Waste Management Europe

erica
VALORE PER L'AMBIENTE

Edoardo Slavik - PFAS Treatment Technologies

Waste Management Europe Conference

SPECIAL FOCUS ON PFAS

The regulatory framework in the environmental field

- In order to focus about **technologies** relating to the **PFAS treatment** in **wastes** and **wastewaters** , it is necessary also to go into detail about **legislation** and **knowledge of production**

- Which wastes contain these molecules and which **concentrations we want to achieve** with the technologies, assuming that the slogan "ZERO PFAS" **has no technical basis?**

- While in the field of **drinking water**, groundwater, **food** and food packaging, the legislation is still present and constantly evolving, in the **environmental field** (wastewater, waste, water discharges) **legislation** is still rather conflicting and fragmented in Europe and in Italy.

- Similarly, also **technologies** are much less applied and tested in the field of waste treatment.

EUROPEAN REGULATORY FRAMEWORK – BAT

Waste and wastewaters

On **10th August 2018**, European Decision (EU) 2018/1147 established conclusions on **Best Available Techniques (BAT)** for waste treatment, pursuant to Directive 2010/75/EU of the European Parliament and of the Council (published in the Journal Official of the European Union of 17 August 2018), and in chapter 1.2 - "Monitoring", provides **only monitoring (without limits to be applied) in discharges of PFOA and PFOS**, considered the most dangerous compounds due to their persistence and bio-accumulation, as well as more representative for the entire PFAS category.

To date, are not present in the documents of European Integrated Pollution Prevention and Control Bureau (EIPPCB), **BREF** or texts containing specific **BATs** by JRC (Joint Research Centre) for the removal of PFAS from waste and wastewaters; therefore the combined approach is still to be built and the regulation and application of limits must take into account the **appropriate timing** of adaptation and **experimentation** of removal techniques and technologies, as well as any limitations on production.

ITALIAN REGULATORY FRAMEWORK

Waste and wastewaters

- In **Italy**, the regulatory limits for PFAS concentrations in **groundwater** are established by the Ministry of the Environment in regulation of 6th July 2016 (DM 6/7/2016)
- There is a specific regulation that concerns the **Environmental Quality Standards** (EQS – SQA the Italian acronym) to be achieved for surface waters (D.Lgs. n. 172/2015), while it is **not yet present at a national level**, a regulation regarding **liquid discharges** nor for the specific treatment of waste and landfill leachates.
- After D.Lgs. n. 172/2015, there are 6 PFAS to be monitored in **surface waters** with quality objectives to be achieved by **22 December 2027** (**PFBA**, **PFBS**, **PFPeA**, **PFHxA**, **PFOA**, **PFOS**).
- Currently this could also be the objective for defining **discharge limits** for wastewaters, in the absence of other specific laws

ITALIAN REGULATORY FRAMEWORK
Waste and wastewaters

- The *Istituto Superiore di Sanità* (Italian Institute of Health), already since **2014** suggested to the Local Authorities the limit values to be adopted for discharge into surface water for **a limited portion of the Veneto** territory affected by specific **PFAS pollution**.
- At a **National level** the topic of PFAS in liquid discharges has been discussed for years and various legislative schemes have been proposed, **without** ever reaching **approval**.
- **Veneto Region** has faced specific pollution in its territory affecting aquifers and aqueducts. The huge investments to overcome this situation were aimed at equipping the aqueducts with techniques for the **removal** of PFAS (**GAC**) and at the construction of **long pipelines** to withdraw drinking water from areas upstream of the specific pollution. During **2019**, however, the Regional Authority also proceeded with regulating the presence of PFAS compounds in the discharges of industrial installations that treat liquid waste, producing Supplementary Indications with which "***provisional and experimental discharge values***" were set for PFAS substances.

ITALIAN REGULATORY FRAMEWORK

Waste and wastewaters

- The **Piemonte** (Piedmont) **Region**, where there is still a company that produces fluorinated substances, has promulgated a **specific law** to regulate PFAS in the discharges of certain companies. This is regional law **25/2021**, which was then followed by explanatory indications in 2022. Restrictive limits are set on PFAS discharging and also substances belonging to the PFAS category, but not yet analytically identified, are regulated.
- The **Lombardy Region** issued guidelines for the application of BAT in 2020 where, regarding PFAS, it is stated that it **is not correct** to apply limits to these parameters. The Lombardy Region has therefore adopted an approach more congruent with European indications, carrying out accurate **monitoring** in 2018, 2021 and 2022 for surface water and liquid discharges.
- Adopting discharge limits for PFAS compounds, focused only to plants that treat liquid waste and for exclusive partial territories, has resulted in a **migration** of waste to plants located in other areas not subject to these regulations.

PFAS
Production limitations

- **For over forty years** PFAS have been freely produced, traded and used; only at the beginning of 2000's with the limitation of the production of PFOS by 3M, the world approach towards these substances changed
- At the moment only 3 PFAS have been banned or restricted from production by REACH through inclusion in the **POPs** category: **PFOS** (and precursors), **PFOA** (and precursors), **PFHxS**; **PFHpA** and its salts was recently added in **ECHA Candidate List**.
- To overcome these restrictions and to partially face the environmental and health risks associated with long-chain PFAS, manufacturers have switched perfluorinated compounds to **shorter carbon chains** and in particular to compounds such as PFBA and PFBS
- At the beginning of **2023**, **ECHA** (European Chemicals Agency) received a formal **request for restrictions**, under REACH, on the production of PFAS. The request was presented by 5 Countries of the Union: Denmark, Germany, Nederlands, Norway and Sweden

PFAS
Landfill leachate

- As well known, PFAS have great **thermal**, **chemical** and **biological stability**, as well as hydro and oleophobic properties. Such molecules have been used in a wide range of industrial and commercial applications since the 1950s
- Consumer products used, such as industrial waste, **disposed in landfills** are subject to rain, to chemical reactions and degradation processes that lead to the release of PFAS in the leachates. Basically **all landfill leachates** contain more or less large quantities of PFAS
- The legislation provides for the management of the landfill, after closure, for **30 years**, thus also including the disposal of landfill leachate
- Landfill leachates are largely disposed in civil **WWTP** and potentially impacting civil sewage sludge and discharges with micropollutants; leachates will remain a **source of PFAS** release into the water cycle even in the event of a **ban** on these class of compounds (proposed under evaluation by **ECHA**).

- It has been estimated that about **70%** of the PFAS intake by the human species occurs through drinking water and food.
- So, the issue of PFAS has long been addressed and studied in relation to human use and therefore focused on **drinking water** and **underground water**, as a primary issue, and on surface water in the second place
- More recently the problem of **reclamation** has been addressed.
- The more recent issue of **wastewater**, **industrial waste** and **landfill leachates** presents fewer scientific studies and has to face completely different **analytical** issues

Technologies

Technologies

Drinking and underground waters

Table ES.1 Summary of PFAS removals for various treatment processes.

Removal <10%	Removal 10-90%	Removal > 90%

Compound	M.W. (g/mol)	AER	COAG/ DAF	COAG/ FLOC/ SED/ G- or M-FIL	AIX	GAC	NF	RO	MnO_4, O_3 ClO_2, Cl_2, CLM, UV,
PFBA	214	assumed	assumed						
PFPeA	264								
PFHxA	314								
PFHpA	364								
PFOA	414								
PFNA	464		unknown		assumed	assumed			
PFDA	514		unknown		assumed	assumed			
PFBS	300								
PFHxS	400								
PFOS	500								
FOSA	499	unknown	unknown		unknown	assumed	unknown	assumed	unknown
N-MeFOSAA	571	assumed	unknown		assumed	assumed	assumed		unknown
N-EtFOSAA	585		unknown		assumed	assumed	assumed		unknown[a]

a - <10% removal by Cl_2 and $KMnO_4$; "assumed": treatment performance is assumed based on the PFAA size/charge and/or known removal data of shorter or longer chain homologues

AER: Aeration, AIX: Anion Exchange, CLM: Chloramination, Cl_2: Hypocholorous/Hypocholorite, ClO_2: Chlorine Dioxide, COAG: Coagulation, DAF: Dissolved Air Flotation, O_3: Ozone, FLOC: Flocculation, GAC: Granular Activated Carbon Filtration, G-FIL: Granular Filtration, M-FIL: Microfiltration, MnO4: Permanganate, RO: Reverse Osmosis, SED: Sedimentation, UV: UV Photolysis, UV-AOP: UV Photolysis with Advanced Oxidation (Hydrogen Peroxide)

Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances

Water Research Foundation

2016

Erica applied research for landfill leachate – GAC Technology

- **2017** - **Politecnico di Milano**: research coordinated by Prof. Francesca Malpei, full professor of the "Waste water treatment" course: "**Treatability of wastewater and leachate containing perfluorinated substances**"
- **2017** - **Laboratory batch** tests to obtain adsorption isotherms, which can be interpreted using Langmuir and Freundlich models; **continuous laboratory** tests using pressurized filtration on sand and activated carbon cartridges at a laboratory scale (simulating real plant conditions); selection of the best combination of different **activated carbons**: **2 types** with distinct nature and porosity, to be placed in series
- **2018** - Following the encouraging results obtained from the tests and the positive feedback from the Authorities, it was decided to continue the experimentation by establishing a real **industrial pilot plant** (potential capacity of approximately **10 mc/day**).

Erica applied research for landfill leachate - GAC

- **2018** - **First** industrial pilot plant experimentation: facility belonging to the **S.T.A. Società Trattamento Acque**, located in the province of **Cremona**. The facility was already authorized for landfill leachate treatment.
- **2019** – In order to better understand the data obtained from the industrial experimentation conducted in 2018, an additional consultancy contract was established with the Department of Civil and Environmental Engineering (DICA) of **Politecnico di Milano**. The final report of this consultancy, titled "**Analysis of Performance Data of Activated Carbon for PFAS Removal**", was prepared in March 2019 by Professor Manuela Antonelli.
- **2019** - The **second** industrial pilot plant experimentation was carried out in 2019 at the wastewater treatment plant of **Ireti S.p.A., Iren Group, Parma**.
- **2019/2020** - Research contract titled '**Execution of Leachate Flocculation Tests**', assigned to Professor Manuela Antonelli of **Politecnico di Milano**

The pilot plant

Pilot Plant in Casalmaggiore (CR)

Design of an industrial plant

3 patents have been issued for the technology

PFAS REMOVER
INSPIRED BY erica

PATENT PENDING

Industrial plant

Dedicated to landfill leachate - Start up Gen 2024

Castiglione delle Stiviere (MN) - **15 m^3/h**

- Installed in a Wastewaters Treatment Plant Site
- Operating **upstream** of the biological plant, only on landfill leachates

GAC efficiency on PFAS removal

- Efficiency of activated carbon of PFAS Removal is well known for **“clean” water**
- Efficiency of GAC applied directly on **landfill leachate**
  - Excellent percentage reduction of **long-chain PFAS**: with 'fresh' carbon, reductions exceed **98-99%**, which remain consistently higher than **85-90%**, sometimes reaching **95%** for extended periods, varying based on leachate characteristics.
  - Regarding **short-chain PFAS** it's confirmed that, similar to drinking water, adsorption appears to be more difficult. Anyway the technology allow reduction yields **exceeding 70%** even over extended periods. Potential imposition of limits on these compounds would result in increased **costs** due to **more frequent carbon reactivations**
  - Using specifically **selected flocculants**, it can be achieved a modest removal efficiency of COD (around 10%) and almost no removal of PFAS (thus avoiding their potential presence in the suspended fraction) but **highly efficacy** as a **pre-treatment for removing suspended solids** (up to 80-90%) and **colloidal substances**, enabling the adsorption columns to operate under more favorable conditions and resulting in high potential economic benefits

GAC efficiency on PFAS

- ⬆ Low energy consumption, economic and environmental **sustainability**
- ⬆ Good **long chain** PFAS removal
- ⬇ Difficult **short chain** removal
- ⬆ Complete PFAS **destruction** through GAC **regeneration/reactivation**
- ⬇ Not applicable on all streams (for example with very high COD or with fatty substances)
- ⬆ Where already installed, at the end of the treatment chain, activated carbon batteries for different uses (for example color reduction) obviously have benefits also in reducing PFAS

Continue exploring the specific treatment of landfill leachates and verify possible integrations with the activated carbon PFAS Remover process:

CNR and **Politecnico di Milano**

Claudio Di Iaconi - Consiglio Nazionale delle Ricerche, Istituto di Ricerca sulle Acque

Silvia Franz - Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"

A new research frontier

A new research frontier

with CNR-IRSA Bari and Politecnico di Milano (**2023**)

- Research project pertains to the laboratory-scale assessment of the effectiveness of the proposed scheme for PFAS removal in landfill leachate treatment through:
  - Activation of a laboratory-scale **SBBGR** (Sequencing Batch Biofilter Granular Reactor) system for landfill leachate treatment.
  - Enhancement of the SBBGR system with ozone and ozone/hydrogen peroxide (**BIO&CHEM process**) upon reaching steady-state conditions of the SBBGR system.
  - Polishing treatment with **photoelectrocatalysis** of the SBBGR/BIO&CHEM process effluent.
  - Polishing treatment with **photolysis** with **excimer lamps** of the SBBGR/BIO&CHEM process effluent.
  - Effluents to be tested with GAC **PFAS Remover** process

SBBGR Results – Bio treatment of landfill leachate – PFAS (main)

		INFLUENT (ng/L)	EFFLUENT (ng/L)
PFBA	$C_4HF_7O_2$	9639	8118
PFBS	$C_4HF_9O_3S$	68280	58770
PFPeA	$C_5HF_9O_2$	1722	1380
PFHxA	$C_6HF_{11}O_2$	3145	1610
PFHxS	$C_6HF_{13}O_3S$	226	< 1
PFHpA	$C_7HF_{13}O_2$	972	< 1
PFOA	$C_8HF_{15}O_2$	10010	< 1
PFOS	$C_8HF_{17}O_3S$	396	< 1
PFDA	$C_{10}HF_{19}O_2$	< 1	< 1
6:2FTSA	$C_8H_5F_{13}O_3S$	1721	< 5

Comments and considerations

SBBGR – Bio process

- Good **COD** reduction, total **BOD5** removal
- **NH3** completely removed, **TN** removal > 90%
- No **color** reduction
- **Sewage sludge**: 0.04 – 0.05 kg TSS / Kg CODRem. **8** times less than traditional systems
- **PFAS** with C > 6 **completely removed**
  - ✓ Adsorbed?
  - ✓ Destroyed?
  - ✓ Adsorbed/destroyed?

Concentration – industrial plants

Concentration by reverse osmosis and triple effect evaporation

GREENTHESIS GROUP

THINK GREEN, ACT SMART

- GEA – Sant'Urbano (PD)
- Start Up 2021
- Installed directly in landfill site and operated by GEA

Concentration – industrial plants

Concentration by reverse osmosis and triple effect evaporation

GEA – Sant'Urbano (PD)

- Reverse osmosis 10 m^3/h → 7 m^3/h permeate – 3 m^3/h concentrated reject
- Evaporator 3 m^3/h → 1,5 m^3/h concentrated reject – 1,5 m^3/h back to RO
- ↑ Very effective system for reducing PFAS
- ↓ High difficult to dispose of the concentrate, high energy consumptions

Legnago Servizi (Le.Se.)

- Installed directly in landfill site and operated by third parties
- Tender for installation, management and disposal (Tecnologie Ambientali)
- Same ↑ and ↓ as above

Other Technologies

Only at Lab or Pilot Scale on waste and wastewaters?

Many technologies have been tested or are under study, but are they all applicable to waste?

- Ion Exchange Resins
- Incineration
- Incineration with spraying of the waste directly in flame
- Macro Porous Polymer Extraction (MPPE)
- Supercritical water oxidation (PFAS Annihilator)
- Alternative sorbents: zeolites, activated biochars , modified clays, graphene…
- Foam and ozone fractioning
- Non thermal plasma
- Electro-oxidation
- Photo-Electro-Catalysis
- DMSO + NaOH
- …

Technologies
Conclusions

- Many technologies for the removal and destruction of PFAS are being studied and tested, some already **applied industrially**
- There are no **universal technologies** that can be applied in every situation and many of these have so far been tested extensively only on **drinking water**. It takes **time** to fully understand the applicability to **liquid discharges** and **waste**
- Time is also needed to develop the appropriate **analytical methodologies** to understand whether PFAS are completely destroyed or simply transformed into **undetectable molecules**, but the dangers of which are unknown
- While waiting for any decisions regarding **production restrictions**, the problem cannot simply be **transferred** to the managers of waste and wastewaters treatment plants, assigning limitations to discharges, in the absence of **BREF**, **BAT** and consolidated and approved technologies

Technologies

Conclusions

- Joint **working groups** are needed where producers, researchers, waste treatment associations and legislators, can focus on common objectives and how to come to **sustainable solutions** (**Today** we are doing just that!)
- In-depth **monitoring** is necessary to identify the sources of PFAS entry PFAS into the waste and wastewater supply chain
- As required by law, the **costs** of the technologies must be commensurate with the **benefits** obtainable in environmental and health terms
- **Unitary legislation** is needed to avoid technological and economic disparities between territories

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