Chair:
Prof. Roberto Canziani

DOCTORAL PROGRAM IN SANITARY - ENVIRONMENTAL ENGINEERING

1. VOCs removal from gaseous emissions. Pilot-plant experiments on biotrickling filters and rotating biological contactors

2. Mobile Lab for air quality monitoring

Introduction

"Although many people are concerned about the status of the environment, environmental engineers are the technical professionals who provide safe drinking water, treat and properly dispose of wastes, maintain air quality, control water pollution, and remediate sites contaminated due to spills of improper disposal of hazardous substances. They monitor the quality of the air, water, and land. And, they develop new and improved means to protect the environment". (Mackenzie L. D. Cornwell D.A., 1998, Introduction to Environmental Engineering. Mc Graw Hill 3rd Edition; Boston, Mass. USA).

The definition of Environmental Engineering, as published by the Environmental Engineering Division of the American Society of Civil Engineers - ASCE is the following:

"Environmental engineering exerts sound engineering thought and practice in the solutions of problems of environmental sanitation, notably in the provision of safe, water supply, the proper disposal of wastewater and solid wastes; the control of water, soil and atmospheric pollution, and the social and environmental impact of these solutions. Furthermore it is concerned with engineering problems in the field of public health and with the effects of technological advances on the environment."

According to these authoritative references, doctoral studies in Sanitary - Environmental Engineering at Politecnico di Milano provide engineers with advanced tools to lead research and development on technologies for pollution prevention and control.

Educational strategy

The long-desired innovation in services and industry should not be a fleeting fruit of fantasy, but a long-lasting product coming from a sound research activity which only University can grant, especially to small and medium-sized enterprises, which cannot afford the burden of autonomous research. The educational strategy of the Doctoral Programme in Environmental Engineering has been based on the transfer of fundamentals of Sanitary and Environmental Engineering to the doctoral students. The main objective is the formation of professionals that can develop autonomous research and that can easily master their field of competence, even for the most advanced topics, so that they can promote innovation and update the specific knowledge in their research field.

In the framework of its general objectives, two main elements are highlighted: a strong structure of the fundamental preparation and a more strict connection with industry and research institutes. For a typically interdisciplinary topic such as Environmental Engineering, "teaching" activities are very delicate, mainly for the wide cultural base that is requested. Specific training courses in biology and organic chemistry are offered. Preparatory training courses provide a synthesis and integration for all doctorate students: basic training courses take advantage of the long experience and know-how in laboratory activities, and offer training activities on essential research tools such as Environmental Engineering Laboratory, Environmental Monitoring, and Environmental Engineering Reactors. Contacts with bodies other than Universities have been established through the participation both to specialised seminars and refresher courses given by experts from industry, together with short training "stages" of the PhD students at highly qualified firms. Finally, stay abroad for at least 3 months is considered essential for PhD students in Sanitary-Environmental Engineering, in order to complete their formation and to exchange research experience and expertise.

Contents of the Doctoral Program in Environmental Sanitary Engineering

The full range of research themes offered by the PhD Course in Sanitary Engineering will cover the following list, in which PhD theses will be developed.

1. Water supply technology and treatment, disposal and reuse of wastewater, advanced biological and physical-chemical water and wastewater treatment, sludge minimization.
2. Solid wastes management (collection, recovery, recycling, incineration with energy recovery and final disposal).
3. Phenomenology of atmospheric environment and treatment of gaseous emissions: statistical models of air quality data, sampling and speciation of fine particulate in the

3. Analytical laboratory

atmosphere, emission models from mobile sources, emissions of micro-pollutants from waste incineration processes, organic volatile control by biofiltration techniques.
4. Contaminated soils and remediation technologies, groundwater protection and treatment, risk assessment, statistical analysis and mapping of contamination data, in-situ and on site bio-remediation;
5. Sustainability issues and environmental management systems (ISO 14001, EMAS, LCA, Ecolabel); indicators and indices: data qualification and statistical analysis.

Type of professional skills and possible positions achieved by graduated Doctors.
The typical interdisciplinary character of the environmental issues and the more and more "integrated" approach to problem solving in

this field has been repeatedly underlined by U.E. directives and will require experts in environment-related topics which can not only plan and design interventions, but also assess their implications on the environment. Typical outlets into the job market are Universities, Research Centres, public bodies and Authorities, private companies. Even medium and small enterprises which cannot afford to develop a specific "know-how" on their own, may require high professional profiles that can ensure adequate updating and innovation necessary to maintain competitiveness. Finally, a PhD in Sanitary-Environmental Engineering should provide highly qualified personnel to cover key positions and roles in research centres, top level management in Public Bodies and Authorities involved in environmental policy, and senior consultants for engineering companies.

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LCA OF PORTLAND CEMENTS PRODUCED IN ITALY AND IN BRAZIL

Junior Ademir Fidelis

Life Cycle Assessment (LCA) is a powerful decision-making tool that is used in environmental management, and is used mostly for comparison purposes between products, processes, and services. The manufacturing of cement is responsible for 5% of global CO_2 emissions. In addition, the cement supply chain also contributes to several other key impacts. Increasingly, companies need to produce environmental and economic benefits by reducing their environmental impacts and increasing the efficiency of their processes.

The basic principle of the LCA methodology is to serve as a tool for the identification and quantification of environmental impacts in accordance with the standards set by the ISO 14040 series.

The modern structure of LCA can be summarized through four key stages: goal definition and scoping, life cycle inventory, impact assessment, and interpretation. *Goal definition and scoping* being the preliminary stage, is where the purpose of the study is defined; and the functional unit, boundaries of the system, data requirements, the assumptions and limits determined. The *Life cycle inventory* is the first part of the work devoted to the study of the life cycle of the process or activity. Its main purpose is to reconstruct the route by

which the flow of energy and materials allows for the operation of the production system under consideration through all the processes of transformation and transportation. The *Life cycle impact assessment* is the study of the environmental impacts caused by the process or activity. It aims to highlight the magnitude of the changes generated as a result of resource consumption and environmental releases calculated within the inventory. The *Life cycle interpretation* is the final part of LCA and aims to propose any changes necessary to reduce the environmental impact of processes or activities.

The present research work has been conducted for three important cement companies in the world; one in Italy and two in Brazil. With the help of LCA software, comparisons have been made between four Portland cement types from a Brazilian company and three Portland cements from plants located in Brazil and Italy. The analysis was performed through a "cradle to gate" approach. The environmental impacts have used the CML 2001 methodology and from its ten categories of impacts, it was decided to focus on only those considered of major importance for processes related to the cement industry. Therefore,

indicators that characterize the various categories of impact and selected for this study include: global warming, resources depletion, acidification, human toxicity and formation photosmog. In addition, energy analysis was assessed according to the Gross Calorific Value and the Cumulative Energy Demand Method.

The first comparison concluded that the 'Quick setting and sulphate resistant cement' (3) contributes the highest impact. The research made with the cements from BR1 show that the impacts are directly proportional to the amount of clinker used. Hotspots present in more than six categories of impact include: the clinkerizzazione, petcoke production and the transportation of fly-ash. The clinkerisation is responsible for between 75-85% of all GWP100. The second hotspot highlighted is petcoke which is used as the main fuel in the clinkerizzazione and is responsible for most emissions of SO_2 and NO_x. A review in detail of the production of petcoke confirms that the greatest impact is from the production of its raw material - this being crude oil. It is responsible for 56 to 91% of all impacts and the use of petcoke makes the production phase of clinker the most energy consuming and polluting.
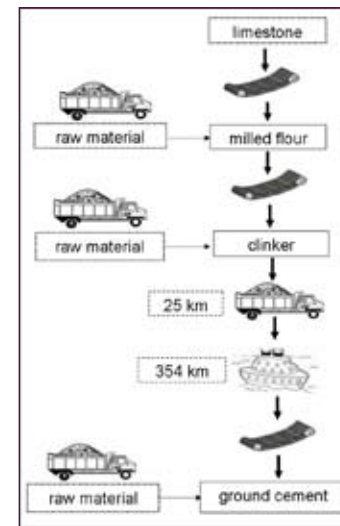
1. Diagram simplified of transport system used in the first comparison

The third hotspot identified is the transport of fly-ash used as a pozzolanic material in the final product and which in these cements is very representative. The impact caused by this operation has no relation with the relevant substance but with the distance travelled, amount transported, the type of transport and its capacity. A review in detail of the components shows the transport of fly ash, and the contributor of the largest impacts, is the consumption of diesel for the truck. This is responsible for between 48 and 88% of all the impacts associated with the transport of fly-ash and this in turn helps to make the final phase

of grinding the second most impactful for cement. The method Analytic Hierarchy Process (AHP) used to weigh and assess the impacts shows that impacts increased by 18%, 32% and 34% respectively for cements (2), (4), and (3). This confirms the results found in each analysis. The second comparison showed that Portland cement from the ITA has more environmental impacts than that from BR1 and BR2. The AHP method showed that the impacts increase by 7% and 54% for cements (2) and (3) respectively. This confirms the results found in each analysis. The third comparison shows that the increased use of RDF or rice husks instead of petcoke in the ITA brings insignificant changes to the impacts. In general, the clinkerisation, the consumption of petcoke in the oven, diesel for transport and electricity for the final grinding are the major contributors of environmental impacts along the supply chain of cement, and are all due to the consumption of fossil fuels. The AHP method showed that impacts decrease by 5% and 15% for cements (2) and (3) respectively. This confirms the results found in each analysis. Finally, the analysis carried out with SimaPro and GaBi demonstrate that the two are suitable software tools for life cycle assessment in cements.

The analysis performed with the SimaPro and then with Gabi serve to show that both approaches are suitable for the evaluation of the software life cycle in the cement. The difference between the results is based on the choice of input and output and the characterization factors available in the database software. Although the method and its version are the same for both assessments; a number of points were observed that may explain the differences found between the studies performed. The PhD thesis developed at the Technical University of Milan and through the internship at the University of Manchester has helped to understand the importance and the complexity of an LCA study. The review has permitted a greater understanding of the difficulties in applying LCA methodology including the use of secondary data, management of missing data, assumptions and simplifications and the use of proper technical terminology of the processes and materials. The available time allowed the research to properly investigate the comparison between the cements studied and to investigate the factors that most influence the environmental impacts identified. Besides, it was possible familiarize with two major LCA software - SimaPro and Gabi.

PREVENTION OF CONTAMINATION RISK DETERMINED BY ROAD TRAFFIC ACCIDENTS IMPLICATING TRANSPORT OF HAZARDOUS LOADS

Maria Kolintzaridou

The executed study has been concentrated on the attempt to supply the risk pollution due too road traffic accidents, that are involved in the transport of dangerous goods, aiming of proposing pollution control systems and measures for the protection of the exposed aquifers.

The study has been concentrated in all the territory of Lecco (Italy), with special focus on a sample road which joins the localities of Varenna, Esino Lario and Parlasco and where dangerous goods transportation accounts for 0.50% of the entire local traffic of the Province of Lecco, most of it concerning fuels (benzine, diesel oil and fuel oil miscellaneous). Subsequently, it has been determined that sensitive areas are up to 21% of the total surface of such Municipalities. Since their territory is mostly mountainous, several galleries are present, factor that further affects the highly remarkable risk linked to this road infrastructure. In the sample road that has been examined, landslides risk caused by natural events introduces a further risk connected to the transport of dangerous goods, being an interference point between road and vulnerable areas. Finally, the risk linked to the possible pollution of waters appears a real threat in any place of the area, considering the

geologic conformation of the northern part of the Province and the possible correlation of accidental discharge with the precipitation's high probability of the zone, with detail reference to the intense precipitations of short duration, alternated to dry periods, factors that contribute substantially to the increase of the pollutant load. Some of the factors leading to the risk of landslide has been evaluated in correspondence of the road under investigation, where water can easily infiltrates in the cliff rocks, due to the complex fracture system interesting all the mass. In order to determine the landslide tendency of the zone and its incidence on the verification of road accidents it has been made a reference to an in-depth study of the hydrogeological and lithological parameters, to a structural geologic survey and to an inspection, aiming to define the two main hydro-geological structures which are typical of the study area. Such structures constitute the models of the water circulation, on which the mathematical models are successively applied in order to determine the travel time of the pollutant agent. At last it is been made a reference to the location of the preferential ways of waters basements sliding, so that an esteem of the vulnerability

of the water course was able to be determined. As result of these considerations its been arrived to the determination of landslide events to small or medium scale in the zone study of object. Our road subject has been chosen for its elevated risk of little cliff landslides, able to create accidents and to deform the street center, and successively it has been calculated the arrival time of contaminating agents to the receiving water bodies mainly exposed. Their exposure is defined by their localization and by the brevity of time of distance of the mainly present hydrogeological formations in the zone. It has been ulteriorly tried to quantify the effective vulnerability of the zone using parametric methods such as SINTACS and Method Base CNR. It's been arrived to the conclusion that the majority of the area turns out to be characterized by a degree of medium high vulnerability. In the remaining part of the zone, the vulnerability generally passes locally to average.

Times of arrival of the pollutant agents to the water bodies mainly exposed have been estimated by implementing analytical solutions or numerical modelling. As for the latter, the piezometric levels of an aquifer of which its basic parameters are known have been calculated, so that distance and appearance
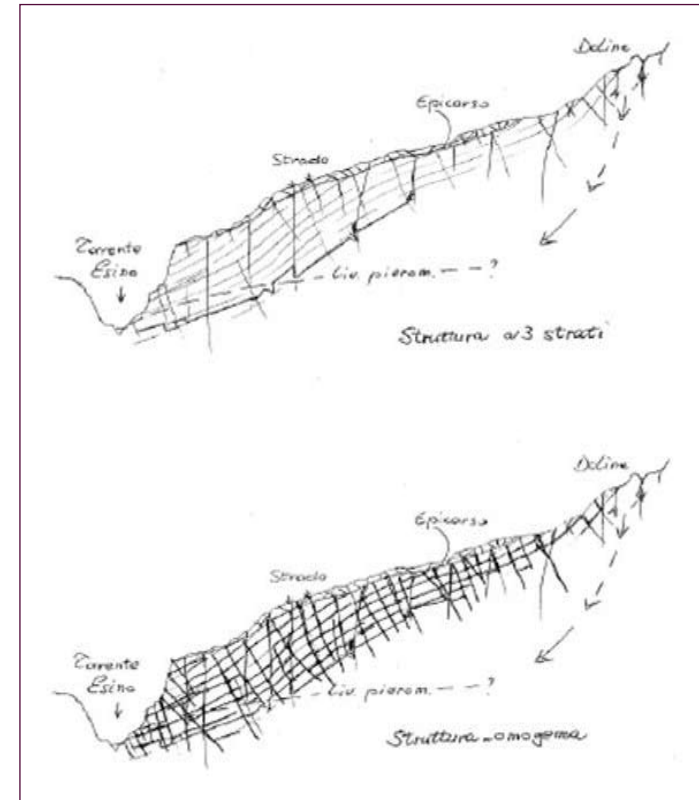
1. Schematics of the fracture systems of the cliff in the study area

time at the target water body have been estimated in the order of two or three months for the the three-layers aquifer (Figure 1,upper) as well as for the homogenous structure (Figure 1, lower).

Given the short arrival times in the Esino torrent, the pollution load discharged during the accident will easily affect lake

Como. It can be concluded that the forecast of arrival times of pollutants is possible, even if many practical aspects have not been defined yet, such as a detailed mapping of the variation in time and distance from the accidental discharge to the body exposed.

CONTAMINANT VAPOUR EMISSIONS
FROM POLLUTED SOIL AND GROUNDWATER

Sara Puricelli

The Soil Framework Directive, discussed by the European Council of Ministers and the European Parliament, and in Italy, the Legislative Decree 152/2006, affirm the centrality of Risk Assessment for long-term exposure of humans in order to identify contaminated sites and their remediation target limits. Exposure pathways often involve inhalation of Volatile Organic Compounds (VOCs), which are major soil and groundwater contaminants at many polluted sites and partition easily into air. To evaluate exposure to them, assessments or measurements of their concentration in air are necessary.

Traditional approaches involve application of transport modelling tools starting from concentrations in the secondary source or in soil gas, but their results are not very representative because they are based on non site-specific hypotheses and simplified conceptual models. Both analytical and numerical transport models are available in literature. Another common approach is sampling ambient air, bypassing the modelling step, which however may be affected by background values, local sources, wind speed for outdoor measurements, and air conditioning/heating for indoor measurements. Finally, a more recent approach is the measuring of emission flow at ground surface, but it is still generally used only at experimental scale for VOC applications.

Enclosure devices such as flux chambers (FC) or wind tunnels, seem to be an innovative proper methods. They measure the vapour flux emitted through the soil towards the atmosphere, isolating a volume of air layering over the surface without causing perturbations; this gives the input term for dispersion models to define vapour concentration in air required by Risk Analysis. Flux measurements allow all the contributions from soil to be evaluated without needing prior deep knowledge of soil; however, they cannot be applied indoors where critical permeable zones (cracks, conducts, walls junctions/corners) are difficult to enclose within the covered structure. Therefore, FC application is still controversial and requests further studies in order to define proper device configuration and monitoring protocols. Available commercial FCs are often built without a detailed study on critical issues.

The experimental part of the work of this Ph.D. thesis started thanks to a research grant given by Politecnico di Milano and the Region of Lombardy. It entailed the project and the execution of tests to study a dynamic FC with the aim to obtain an ideal FC setup to monitor emissions of volatile compounds from contaminated soils. A number of tests were performed at DIIAR Laboratory of Politecnico di Milano, both on a commercial apparatus and a new arranged setup, to evaluate the FC technical characteristics and main operative parameters, such as mixing conditions, purge duration and inertness of material. Tests performed on the commercial chamber, in fact, resulted unsatisfactory since it was not homogeneously mixed due to the inappropriate sweep gas injection system and the dome shape. Purge duration, also, took more than 2 h 30 min because the material it was made of adsorbed organic compounds. A new setup was defined, which replaced the dome with a flat PTFE cover, old inappropriate gasket with a PTFE one and changed the inflow gas injection system for a Teflon spiral. This new chamber resulted homogeneously mixed, with purge duration shorter than 2h. An ambient air treatment system was set up to be used as sweep gas and monitoring procedure was drawn up. In particular, sampling line details and analytical protocol were defined. The importance of recording physical parameters, such as temperature, humidity and pressure difference between outside and inside the FC, was affirmed as a recommended monitoring rule.

This defined configuration was used to carry out FC measurements (see Fig.1) at a site located in the North of Italy potentially contaminated by petroleum hydrocarbons. Three seasonal campaigns were performed, and data of groundwater, soil gas, and ambient air monitoring were also provided thanks to collaboration with the regional environmental Agency.

The field activity gave the opportunity to compare results from different approaches used to evaluate vapour inhalation pathway for Risk Assessment: air concentrations assessed from both FC measurements fluxes and modelled fluxes (by using concentrations in groundwater and soil gas in Johnson and Ettinger model), and air measurements. As a general trend, the applied model tended to overestimate, even if a good agreement or a slight underestimation was found for some pollutants at some sampling locations, suggesting models to offer an unreliable and not always precautionary assessment of vapour transport in soil. Dispersion box model was applied to calculate air concentrations from each approach to compare with the measured air concentrations. This information was used for Risk Analysis. Air concentration measurements resulted to overestimate risk in comparison with all the other approaches because of the pollutant environmental background.

Finally, a non-conventional remediation technique to treat soil contaminated with VOCs was assessed through laboratory tests performed at Civil and Environmental Laboratory of Newcastle University –UK-. Biochar-amended soil was compared to natural soil (both by batch and column tests) to study the effects on vapour transport, in particular as far as biodegradation and adsorption were concerned. A numerical code was written in Matlab to describe vapour transport in the test-specific conditions and geometry and to interpret the experimental results. The research showed that the biodegradation of petroleum hydrocarbons was not constant over time and was interdependent of the presence of other compounds, leading to sudden rises and falls in the gas-phase concentrations. Their behaviour was probably more complex than stated in the original modelling assumptions. It appeared, however, that biochar increased sorption of aromatic compounds without having negative effects on microbial activity. In particular, toluene vapours were effectively adsorbed on the amended matrix

1. Picture of FC system used for field activity

allowing increase in the degradation of cyclic and branched alkanes, which were only poorly degraded in soil without biochar. In general, in both column tests, biodegradation rates were lower than those simulated using data from batch results, probably because soil nutrients, in particular nitrogen, were not sufficient to support a long-term biodegradation activity. Nevertheless, it is encouraging to note that no detrimental effect of the biochar on the natural attenuation of the more readily biodegradable and more volatile petroleum hydrocarbons was observed in this study. Further investigations, however, need to be performed to evaluate biochar amendment for different soil types and for different biochar types, too.

TREATMENT OF INDUSTRIAL WASTEWATERS BY ANOXIC-AEROBIC AND ANAEROBIC MEMBRANE BIOREACTORS

Aronne Teli

SANITARY - ENVIRONMENTAL ENGINEERING

Membrane bioreactors (MBRs), combining an activated sludge process with a solid–liquid separation by membrane filtration, have proven to be an effective treatment for domestic as well as industrial wastewaters, also containing slowly biodegradable organics. However, membrane fouling and its consequences in terms of maintenance and operating costs resulted in the major obstacle for a wider application of MBRs. Therefore, fouling control is a key issue and several design and operational strategies can be implemented to achieve this scope such as membrane scouring, relaxation, backwashing, sustainable flux operation, etc. Moreover, flux enhancers, including metal salts, cationic polymers and powder activated carbon, have recently been introduced to hinder fouling occurrence. At the same time, they can improve permeate quality as pollutants can be flocculated or adsorbed and thus retained by the membrane. Therefore, this application is of particular interest in the treatment of industrial wastewater containing recalcitrant organics not completely biodegradable in a MBR. On the whole, the scope of the thesis is to investigate the effectiveness of flux enhancers dosing in an anoxic-aerobic pilot MBR treating textile

wastewaters (topic A) and to investigate treatability and anaerobic biodegradability of a highly problematic industrial wastewater (metal working fluids, MWFs) by an anaerobic pilot MBR (topic B). In particular, topic A focused on fouling control and permeate quality enhancement, especially with reference to specific textile macro-pollutants, i.e., dyes and surfactants. Low dosages of flux enhancers were considered to limit any possible detrimental effects on the biological activity and to guarantee economic sustainability for a possible implementation in full scale MBRs. The pilot (Figure 1), equipped with two lab-scale Siemens modules (surface area, 0.5 m²; pore sizes, 0.04 μm), was located in a full scale wastewater treatment plant and fed with mixed domestic-textile wastewaters (70% of the COD loading). It operated for 7.5 months without any flux enhancers (stage 1) and 2.5 months with polyaluminium chloride (stage 2), that was previously selected on the basis of a jar test campaign. On the whole, the addition of polyaluminium chloride (PACl) enhanced the permeate quality appreciably and controlled fouling occurrence properly. In particular, as for permeate quality, considerable improvements for COD (91.0

1. Picture of the anoxic-aerobic pilot MBR

vs. 81.0%), total phosphorus (87.8 vs. 23.6%), colour as the absorbance at 426 nm (83.6 vs. 72.0%), and anionic surfactants (84.3 vs. 79.2%) were detected. On the other hand, PACl showed negligible effects on nitrogen compounds and non ionic surfactants. As for fouling, the average irreversible fouling rate in stage 2 (with PACl) was approximately half the value observed in stage 1 (1.04×10^9 vs. 1.90×10^9 m⁻¹ d⁻¹). With regards to reversible fouling, PACl gave a significant reduction in the cake layer resistance forming on membranes (R_c), overall presenting values comparable with the membrane resistance (R_m). Such results were achieved even if a drop in flocs strength and structure occurred during stage 2, as strength indexes (SI_1, variation from 42.5 to 23.5 mg g MLVSS⁻¹; SI_2, from 7.5 to 15%) and the

specific resistance to filtration (from 6×10^{13} to 9×10^{13} m kg⁻¹) showed. Also, the definition and the implementation of a new modified flux-step method for the evaluation of fouling propensity indicated a worsening in critical flux (Jc, from 20 to 15.2 LMH) and in the compressibility factor (CF, from 1.25×10^9 to 3.5×10^9 bar⁻¹ m⁻²). In conclusion, as for topic A, the MBR technology combined with PACl addition can be considered as an effective option for the treatment of textile wastewater and, in general, for industrial effluents because of enhancing the permeate quality appreciably and controlling fouling properly. With regards to topic B, metal working fluids (MWFs) are products widely used in the metalworking industry for cooling and lubricating during the machining process, and, used MWFs cause high levels of contamination so that their treatment must be handled carefully. Biological processes offer an alternative solution to usual treatments (electrochemical, chemical and physical processes) although the complexity of MWFs composition can bring significant difficulties in operating bioreactors. In particular, anaerobic membrane bioreactors are suitable to select bacteria consortia able to degrade and convert into methane complex

organics. In this study a fresh MWF was used and its anaerobic biodegradability and inherent toxicity were firstly investigated. In particular, biochemical methane potential (BMP) assays were executed showing a biodegradation approximately of 0.8% over a period of 150 days. Moreover, volatile fatty acids (VFAs) production assays, carried out in parallel, suggested that the adaptation of the hydrolytic/heteroacetogenic bacteria (upper pathway of anaerobic digestion) did not occur significantly during the tests. Anaerobic toxicity assays, also employed in this study, showed that the acetoclastic methanogenesis (lower pathway of anaerobic digestion) was inhibited. Then, the start-up of a two phase submerged anaerobic MBR, equipped with Kubota flat sheet modules (surface area, 0.1 m²; pore sizes, 0.4 μm), was executed. In particular, the first reactor was thought to be a protective barrier for the growth of methanogens bacteria present in the second reactor, because more sensible to inhibitors. However, methane production was observed only in first days of pilot operation showing a degradation of 1.65%. Then, particle size analysis showed that the fresh MWF was prone to attach on biomass and to wrap biological flocs

leading to a possible limitation of the transport of soluble substrates. On the other hand, this attachment propensity on biomass resulted in a stable filtration with TMP variations between 0 and 0.020 bar in 40 days of operation. In conclusion, results showed that anaerobic biomass need a long period of time to become acclimatized to MWFs. Therefore, to achieve this goal, strategies including co-substrate addition or the systematic introduction of different sources of biomass can be executed to enrich the enzymatic pool of the bacterial community.