World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:8, No:1, 2014

Efficiency of Modified Granular Activated Carbon Coupled with Membrane Bioreactor for Trace Organic Contaminants Removal

Mousaab Alrhmoun, Magali Casellas, Michel Baudu, Christophe Dagot

Abstract**—**The aim of the study is to improve removal of trace organic contaminants dissolved in activated sludge by the process of filtration with membrane bioreactor combined with modified activated carbon, for a maximum removal of organic compounds characterized by low molecular weight. Special treatment was conducted in laboratory on activated carbon. Tow reaction parameters: the pH of aqueous middle and the type of granular activated carbon were very important to improve the removal and to motivate the electrostatic Interactions of organic compounds with modified activated carbon in addition to physical adsorption, ligand exchange or complexation on the surface activated carbon. The results indicate that modified activated carbon has a strong impact in removal 21 of organic contaminants and in percentage of 100% of the process.

Keywords**—**Activated carbon, organic contaminants, Membrane bioreactor.

I. Introduction

IN the world, the question of presence the micropolluant as pharmaceuticals and personal care products (PPCPs) in water is one of main problems of environment, because of sanitary and dangerous consequences for this type of micropolluant and the insufficiency of purification networks. Hospitals are important sources of these compounds: a great variety of micro-contaminants result from diagnostic, laboratory and research activities on one side and medicine excretion by patients on the other. They include active principles of drugs and their metabolites, chemicals, heavy metals, disinfectants and specific detergents for endoscopes and other instruments, radioactive markers and iodinated contrast media [1], [2]. In France, the total number of hospitals has raised from 1540 in 1990 to 2856 in 2005. Environ 1.071.000 m3/d hospital wastewater was generated, corresponding to approximately 5 % of municipal wastewater in 2005.

The Membrane Bioreactor (MBR) technique is a promising alternative to conventional treatment as membranes can achieve a high degree of water purification. The combination

Of membrane filtration and biological treatment avoids secondary clarification and tertiary steps [3]. Recently, more attention has been paid to the membrane bioreactor (MBR) technology for hospital wastewater treatment because of its higher efficiency in pollutant removal, excellent effluent quality, low sludge production, compact size and lower energy consumption [3]. Because of their ability to reach higher contact times and then to maintain in reaction a slow-growing biomass, microorganism species are more diversified with higher physiological capacity and are more adapted to resistant compounds. Although the effectiveness of MBR treatment for eliminating trace organic contaminants has been well demonstrated in the literature, recent studies have also shown the limitations of MBR in removing certain persistent compounds [4]-[6]. Therefore, it is necessary to implement a post-treatment process after MBR particularly in indirect potable water recycling applications or when discharging the effluent to an ecologically sensitive environment.

Numerous authors have investigated the MBR for the treatment of effluent containing pharmaceuticals [5], [2]. All these studies were carried out using microfiltration (MF) or ultra filtration (UF) membranes. In this study, the removal of trace organic contaminants via sequential application of GAC adsorption following MBR treatment (MBR-GAC) was investigated. Using the granular activated carbon (GAC) adsorption has been commonly in treatment process of industrial water and it is very effective for the removal of pesticides and other emerging trace organic contaminants in drinking water treatment [7], [8]. Recently, a few have investigated the use of GAC adsorption for the removal of trace organic micropolluant from biologically treated effluent [9]-[11]. The hospital wastewater treated by membrane reach to GAC post-treatment which to specifically target the residual trace organic contaminants in MBR permeate.

The purpose of this paper was to summarize the long-term performance experience of a MBR- GAC system for hospital wastewater treatment and to provide data on the elimination efficiency of an on-site biological wastewater treatment. To verifier this objective: (i) pilot-scale MBR coupled with post treatment GAC was installed to receive and treat real hospital wastewater, (ii) an efficient and representative samples was taken to representatively collect influent and effluent from the MBR; and (iii) SPE-HPLC-MS/MS analytical method was developed and optimized to quantify the concentrations of approximately 30 target analytics including pharmaceuticals and human metabolites (laboratory INASCO, Poitiers, France).

M. Alrhmoun, M. Casellas, M. Baudu, and C. Dagot are with laboratory of GRESE EA 4330, University of Limoges, France (e-mail: moussab1984@ hotmail.com, Casellas@ensil.unilim.fr, michel.baudu@unilim.fr Dagot@ ensil.unilim.fr).

II. Material and Methods

A. Study Area

The hospital effluent (HE) samples used in this study were collected from the sewerage system which comprises only sewers from clinical activities of the hospital. Average characteristics of wastewater and activated sludge used as inoculums during the experiments are detailed in Table I.

TABLE I
PHYSICOCHEMICAL CHARACTERISTICS OF THE HOSPITAL EFFLUENT (HE), AND ACTIVATED SLUDGE (AS)

	COD (mg/L)		N (mg/L)		SM (g/L)	VM (g/L)
	Total	Soluble	Total	Soluble		
HE	333.801	177	128	84	0.1965	0.061
AS	1201	145	-	-	7.25	1.52

B. Lab-Scale MBR and GAC Post-Treatment Column

The reactor consisted of a membrane bioreactor with a working volume of 400 L and a membrane module in an external circulation loop. The membrane module was a polypropylene and type of fibers creuses (MF) membrane with 1m² of surface area and pore size of 0.2µm (ALTING, MICRODYN, France) (Fig. 1). A Ruston turbine (80-120 rpm) was installed to keep the bioreactor completely mixed. An identical lab-scale cross-flow MBR was run and inoculated with activated sludge from a municipal wastewater treatment plant (dry weight, 2.5 g/L). The influent was a hospital effluent (average flux 100 L/day).

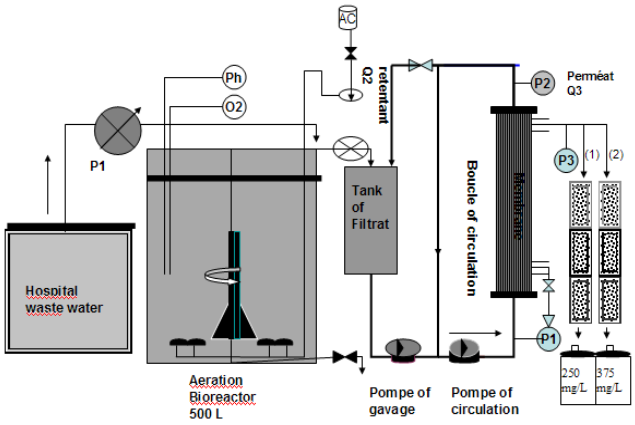


Fig. 1 Schematic diagram of the membrane bioreactors

Table II shows all the operational conditions. Daily monitoring revealed that the pH of the mixed liquor was in the range of 7.3e7.5. The aeration cycle was automatic based on tow limits. Pressures were measured at the inlet (P1), outlet (P2), and permeate side of the membrane (P3) in order to determine the trans-membrane pressure (TMP). At constant permeate flux, TMP indicates the extent of membrane fouling and it was calculated as follows:

$$TMP = [(P1 + P2) /2 - P3] \quad (1)$$

TABLE II
KEY OPERATIONAL PARAMETERS OF MBR SYSTEMS INVESTIGATED

Condition of bioreactor operation	
Operating parameters	Operating range
Concentration of oxygen	1- 5 mg O2/L
PH	6.9 -8
T C°	14.5- 20
Agitation	80-120 tr/min
Volume (L)	400 L
flow of outlet (L.d-1)	1300-1700 L / j
SRT (d)	15-20 days
HST	22 h
Aeration	Auto - 1-5 mg.O2/L
Time of presence O_2 (h)	6
Flux outlet (14-20°C) (L.m-2.h-1)	40-50 L/h
Mode of filtration	position horizontal
Tangential speed along the membrane (m / s)	0.286m/s
Type of treatment	Decantation
Cycle of operation	
Time of decantation	20 min
Time of transport	20 min
Temps of filtration	20 min
Temps of alimentation	40 min
Volume of tank	150 L
Volume of tank the washing	150 L
Flow of pump Booster	900 L/h
flow of pomp of circulation	800-950 L/h
flow of inlet	4,25 L/ h
TMP	0,1 - 0,25 bar

The MBR permeate was further treated by a laboratory scale GAC column. The GAC adsorbent (GAC-1240) was supplied by ‘’Norit Activated Carbon’’. The physical and chemical characteristics of this GAC are summarized in Table III and Fig. 2.

Prior to the experiment, the GAC was washed with distilled water to remove fine particles and then dried at 105C° for 24h. Two columns of borosilicate glass with internal diameter of 5cm and active length of 75cm were used in this study. The first column was filled with activated carbon in concentration 250gr of GAC/ L and the second in concentration 375gr of GAC/ L. However, the quantity was devised to three equals’ parts the first part was washed by HCL (1N) in concentration 30% for 2h then dried at 30°C for 24h with pH = 4.5. The third part was washed by NaOH (1N) in concentration 30% for 2 h then dried at 30°C for 24h with Ph= 9 then the second without any treatment.

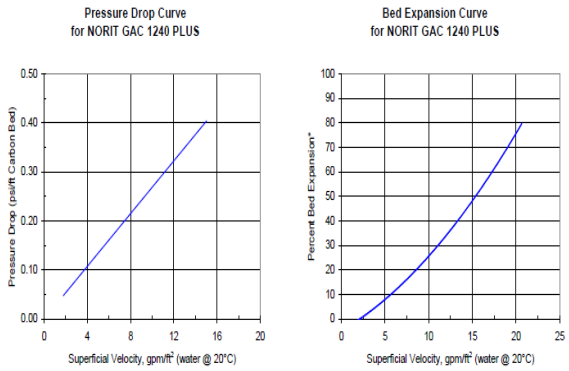


Fig. 2 Represented the pressure Drop Curve and the bed expansion curve for GAC1240 plus

TABLE III
CHARACTERISTICS OF THE GAC-1240 PLUS

Parameter	Values
Iodine number	mg/g 950 min.
Molasses number	210 min.
Abrasion number (AWWA)	78 min.
Iron, acid soluble, % as Fe	0.01 max.
Acid soluble ash, %	0.5 max.
Moisture, % as packed	3 max.
pH, water extract	5.0 to 8.0
Mesh size (U.S. Sieve Series)	
Greater than 10 mesh (2.00 mm),	5 max.
Less than 40 mesh (0.42 mm),	0.5 max.
Pore volume (cc/g)	0.046b
Pore diameter (nm)	3.232b

All the parts supplied by the columns in order and the same operation repeated for the second columns with concentration 375gr of GAC /L. (Fig. 1). This study was conducted over total 275 days, with 85 days of MBR-only operation, 145 days of operation in MBR+ support media mode and 45 days of MBR- GAC operation.

C. Analytical Methods

Wastewaters and sludge physic-chemical characteristic measurements were done every two day. Measurements of total and volatile suspended solids (TSS and VSS) were done according to the normalized method (AFNOR, NF T 90-105). Chemical Oxygen Demand (COD) was measured by the closed reflux colorimetric method (ISO 15705:2002), and total nitrogen (TN) was assessed using the alkaline per sulfate digestion with colorimetric reactive (Hatch company). The COD and TN were carried out on both total and soluble fraction (after samples filtrated at 1.2µm). Ionic species in solution were determined on samples filtrated at 0.22µm using ion chromatography (DIONEX 120) according to the standard method (AFNOR, NF EN ISO 10304-1). The used detector was conducted metric, and the analytical error was ±5%.

D. Sampling

A peristaltic pump was used for sampling of the pilot plant influent. Fresh MBR-effluent was sampled continuously by a peristaltic pump before it entered the MBR permeate tank. The flow from the sampling pumps was directed into cooled glass bottles located in a refrigerator at 4°C. Cooling elements were used during sample transport from the pilot plant to the lab for the analyses. Three sampling campaigns took place for Inlet, outlet of BRM and outlet of GAC post a preliminary over 5 weeks in June 8, 2013.

E. Sample Preparation

The wastewater samples were filtered through a 0.7-µm GF/F glass−fiber filter (Whatman, Dassel, Germany) and further through a 0.2-µm regenerated cellulose filter (Sartorius AG, Gotingen, Germany). For the analysis of 52 micro pollutants, samples were diluted ratio 1:100 and 1:10 with nano-pure water or left undiluted, depending on the matrix. Subsequently, 50 isotope labeled internal standards in three mixtures were spiked. Prepared samples were stored at 4°C in the dark for 1−20 days before they were analyzed. For analysis, 20mL of the filtered and internal standard containing sample in an amber glass vial was inserted into a cooled auto sampler rack, and automatically acidified by formic acid (0.1% formic acid in a sample, v/v) just before injection into the online SPE-HPLC- MS/MS system to avoid hydrolysis.

F. Analysis of Trace Organic Contaminants (PPCPs)

Two different analytical methods were applied to determine the concentration levels of the PPCPs in the wastewaters samples. Analyses were performed by the IANESCO. Water samples were enriched by liquid-solid phase (SPE) by using Osis HLB cartridges (6ml, 200mg) from waters. The SPE extracts were injected in liquid chromatography- mass spectrometry (LC-MS/MS). Acquisition was performed in selected reaction monitoring (SRM) mode and tow transitions (quantification, confirmation) were obtained for each compound. Quality control (QC) was assured by measuring two transitions for each analytic and each internal standard, comparing retention time of an analytic with the retention time of the internal standard in each sample, duplicates, numerous blanks, and QC standards.

III. RESULTS AND DISCUSSION

A. The Process Performances

The total and soluble COD removal efficiency was always respectively greater than 87.9 % and 86.9. During start-up TSS and VSS concentrations in the MBR increased almost continuously (depending on our wastewater characteristics the increased was slowly and not very remarkable). Effluent solids concentrations were always very low (<0.0012 g/L) confirming the excellent solids removal of micro-filtration systems. The removal of TSS was 99.5% obtained only by the filtration by membrane and that indicate to the perfect solids retention capacity of the membranes. By the way, more than 97% of the VSS influent was removed. Particular attention has to be paid to the nitrogen removal efficiencies. The total and soluble Nitrogen removal efficiency was always respectively greater than 91% and 90%. It is not worth to confirm that the denitrification potential of a wastewater is linked not only to the COD availability in the influent but also to its ready

biodegradability. Performance of the MBR with respect to the removal of TOC and TN was stable during the entire study (Table IV).

TABLE IV
EVOLUTION THE EFFICIENCY REMOVAL OF ORGANIC POLLUTANTS BY MBR

Removal %	TSS	VSS	TCOD	SCOD	TN	SN
MBR	99.5	97.4	87.9	86.9	91	90.4

B. Removal of Trace Organic Contaminants by MBR

The main mechanisms responsible for the removal of pharmaceutical compounds in the MBR-system are sludge sorption and biodegradation by microorganisms present in the wastewater [12]. The total removal efficiency (sludge sorption+ biodegradation + membrane retention) of each pharmaceutical compound was determined MBR according to (1):

$$\text{Removal \%} = (C2-C1) / C2 \times 100$$

where:

C1: the experimental concentration determined for each pharmaceutical compound in each reactor influent by LC / (MS MS) analysis.

C2: the experimental concentration of each pharmaceutical compound in each reactor effluent by the LC / (MS-MS) analysis.

The concentrations of the various pharmaceutical compounds and their transformation products during the spiking period were determined by LC/MS-MS applying electro spray ionization (ESI) under high resolution MS conditions. Table V shows the concentration of the PPCPs in influent, outlet and the removal % for the MBR after 275 days of the operation. It can be clearly observed the highest removal efficiency (environ 95%) or complete removal of Ketoprofen, Naproxen, Paracetamol, Ibuprofen, Caffeine, Gemfibrozil, Pravastatin, Carboxy-ibuprofen, Iohexol in BRM for the compounds which (log D< 3).

In our study after 275 days of operation and in high efficiency of removal for the N and the COD we can confirm that the BRM was reached to stable operation. Therefore, the high and/or variable removal of these compounds can be attributed to their physicochemical proprieties as the electronics strong in presence functional groups (amide, chlorine and carboxylic) [6], (see Fig. 3). In addition to that effect of hydrophobic interactions and its changes with the time. Hydrophpic compounds (log D> 3) adsorbed on sludge can be retained by membrane and further biodegradation by biomasses in the reactor can occur. The reporters [4]-[6] confirmed our results. In another side, the reporters [14], [16]-[18] have been reported variations in the removal of these compounds, for example joss et al found the efficiency of removal of Ketoprofen 30% and Naproxen from 55 to 85%. This means that in addition to physiochemical proprieties of trace organics, their removal also depends on operations conditions such as the temperature [19], [20], the HRT [21] and the PH [22].

TABLE V
TRACE ORGANIC CONTAMINANT REMOVAL EFFICIENCY OF THE MBR OVER 275 DAYS OF OPERATION

Pharmaceutical compound	Influent (µg/L)	Removal (%) MBR	MBR-GAC	References
Codeine	0,18	100	100	
Ketoprofen	6,4	97	100	(30%) [13]
Paracetamol	177	100	100	
Diclofenac	0,1	30	100	(5–45%) [14]
Naproxen	3,7	94,6	100	(55-85%) [14])
Ibuprofen	1,4	96,4	100	(90-100%) [14]
Roxithromycin	0,21	57,1	100	(<60%) [15]
Sulfametoxazole	1,6	18,8	100	
Metronidazole	4,8	56,3	100	15–18% [13]
Trimethoprim	1,4	14,3	100	90% [15]
Hydrochlorothiazide	2,8	10,7	100	
Furosemide	5,1	74,5	100	35–40% [13]
Caffeine	41	96,1	100	
Gemfibrozil	0	100	100	
Pravastatin	0,42	100	100	45% [13]
Metoprolol	0,1	10	100	
Atenolol	0,77	70,1	100	70% [13]
Acide Fenofibric	2,1	71,9	100	
Carboxyl-ibuprofen	16	100	100	80% [14]
Iopromide	1,1	74,5	100	60-80% [13]
Iohexol	167	99,8	100	

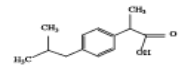
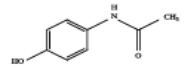
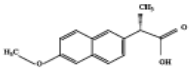
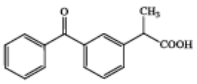
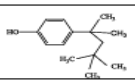
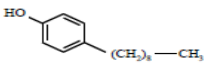
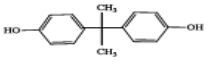
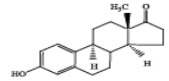
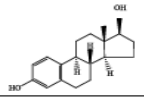
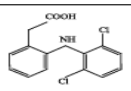
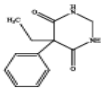
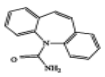
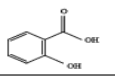
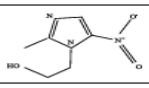
Category	Compound	CAS number	Molecular weight (g/mol)	Log K_{OW}[a]	Log *D* at pH 7 [a]	Dissociation constant (pKa)[a]	Water solubility (mg/L)[b]	Charge	Structure of compounds
Pharmaceutically active compounds	Ibuprofen ($C_{13}H_{18}O_2$)	15687-27-1	206.28	3.50 ± 0.23	0.94	4.41 ± 0.10	21	Negative	
	Acetaminophen ($C_8H_9NO_2$)	103-90-2	151.16	0.48 ± 0.21	0.47	9.86 ± 0.13 1.72 ± 0.50	14000	Neutral	
	Naproxen ($C_{14}H_{14}O_3$)	22204-53-1	230.26	2.88 ± 0.24	0.73	4.84 ± 0.30	16	Negative	
	Ketoprofen ($C_{16}H_{14}O_3$)	22071-15-4	254.28	2.91 ± 0.33	0.19	4.23 ± 0.10	16	Negative	
Surfactants and industrial chemicals	4-tert-octylphenol ($C_{14}H_{22}O$)	140-66-9	206.32	5.18 ± 0.20	5.18	10.15 ± 0.15	5	Neutral	
	4-n-nonylphenol ($C_{15}H_{24}O$)	104-40-5	220.35	6.14 ± 0.19	6.14	10.15	6.35	Neutral	
	Bisphenol A ($C_{15}H_{16}O_2$)	80-05-7	228.29	3.64 ± 0.23	3.64	10.29 ± 0.10	120	Neutral	
Steroid hormones	Estrone ($C_{18}H_{22}O_2$)	53-16-7	270.37	3.62 ± 0.37	3.62	10.25 ± 0.40	677	Neutral	
	17-β-estradiol ($C_{18}H_{24}O_2$)	50-28-2	272.38	4.15 ± 0.26	4.15	10.27	3.9	Neutral	
	Diclofenac ($C_{14}H_{11}Cl_2NO_2$)	15307-86-5	296.15	4.55 ± 0.57	1.77	4.18 ± 0.10 -2.26 ± 0.50	2.4	Negative	
	Primidone ($C_{12}H_{14}N_2O_2$)	125-33-7	218.25	0.83 ± 0.50	0.83	12.26 ± 0.40 -1.07 ± 0.40	500	Negative	
	Carbamazepine ($C_{15}H_{12}N_2O$)	298-46-4	236.27	1.89 ± 0.59	1.89	13.94 ± 0.20 -0.49 ± 0.20	18	Neutral	
	Salicylic acid ($C_7H_6O_3$)	69-72-7	138.12	2.01 ± 0.25	-1.13	3.01 ± 0.10	2240	Negative	
	Metronidazole ($C_6H_9N_3O_3$)	443-48-1	171.15	-0.14 ± 0.30	-0.14	14.44 ± 0.10 2.58 ± 0.34	9500	Neutral	

Fig. 3 Physiochemical properties of traces organics found in hospital waste water

C. Removal of Trace Organic Contaminants by MBR- GAC System

The removal effectiveness of the activated carbon adsorptive treatment system depends on the properties of the adsorbent (specific surface area, porosity, surface polarity, and physical shape of the material) and the characteristics of the compound (shape, size, charge and hydrophobicity). Adsorption mechanisms consist of the chemical (electrostatic interaction) and physical bindings of molecules to the surface of an adsorbent. The latter is often more important due to the capability to form multi-layer bindings [23]. In fact, it was recently reported that the greatest removal of amoxicillin by activated carbon was achieved under pH conditions corresponding to a zero net charge on the activated carbon surface [24].

The sorption efficiencies of organics traces to activated carbon may be significantly altered by several factors, such as the types of activated carbon used, the initial concentrations of target compounds and the pH, temperature and dissolved organic carbon (COD) concentration of the solution [25]-[28].

The capacity of activated carbon to adsorb a particular compound can, to some extent, be predicted based on the 'hydrophilic' or 'hydrophobic' nature of the chemical [23]. The hydrophobic (non-polar) or hydrophilic (polar) properties of pharmaceutics compounds can be determined from their LogD (or pKa-adjusted Log Kow) values. It has been reported that non-polar compounds with Log Kow > 2, may be effectively removed with activated carbon by hydrophobic interaction [23]. However, the adsorption of more polar or charged compounds to activated carbon is much more difficult to predict due to additional effects of polar interactions and ion exchange [23]. For that in our study we have been changed the ionic forces of activated carbon by treating with acidic and basic solution in high concentration. Many pharmaceutics compounds, such as tetracycline and sulfonamides are often present in negatively charged form at normal operating pH conditions [29]. Therefore, the use of ionic treatment processes may be effective for the removal of this anionic micropollutant [30] and that according with our results in this study. Ion exchange is the main mechanism in the ionic treatment for negatively and positively charged pharmaceutics.

Full-scale studies are required to determine the optimal configuration and operating conditions of adsorptive systems, which are effective and economically feasible for pharmaceutics compounds removal. In another side, in this study, we can confirm that initially GAC post-treatment could significantly improve the removal of the compounds which demonstrated low to moderate removal by MBR treatment (i.e., diclofenac, Roxithromycin, Sulfametazole, Hydrochloric-thiamine, Furosemide, Metoprolol, Atenolol, Acide Fenofibric, Iopromide, Trimethoprim, and metronidazole) see Table V.

IV. Conclusions

This study reported the stabilization of extern MBR system in biological treating of the hospital effluent during the operation a period over of 275 days. The results confirmed the high efficiency removal of COD and Nitrogen. The MBR system treatment can effectively remove Ketoprofen, Naproxen, Paracetamol, Ibuprofen, Caffeine, Gemfibrozil, Pravastatin, Carboxyl-ibuprofen, and Iohexol. The GAC column following the MBR treatment was demonstrated a high (95-100%) removal for all the organics traces in the hospital waste water. The ionic force of activated carbon and the electronic charge of organic micropollutant were two parts of chemical and electronic interaction which have been as important mechanism for complete and effective removal of organic micro pollutant of the waste water treated by MBR.

References

[1] Kümmerer K. Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources a review. 2001 Chemosphere, 45, (6–7), 957-969

[2] Carballa, M., Omil, F., Lema, J.M., Llompart, M., Garcia-Jares, C., Rodriguez, I., Gomez, M., Chromatography–mass spectrometry: methods and preliminary results including toxicity studies with Vibrio fischeri. J. Chromatogr. A 2004- 938, 187–197.

[3] Franc-ois Zaviska , PatrickDrogui , AlainGrasmick , AntoninAzais a,b, MarcHe´ran ; Journal of Membrane Science Nanofiltration membrane bioreactor for removing pharmaceutical compounds. 2012 Journal of Membrane Science 429 (2013) 121–129.

[4] Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H., 2005. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Res. 39, 4797e4807.

[5] Joss, A., Keller, E., Alder, A.C., Göbel, A., McArdell, C.S., Ternes, T., Siegrist, H., 2005. Removal of pharmaceuticals and fragrances in biological wastewater treatment. Water Res. 39, 3139e3152.

[6] Tadkaew, N., Hai, F.I., McDonald, J.A., Khan, S.J., Nghiem, L.D., 2011. Removal of trace organics by MBR treatment: the role of molecular properties. Water Res. 45, 2439e2451.

[7] Kim, S.H., Shon, H.K., Ngo, H.H., 2010. Adsorption characteristics of antibiotics trimethoprim on powdered and granular activated carbon. J. Ind. Eng. Chem. 16, 344e349.

[8] Behera, S.K., Oh, S.Y., Park, H.S., 2012. Sorptive removal of ibuprofen from water using selected soil minerals and activated carbon. Int. J. Environ. Sci. Technol. 9, 85e94.

[9] Dickenson, E.R.V., Drewes, J.E., 2010. Quantitative structure property relationships for the adsorption of pharmaceuticals onto activated carbon.Water Sci. Technol. 62, 2270e2276.

[10] Grover, D.P., Zhou, J.L., Frickers, P.E., Readman, J.W., 2011. Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: impact on receiving river water. J. Hazard. Mater. 185, 1005e1011.

[11] Hernández-Leal, L., Temmink, H., Zeeman, G., Buisman, C.J.N., 2011. Removal of micropollutants from aerobically treated grey water via ozone and activated carbon. Water Res. 45, 2887e2896.

[12] José Luiz Tambosi a,b, Rênnio Felix de Sena a,b, Maxime Favier b, Wilhelm Gebhardt b, Humberto Jorge José a, Horst Friedrich Schröder b, Regina de Fátima Peralta Muniz Moreira a, a Laboratory of Energy and the Environment, Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Campus Universitário, Trindade, 88040-900.

[13] Jelic A, Gros M, Ginebrenda A, Cespedes-Sánchez R, Ventura F, Petrovic M, et al. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res 2011; 45:1165–76.

[14] Joss A, Keller E, Alder A, Göbel A, Mcardell C, Ternes T, et al. Removal of pharmaceuticals and fragrances in biological wastewater treatment. Water Res 2005; 39: 3139–52.

[15] Göbel A, Mcardell CS, Joss A, Siegrist H, Giger W. Fate of sulfonamides, macrolides, and trimethoprim in different wastewater treatment technologies. Sci Total Environ n2007; 372:361–71.

[16] Urase, T., Kagawa, C., Kikuta, T., 2005. Factors affecting removal of pharmaceutical substances and estrogens in membrane separation bioreactors. Desalination 178, 107e113.

[17] Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., Takada, H., 2006. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res. 40, 3297e3303.

[18] Kimura, K., Hara, H., Watanabe, Y., 2007. Elimination of selected acidic pharmaceuticals from municipal wastewater by an activated sludge system and membrane bioreactors. Environ. Sci. Technol. 41, 3708e3714.

[19] Hai, F. I., Tessmer, K., Nguyen, L. N., Kang, J., Price, W. E., Nghiem, L. D., 2011. Removal of micropollutants by membrane bioreactor under temperature variation. J. Membr. Sci. 383, 144e151.

[20] Vieno, N.M., Härkki, H., Tuhkanen, T., Kronberg, L., 2007. Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. Environ. Sci. Technol. 41, 5077e5084.

[21] Kim, S., P. Eichhorn, J.N. Jenson, A.S. Weber, and D.S. Aga, Removal of antibiotics of waste water: Effect of hydraulic and solid retention time on the fate of tetracycline in the activated sludge process. Environmental science technology, 2005. 39(15): P. 5816-5823.

[22] Tadkaew, M. sivakumar, F. I., McDonald, J. A., Khan, S. J., Nghiem, L. D., 2010. Effect of mixed liquer Ph at removal traces organics in a membrane bioreactor. Bio. Tech. 2010. 163 (0) P. 287-303.

[23] Snyder, S. A., Westerhoff, P., Yoon, Y. & Sedlak, D. L. 2003. Pharmaceuticals, Personal Care Products, and Endocrine Disruptors in Water: Implications for the Water Industry. Environmental Engineering Science, 20, 449-469.

[24] Putra, E. K., Pranowo, R., Sunarso, J., Indraswati, N. & Ismadji, S. 2009. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics. Water Research, 43, 2419-2430.
[25] Rivera-Utrilla, J., Prados-Joya, G., Sánchez-Polo, M., Ferro-García, M.A., Bautista- Toledo, I., 2009. Removal of nitroimidazole antibiotics from aqueous solution by adsorption/bioadsorption on activated carbon. J. Hazard. Mater. 170, 298e305.
[26] Choi, K. J., Kim, S. G. & Kim, S. H. 2008. Removal of tetracycline and sulphonamide classes of antibiotic compound by powdered activated carbon. Environmental Technology, 29, 333-342.
[27] Ji, L. L., Chen, W., Duan, L. & Zhu, D. Q. 2009. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. Environmental Science & Technology, 43, 2322- 2327.
[28] Aksu, Z. & Tunc, O. 2005. Application of biosorption for penicillin G removal: comparison with activated carbon. Process Biochemistry, 40, 831-847.
[29] Adam, M. L., Comfort, S. D., Morley, M. C. & Snow, D. D. 2004. Remediating RDX-contaminated ground water with permanganate: Laboratory investigations for the Pantex perched aquifer. Journal of Environmental Quality, 33, 2165-2173.
[30] Robberson, K. A., Waghe, A. B., Sabatini, D. A. & Butler, E. C. 2006. Adsorption of the quinolone antibiotic nalidixic acid onto anion-exchange and neutral polymers. Chemosphere, 63, 934-941.