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Wastewater polycyclic aromatic hydrocarbons removal by membrane bioreactor

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ABSTRACT

The capacity of removal polycyclic aromatic hydrocarbons (PAHs) by membrane bioreactor (MBR) has been studied. The study has been developed at pilot scale using a pre-denitrifying MBR and several stages have been checked at bench-scale. Concentration of PAHs was determined by gas chromatography (GC) and mass spectrometry (MS) with twister and a balance on the MBR system was achieved. The system was feeded with raw wastewater which contains usually pyrene, phenanthrene and fluoranthene at low concentration (<0.3 ppb). Treated wastewater concentration was under detection limits for all detected PAHs and sludge accumulation was not observed. Under operational MBR conditions, several removal mechanisms and different removal rates for each compound are presented along the treatment process. Bench-scale experiments reveal that PAHs removal is mainly due to sorption and air stripping, however the volatilization and biodegradation present a questionable insignificant contribution. Toxicity by PAHs during MBR treatment can not be expected due to the low bio-available for the microorganisms mainly as a result of the high removal by air stripping.

Keywords: Polycyclic aromatic hydrocarbon; Wastewater; Phenanthrene; Flouranthene; MBR; Pyrene

1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds with two or more fused aromatic rings with a relatively low solubility in water and a high octanol/water partition coefficient (K_{ow}). These substances are originated from pyrolysis of organic compounds under temperature conditions ranging from 500°C to 900°C specially by incomplete combustion during industrial and other human activities, such as processes of coal and crude oil, combustion of natural gas or wood, combustion of refuse, vehicle traffic, cooking and tobacco smoking, as well as natural processes such as carbonization [1,2].

Wastewater levels of PAHs depend on the industrial effluents added to the domestic and runoff discharges [2,3]. PAHs in domestic wastewater varied from 0.005 to 14.3 μg l^{-1} and in mixed urban wastewater from 2.7 to 26.4 μg l^{-1} [4]. A predominance of low molecular weight compounds was observed in urban wastewater where phenanthrene (PHE), naphthalene, fluoranthene (FLT) and pyrene are usually the most abundant compounds [2].

Several PAHs are considered as widespread environmental pollutants, hazardous to ecosystems and a human health risk due to its carcinogenic and mutagenic properties close to its persistence and lipophilicity [5,6].

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Because of this, some PAHs are included in priority pollutants lists compiled by USEPA and European Union with the objective of reducing the release of these compounds to the environment [7].

The occurrence and fate of PAHs during wastewater treatment plant by conventional activated sludge has been studied previously [3]. Treated wastewaters show lower levels of PAHs as a result of the removal through different processes. As consequence of their physico-chemical properties, PAHs are mainly removed from wastewaters by sorption to the sludge [8]. Others mechanisms such as volatilisation, advection, biotransformation/biodegradation or air-stripping must be taken into account as wastewater PAHs removal related to the influent characteristics in WWTP, the process design and operating conditions of the system [3,9]. Anoxic reactors with stirring, sorption, volatilisation and biotransformation can be considered as mechanisms of PAHs removal whereas in aerobic reactor may be removed through sorption, volatilisation, air stripping and biotransformation/biodegradation [9–11].

Submerged membrane bioreactor (MBR) is an alternative membrane application in wastewater treatment. This technology combines the biological activated sludge process with solid/liquid physical separation by membrane, avoiding the need for a previous sedimentation step. In this way, a new system has evolved which merges the first, the second and the third treatment phases, allowing the construction of more compact plants capable of producing directly reusable effluent [12]. In such, system different configurations may be used in function of the final water quality. So, PAHs removal mechanisms in MBR can defer with respect to conventional activated sludge.

The objective of the present study aimed to know the main mechanisms concerning to PAHs removal from urban wastewater by MBR technology. For this purpose, PAHs were determined in raw and treated wastewater by a pilot scale MBR and several stages of the process were checked at lab-scale including respirometric assays to know the potential toxicity.

2. Materials and methods

2.1. Pilot plant study

A first stage of the study was achieved at pilot-scale by a pre-denitrifying MBR located in the Granada urban wastewater treatment plant (Spain). The MBR consisted of an external membrane system (ZeeWeed 500 membranes) equipped with polyvinylidene fluoride (PVDF) outside-inside hollow fibres with an average pore size of 0.04 μm (Fig. 1).

Raw wastewater (previously pretreated) passed through a brush screen (1 mm) and was put into anoxic reactor. Activated sludge of anoxic reactor was pumped to aerobic reactor which fed membrane tank. The membrane tank concentrate returned as overflow to the anoxic reactor and permeate ($F = 0.8\ m^3\ h^{-1}$) passed to the backwashing tank. A constant purge of $1.05\ m^3\ d^{-1}$ was achieved in order to obtain 25 d of sludge retention time. The operational hydraulic retention time was 35 h.

Samples were taken daily from influent, effluent and purge during a week. This was facilitated by automatic sampling devices located at the corresponding pipes. A portion of the sample was collected in a brown glass bottle (100 ml), which was filled completely and hermetically sealed. Persistent organic pollutants (POPs) were analysed in all samples.

2.2. Lab-scale study

Bench-scale bioreactors operated in parallel were used for several assays. The volume of the reactors were 10 l; all of them have a stirring system. Furthermore, two of them present air injection system and were filled with activated sludge from the pilot-plant aerobic reactor. The other bench-bioreactors were filled with activated sludge from the anoxic reactor.

The reactors were spiked with different amounts of pyrene, PHE and/or FLT, in order to obtain high PAHs concentrations. For the PAHs fate and behavior determination after 24 h, the doped activated sludge was separated into solid and liquid phase by decantation using a 250 ml test-tube. Both phases were used for PAHs extraction and analysis. The samples were manually collected.

In order to determinate the possible toxicity of the PAH and the potential sludge biodegradation capability, the activity of the biomass and the oxygen consumption rate were evaluated using a respirometer. Cyclic and dynamic configurations were used for different assays. The cyclic configuration was used with the oxygen uptake rate (OUR) assays for determining the response during a long time exposition. A dynamic configuration was used with the Rs (Dynamic Respiration Rate) assays for determining the possible acute toxicity.

2.3. Analytical determination of PAHs

All the samples were collected in brown glass bottle (100 ml), which was filled completely and hermetically sealed. PAHs were analysed in all samples. PAHs were extracted from sludge and wastewater samples using a stir bar sorptive extraction method (SBSE), called twister. PAHs were quantified using liquid–liquid extraction gas chromatographic/mass spectrometric method [13].

2.4. Isolation of PAH-degrading microorganism

Microorganism strains in the pilot-plant sludge were grown in basalt salt medium (BSM) (0.1 ml of anoxic or

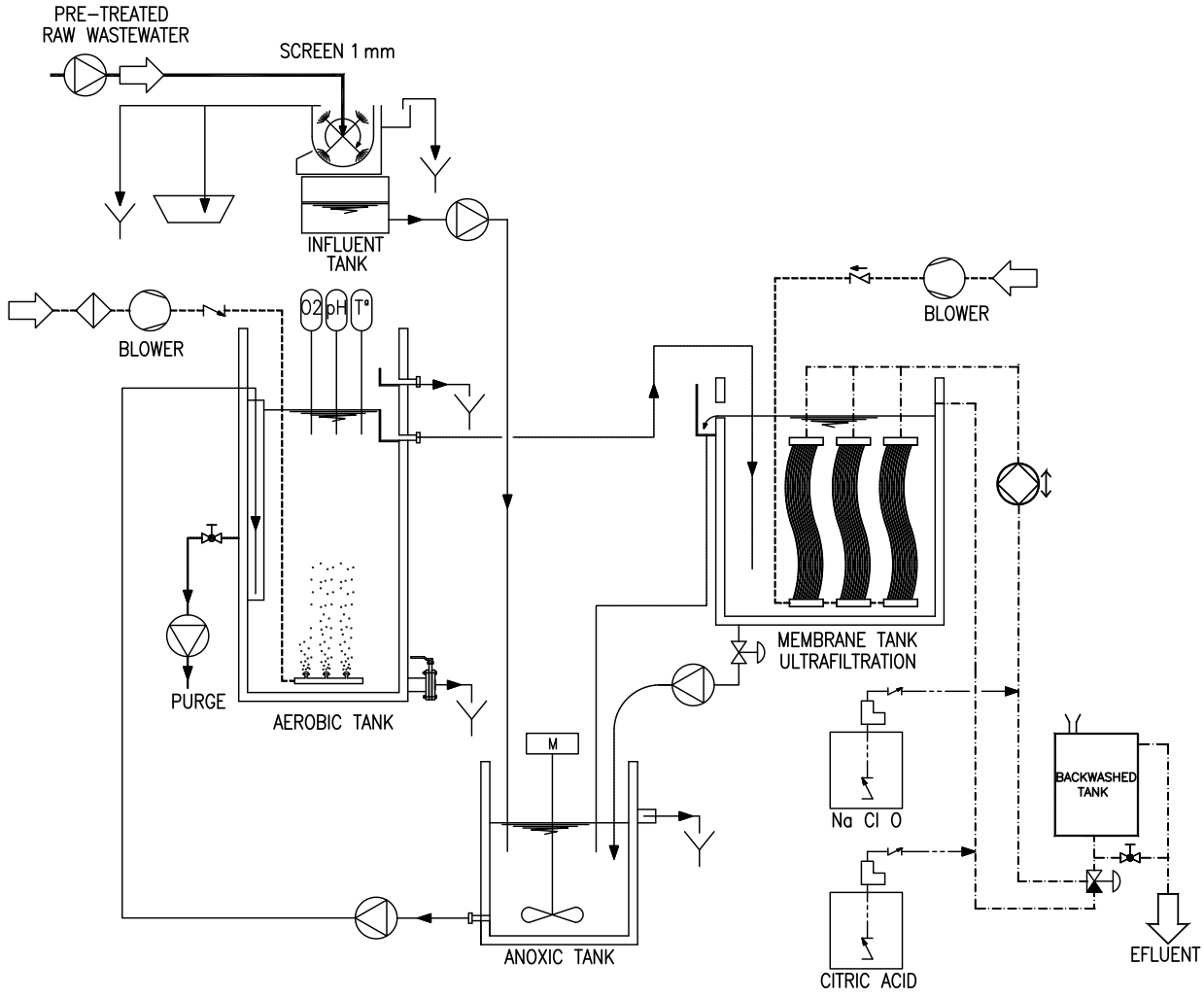

Fig. 1. Layout of pilot plant.

aerobic sludge per 20 ml of basal salt medium) to which solution of acetone and pyrene at a level of 1 mg ml^{-1} were added like aerosol on the top. A BSM formula was adapted from [14]. The culture dishes were incubated at 20°C in the dark and colony growth was checked during a month.

3. Results and discussions

Several POPs occurrence in Granada wastewater were analyzed, and only some PAHs were found (Table 1). So, the behaviour and possible fate of PAHs into the MBR was studied.

The low PAHs concentration for Granada urban wastewater could be expected due to the low industrial wastewater discharges. Pyrene, fluorantene and phenantrene were the main PAHs analysed, a predominance of low molecular weight compounds just as Blanchar et al. [2] observed for urban wastewater.

Table 1
POPs (µg l^{-1}) occurrence in MBR pilot scale plant

Pollutant	Raw wastewater	Effluent	Purge
Triazenes	<0.02	<0.02	<0.02
Organophosphorade compounds	<0.03	<0.03	<0.03
Organochlorine compounds	<0.05	<0.05	<0.05
Polycyclic aromatic hydrocarbons (PAHs)	0.48	<0.05	<0.05
Phenanthrene	0.09	<0.05	<0.05
Fluoranthene	0.11	<0.05	<0.05
Pyrene	0.28	<0.05	<0.05
Other PAHs	<0.5	<0.5	<0.5
Polychlorinated Biphenyls (PCBs)	<0.05	<0.05	<0.05

After MBR treatment effluent PAHs concentration under the detection limit was observed. A high efficiency at removing PAHs was observed for MBR technology. So, sorption, volatilisation, air stripping or biotransformation/biodegradation mechanisms were occurred [9,11]. PAHs were not detected in purge samples at which sorption was not significant mechanisms for PAHs removal.

After a month of incubation, the cultures achieved with the aim to know the presence of PAH-degrading microorganism developed a transparent halo on the pyrene–acetone top cake. The positive cultures were achieved for activated sludge from aerobic and anoxic bioreactor. The colonies were developed by fungi and its number was small with one or two colony only in a few Petri dishes. These results show the posibility of biotransformation/biodegradation mechanisms for PAHs removal during MBR treatment. However, the significance of these mechanisms was not prominet according to [10].

Bench scale experiment revealed than PHE presence after 24 h under aerated conditions is lower than 85% with respect to non aerated sludge (Fig. 2). Sediment phase shows a higher concentration than liquid phase for activated sludge from aerated and non aerated bioreactor. Just as showed for naphthalene during secondary treatment, PHE was dragged up by air stripping, an important removal mechanism for the lower molecular weight PAHs [3,9].

A similar behaviour was observed for FLT which was draged up mainly from sediment phase. However, a higher concentration in the liquid phase was observed (Fig. 2). This may be due to the higher molecular weight and other different physico-chemical properties which gave rise to a lower removal. The presence of FLT in the aerated bioreactor was 50% lower than in the non aerated bioreactor a higher rate than the observed by Manoli and Samara [3].

Significant differences are probed between the air injected and the non-aired bench-scale reactor. This indicates the important role of the aeration improving the air-stripping like the main removal way. Experimental removals of individual PAHs ranged between 0% and 86% were observed in the sediment phase, and between 50% and 100% in the liquid phase. The PAH removal efficiency from wastewater and sludge varies with the properties of different PAHs. Low molecular weight PAH (phenathrene) was more easily removed than larger molecule (fluoaranthene). Volatilisation was an important mechanism during non aerated treatment, but its total contribution to PAHs removal was not significant respect to air stripping.

A 0.4 mg l^{-1} of pyrene was spiked on activated sludge which was stirred and aerated during 24 h. Pyrene was mainly distributed between liquid phase (1/3) and sediment phase (2/3). Liquid phase pyrene was easily removed during the first 12 h. However, the sediment phase had presented pyrene after 24 h, with a 50% removal over initial concentration (Fig. 3). Again, pyrene was mainly dragged up by air stripping, but physico-chemical properties gave rise to a lower removal from sediment.

During conventional wastewater treatment plant, forceful relationship is observed between removal

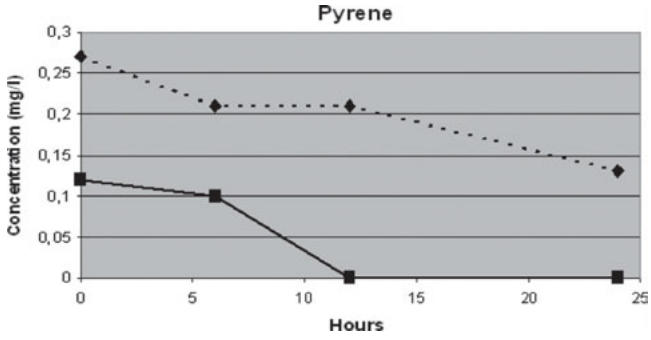

Fig. 3. Pyrene concentration: Evolution of the concentration in the sediment (◆) and liquid phase (■) during the stirring and air injection process.

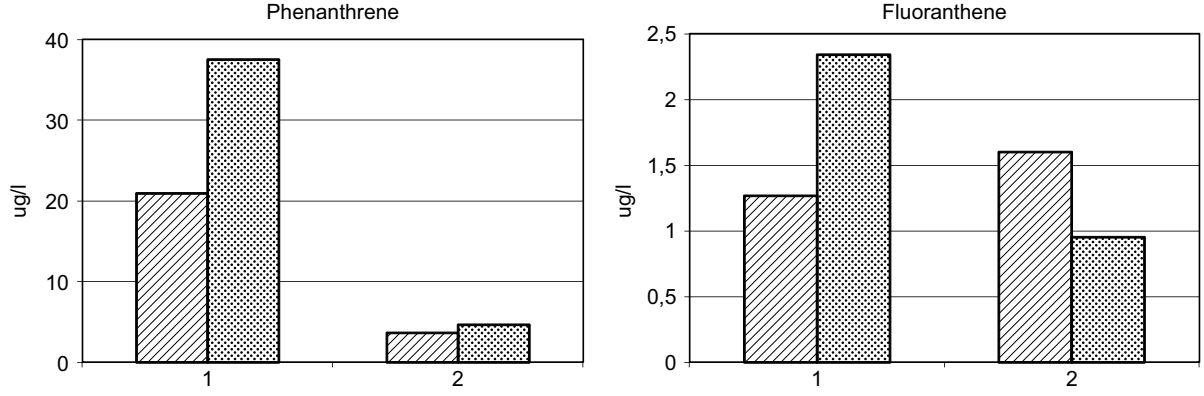

Fig. 2. Activated sludge phenanthrene and fluoranthene concentration after 24 h: (1) Stirred bioreactor; (2) stirred and aerated bioreactor. Liquid phase (crossed bars) and sediment phase (black bars).

efficiency from the solid phase and log K_{ow} of PAHs suggesting that high molecular weight PAHs are principally removed trough sorption to sludge particle and later removal during the separation solid–liquid phases [3]. However, by MBR system sorption to sludge particle remove PAHs from liquid phase and air stripping during aerated treatment drag up PAHs to the atmosphere.

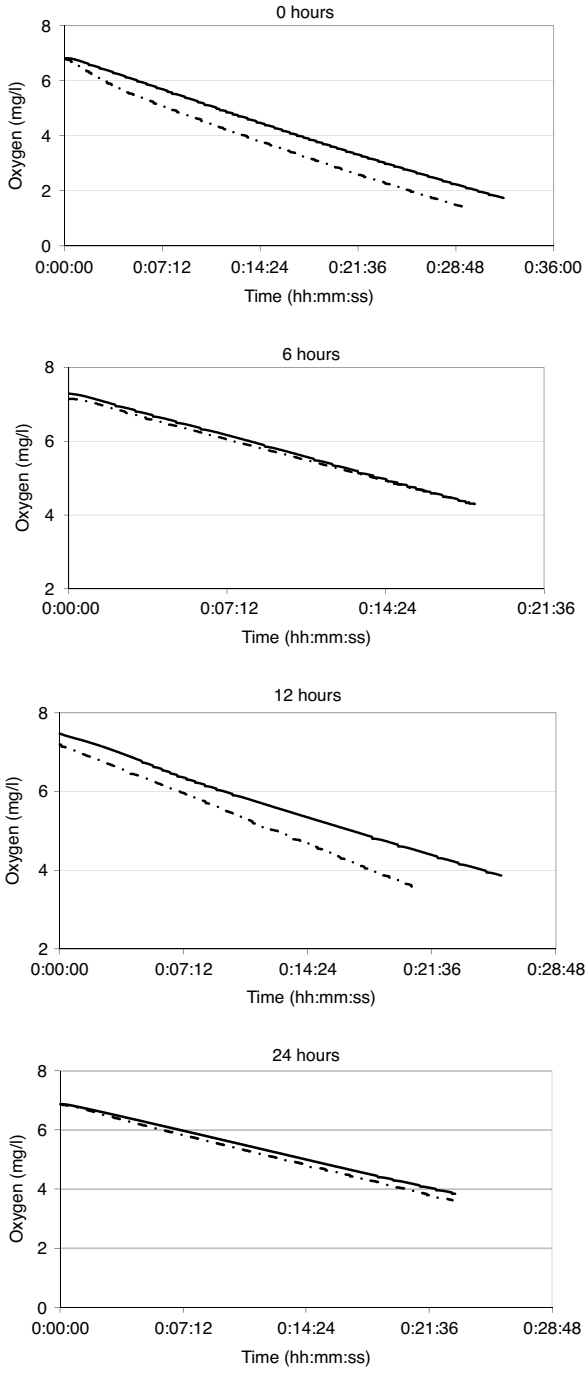

Fig. 4. Oxygen consumption rate: OUR respirometry assays. Raw (full line) and spiked sludge (broken line) (0.04 mg pyrene l^{-1}).

Fig. 4 shows the results of the respirometric assays using the OUR into the sludge without air injection. Similar slopes for the raw and the spiked sludge samples were obtained, which suggest that toxicity was not detected with a pyrene concentration of 0.04 mg l^{-1}.

Fig. 5 illustrates the responses of the sludge with different amounts of pyrene (0.04–0.8 mg l^{-1}). The dynamic respiration rates (mgO_2 l^{-1} h^{-1}) were calculated with the respirometric assays. At first, the raw sludge from the pilot plant was induced to the endogenesis. Then, the respiration rate of the sludge was calculated measuring the consumption after the addition of carbon substrate (200 mg sodium acetate l^{-1}). Using the same sludge sample again, it was feed with the substrate and pyrene. The different oxygen consumption rate between the raw and the spiked sludge showed a very similar respiration rates, therefore, the pyrene did not present toxicity for the sludge with concentration below 0.8 mg l^{-1}.

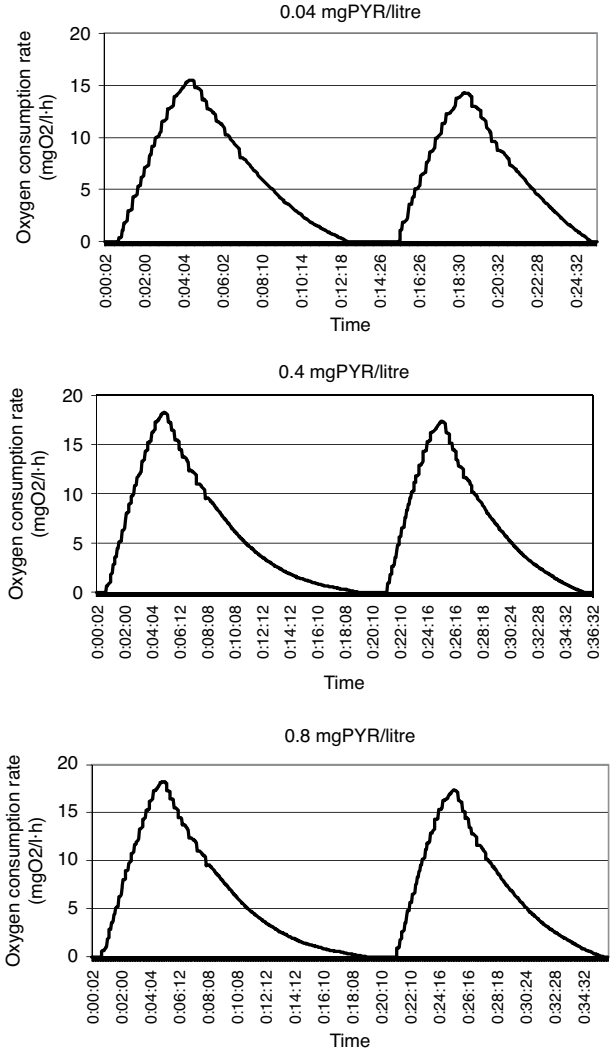

Fig. 5. Oxygen consumption rates with different pyrene concentration: (a) 0.04 mg l^{-1}, (b) 0.4 mg l^{-1} and (c) 0.8 mg l^{-1}.

The non-toxicity showed by the sludge with pyrene concentration below 0.8 mg l^{-1}. and the similar response when that concentration was increased indicate that the pyrene has not been bio-available for the microorganism during the assays. It is due to the hydrophobic property of pyrene, its tendency to concentrating adsorbed to the sludge and mainly to air stripping.

4. Conclusions

The PAH removal efficiency from wastewater by MBR technology varies with the properties of different PAHs. Low molecular weight PAH (phenathrene) was more easily removed than larger molecule (fluoaranthene). High molecular weight PAHs were principally removed trough sorption to sludge particle and later removal to the atmosphere from liquid and sediment phase by air stripping during aerated treatment. The high significance of air stripping limits biodegradation and volatilization mechanisms.

Toxicity by PAHs during MBR treatment can not be expected due to the low bio-available for the microorganism mainly due to high removal by air stripping.

Acknowledgements

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References

[1] USEPA. Agency for Toxic Substances and Disease Registry. Toxicological profile for polycyclic aromatic hydrocarbons (PAHs): update. Atlanta, GA, US Department of Health and Human Services, Public Health Services, 1994.

[2] M. Blanchard, M.J. Teil, D. Ollivon, L. Legenti and M. Chevreuil, Polycyclic Aromatic hydrocarbons and polychlorobiphenyls in wastewater and sewage sludges from the Paris area (France), Environ. Res., 95 (2004) 184–197.

[3] E. Manoli and C. Samara, The removal of polycyclic aromatic hydrocarbons in the wastewater treatment process: experinmental calculations and model prediction. Environ. Pollut., 151 (2008) 477–485.

[4] J. Sánchez-Ávila, J. Bonet, G. Velasco and S. Lacorte, Determination and occurence of phtalates, alkylphenols, bisphenol A, PBDEs, PCBs and PHAs in an industrial sewage grid dischrarging to a municipal wastewater treatment plant. Sci. Total Environ., 407 (2009) 4157–4167.

[5] M. Blanchard, M.J. Teil, A.M. Carru, D. Ollivon, B. Garban, A. Chesterikoff and M. Chevreuil, PCB and PHA impacts on cytochrome P-450 dependent oxidases in roach (Rutilus rutilus) from the Seine river (France), Arch. Environ. Contam. Toxicol., 37 (1999) 242–250.

[6] A.J. Sweetman and K.C. Jones, Declining PCB concentrations in the UK atmosphere: evidence and possible causes, Environ. Sci. Technol., 34 (2000) 863–869.

[7] E. Manoli and C. Samara, Occurrence and mass balance of polycyclic aromatic hydrocarbons in the Thessaloniki sewage treatment plant, J. Environ. Qual., 28 (1999) 176–187.

[8] F. Busetti, A. Heitz, M. Cuomo, S. Badoer and P. Traverso, Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and soil samples from an Italian wastewater treatment plant, J. Chromatogr., 1102 (2006) 104–115.

[9] G. Byrns, The fate of xenobiotic organic compounds in wastewater treatment plant, Water Res., 35 (2001) 2523–2533.

[10] A.K. Haritash and C.P. Kaushik, Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PHAs): A review. J. Hazard. Mater., 169 (2009) 1–15.

[11] A. Katsoyiannis and C. Samara, Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance. Environ. Res., 97 (2005) 245–257.

[12] C. Wisniewski, Membrane bioreactor for water reuse, Desalination, 203 (2007): 15–19.

[13] APHA, AWWA, WPCF. Standard Methods for the examination of water and wastewater. 1989.

[14] C. Miller, K. Hall, Y.N. Liang, K. Nieman, D.L. Sorensen, B. Issa, A.J. Anderson and R.C. Sims, Isolation and characterization of Polyciclyc aromatic hydrocarbon-degrading Mycobacterium isolates from soil. Microb. Ecol., 48 (2004) 230–238.