Chemical pollutants in water and wastewater and related Eco toxicity: advanced developing technologies for organic degradation

Sueli Ivone Borrely[1], Antonio Carlos Silva Costa Teixeira[2], Roque Passos Piveli[3], Fabio Campos[3], Maria da Conceição Costa Pereira[1] ,Vanessa Honda Ogihara[1], Marcela Prado Silva [2],, Arlen Mabel Lastre-Acosta[2], Ana Paula dos Santos Batista [2]

[1]Radiation Technology Center, Nuclear Research Institute, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242, 508-000, São Paulo, Brazil. Phone (+55-11-31339817)

[2]Chemical Engineering Department, University of São Paulo,Av. Prof. Luciano Gualberto, travessa 3, 380, 05508-010, São Paulo, Brazil,Phone: (+55-11-3091-2263)

[3]Laboratory of Sanitation – PHA, Polytechnic School of Engeeniring, University of São Paulo, Av. Prof. Almeida Prado, 271, São Paulo, Brazil. Phone (+55-11-30915582)

[*]**Corresponding author:** Sueli Ivone Borrely, Radiation Technology Center, Nuclear Research Institute, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242, 05508-000, São Paulo, Brazil. Phone (+55-11-31339817); E-mail: sborrely@ipen.br

Abstract

Environmental issues nowadays include the presence of contaminants in waters that are increasing in numbers and classes of chemicals. The environmental and human health will always depend on the protection of the air, waters, and soil. The industrial activities are as important as agriculture but a more clean production is imperative. The subject of this chapter is to discuss the xenobiotics contaminants in water and wastewaters and their related toxicity. A second

issue is to show some data related to new possible technologies, under development, and their potency for decomposition of organic contaminants. Acute toxicity results evidenced the importance of this tool for assessing the impacts of toxins to living organisms and here they were used for the evaluation of proposed technologies for wastewater improvement. Three treatment technology options were presented (advanced oxidative processes, AOPs; photolysis by UV radiation, also including the Photo-Fenton processes and Ultra-sound; a special biomidia used as an additive effort to enhance biomass in order to treat landfill leachate in a sewage mixture). The last technique and Integrated Fixed-Film Activated Sludge (IFAS) was assessed for also for toxicity removals. Daphnia similis water flea and Vibrio fischeri bacteria were the target organisms for the evaluation of these processes. Acute effects removal > 20% was achieved for fluoxetine irradiated at 5kGy. ATZ acute effects were efficiently removed after 60 min of exposure to UV radiation and the combined IFAS processes were the most effective process for toxicity removal.

Introduction

One given pollutant may be considered as a substance or effect that adversely alters the environment by changing the growth rate of species, interferes with the food chain or with health at environment. Once we know the ability of aquatic organisms to adsorb variety of chemicals from water, sediments and food, it is ideal to use such a type of aquatic organisms using the concepts of Ecotoxicology. Pharmaceutical compounds have been reported as emerging pollutants. Are pharmaceuticals in the environment a growing problem? According to Lyons, 2014, a global review of pharmaceuticals in the environment, commissioned by Germany's environment ministry, they found that of the 713 pharmaceuticals tested for, 631 were found above their detection limits (mainly in surface waters, such as lakes and rivers, but also in groundwater, soil, manure and even drinking water) [1].

Some chemicals may be found only at low levels in various tissues, whereas others may builds up to significant concentrations. Accumulation of chemicals by organisms in the aquatic environment is based on the interactions of a variety of physical, chemical and biological characteristics and processes [2]. Pesticides degradation and toxicity were also studied (sulfonimides).

The presence of a myriad of pharmaceuticals such as antibiotics in the aquatic environment continues to be a matter of concern since these compounds may favor the selection of antibiotic-resistant bacteria and in some cases cause toxic and endocrine-disrupting effects to humans and other living organisms [3,4]. Conventional biological and

physicochemical treatments processes show limited success for the destruction of antibiotics. On the contrary, AOPs usually show higher rates of removal for these emerging pollutants from water matrices; among AOPs, ultrasonic (US) degradation is growing quickly in interest. In this case powerful oxidizing species such as hydroxyl radicals (●OH) are generated by pyrolysis of water molecules during cavitation [5]. Nevertheless, the use of high-frequency US for the treatment of water contaminated by sulfonamides still deserves further investigation.

Electron Beam Irradiation as an Alternative to Reduce Whole Toxicity in Effluents

In Brazil ecotoxicity of pharmaceuticals have been determined on different living organisms. Fluoxetine hydrochloride, Prozac's active substance, is taken as an example of a high toxic substance that was decomposed by Electron Beam Irradiation, as an alternative treatment (EBI). When talking about high contaminated samples it is common to use ecotoxicity for measuring acute effects on living organisms, before discharging wastewater to the environment [6]. Water fleas are commonly applied for effluents assessments and risk analysis. Daphnia magna is commonly used in Europe, due to the high hardness of water, while Daphnia similis are growing in a hardness range between 20 to 50 ppm (CaCo3). For common toxicity assay the immobility is the end point for daphnia water flea and the EC50 value means the average concentration of chemical (or effluent) which immobilized 50% of daphnids after exposition (usually 48 hours), Figures 1 and 2.

Another application of toxicity assays have been the confirmation if the new techniques for treating wastewater are effective for removing toxicity. It is a way to confirm that the degradation process is not generating more toxic byproducts.

The use of electron beam accelerator for the decomposition of organics is related to the absorbed dose of radiation for a given amount/volume of material. This transferred energy is defined as the absorbed dose. Absorbed dose is reported as Gray, (Gy), according to SI unit (absorbed dose is joule per kilogram (J/kg)). The yield of chemical products produced by ionizing radiation is expressed as the quantity of product obtained divided by the dose, or G value [7].
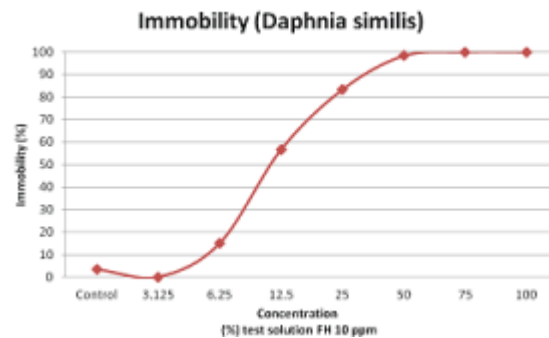
Figure 1: Immobility of Daphnia similis exposed to several concentration of fluoxetine hydrocholoride (48 hours) – average effective concentration = 1.37 ± 0.31 ppm. A typical dose response curve obtained during toxicity measurements.

Figure 2: Example of living-organisms commonly used for toxicity assessments in Brazil.

The water radiolysis is an important mechanism to introduce the oxidative species into the water or wastewater while EB irradiation is applied. In the book Environmental Applications of Ionizing Radiation a lot of information was organized on the basic of radiation chemistry and possible uses of radiation for environment applications.

Accelerators are machines designed for industrial technology and material processing, as well as for radiotherapy. Several needs have grown the interest in dedicated and small machines for environmental benefits [8]. Other studies evidenced the potency of radiation for microbial reduction at 1 kGy (coliforms in secondary treated sewage) but the degradation of organic compounds in wastewater is the relevant interest concerning industrial wastewaters and pharmaceuticals into waters [9,10].

An alternative radiation source is the cobalt-60, if accelerators are not available for such a type of research [11].Electron beam machines may be classified according to the energy of machine, what is a relevant parameter for the penetration of electrons into material. The studies presented here were based on a Dynamitron type accelerator with a 1.5MeV and current up to 25mA. During this irradiation a 4mm thick of sample was used and controlled by the volume of samples displayed in the vessels, (Figure 3).
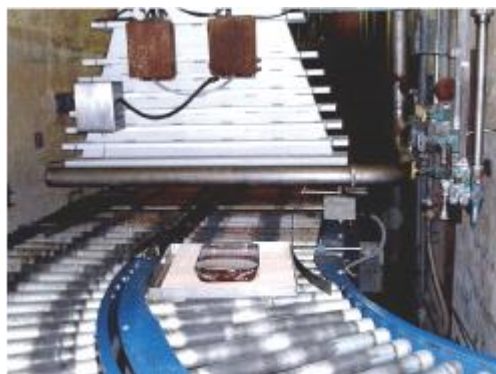

Figure 3: Electron beam scanning system, used during irradiation of liquid samples for pollutant abatement. RD Inc accelerator, fixed energy at 1.4MeV; variable electric current according to required dose (IPEN/CTR).

The mains reactive species obtained through the interaction of radiation into the water are very important for organic compound degradation and even for killing the microorganisms, which means that radiation technology may reduce both organics and microorganisms at the same time. H2O2, H2, e-**aq,** ●OH and H ions are first reactive species introduced into water system by irradiation. The yields of them are presented at Table 1.

pH	e-**aq**	H	OH	H2	H2O2
Liquid Water					
3-11	2.63	0.55	2.72	0.45	0.68
0.46	0	3.65	2.90	0.40	0.78

s(modified from Woods, 1998)

Table 1: Water radiolysis: radical and molecular product yields formed by the irradiation of water after100eV transferred energy, according to pH range.

Hidrochloride fluoxetine decomposition by EB irradiation: from different radiation doses applied for fluoxetine degradation 2.5kGy was enough for an important decomposition. On the other hand, using fluoxetine in water solution > 80% acute effects were reduced by 0.5kGy, D. similis exposed for 48 hours, see (Figure 4).
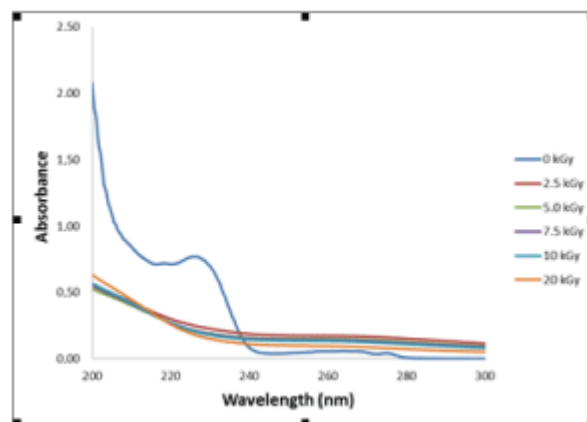

Figure 4 : UV-Vis absorption spectrum of fluoxetine versus radiation (226 nm) [9].

When the same experiment was carried out in the presence of raw sewage (50% in volume) 5kGy was required to get the same efficacy. Lower efficacy was obtained for V. fischeri, from 17% up to 21% at 5kGy. As recommended by Rand (1995), it was noticed the importance of different classes of living organisms be applied for effluents and treatment processes evaluations [2]. Organic acids were detected after irradiation of pharmaceuticals, reducing slightly the samples pH [10].

Pesticides and Pharmaceutical as Emerging Pollutants And Photolysis As An

AOP

Pesticides have been detected in surface waters and ground water all around the world. They have been included amongst Persistent Organic Pollutants (POPs) due to their resistance to natural degradation processes and to the risks they have to human health as well as for the environment. Pesticides can reach surface waters through discharge of industrial synthesis processes and agro-industry wastewaters, from spray equipment and pesticide containers, spills due to improper handling and disposal, agricultural runoff, etc. [12-15].

Silva et al. (2014) studied the removal of atrazine (ATZ) from water by photolysis [16]. ATZ is one of the most commonly used herbicides in the world, a possible human carcinogen and endocrine disruptor [16,17]. The authors discussed the effects of the photon emission rate and ATZ initial concentration on the herbicide photolytic degradation rate, under 254 nm-UV radiation.

The stability of ATZ in aqueous solution in the absence of light, regardless of pH, was confirmed through hydrolysis experiments. Photolysis experiments were performed in a tubular photochemical reactor equipped with a concentric low-pressure mercury vapor lamp, using four different photon emission rates on a per unit reactor volume basis ($E_{P,0}$), namely 3.6×10^{18}, 1.9×10^{18}, 1.1×10^{18}, and 8.7×10^{17} photons L-1 s-1 (Figure 5). ATZ removal by photolysis was shown to follow apparent first-order decays during the first 10 minutes (Figures 5c and 5d) and high percent ATZ removals were achieved after 30 min of irradiation, with more than 80% and 65% removals for $[ATZ]_0 = 5$ mg L-1 and 20 mg L-1, respectively.
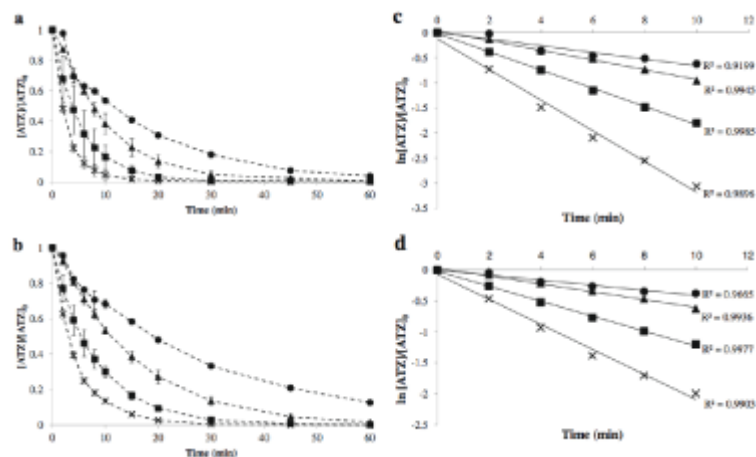
Figure 5: Atrazine (ATZ) degradation during photolysis for different initial concentrations and photon emission rates (3.6×1018 photons L-1 s-1; 1.9×1018 photons L-1 s-1; 1.1×1018 photons L-1 s-1 and 8.7×1017 photons L-1 s-1). (a) and (c) [ATZ]0 = 5 mg L-1. (b) and (d) [ATZ]0 = 20 mg L-1 (Silva et al., 2014).

It was noted that the higher the initial ATZ concentration, the lower the values of the apparent first-order photolysis rate constants k, the higher the pesticide half-lives and the lower the percent removals after 30 minutes of irradiation. Silva et al. (2014) assigned the dependence of the amount of substrate destroyed and apparent rate first-order rate constants with [ATZ]0 by the fact that the higher the ATZ initial concentration, the higher the amount of degradation products formed, therefore competition by incident photons increase.

A direct relationship between ATZ degradation and the photon emission rate was observed, with proportionality constants of 0.085 and 0.056 for 5 mg L-1 and 20 mg L-1 respectively. Dechlorination was the dominant mechanism during the initial steps of ATZ photolysis, as shown in Figure 6 by the comparison between the release of chloride ions in solution and ATZ photolytic degradation. The difference between the amount of Cl- released and the amount of ATZ degraded suggest the persistence of very small amounts of chlorinated degradation products. Moreover, no appreciable carbon removal was observed after 60 minutes of ATZ photolysis owing to the presence of persistent degradation products [16].
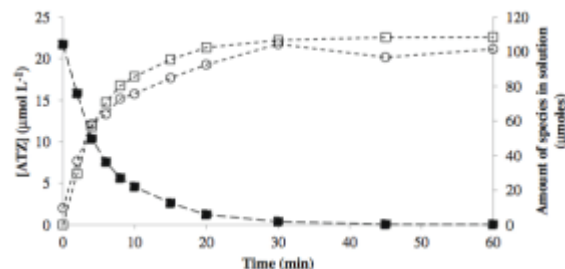
Figure 6: Comparison between the release of chloride ions in solution and ATZ photolytic degradation. $[ATZ]_0 = 5$ mg L-1 and $E_{P,0} = 3.6 \times 10^{18}$ photons L-1 s-1. [ATZ]; amount of Cl− released; amount of ATZ degraded (Silva et al., 2014).

Based on the experiment with the best performance for ATZ removal during photolysis, despite the presence of persistent degradation products, acute toxicity to Daphnia similis was efficiently removed after 60 minutes of exposure to UV radiation. Finally, by means of additional experiments in the presence of a suppressor of singlet oxygen, using a radical scavenger and by varying the amount of dissolved oxygen in reaction medium, the authors pointed out reactive oxygen species (hydroxyl radicals and singlet oxygen) as important actors during the photolytic degradation of atrazine.

Regarding treatment technologies possibilities, Lastre-Acosta et al. (2015) investigated the degradation of sulfadiazine (SDZ) (25 mg L-1) in aqueous solution by high frequency ultrasonic treatment (580, 862, and 1142 kHz) [17]. In this study, the effects of a radical scavenger and the incorporation of Fenton reagent (sono-Fenton) were analyzed. With this aim, an ultrasound multifrequency generator (MeinhardtUltraschalltechnik), operating in continuous mode at high frequency greater than 100 kHz and variable electric power output, was connected to a stainless steel transducer (E 805/T/M) placed directly inside solution and used in sonication experiments. The authors observed higher SDZ percent removals and removal rates for the lowest operating frequency (580 kHz), higher dissipated power and lower pH. The addition of n-butanol (22-fold molar concentration of n-butanol to sulfadiazine) considerably reduced SDZ degradation, with only 16% SDZ removal after 120 minutes and a pseudo-first order rate constant of 1.7×10^{-3} min-1, therefore confirming that the attack of ●OH radicals to SDZ at the interface of collapsing bubbles is an important

mechanism involved in antibiotic degradation. The corresponding values in the absence of n-butanol were 71.5% and 10.1×10^{-3} min-1, respectively [17].

In the range of operating conditions studied, the addition of hydrogen peroxide showed detrimental effects on SDZ degradation rate in comparison with the performance of the ultrasound-driven process alone. On the contrary, the Fenton chemistry combined with US treatment remarkably improved sulfadiazine removal rate. Therefore the sono-Fenton process seems to be more efficient for the removal of the antibiotic than sonolysis alone, as shown in (Figure 7). In fact, the extent of SDZ degradation was higher for the US/Fe(II)/H2O2 process as compared to H2O2 alone, Fe(II)/H2O2, US/H2O2, US and US/Fe(II). In this case, the synergistic effect is clearly demonstrated.
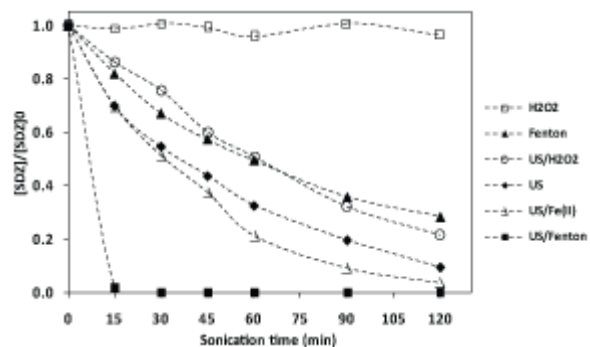

Figure 7: SDZ degradation by different processes (580 kHz, 22 W, [SDZ]0=25 mg L-1, 30 °C; H2O2:SDZ=180 mol/mol for US/H2O2 and H2O2 processes; H2O2:SDZ=198 mol/mol for US/Fe(II)/H2O2 and Fenton processes). (white square) H2O2, (black triangle) Fe(II)/H2O2, (white circle) US/H2O2, (black diamond) US, (white triangle) US/Fe(II), and (black square) US/Fe(II)/H2O2 (Lastre-Acosta et al., 2015).

Electrophilic addition of hydroxyl radicals (HO•) offers the possibility to degrade sulfonamides in aqueous solutions due to the existence of π electrons in their molecules. Among the different processes available for generating HO• radicals [18]. UV-based technologies are considered efficient in aqueous treatment containing recalcitrant sulfonamides [19-22]. These technologies include the photo-excitation of Fe(III)-complexes, the photo-Fenton processes, photo-induced processes, and photo-initiated oxidation processes.

Photo-Excitation of Fe (III)-Complexes

Photo-excitation of Fe(III)-complexes induces reduction of ferric (Fe^{3+}) to ferrous (Fe^{2+}) ions and formation of $HO\bullet$ radicals. Reactions involving Fe(III)-complexes are important in surface water and can promote the degradation of contaminants in aqueous solutions. The presence of diverse organic ligands in Fe(III)-complexes leads to sulfonamides degradation at different reaction rates [23]. Hydrogen peroxide (H_2O_2) can be generated from the photolysis of Fe(III)-oxalate which react with Fe^{2+} to produce $HO\bullet$. Furthermore, the oxidation of organic ligands in Fe(III)-complexes generates organic radicals that may reduce dissolved oxygen (O_2) to yield radical species such as the superoxide radical anion, $O_2\bullet^-$[24]. During photolysis of Fe(III)-oxalate (Figure 8a), the oxidation of the oxalate ligand generates carboxylate radical anions ($CO_2\bullet^-$) which, in the absence of O_2, react with Fe(III)-oxalate to form Fe^{2+} ions. In aerated systems, $CO_2\bullet^-$ reduces O_2 giving $O_2\bullet^-$. Similarly, the photolysis of Fe(III)-citrate produces Fe^{2+} ions and also the 3-hydroxyglutarate anion radical ($3\text{-GHA}\bullet^{2-}$), which generates both the 3-oxoglutarate (3-OGA^{2-}) ion and $O_2\bullet^-$ after reaction with O_2, with fast generation of unstable acetone and carbon dioxide as byproducts (Figure 8b).
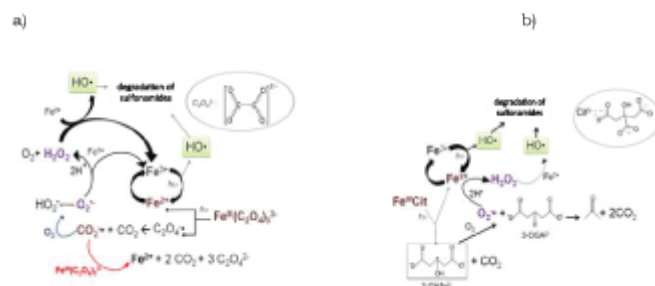
Figure 8: Scheme of photolysis of Fe(III)-complexes: (a) Fe(III)-oxalate and (b) Fe(III)-citrate.

Fe(III)-oxalate was shown to be more effective to sulfonamides degradation than Fe(III)-citrate using UV irradiation. The remaining carbon from Fe(III)-citrate photolysis was shown to be disadvantageous toward sulfonamides degradation. A significant increase in sulfonamides degradation rate was reported using sunlight irradiation in the presence of Fe(III)-oxalate [19].

Photo-Fenton Processes

Among UV-based technologies, photo-Fenton processes may be a suitable technology for the degradation of sulfonamides in aqueous solution. Based on the electron transfer from ferric/ferrous ions system, the decomposition of H2O2 is catalyzed by Fe2+, making UV absorption by hydrogen peroxide (H2O2) not essential for the generation of HO• radicals. However, the highly acidic solution needed to avoid the formation of hydroxylated iron species, the complexation of iron ions by sulfonamide molecules (or their byproducts) which hinder Fe3+ photoreduction, and the regulation regarding the maximum concentration of iron. Studies of sulfonamides degradation performed at low initial concentration (≤ 0.1 mmol L-1/25 mg L-1) resulted in such good efficacy that Solid Phase Extraction (SPE) techniques were required for increasing the sensitivity of the analytical method [15].

SPE technique was conducted at low pH using the Strata-X Phenomenex cartridge since neutral or protonated sulfonamide molecules have good extraction recoveries for hydrophilic sorbent.

Photo-Induced and Photo-Initiated Oxidation Processes

The use of UV-driven technologies has enhanced the efficiency of oxidation processes including photo-induced and photo-initiated oxidation in circumneutral solution. Photo-induced oxidation of organic compounds has been investigated and shown to be an important process for the removal of sulfonamides from natural waters [25,26]. The formation of sulfonamides in the triplet excited state is an important phenomenon during the photo-induced oxidation processes and is related to the generation of reactive species [20,27]. The phenomena induced by the interactions between UV radiation and sulfonamide molecules can promote degradation from reaction with singlet oxygen and radical species during photosensitized processes occurring simultaneously with direct photolysis. The singlet excited state of the sulfamethazine molecule (1C12H14N4O2S*) may undergo intersystem crossing to a triplet excited state (3C12H14N4O2S*) to produce reactive oxygen species (ROS) via electron/energy transfer to dissolved molecular oxygen (3O2). The ROS were able to oxidize SMT molecules at relatively higher initial concentration (≥ 0.1 mmol L-1) compared to that found in natural waters.s

Photo-initiated oxidation processes involve absorption of photons by auxiliary oxidants, such as hydrogen peroxide, to generate HO• radicals. For example, sulfamethazine degradation was evaluated by photo-induced and photo-

initiated oxidation under 254 nm-UV radiation. Slow degradation rates were reported for the photo-induced oxidation of sulfamethazine under low-pressure UV radiation. Besides, relevant improvement of sulfamethazine degradation was observed in the presence of auxiliary oxidants. The pH of sulfamethazine solutions decreased during oxidation, suggesting the presence of acidic transformation products formed from the oxidative cleavage of hydroxylated aromatic rings [21].

Integrated Fixed-Film Activated Sludge (IFAS) As a Co-Treatment of Landifill Leachate In The Presence Of Sewage Using an Integrated Biological System

The solid waste management is one of the important issues in megacities. Considerable costs are involved for the correct disposal of solid wastes. One of the technologies is the landfills, from which water percolates through waste. It promotes and assists the process of decomposition by microorganisms. Nonetheless the biological decomposition is the most significant path for waters cleaning and even when talking about solids residues at landfills. These processes in turn release chemical by-products and rapidly use up any available oxygen, creating an anoxic environment. As a result of an increasing temperature and actively decomposing waste, the changes in pH rises, interfering in the solubilization of metals, many metal ions that are relatively insoluble at neutral may become dissolved in the developing leachate [28,29].

The physical appearance of leachate when it emerges from a typical landfill site is a strongly odoured black-, yellow- or orange-coloured cloudy liquid. The smell is acidic and offensive and may be very pervasive because of hydrogen-, nitrogen- and sulfur-rich organic species such as mercaptans [30,31]. The decomposition processes themselves release more water, which adds to the volume of leachate. The residues released in the leachate may also form a large component of the landfill gas.

On the other hand, how to treat the tons of liters of landfill leachate? The limitation for carbon biological degradation and general pollutants is that many designed biological systems were not suitable for decomposition leachate (from landfill), same for the pesticides, pharmaceuticals and biocides.

Once the biological treatment is based on microorganisms decomposition, such type of residues (from leachate) may often act as source of toxins, damaging the sludge activity. In Brazil many biological systems for municipal

Wastewater Plant (WWTP) receive the landfill leachate for treatment into the biological system. How may a hard mixture of chemicals affect the activated sludge? Considering the possible mixture of sewage and landfill leachate the ratio for the combination is quite important. Toxicity data was obtained to assess those values as well as to evaluate the application of an auxiliary midia for the improvement of the biological decomposition of organic matter.

In a landfill that receives a mixture of municipal, commercial, and mixed industrial waste, landfill leachate may be characterized as a water-based solution of four groups of contaminants: dissolved organic matter (alcohols, acids, aldehydes, short chain sugars etc.), inorganic macro components (common cations and anions including sulfate, chloride, iron, aluminium, zinc and ammonia), heavy metals (Pb, Ni, Cu, Hg), and xenobiotic organic compounds such as halogenated organics, polychlorinated biphenyl, PCBs and also pharmaceutical residues [29,31,32].

An Integrated fixed-film activated sludge was studied as one of the technologies for treatment of such leachates and the system was designed for treating a mixture of landfill leachate and raw sewage, applying a new media as support of microorganisms, called as Integrated Fixed-Film Activated Sludge (IFAS).

Parameters	1ª step (5%)	2ª step (10%)	3ª step (20%)
COD total (mgO2.L-1)	510	500	610
BOD5,20 total (mgO2.L-1)	220	220	290
TOC (mgC.L-1)	59	71	84
TKN (mgN.L-1)	110	160	230
NH4+-N (mgN-NH4+.L-1)	60	110	120
Alcalinity (mgCaCO3.L+1)	200	400	600

Table 2: Chemical characterization according to the percentage of landfill leachate into the sewage influent mixture (steps 1, 2 and 3).

A biological reactor was used during the treatement process for the domestic sewage and landfill leachate mixture. Hibrid system was constructeded on a pilot scale at Sao Paulo Univesity, Centro Tecnológico de Hidráulica (CTH/EPUSP), Departamento de Engenharia Hidráulica e Ambiental. The biomidia applied during the conjugated process was presented as (Figure 9).

Figure 9: The small and clean biomidia applied for the biofilm improvement and the dirty used biomidias (Anox Kaldnes®), obviously related to the exposure of the biomidia to the effluent, during the treatment proposed studied.

The reactor material was acrylic, designed in two parts: 270 liters for the first anoxic chamber for pre-denitrification. The second part for 800 liters, in an oxigenated chamber and 4 difusors, installed at the bottom of the system. The compressor/difusors introduced air into the system in order to achieve from 3.0 up to 4.0 mg.L-1 of dissolved oxygen. The second part of the system was a circular secondary decantador, receiving 2 m³.d-1 of the mixture. Sludge recirculation was 0,5. The biomidia Anox Kaldnes® was applied for both systems. The filling volume was 70% of total volume to aeration tank and 50% for the anoxic chamber (Figure 10).
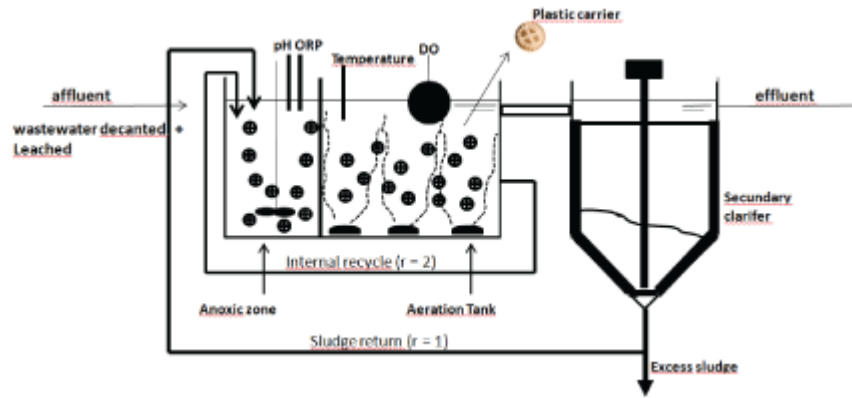
Figure 10: The designed system included biomidia Anox Kaldnes® , aeration tank, secondary clarifier and measurements apparatus.

The toxicity was an important parameter for the evaluation of the efficacy of proposed treatment as well as to evaluate the toxic charge (EC50 X volume of influent) of the influent of IFAS system. Vibrio fischeri bacteria and Daphnia similis crustacean were the biological indicators used for toxicity assessment and the samples applied during the IFAS in a ratio of 5%, 10% and 20% of landfill leachate in raw sewage, reported as influent. One of the most important questions was the amount of leachate is feasible into an activated biological treatment system? Peristaltic pump injected leachate into the system, followed by characterization and organic matter. The toxicity assessment was carried out for the mixture content for different percentage of landfill leachate (5, 10 and 20% of the total volume).

Taking operational conditions into account and the characteristics of influent (Table 2) the application of organic charge and nitrogen charge (in volume) varried from 0.4 up to 0.9 kgBOD.m3.d-1 and 0.32 up to 0.7 kgN.m3.d-1. It was possible to note the contribution of leachate addition in different parameters, such as Total Nitrogen (TN), amoniacal nitrogen (NH4+-N) and alcalinity, higher after 10% and 20% of landifil leachate. The volatile solids content into the reactor varried according to the literature database (2000 a 5000 mg.L-1), (Figure 11).
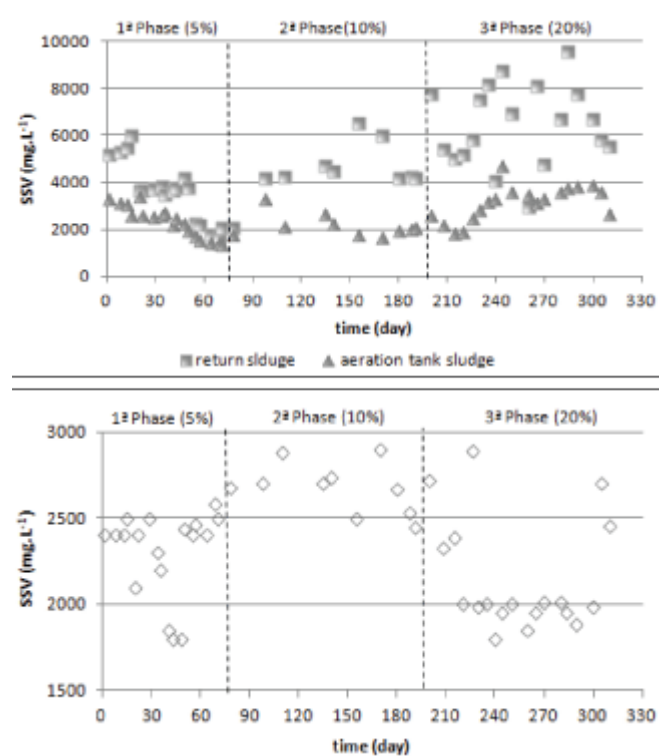
Figure 11: a) Volatile Suspended Solids, (VSS), versus time, at aeration tank and at sludge return - operation period; b) The influence of treatment into SSV as a function of biofilm adhered to the biomidia and time (Campos, F., 2014).

The fixed biomass decreased in the 3o. Step of the process - Kaldnes® (K1), 300 m2.m-3, reaching 8 gSSV.m-2 as adhered biofilm. The SSV biofilm is about 15 gSSV.m-2 [33,34].

The main objective of any WWTP is to remove organic mater and nitrogen. Another important issue is the solids which contain relevant chemical and biological contaminants such as parasite eggs, coliforms, virus etc. In this developed system, under stable operational conditions the efficacy of the three steps (including 5/10 and 20% of

leachate) the accounted for 85% of BOD5,20 and 90% as COD removal. Regarding nitrogen, 90% was the TNK and NH4+ for the two firs steps and 80% for the last one. As the WWTP receive leachate to be treated with the sewage more studies are necessary for achieving a safe treatment condition such as controlable toxic charge, sludge quality and treated sewage controling and quality [35].

The proposed IFAS was quite effective for BOD and amonia removal, resulting also in less toxic effluents, specially for the step 3, where 20% of landifill leachate was added to the sewage. 72% of whole toxicity was achieved for Vibrio fischeri bacteria for 15 minutes exposure (Figure 12).
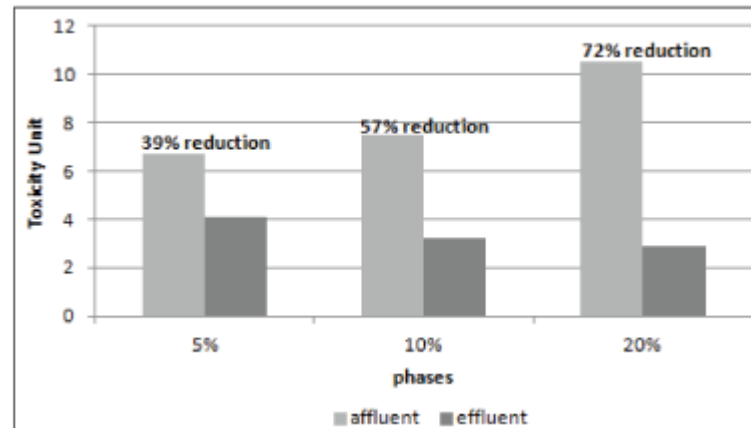

Figure 12: Efficacy of the combined processes onto the acute toxicity (V.fischeri) at different amount of landfill leachate in the mixture.

Regarding to acute ecotoxicity data, the highest percentual of leachate received from the landifill was 20% in the sewage mixture, keeping the same efficiency for organic matter and nitrogen. Nonetheless the residual toxicity was detected for Vibrio fischery (measured by Microtox®). The D.similis crustacean was less sensitive than the vibrio bacteria. These data reinforce the needs for toxicity assessment involving more than one biological class of living organisms for the evaluation of wastewater and their treatments, chronic effects assays are also recommended, before discharge of treated wastewater into the rivers.

Concluding remarks: Why treatment technologies are important? These examples were chosen due to the relevance of chemical classes of contaminants and developing technologies. And how Ecotoxicology can contribute to this proposed subject and to reduce contamination? These ecotoxicity assays are also used for fixing standard limits and for assuring safety discharges to the environment, our further actions for preservation. From this chapter it was possible to confirm the efforts that have been carried out to reduce the presence of pharmaceuticals and other chemicals in waters. There is no other way to protect environment if not education, collaboration, safety and technologies.

References

1. Lyons G (2014) Pharmaceuticals in the environment: a growing threat to our tap water and wildlife. A Chem. Trust report.

2. Rand GM (1995) Fundamentals of Aquatic Toxicology: effects, environmental fate and risk assessment, (2nd ed), Taylor & Francis, Washington.

3. Chatzitakis A, Berberidou C, Paspaltsis I, Kyriakou G, Sklaviadis T, et al. (2008) Photocatalytic degradation and drug activity reduction of chloramphenicol. Water Research, 42, 386.

4. Mendez-Arriaga F, Torres-Palma RA, Petrier C, Esplugas S, Gimenez J, et al. (2008). Ultrasonic treatment of water contaminated with ibuprofen. Water Research, 42, 4243.

5. Bagal MV, Gogate PR (2014) Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. Ultrasonic Sonochemistry, 21, 1.

6. Borrely SI, Gonalves AA, Oikawa H, Duarte CL, Rocha FR, et al. (2004) Electron beam accelerator for detoxification of effluents. When radiation processing can enhance the acute toxicity? Radiat. Phys. and Chem., 71, 453-456.

7. Cooper, Randy & O'shea (1998) Advanced Oxidation Processes for Water and Wastewater. John Wiley & Sons, Inc., New York.

8. Han B, Kim JK, Kim Y, Choi JS, Jeong KY, et al. (2012) Operation of industrial-scale electron beam wastewater treatment plant. Radiat. Phys. and Chem., 81: 1475-1478.

9. Ogihara-Silva VH (2014) Avaliao da toxicidade e da degradao do farmaco cloridrato de fluoxetina, em soluo aquosa e em mistura com esgoto domstico, empregando irradiao com feixe de eletrons. Master thesis. IPEN/USP. Brasil.

10. Homlok R, Takcs, E, Wojnrovits L (2011) Elimination of diclofenac from water using irradiation technology, Chemosphere, 85: 603608.

11. Guo Z, Zhou F, Zhao Y, Zhang C, Liu F, et al. (2012) Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms. Chemical Engineering Journal, 191, 256.

12. Curini R, Gentili A, Marchese S, Marino A, Perret , et al. (2000) Solid phase extraction followed by high-performance liquid chromatography-ion spray interface-mass spectrometry for monitoring of herbicides in environmental water. Journal of Chromatography A, 874.

13. Carabias-Martinez R, Rodriguez-Gonzalo E, Revilla-Ruiz P (2006) Determination of endocrine-disrupting compounds in cereals by pressurized liquid extraction and liquid chromatographymass spectrometry. Study of background contamination. Journal of Chromatography A, 1137.

14. McMurray, TA Dunlop, PSM, Byrne, JA (2006) The photocatalytic degradation of atrazine on nanoparticulate TiO2 films. Journal of Photochemistry and Photobiology A: Chemistry, 182, 43.

15. Silva MP, Batista APS, Borrely SI Silva, VO Teixeira ACSC (2014) Photolysis of atrazine in aqueous solution: role of process variables and reactive oxygen species. Environmental Science and Pollution Research, 21, 12135.

16. Hleli S, Martelet C, Abdelghani A, Burais N, Jaffrezic-Renault N, et al. (2006) Atrazine analysis using an impedimetric immunosensor based on mixed biotinylated self-assembled monolayer. Sensors and Actuators B, 113, 711.

17. Lastre-Acosta AM, Cruz-Gonzlez G, Nuevas-Paz L, Juregui-Haza UJ, Teixeira, ACSC, et al. (2015) Ultrasonic degradation of sulfadiazine in aqueous solutions. Environmental Science and Pollution Research, 22, 918.

18. Legrini O, Oliveros E, Braun AM (1992) Photochemical processes for water treatment. Chemical Reviews, 93, 671.

19. Batista APS, Cottrell BA, Nogueira RFP (2014) Photochemical transformation of antibiotics by excitation of Fe(III)-complexes in aqueous medium. J. of Photochemistry and Photobiology A: Chemistry, 274, 50.

20. Batista APS, Nogueira RFP (2012) Parameters affecting sulfonamide photo-Fenton degradation-iron complexation and substituent group. Journal of Photochemistry and Photobiology A: Chemistry, 232, 8.

21. Batista APS, Pires FCC, Teixeira ACSC (2014) Photochemical degradation of sulfadiazine, sulfamerazine and sulfamethazine: Relevance of concentration and heterocyclic aromatic groups to degradation kinetics. Journal of Photochemistry and Photobiology A: Chemistry, 286, 40.

22. Silva MP, Batista APS, Borrely SI Silva, VO Teixeira, A.C.S.C. (2014) Photolysis of atrazine in aqueous solution: role of process variables and reactive oxygen species. Environmental Science and Pollution Research, 21, 12135.

23. Faust BC, Zepp, RG (1993) Photochemistry of aqueous iron(III)-polycarboxylate complexes: Roles in the chemistry of atmospheric and surface waters. Environmental Science and Technology, 27, 2517.

24. Jeong J, Yoon J (2005) pH effect on ?OH radical production in photo/ferrioxalate system. Water Research, 39, 2893.

25. Lam, M W, Mabury S A(2005) Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters. Aquatic Sciences, 67:177

26. Boreen AL, Arnold WA, McNeill K (2004) Photochemical fate of sulfa drugs in the aquatic environment: Sulfa drugs containing five-membered heterocyclic groups. Environmental Science and Technology, 38, 3933.

27. Moore DE (1998) Mechanisms of photosensitization by phototoxic drugs. Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis, 422, 165.

28. Aucott M (2006) The fate of heavy metals in landfills: A Review, Pollution Prevention and the NY-NJ Harbor Project of the New York Academy Sciences.

29. VanLoon, GW and Duffy SJ (2005) Environmental chemistry a global perspective. 433-458, New York.

30. Christensen TH, Kjeldsen P, Bjerg PL, Jensen DL, Christensen JB, et al. (2013) Biogeochemistry of landfill leachate plumes. HBRC Journal, 9(2) 187-192.

31. Campos F (2014) Influncia do recebimento de lixiviado de aterro sanitrio sobre o tratamento de esgoto em processo de lodo ativado e reator integrado de lodo ativado com biofilme em leito mvel. PhDThesis Faculdade de Sade Publica, Universidade de So Paulo.

32. ecen F , akirolum D (2001) Impact of Landifill Leachate on the Co-Treatment of Domestic Wastewater, Biotechnology Letters, 23, 821.

33. ABNT NBR 12209 (2011) Elaborao de projetos hidrulicos-sanitarios de estaes de tratamento de esgotos sanitrios.

34. Gaul T, Marker S, Kunst S (2005) Start-Up of Moving Bed Biofilm Reactors for Deammonification: The Role of Hydraulic Retention Time, Alkalinity and Oxygen Supply. Water Science & Technology, 2, 7: 127133.

35. Wiszniowsk J, Surmacz-Gorska J, Robert D, Weber JV (2007) The Effect of Landfill Leachate Composition on Organics and Nitrogen Removal in a Activated Sludge System With Bentonit Additive. Jornal of Environmental Management, 59-68.

36. Woods R (1998) Radiation chemistry and its application to environmental pollution. In Environmental applications of ionizing radiation, 1-31. New York.