Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile

A novel method for PFAS removal in water for human use.

Alberto Ubaldini, Antonietta Rizzo, Chiara Telloli, Sergio Lo Meo

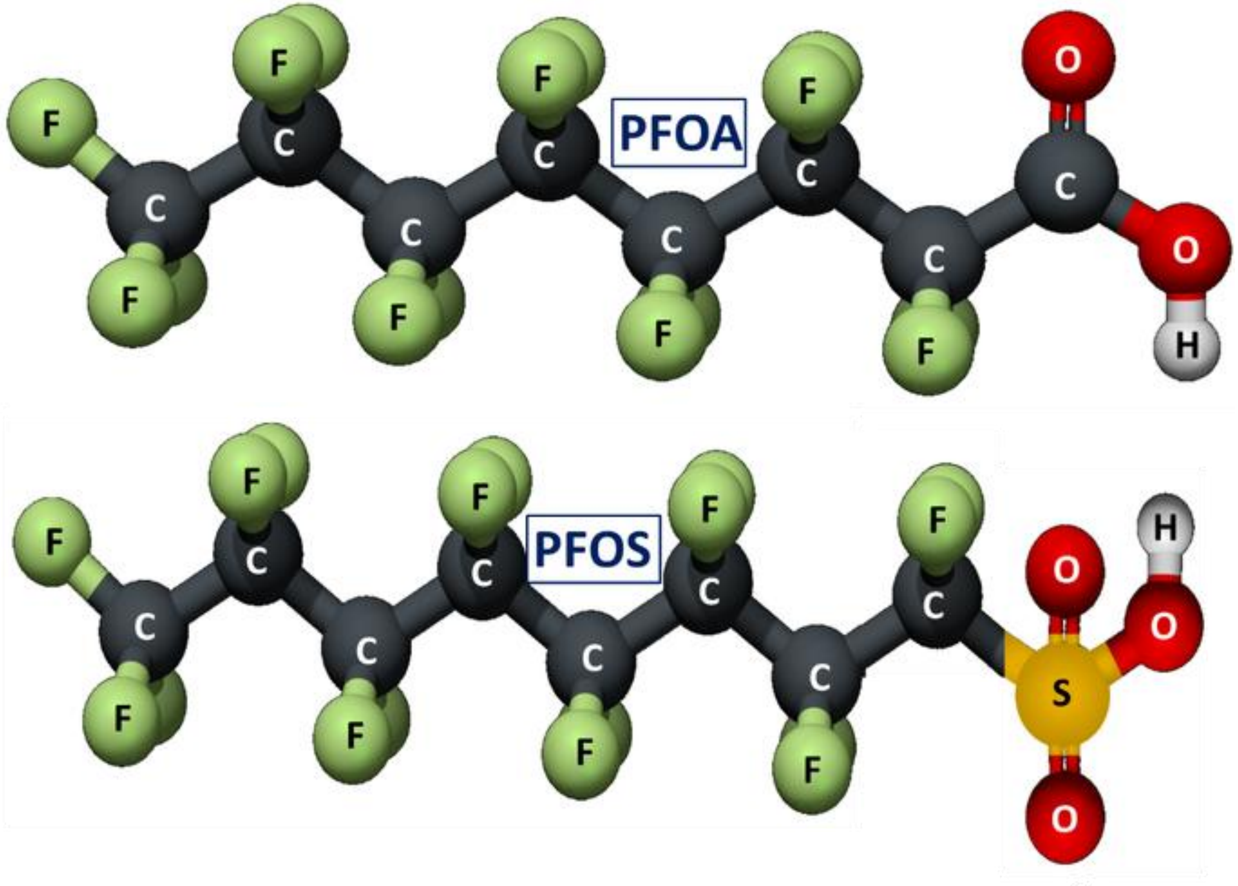
Bologna, 23/09/2020

Outline

- Introduction
- State of art of removal methods
- Electro-beam removal technology
- Conclusion

The PFAS

The perfluoroalkyl substances (PFAS) is a family of organic compounds formed by a totally fluorinated alkyl chain of various lengths (i.e. where C - F bonds are present, very strong and stable) and by a hydrophilic group: generally an acid, carboxylic or sulphonic.



They are synthetic substances, produced by polycondenzation processes of tetrafluoroethylene or electrochemical fluorination of organic substrates. The most common molecules of this family are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)

ANALYTE	ACRONYM	FORMULA	CAS-NUMBER
Perfluorobutanate	PFBA	$C_3F_7COO^-$	375-22-4
Perfluoropentanate	PFPA	$C_4F_9COO^-$	2706-90-3
Perfluorohexanate	PFHxA	$C_5F_{11}COO^-$	307-24-4
Perfluoroheptanate	PFHpA	$C_6F_{13}COO^-$	375-85-9
Perfluorooctanate	PFOA	$C_7F_{15}COO^-$	335-67-1
Perfluorononanate	PFNA	$C_8F_{17}COO^-$	375-95-1
Perfluorodecanate	PFDA	$C_9F_{19}COO^-$	335-76-2
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_2O^-$	29420-49-3
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_2O^-$	3871-99-6 (potassium salt)
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_2O^-$	2795-39-3 (potassium salt)
6:2 fluorotelomer sulfonate	6:2 FTSA (THPFOS)	$C_6F_{13}C_2H_4SO_3^-$	27619-97-2
Perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	754-91-6
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	$C_8F_{17}SO_2N(C_2)CH_2CO_2H$	2991-50-6
INTERNAL STANDARDS			
Perfluoro-n-(1,2,3,4-13C4)butanate	$[^{13}C_4]$-PFBA	$(2,3,4\text{-}^{13}C_3)F_7{}^{13}COO^-$	n.a.
Perfluoro-n-(1,2-13C2)hexanate	$[^{13}C_2]$-PFHxA	$C_4F_9(2\text{-}^{13}C)F_2{}^{13}COO^-$	n.a.
Perfluoro-n-(1,2,3,4-13C4)octanate	$[^{13}C_4]$-PFOA	$C_4F_9(2,3,4\text{-}^{13}C_3)F_6{}^{13}COO^-$	n.a.
Perfluoro-n-(1,2,3,4,5,6,7,8-13C8)octanate	$[^{13}C_8]$-PFOA	$(2,3,4,5,6,7,8\text{-}^{13}C_7)F_{15}{}^{13}COO^-$	n.a.
Perfluoro-n-(1,2,3,4,5-13C5)nonanate	$[^{13}C_5]$-PFNA	$C_4F_9(2,3,4,5\text{-}^{13}C_4)F_8{}^{13}COO^-$	n.a.
Perfluoro-n-(1,2-13C2)decanate	$[^{13}C_2]$-PFDA	$C_8F_{17}{}^{13}CF_2{}^{13}COO^-$	n.a.
Perfluoro-1-hexane(18O2)sulfonate	$[^{18}O_2]$-PFHxS	$C_6F_{13}S[^{18}O_2]O^-$	n.a.
Perfluoro-1-(1,2,3,4-13C4)octanesulfonate	$[^{13}C_4]$-PFOS	$C_4F_9(1,2,3,4\text{-}^{13}C_4)F_8SO_2O^-$	n.a.
Perfluoro-1-(1,2,3,4,5,6,7,8-13C8)octanesulfonate	$[^{13}C_8]$-PFOS	$(1,2,3,4,5,6,7,8\text{-}^{13}C_8)F_{17}SO_2O$	n.a.
6:2 fluorotelomer sulfonate $(1,2\text{-}^{13}C_2)$	$[^{13}C_2]$-6:2 FTSA	$(1,2\text{-}^{13}C_2)C_6H_4F_{13}SO_3^-$	n.a.
Perfluoro-1-(1,2,3,4,5,6,7,8-13C8)octanesulfonamide	$[^{13}C_8]$-FOSA	$(1,2,3,4,5,6,7,8\text{-}^{13}C_8)F_{17}SO_2NH_2$	n.a.

Industrial uses

PFAS compounds have high chemical and thermal stability, good surfactant properties and have been of great interest for various industrial applications since the 1950s.

They are resistant to fire, oil, stains, grease and repel water. They have a wide range of industrial and commercial applications, such as cleaners, textiles, leather, paper, paints, fire-fighting foams and wire insulation.

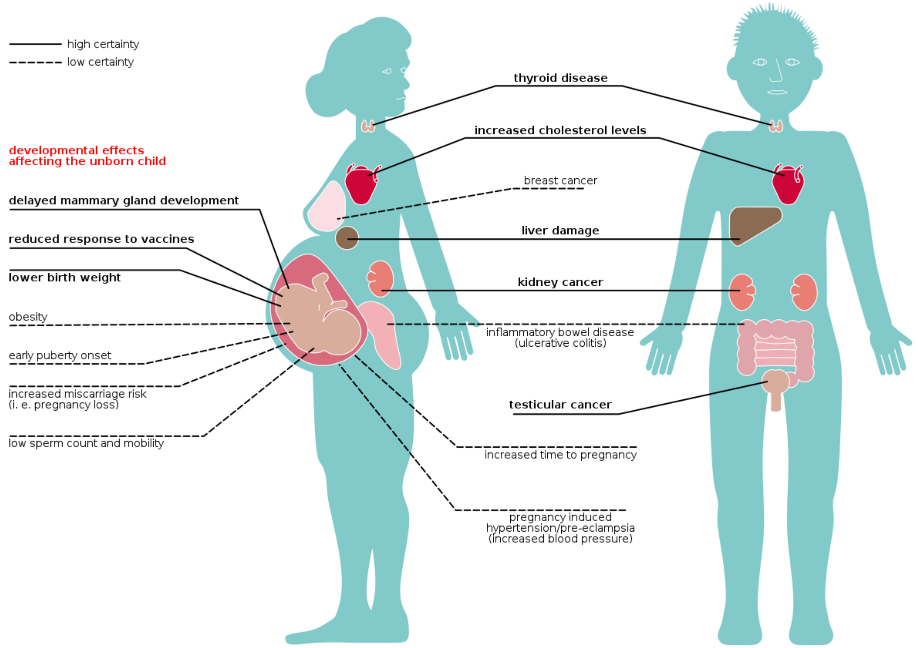
PFAS are often found in cookwares, frozen food wrappings, clothing and upholstered furnitures, cleaning products, electronics manufactures, automotive chemicals such as fuel additives and others.

The problem

PFAS were initially considered inert molecules since they lack a chemically active group and for this reason not a serious concern for environment. However, precisely because of their chemical stability, they have a considerable persistence in the environment, being resistant to natural degradation, i.e. not easily biodegradable by bacteria and other microorganisms.

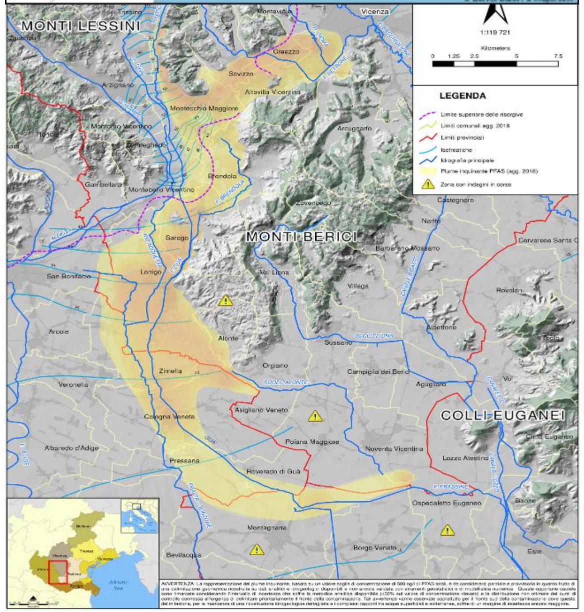
Recent studies have shown that they are a serious threat to human health and a source of environmental pollution. They can cause tumors, endocrine disorders and increase the neonatal mortality rate. They easily enter the food chain, having also been detected in fish, eggs and similar products and easily bioaccumulate.

Due to these possible adverse health effects, the authorities of many countries have begun to take measures to limit and in some cases completely ban the use of certain PFAS



The Italian situation

The disposal of products containing PFAS, the discharge of industrial and urban wastewater and the use of aqueous films that form foams in firefighting have led to widespread contamination of surface and groundwater, including many supplies of drinking water. In particular, in Italy there are high levels of these substances, which have been detected in the major rivers, in Tuscany and in the Tiber, but above all in the Po which is the most polluted of the major European rivers.



In the Po Valley basin, highly critical situations were detected in Lombardy and especially in Veneto, a region where a high concentration of PFAS is observed west of the Berici Mountains. Studies conducted by the ARPAV and the CNR, have highlighted a large area of contamination that extends over 150 km2 with more than 20 municipalities involved, including the provinces of Padua, Verona and Vicenza.

Treatment Technologies for PFAS removal from water

PFAS concentration in water for human uses can be reduced using existing technologies. They include:

Activated Carbon Treatment

Activated carbon treatment is the most studied treatment for PFAS removal. They are commonly used to adsorb natural organic compounds, taste and odor compounds, and synthetic organic chemicals. Adsorption is both the physical and chemical process of accumulating a substance

Ion Exchange Treatment

Ion exchange resins are made up of highly porous, polymeric material. The positively charged anion exchange resins are effective for removing negatively charged contaminants, like PFAS.

High-pressure Membranes

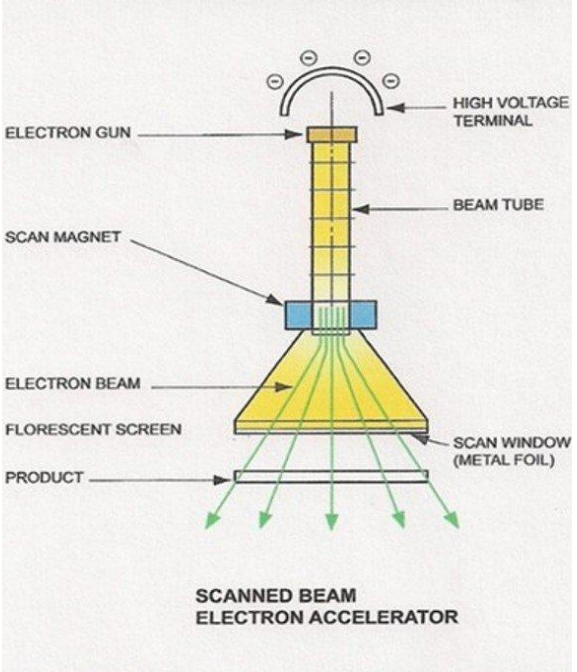
High-pressure membranes, such as nanofiltration or reverse osmosis, have been extremely effective at removing PFAS. Reverse osmosis membranes are tighter than nanofiltration membranes. This technology depends on membrane permeability.

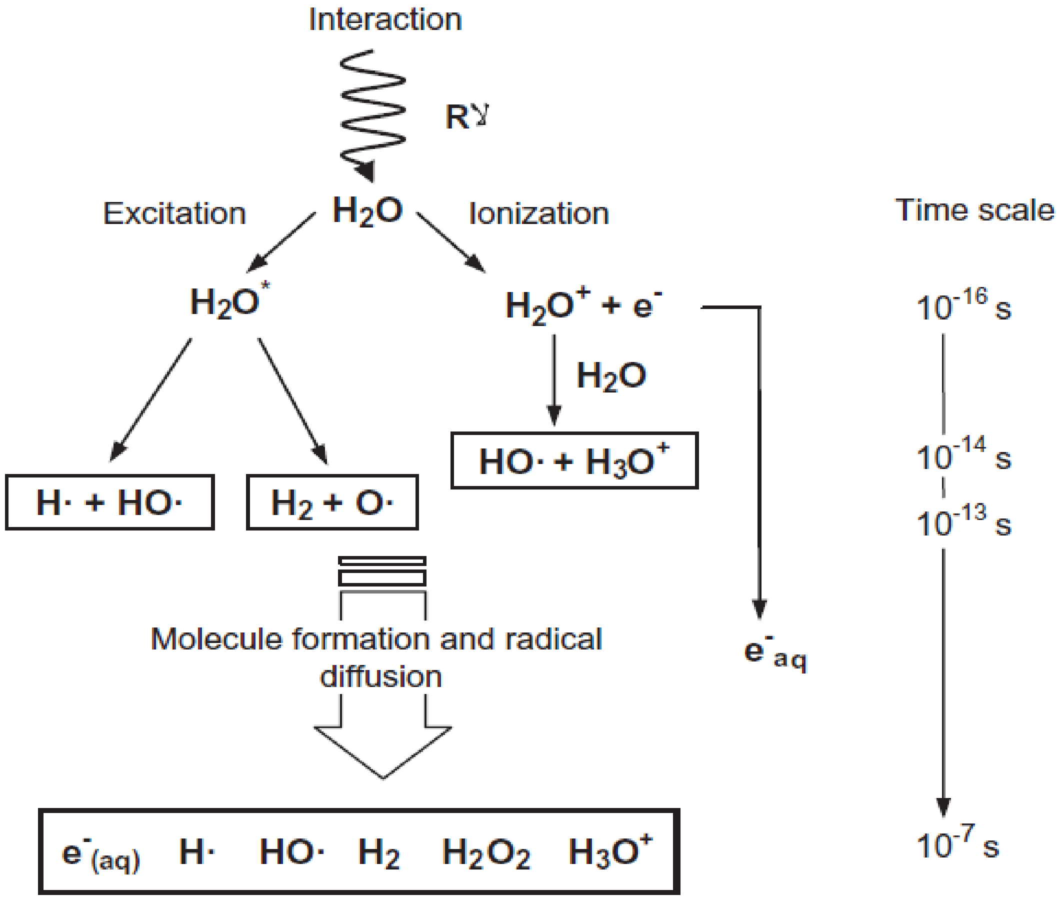
The electron – beam method

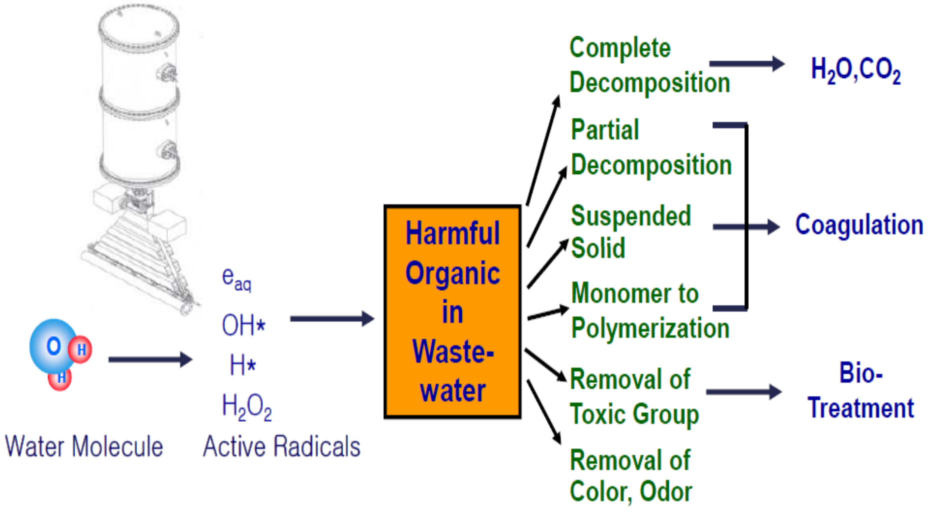
The electron beam is a process that involves the use of accelerated electrons with high energy to treat an object, or medium, for a variety of purposes such as surface treatments, modification of physico-chemical properties of materials by specific reactions, sanitation of objects, sterilization of food and others.

In the case of water treatment, it is successfully used for the removal and abatement of a large number of pollutants, especially of an organic nature.

The process is based on the fact that when a volume of water is irradiated with high-energy electrons, a series of chemical-physical processes take place that lead to the formation of highly reactive chemical species, such active ions, free hydroxyl radicals, free hydrogen atoms and solvated electrons including OH^-, O^{2-}, H^+, $HO_2^{\cdot}$, O_2^- $H^{\cdot}$, H_2, O_2, H_2O_2.
All these chemical species are "aggressive" towards many substances and are able to degrade them. Indeed, they have much higher oxidation potentials than ozone, hydrogen peroxide or chlorine





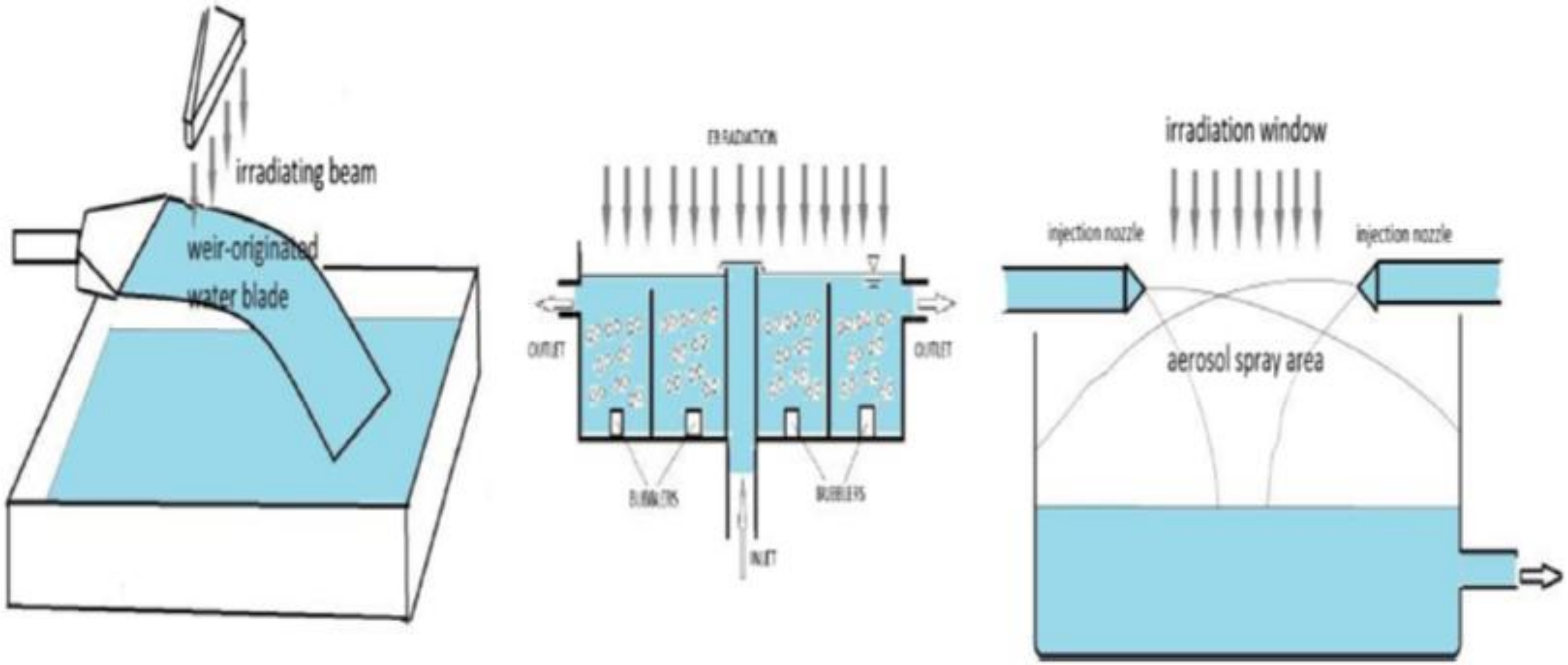


The chemical reactions that occur with irradiation are similar to those that occur in classical oxidative processes, but it is extremely more intense and rapid due to the greater density of different radical species.

The reactions of the contaminants present in the water are practically instantaneous with intensity and end point controlled by the given irradiation dose. The radical species generated will return very quickly (in the order of a few milliseconds) to their original state of water, if they do not immediately react with polluting molecules.

The electrons are released by a device and accelerated by a grid. The electrons emerge from the window with an energy proportional to the voltage applied to the anode and in quantity depending on the cathode current. By adjusting these parameters, it is possible to control, respectively, the penetration of the beam (proportional to the energy) and the dose rate (proportional to the current).

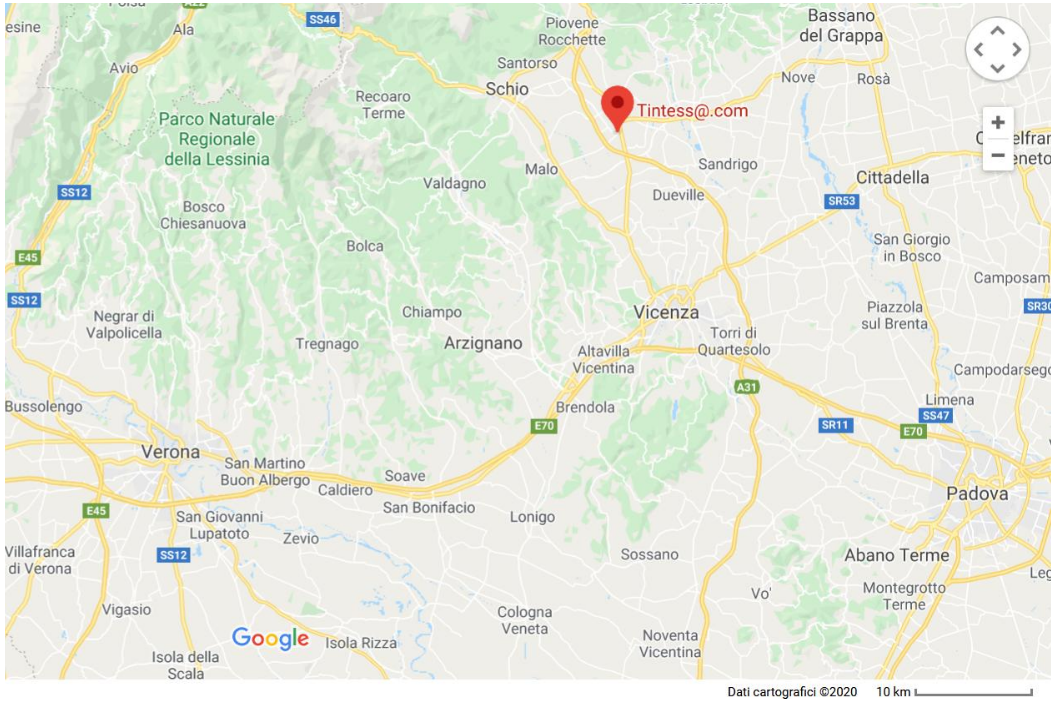
EB machines used in the field of water and wastewater treatment work generally between 600 keV and 1.5 MeV .



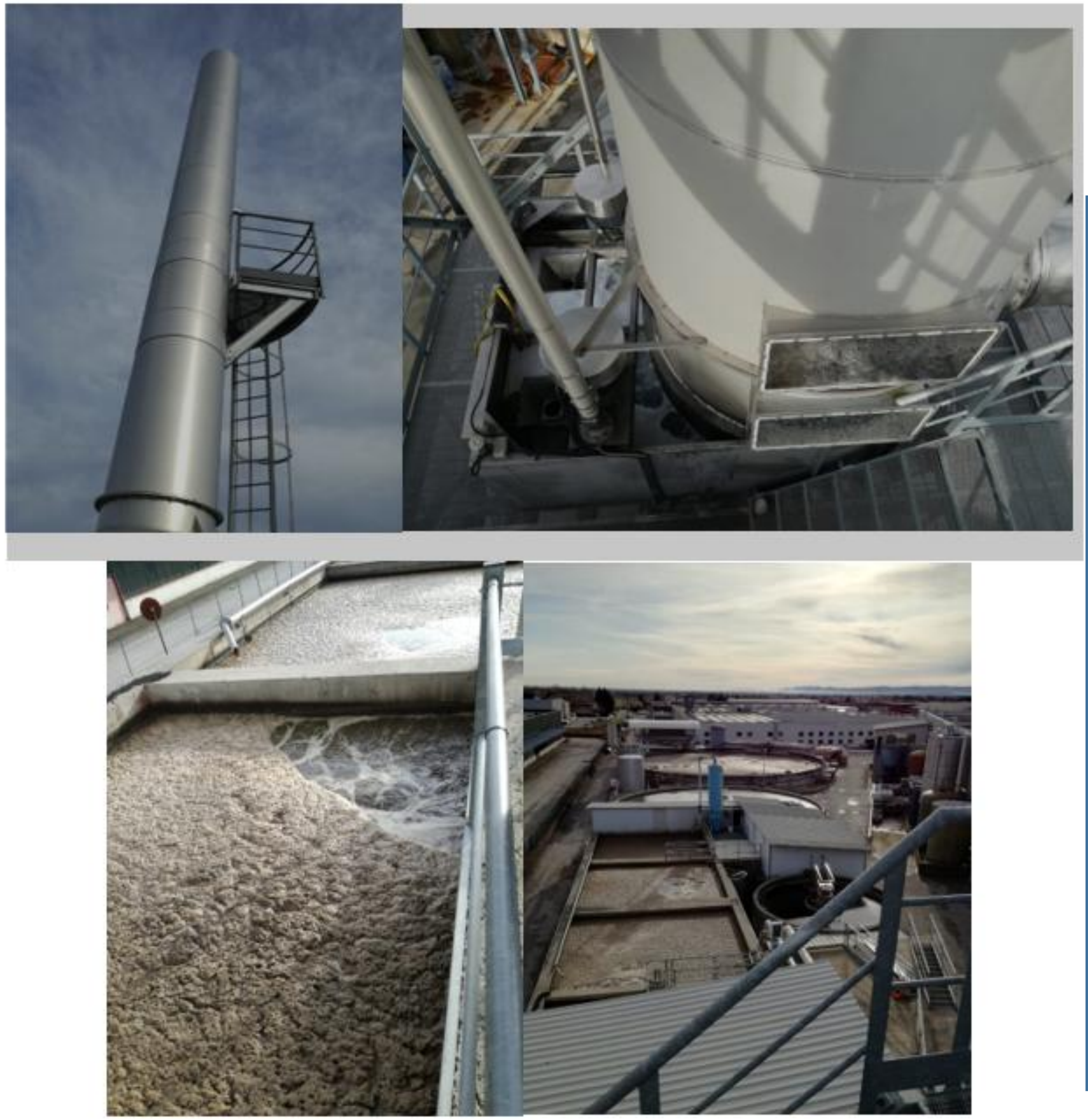
The case study of the company Tintess S.P.A

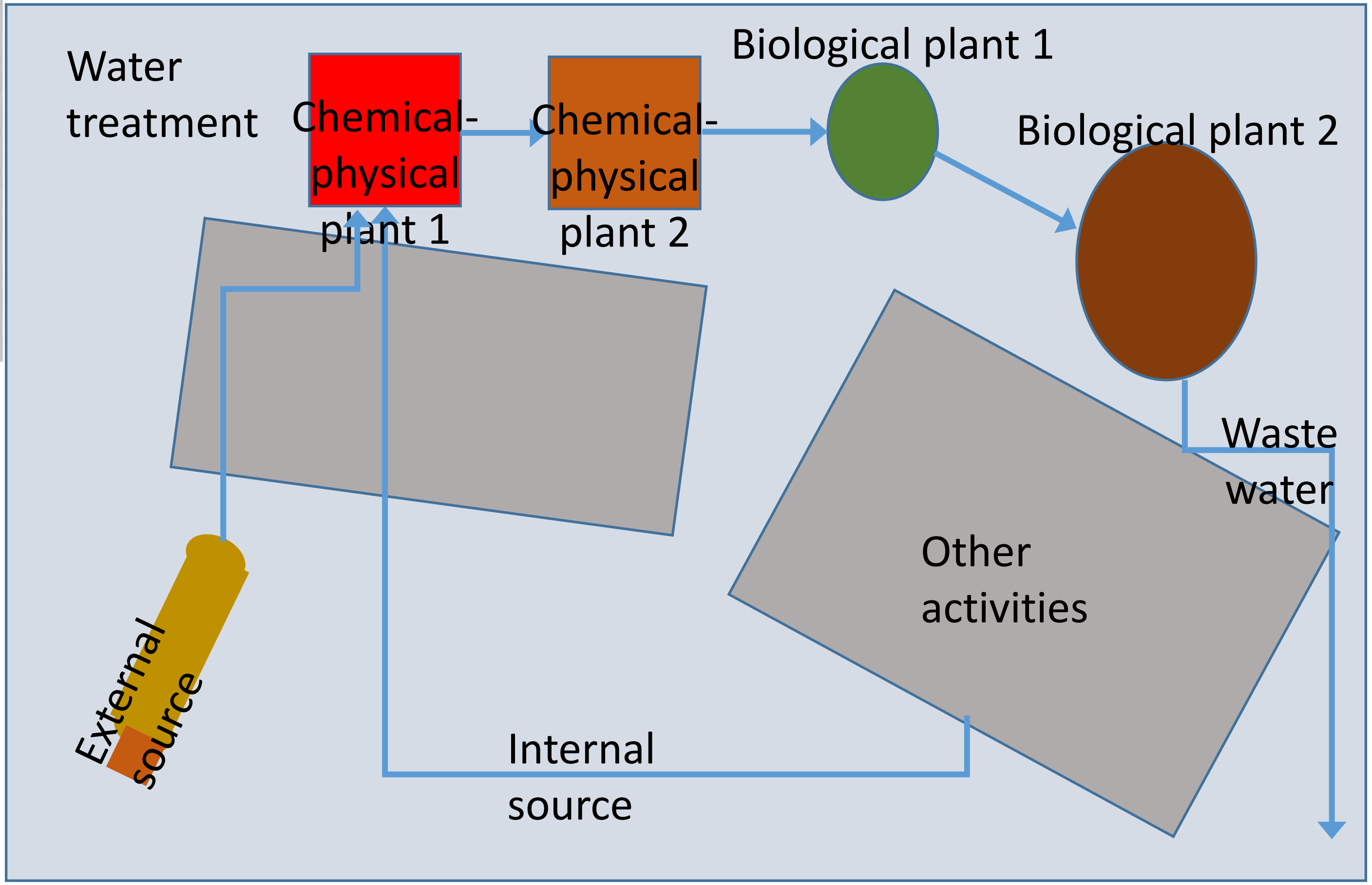
Tintess Depurazione Acque is one of the most advanced and efficient Italian companies engaged in the purification of industrial waste water. Born and raised in an area with a great industrial vocation, since 2007 it has been operating and investing driven by a precise awareness: it is possible to enrich and innovate the production processes of many sectors, making them more profitable, increasing their environmental sustainability together and thus preserving their integrity. and ecosystem health.

https://www.tintessacque.com/

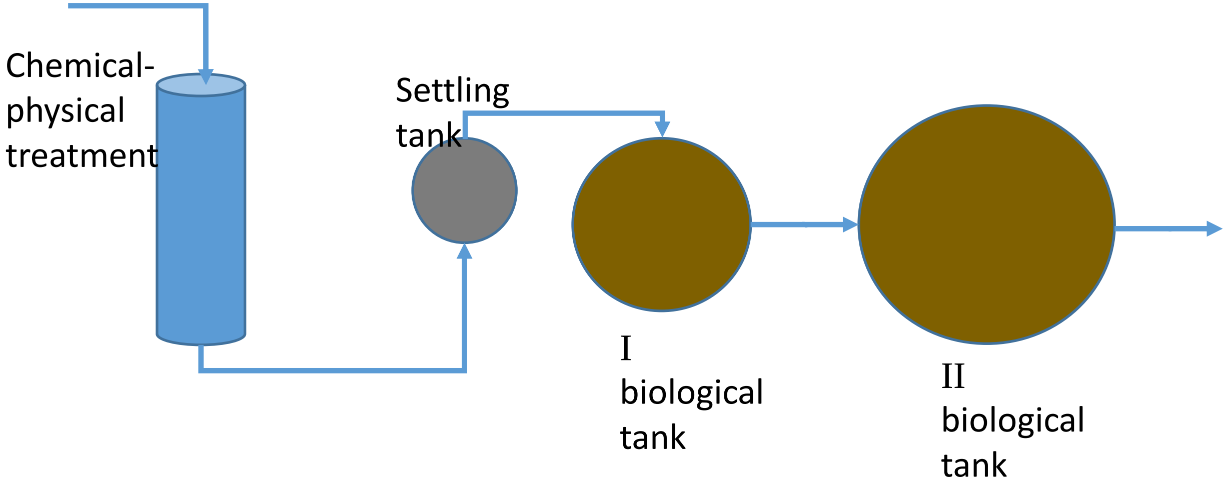


The company Tintess S.P.A. has an excellent wastewater treatment plant with two biological treatment tanks downstream of a chemical-physical treatment system. In general, at the end of the process, most of the pollutants are eliminated

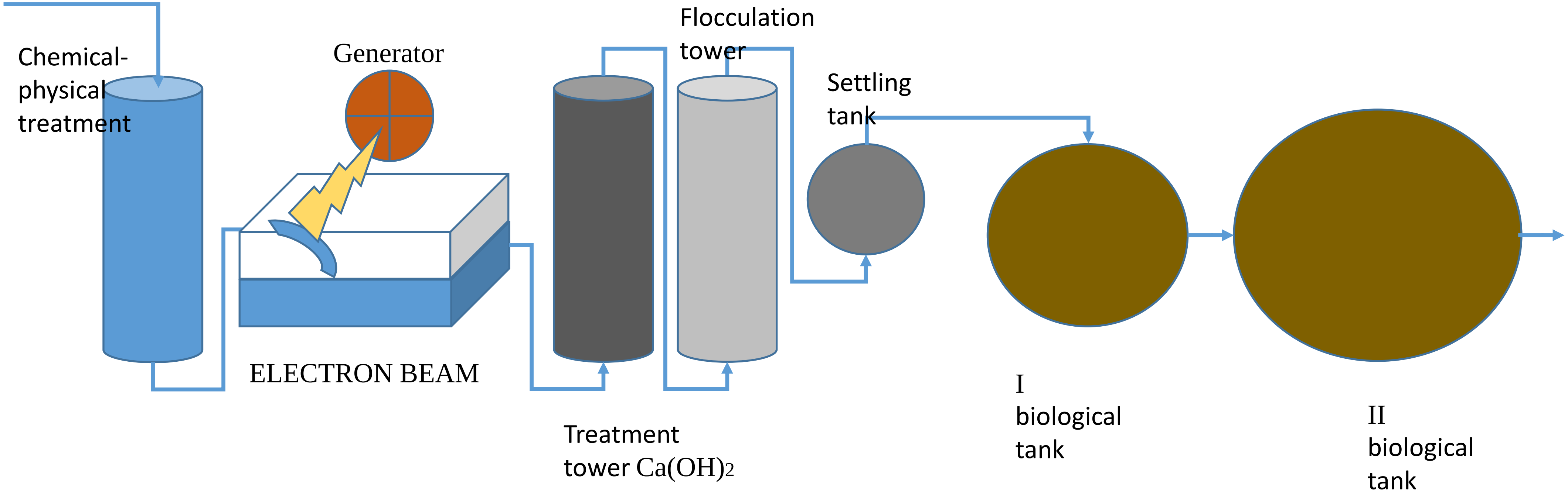




Current plant



Possible modification to the system



Laboratory activity

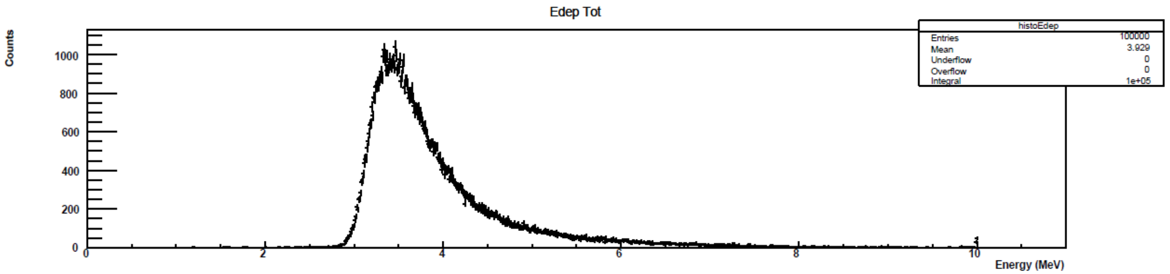
a) In-depth study of the current conditions of the purification system;
b) Withdrawals of water from the current situation downstream of the chemical-physical treatment and before biological treatment;
c) Analysis with mass spectrometry (MS) to determine the fluorine content;
d) Withdrawal of water from the current situation at the end of the process, after the second biological treatment;
e) Further analyzes to study the final fluorine content;
f) Study of the aging effects of the samples and possible ex-situ pollution (measurements on the same batches, but at different times);
g) Design of the machine for the treatment with electron-beam;
h) Irradiation of the samples after the current chemical-physical treatment;
i) Study of the final abatement of fluorides with chemical-physical methods;
j) Mass spectrometric analysis (MS) on the treated samples.

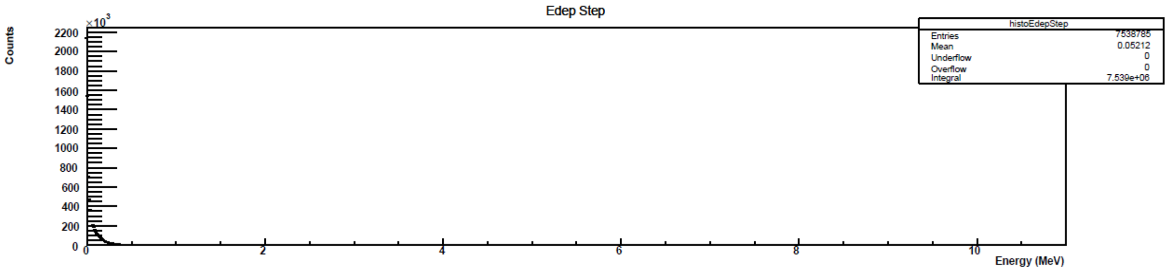
(final) activities on the plant

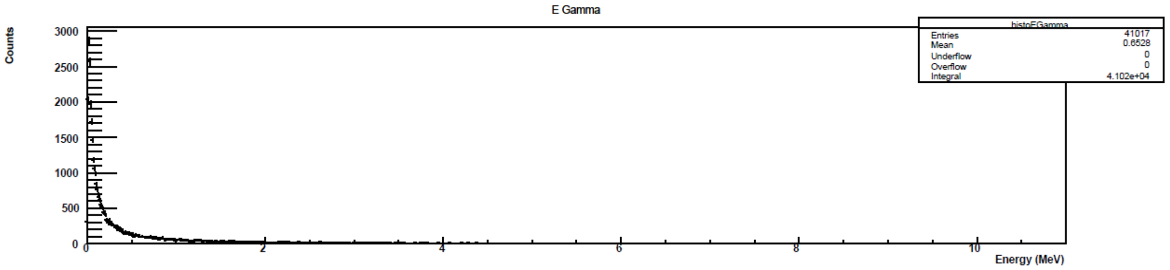
a) Design of any changes to the system;
b) Installation of additional treatment tanks;
c) Verification of the effectiveness of the method on a real scale.

Preliminary laboratory scale experiments (total volume of few ml) have shown that the process can be effective.
Solutions of PFOA, at a concentration higher than that typically observed in real samples, were irradiated with electron beams with energy up to 0.2 MeV and the formation of inorganic fluorides, which can be removed by traditional technologies and chemical methods, was observed.

It was also possible to estimate with the computer the depth of penetration of the beam as a function of its energy, demonstrating that a few MeV are sufficient to have a few cm of penetration.
In this way it will be possible to design a larger scale plant to verify the method on real samples







Conclusion

The presence of PFAS in Italian surface waters is a problem that is currently presenting itself with gravity. Currently existing technological solutions are not sufficient to mitigate the problem in an acceptable way.

It is therefore necessary to study new ways and in this report we investigate the potential of an innovative system based on irradiation with an electron beam of samples from an industrial wastewater treatment plant.

This method is very promising and there are studies of its application to numerous purification plants of gaseous and solution pollutants. For this reason a positive result can also be expected in this case.