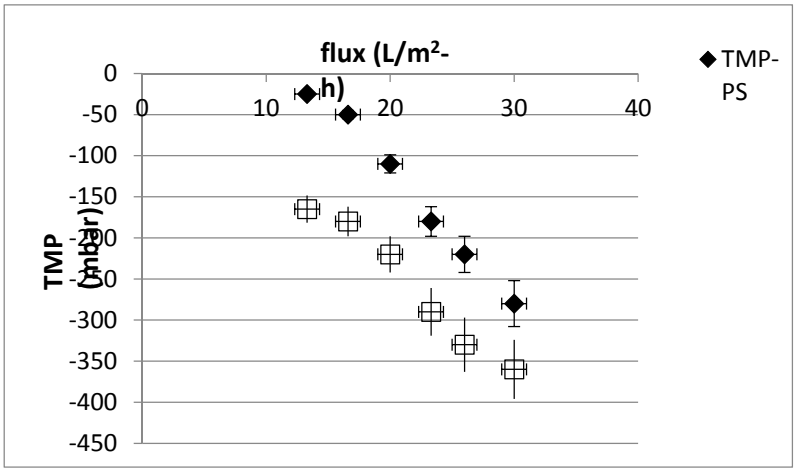

Figure 2. The TMP and flux rate relationship in both plants. Where, TMP-PS stands for the pilot plant and TMP-FS for the VRM plant.

Konacik MBR Plant

This is a full scale plant located on the Aegean coast of Turkey with a nominal capacity of 1100 m^3/d. The plant operates with positive pressure rather than suction. During operation cycle flux stops at regular intervals and membranes are relaxed for one minute without flow. Details of this plant are summarized in Table 2. Unlike the other two MBR plants this plant has a pre-anoxic tank for nitrogen removal.

Table 2. Properties of the MBR Plants

	Clear-Box	VRM Plant	Konacik
Storage tank volume (m^3)	0.35	10	115
Aeration Tank Volume (m^3)	0,75	85	Anox: 180 Aerobic: 600
MBR tank volume (m^3)	0,75	23	64 x 2
Membrane Type	plate and frame	plate and frame	Plate and frame
Total Membrane Area (m^2)	3	540	2560
Membrane Material	polyethersulfones (PES)	PES	PES
Nominal Pore Size (µm)	0.038	0.038	0.04
Sludge Retention Time (days)	10	10	25
Flux (L/h-m^2)	13.3-26	13.3-30	18
Dissolved Oxygen (mg(L) **Aeration Tank** **VRM Tank**	 1.5-2.0 -	 1.5-2.0 0-0.1	
SRT	10	10	25
HRT	18	18	16
Type	Flat sheet	Flat sheet	Flat sheet
MLVSS			
Flow	200 m3 d-1	1 m3 d-1	
N-Removal	NO	NO	YES
Feed	Natural domestic	Natural domestic	Natural domestic

Results and Discussion

Konacik Plant

The diltiazem and carbamezapine, the two most commonly prescribed pharmaceuticals as blood thinners and antiepileptics, respectively, are not at all treated in this plant. Whereas the painkiller acetaminophen was completely removed by biodegradadtion.

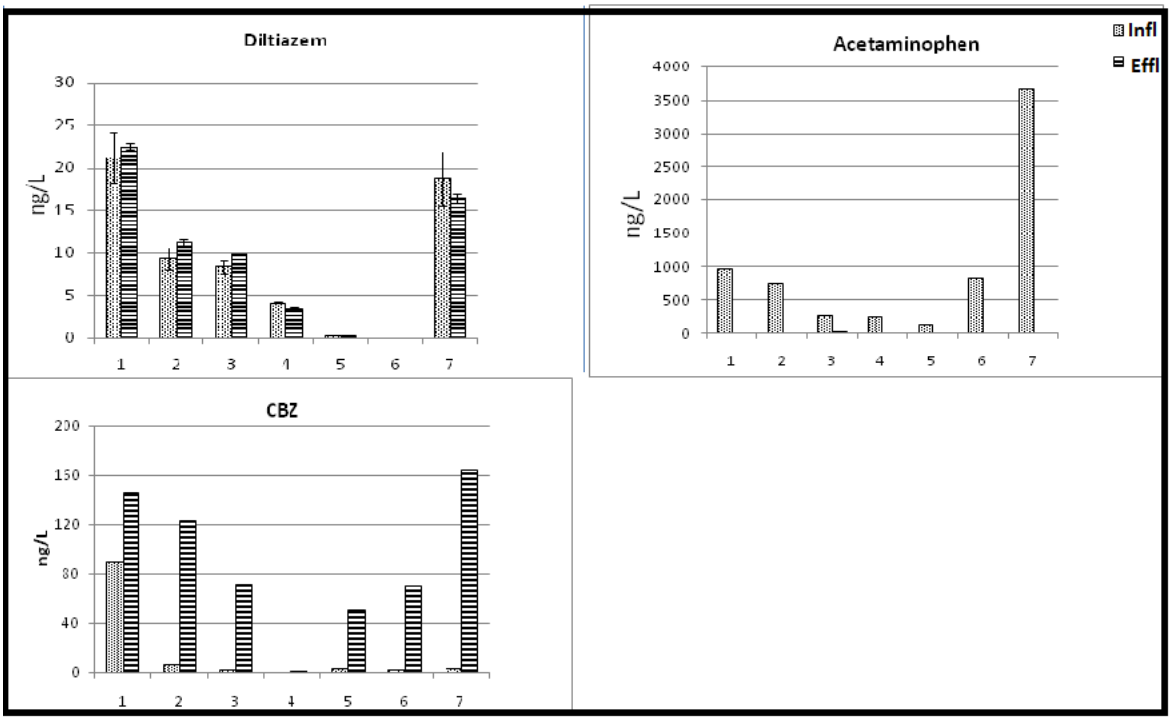

Figure 1. Removals of selected micropollutants in Konacik MBR plant.

METU VRM Plant

The diltiazem was not removed biologically and was present in the aeration tank supernatants but absent in the filtrates. This was contrary to the findings of Konacık and METU-Pilot plants. Removals of the other EDCs in this plant are depicted in Fig. 2.

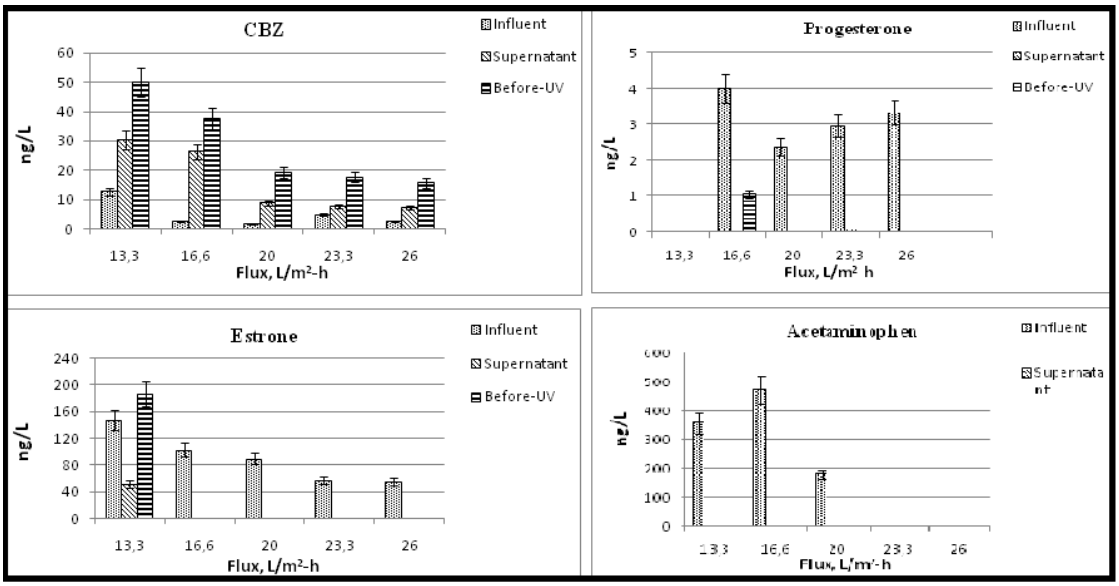

Figure 2. Removals of selected micropollutants in METU-VRM MBR plant.

METU (ClearBox) Pilot MBR Plant

Removals of selected EDCs in the pilot MBR is depicted in fig. 4. It is readily seen from this figure that the natural hormones, estrone and progesterone, and the painkiller acetaminophen were completely eliminated from effluents by biodegradation. Whereas carbamezapine and diltiazem were not removed at all in this plant.

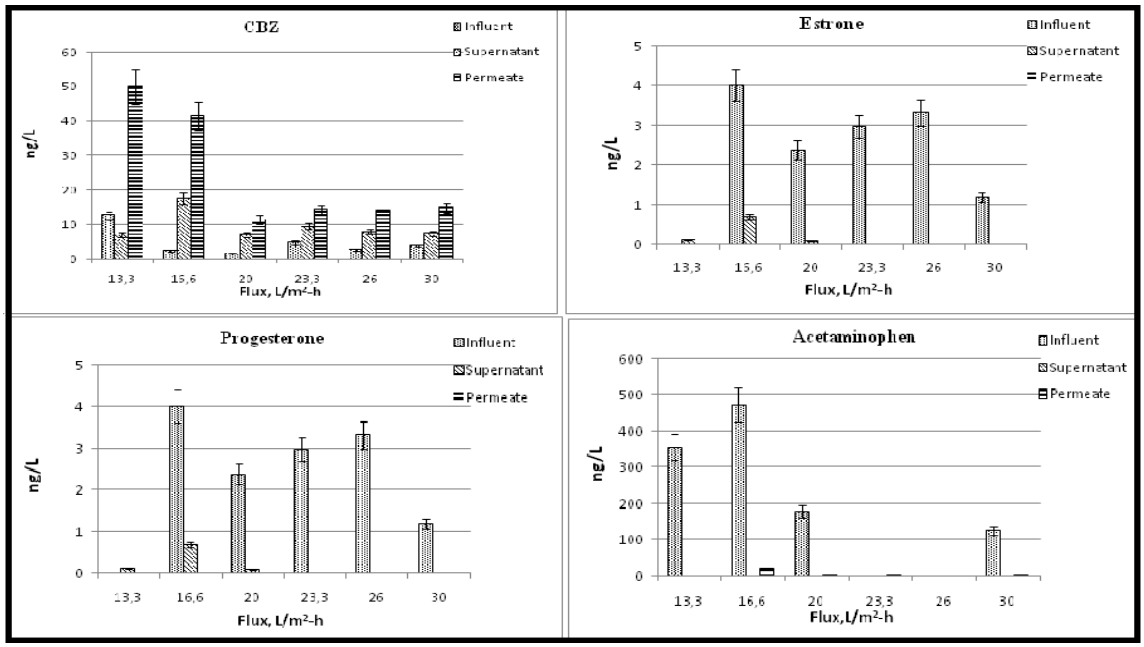

Figure 3. Removals of selected micropollutants in METU-Pilot MBR plant.

Conversely studies with classical activated sludge type plants revealed entirely a different picture, where even the most recalcitrant EDCs, such as carbamezapine and diltiazem, which are not removed at all in MBRs, were found almost totally removed in the effluents of activated sludge type plants. Close examination of the removal mechanisms indicated that removals were entirely due to adsorption onto sludge; thereby shifting focus on decontamination of waste sludge. Several processes has since been developed in our laboratory to decontaminate EDCs-laden sludge whist stabilizing it.

Conclusion

It can be concluded that the commonly prescribed pain killer, acetaminophen, and the natural hormones, progesterone and estrone, were completely biodegraded in the three MBR plants studied. Whereas carbamezapine was not degradable at all in the plants and diltiazem, was found non-treatable in two of the MBR plants but was completely treatable in the third one. The flux rate does not seem to have any great effect on micronutrients removal. Conversely studies with classical activated sludge type plants revealed entirely a different picture, where even the most untreatable EDCs in MBRs, such as carbamezapine and diltiazem, were found almost entirely removed in the effluents of activated sludge type plants. Evidently the removals were entirely due to adsorption onto sludge; thereby shifting focus on decontamination of waste sludge. Several processes has since been developed in our laboratory to decontaminate EDCs-laden sludge whist stabilizing it.

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