

The pollution of water resources and interventions to mitigate and control environmental impact

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Abstract

The urban sewage coming from residential or commercial compounds are mainly characterized with wastes of human metabolism or activities linked to the use of compounds as cleaning, washing, watering and so on.

Especially in the sewage of metropolitan areas, new categories of pollutants, so called “Emerging Pollutants” (EP), were found. The polluting contents of EP are those that are residual coming from medicines, products used for skin and hair care, antibiotics for human and animal use, endocrine interferents, illegal drugs and so on.

On this ground the paper wants to focalize on the Italian regulations and relating statutory treatments of water at the present time which do not take into consideration this new shape of pollution. After a short sketch of statutory treatments scheduled by regulations, the paper also tries to envisage in which way it might be possible to cope with this new polluting problem by advanced waste water treatments. For reason of room, the “water line” of urban sewage purification will be treated, leaving the “mud line” to another future paper.

Keywords: urban sewage, emerging pollutants, control.

1 Preliminary remarks

Pollution can be defined by the contents in water of so-called “load parameters” classified in typologies as shown in Table 1. Draining waters coming from household sewage’s present values significantly unequal compared



to natural water as shown for some of them in Table 2. The typologies of pollutants in function of the kind of polluting agents are briefly reported in Table 3.

Table 1: Load parameters.

A) Autochthonous Load Parameters	C) Anthropic Load Parameters	E) Toxic Load Parameters
A1) pH		
A2) temperature	C1) BOD5	E1) Arsenic
A3) electrical conductivity	C2) COD	E2) Cadmium
A4) total hardness	C3) total phosphorus (as P)	E3) total chromium and hexavalent chromium
A5) sulfate	C4) ammonia nitrogen	E4) Mercury
A6) chlorides	C5) nitrous oxide	E5) nickel
A7) nitric	C6) extractable substances in petroleum ether	E6) Lead
A8) dissolved oxygen	(mineral oils, animal fats and vegetable)	E7) copper
A9) sodium	C7) anionic	E8) zinc
A10) iron	C8) soluble orthophosphates	E9) cyanide
A11) Manganese		E10) sulphides
B) Optical Load Parameters	D) Bacteric Load Parameters	E11) sulfite
B1) turbidity		E12) total phenols
B2) coarse materials	D1) total coliforms	E13) pesticides
B3) materiali sedimentabili	D2) fecal coliform	E14) fluorides
B4) Total suspended solids	D3) faecal streptococci	E15) free chlorine
B5) volatile suspended solids	D4) sulphite-reducing clostridia	

Table 2: Comparison between draining and natural water.

PARAMETERS	NATURAL WATER	DOMESTIC SEWAGE
pH	7,5- 8,5	6,8-7,5
Total suspended solids (mg/l)	5-80	200-50000
BOD5 (mgO ₂ /l)	1-15	80-20000
COD (mgO ₂ /l)	5-50	200-100000
ammonia nitrogen (mgN/l)	0-7	10-300
Nitrous oxide (mgN/l)	0-0,3	0-0,5
nitrate nitrogen (mgN/l)	0,5-10	0-1
total nitrogen (mgN/l)	5-10	20-500
total phosphorus (mgP/l)	0-3	1-100
chloride (mgCl/l)	20-100	50-1000
Total coliforms (cfu/ml)	1-200	10 ⁵ -10 ⁷
total surfactants (mg/l)	0-1	5-50



Table 3: Types of pollutants.

Conventional pollutants	Total suspended solids Solid colloidal BOD, COD, TOC Ammonia, nitrates, nitrites, total nitrogen Phosphorus Bacteria, cysts, oocysts of protozoa, viruses
Non-conventional pollutants	Refractory organic substances Volatile organic compounds Surfactants Metals Total dissolved solids
Emerging pollutants	Prescribed and non-prescription drugs Care products and hygiene personal Antibiotics for human and animal Endocrine disruptors Illicit drugs

2 Italian regulations

Current regulations do not take into account so-called “Emerging Pollutants” (EP), shown in Table 3, since the pollution of water is presently ruled by Legislative Decree (LD n.152/2000 that basically is strictly related to the Cadre Directive on Water (CDW) 200/60/CE and the European Decision (ED) n.2455/2011/ CEE too.

The Italian LD specifies the parameters that must be controlled (Annex n.1 to LD) and defines the various standards for BOD, COD, etc. The LD dictates, in addition, the obligation to monitor additional parameters (surfactants, hydrocarbons, etc. etc.) with relation to those concentration limits previously appointed by Ministerial Decree (MD) n.307/2003. Moreover, the LD imposes that the so-called “Apposite Treatment” (AT) must be carried out before delivering waste waters in “Environmental Terminal Delivery” (ETD) (sea, lake, soil, etc. etc.). The term AT is defined by Italian rules as “those treatments of waste water by means of those processes and systems able to guarantee the compliance of terminal Receiving Environmental Bodies (REB) with their quality targets, whether the REB is a surface or underground water body or the ground”. The AT must further be able to bring back into the limit of rules the concentrations of polluting contents of water by the so-called method of Equivalent Inhabitants” (EI) that originated the household sewage. The term EI is clearly defined by Italian rules as “the amount of biodegradable loads” (ABL) that need a BOD₅ equal to 60 gr/day.

3 The treatments

The AT mentioned in Italian regulations needs a scale of processing in subsequent temporal order such as to ensure the “quality standard” of ETD. A logical pattern flow to face the problem of purification could be that reported in



figure 1, where p* are that points of flow where it could be necessary to apply a suitable test analysis to check the presence and concentrations of EP.

The order of AT in Italian Regulations foresees:

- Preliminary treatment which must separate out of sewages the solid matter (detritus, sands, oil, etc).
- Preliminary treatment which must remove Total Suspended Solid (TSS) essentially constituted by organic matter with the target to reduce the BOD5 down to 20% and TSS down to 50%.
- Secondary treatment which must remove both Biodegradable Organic Matter (BOM) and not settling Colloid Solid (CS) to obtain the end further average reduction respectively of 80% of BOD5, 75% of COD and 90% of TSS.
- Tertiary treatment which must reduce the load of nutrient elements (P and N) and those substances not much biodegradable also called “bioresistant”.

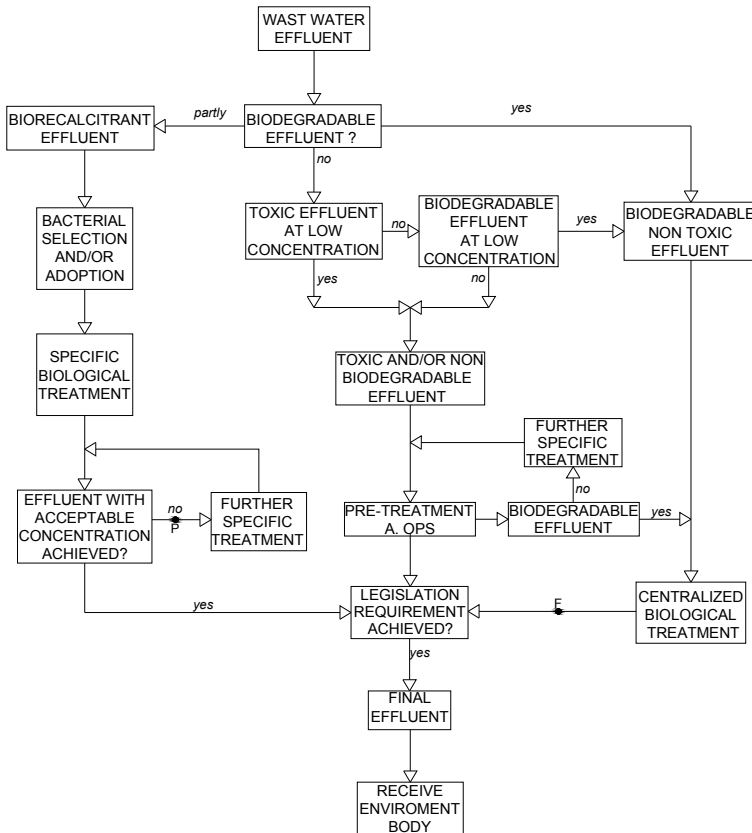


Figure 1: Logical pattern flow.



The modern technologies makes available a wide range of high efficiency plants and systems able to carry out treatments reports in Table 4 and there is too large a technical bibliography showing the various chemical processes (and their correlated plants) both from physical processes and physical-chemical reactions' points of view [1–3].

Table 4: The main processing present in the various orders of AT.

PRE-TREATMENT	PRIMARY	SECONDARY	TERZIARY	DISINFECTION TREATMENT
Separation gridding	Primary sedimentation	Biological oxidation	Nitrogen removal	Chlorination
De-sand Blasting and De-oiling	Clarify flocking	Anaerobic digestion	Phosphorus removal	Ozonization
Equalizing and Homogenizing	Flottation	Secondary sedimentation	filtration	Ultraviolet rays treatment
Pre-airing			Absorption	
Neutralizing				

In this paper, the authors, on the other hand, want to draw attention to the new kind of water pollution called “Emerging Polluting” and their environmental clean up.

4 Emerging Pollutants (EP)

Among the emerging pollutants, the main samples are medicines, drugs and products of personal hygiene and beauty care (PPCPs), endocrine interfering (EDC) and total solid dissolved (TSD) too.

Moreover, there are some products too normally utilized in the urban environment such as disinfectants, nitrosodimethyl ammine (NDMA), fuel additives, such as methyl-tert-butyl-ether (MTDE) and fire retardants, such as hexabromocyclodecane (HBCD) and polybrominated diphenyl ethers (PBDE) [4].

A common distinctive feature of EP are to be so small sized that they are below surveying standards established by current Italian regulations as shown in figure 2.

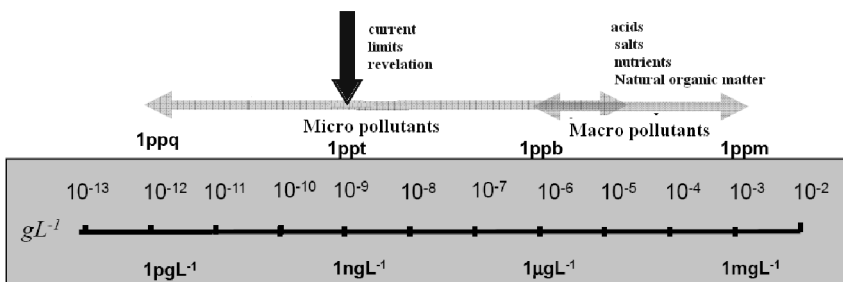


Figure 2: The surveying limits of current Italian rules.

Figure 3 shows sizes and molecular weight of PPCPs and EDC compared with other substances.

Figure 4 below shows the EP concentrations found in effluents of some purification plants.

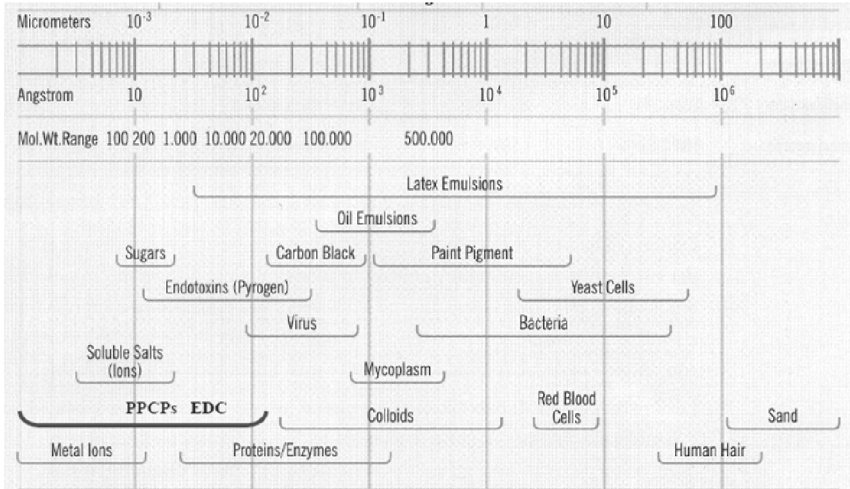


Figure 3: Sizes and molecular weight of PPCPs and EDC compared with other substances.

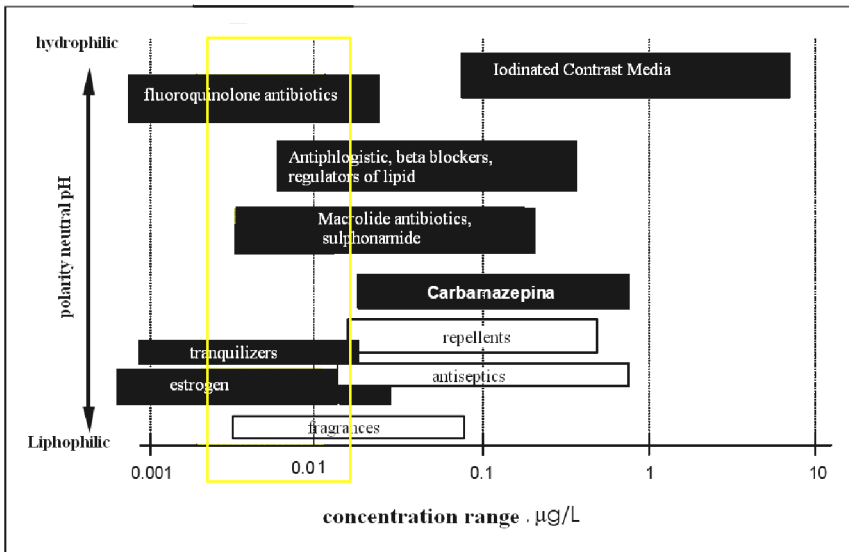


Figure 4: The EP concentrations found into effluents of some purification plants.

The regulation of draining water coming from purification plants before or after running the time must be completed to take in account of EP presence into draining water and of their adverse effects on environment and on human health

The suggestions of actions to complete the regulations are:

- To specify what markers must put under investigation into the surface and draining water to classify the presence of EP as pollutants
- To define the methodology of analysis that must be done and to trial the methodologies by pilot plants
- To carry out after the choice of methodology, the tertiary treatments able to achieve the best effectiveness both in technical and economical ways

5 The treatments in advanced course of study

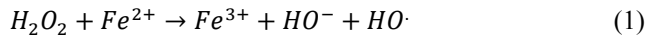
The tertiary treatments in advanced course of study to face EP problem as things stand now mainly bring to:

- Micro and ultra filtration
- Photochemical process
- Inverse osmosis and nanofiltration
- Photo-Fenton process

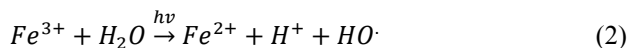
The Photo- Fenton process could be that one with larger future development as it is the likelihood to make use of renewable energy (solar energy) to improve the effectiveness of process both as speed of reaction of process and reduction of power source,

6 Photo-Fenton process

The efficient process to face the EP in waste water treatment could seen Photo-Fenton (Ph-F) process [4–6]. The Ph-F process improve the efficiency of Fenton reaction(1), also called dark- Fenton

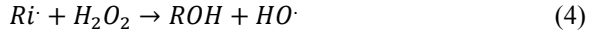
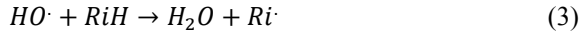


It is well known that hydroxyl radical ($HO\cdot$) [7–9] is one of the most powerful oxidant universally recognized. The mechanism of oxidation of (1) has been expanded and revised by many Scientists until experiments of Wadley and Wait in 2004 These Scientist demonstrated that hydroxyl radicals produced by Fenton reaction by decomposition of hydrogen peroxide when reacting with ferrous ions if stimulating with sunlight or an artificial sources of wavelengths (180 – 400 nm) increases the rate of contaminant degradation mainly stimulating the reduction of Fe^{3+} to Fe^{2+} . In a very short synthesis equation (1) was turned into equation (2), so called by Person in the 2004 Photo-Fenton reaction

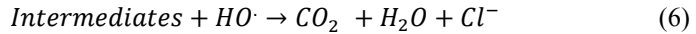


In the Photo-Fenton reaction the concentration of hydroxyl radicals becomes higher with the consequence of promoting a faster degradation of the pollutant.

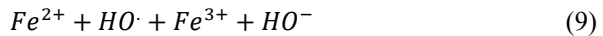
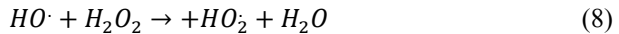
Theoretically, by combination of Fenton and Photo-Fenton reaction, two moles of OH[·] should be produced per mole of H₂O₂ consumed. All scientists agree that hydroxyl radicals formed by complex reaction mechanism oxidize organic species making the start of a radical chain oxidation (3), generating organic radical species which undergo oxidation (4) up to mineralization (5)



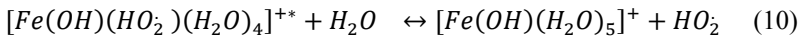
In the case, for example, of chlorinated compound Cl⁻ it is realized in accordance with (6)



The mechanism pathway of Ph-F process according to the classic interpretation is even more complex, but for room reason, we limit ourselves to show reactions (7), (8), and (9) that simplify the main scavenging effect that may occur during the process



At least many authors agree that reaction (10) could describe the real photochemical reduction



Concerning the photo enhanced process (10) it has also been shown that UV irradiation accelerates the recycling of Fe²⁺.

The acceleration might be due to photo induced oxidation of the linked of various iron (III) complexes and this kind of process is faster than the reduction of iron(III) to iron (II) described in reaction (2) [10, 11].

Considering the successive evolution of solar Ph-F, it is possible to suppose that it could be an opportune utilization of solar thermal radiation for the Ph-F process in consideration too of thermal energy connects with solar energy. As a matter of fact, photons in wavelengths included between 300 and 500 nm solar radiations can facilitate photochemical conversion of Fe³⁺ to Fe²⁺, whereas photons in all remaining wavelengths supply thermal energy that increases the temperature of process that results in an optimal reaction condition.

Among the many solar reactors tested, the compound Parabolic Collector (CPC) shows the most efficient light collection for low concentrating system as matter of fact that CPC:

- It has no mobile parts
- It is able to collect almost all the direct and diffuse radiation incident in the capitation area
- It is available for photochemical process in reactor
- May be easily up-scaled owing to the simple engineering concepts involved

Figure 5 shows the global irradiance solar spectrum. Figure 6 shows a model of CPC.

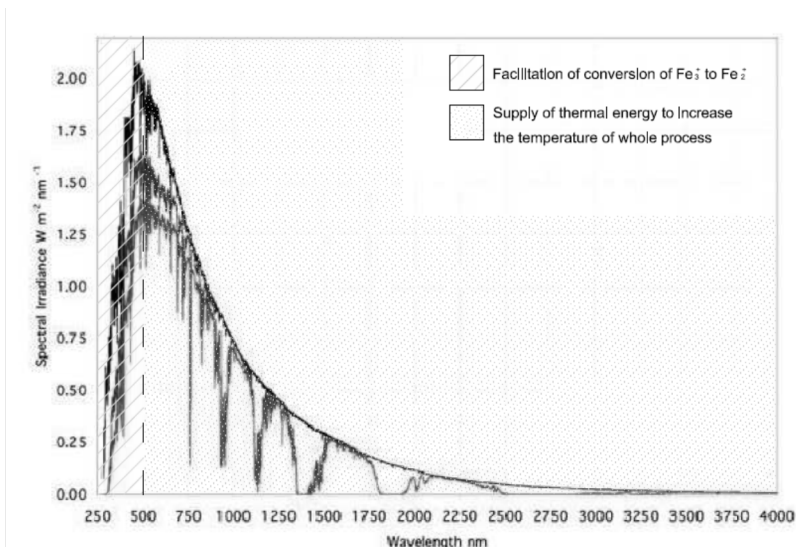


Figure 5: The global irradiance solar spectrum.

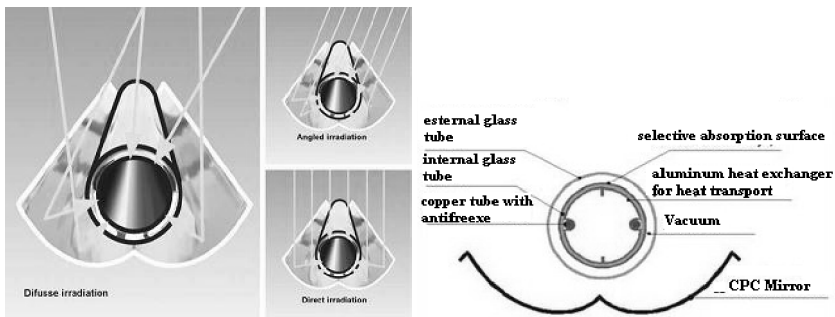


Figure 6: Model of CPC.

7 Conclusions

The presence more and more considerable of concentration of EP into the draining water of purification plants urges us into updating the regulations concerning the pollution of waste water. On this ground the authors believe:

- Upstream of regulation it is necessary to carry out both careful research and classification to determine which kinds of EP and at what concentrations are true concerns for the living and not-living environment.
- In research must be interested the whole Research Organization and the Universities with high specific expertise in fields such as chemistry, pharmacy, sanitary and genetic engineering, environmental control engineering, etc. etc.
- Both the theoretical basic and applied research must give responses to a set of questions as like:
 - o In which way is it possible to pitch-out the true sources of this kind of pollution?
 - o How can people reduce the consumption of PPcPs and EDC?
 - o What are the new molecules (green pharmacy) that can replace the EP compounds in a way so as to involve a compatible interference with the living and not living environment?
 - o What could be the tertiary treatments and relating equipments able to remove or reduce the EP concentrations to within compatible limits to human health?

To reach previous goals the research must carry on!!

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