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Advanced oxidation processes applied to effluent streams from an agrochemical industry

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Firstly, I wish to thank the Organizing Committee of this Congress for this invitation so that, I should have the opportunity to report our project at the Federal University of Santa Maria (UFSM), Brazil, that deals with the application of Advanced Oxidation Processes (AOP's) to effluent streams within an agrochemical industry. During next 20 minutes, I'll define (Fig. 1) and explain advanced oxidation processes; then I'll demonstrate their importance and, last but not least, I'd relate a case study of the application of AOP's to effluent streams of an agrochemical industry in the state of Rio Grande do Sul. This topic is receiving full attention from our research group at the UFSM because of its environmental importance.

In this scheme (Fig. 2) the main AOP's are put together: **Ozonation + UV-Irradiation + Peroxydation + Catalysis,** and their combinations: *Photoozonization, Photocatalysis, Peroxonation, Peroxidation* and others. These processes can be applied separatedly, in association with others, and even sequentially; it depends on the kind of effluent that has to be handled.

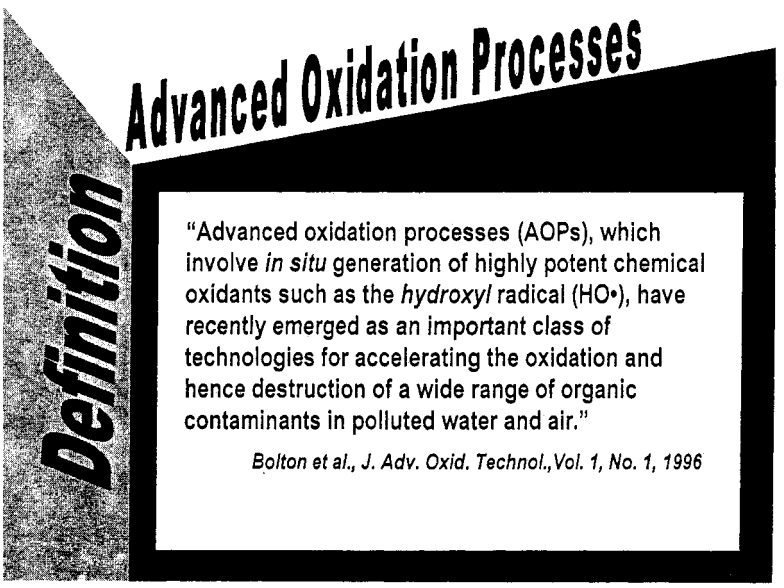


Fig. 1 Definition of advanced oxidation processes.

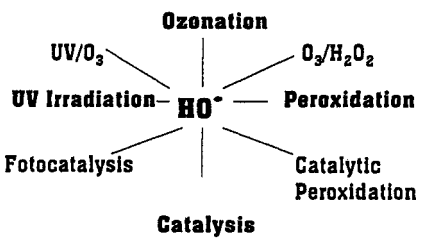


Fig. 2 Advanced oxidation processes.

*Lecture presented at the XI CHEMRAWN Meeting on Environmental Chemistry: Latin American Symposium on Environmental Analytical Chemistry, Montevideo, Uruguay, 15–20 March 1998. Other presentations are published in this issue, pp. 2259–2336.

Moreover, all these AOP's have an item in common: the generation of **hydroxyl radical**, which is extremely reactive, and possesses a very high oxidation potential. As a matter of fact, the hydroxyl radical shows an oxidation potential over 3 Volts, surpassed only by the negative oxidation potential of fluorine.

The reasons for our interest in this topic are illustrated in this figure (Fig. 3): first of all, the declarations of the Brazilian government at the Rio '92 Conference for **Clean Production** in the field of industrial activities within our country. Secondly, the statement by scientists from Cambridge and Stanford in the February '96 issue at **Science**, predicting that the main problem of the human civilization until the year 2030 would be the *lack of potable water.*

Thirdly, almost the entire hydric basin of the state of Rio Grande do Sul - like the rest of our country basins - is submitted to a growing environmental impact, where only little more than 4% of all municipal waste is processed. Speaking about industrial wastes, most of these are unconformable to conventional treatment processes, as is happening in agrochemical industries, whose effluents are so toxic that they inhibit the microbiological processes involved in the treatment system.

Our research group in environmental chemistry is trying since the last years to have a cooperation with regional industries, such as tanneries, agrochemical, cellulose and paper industries. We pay special attention to problems resulting from the disposal of effluents from these industries, and so we began to investigate AOP's, processes of growing importance since the '80. AOP's have been applied to special liquid effluents, particularly, to those of difficult biodegradability, and high toxicity. Recently, AOP's have invaded the domestic environment, specially, as systems for air cleaning and water purifying, in the USA, Europe, and Japan.

This figure (Fig. 4) is from our newspaper „Zero Hora", 20th July 1995. Here is seen the **Jacuí River** basin, the most important hydric basin of the state of Rio Grande do Sul - this is also the most important affluent of **Guaíba River**, the large river seen on postcards from the city of **Porto Alegre,** capital of Rio Grande do Sul.

According to reports from our FEPAM – *Fundação Estadual de Proteção Ambiental* – the **Taquarí River**, the main affluent of the **Jacuí River**, which supplies all river side population with potable water, is the river that is overloaded with organic pollutants, followed by the **Caí**, and then **Sinos** rivers. In these, not only urban wastes and agricultural run off, but industrial effluents are also present.

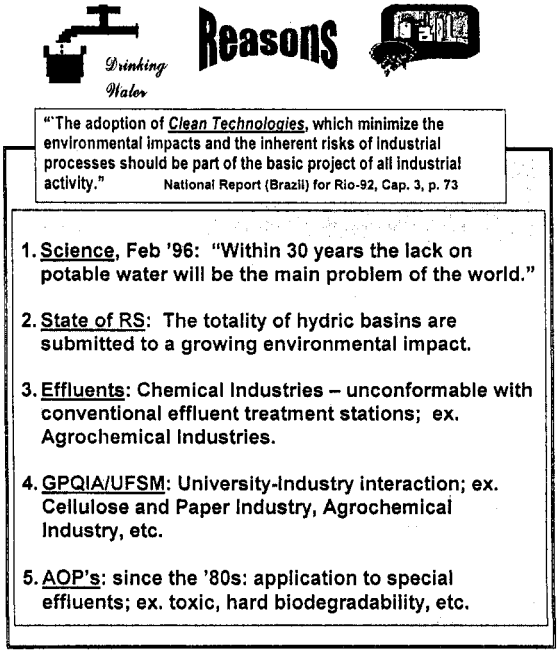


Fig. 3 Reasons for the research.

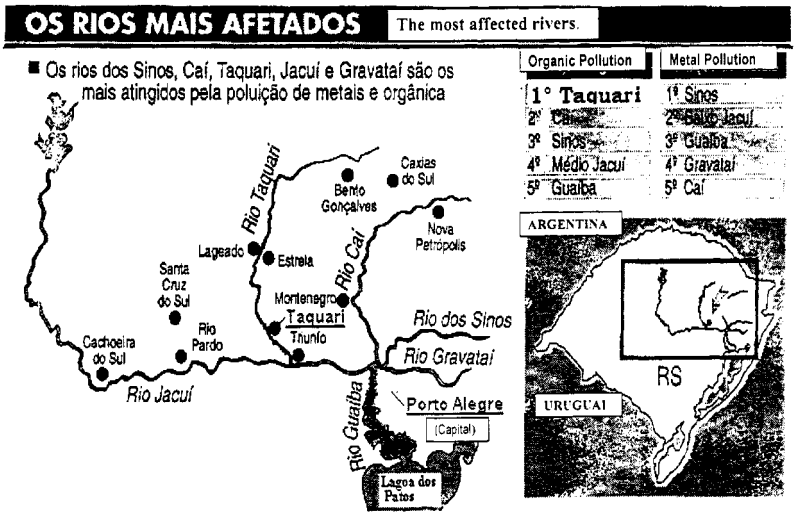


Fig. 4 *Zero Hora* Newspaper 20 July 1995—investigation exposes the pollution of 'gaúchos' rivers'—FEPAM Report signs the Guiba river basin as the most affected one.

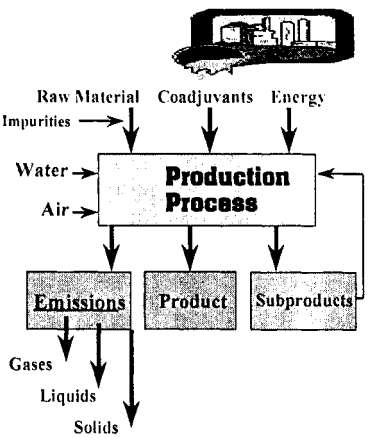


Fig. 5 Process production of the chemical industry & similar.

Additionally, on the margins of this river, the agrochemical industry and the homonym city (Taquarí) are located.

Here we have a scheme (Fig. 5) of usual production process of the chemical industry: **input** = [raw materials (+ impurities) + Coadjuvants + Energy + Water + Air] and **output** = [Product + Subproduct (recycled) + Emissions (gases, liquids and solids)]. The trend in the industrial production is the minimization of water and air consumption, cleaner production, and total reutilization of residues.

This is a representation (Fig. 6) of a conventional plant for effluents treatment of a hypothetical chemical industry. This system can be divided in three main phases –**mechanical, biological, and chemical** – which can vary in conception, of course, according to the nature of the effluents and the final polish required. A simple scheme like this can hide chemical installations.

And here (Fig. 7) we have an idea of the processes and operations involved in a central waste treatment station in a large chemical industry. Actually, Advanced Oxidation Processes are more and more present, being part of the so called ***Special Treatments.***

As we said before, the Agrochemical Industry, which is cooperating with us, is located in the city of Taquarí, on the margins of the homonym river, 100 km from the Capital (Porto Alegre). This industry is of strategic importance for the state of Rio Grande do Sul (the major corn producer in Brazil), whose economy is based on agriculture and cattle rearing.

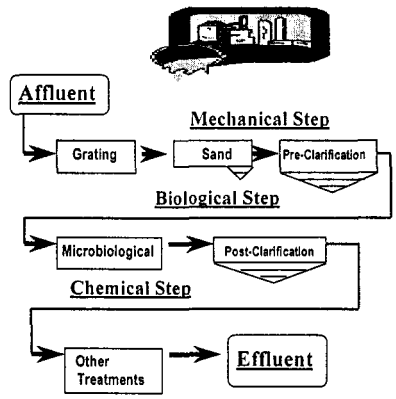


Fig. 6 Conventional unit of effluent treatment.

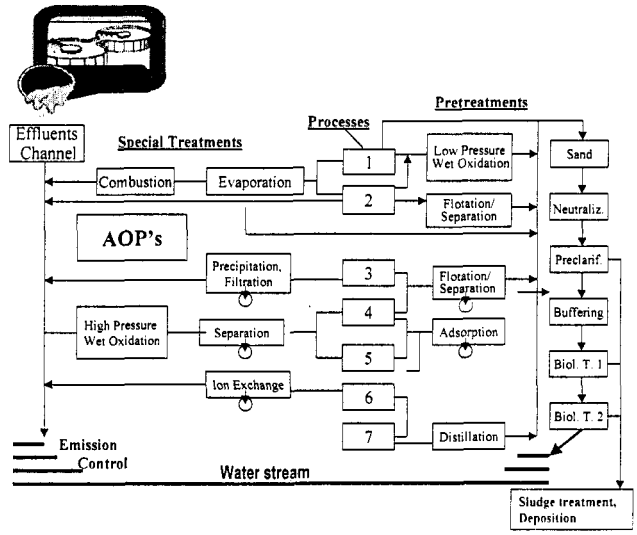


Fig. 7 Chemical industry: effluents treatment.

This industry is suffering enormous pressure from our environmental authorities (FEPAM), particularly, since the end of the '80s. For this reason, we were invited by this industry to collaborate in the development of advanced oxidation processes applicable to its effluent streams, well known for its toxicity and difficult biodegradability.

Among other products, the herbicide ***Trifluraline*** assumes great importance in the industrial context, not only for economic reasons. The effluent streams derived from its production have high salt content, great toxicity, and difficult biodegradability. As we can see (Fig. 8), trifluraline is an herbicide from the nitroaniline group, a pre-emergent, cellular and nuclear division inhibitor. It is highly toxic for humans, its environmental effects are currently under investigation, and these have not been well elucidated.

Here we have a simplified flowschart (Fig. 9) of the final stage in production of trifluraline – the *Trifluormethyl-2-nitro-parachlor-benzene* is nitrated in the nitration reactor resulting in the so-called „Dinitro" product, which is washed, and neutralized, giving raise to the first stream problem – the "Neutralization water" (NW). This *Dinitro* is extracted with the aid of chloroform, and then transported to an amination reactor, where it reacts with dipropylamine at 120 °C, forming *trifluraline* – a dinitroaniline herbicide. Separation is done in a press filter, and then the second and more problematic stream is formed – the "Amination Water" (AW).

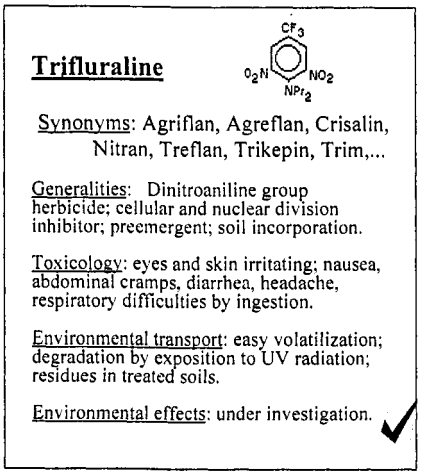


Fig. 8 Trifluraline—properties.

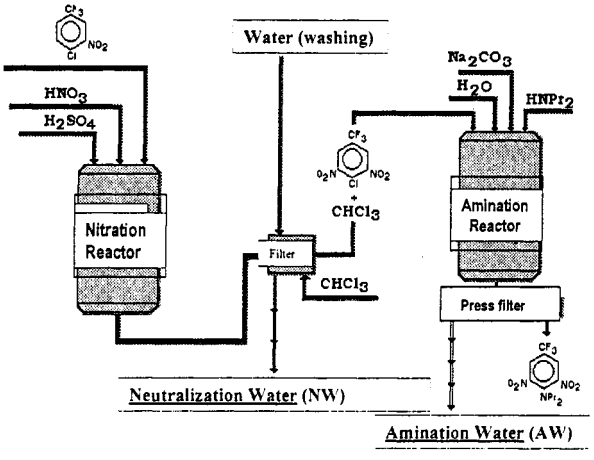


Fig. 9 Trifluraline production.

In this figure (Fig. 10) are given important characteristics of these two toxic streams and some for the tolerance values imposed by FEPAM. The COD values are very high, especially for the "Amination Water". The TOC value is around 4000 ppm. The BOD values logically couldn't be determined due to the high toxicity of the effluents. The chloride content of the amination water, under certain conditions, could surpass 15%. The fluoride concentration isn't such a serious problem, but it is still beyond the permitted level. pH is between 7 and 11, and could be easily corrected to the recommended range. The dinitro and trifluraline residues in the corresponding effluent streams are in ppb/ppm levels, but their toxicity are high enough to make them incompatible for the microbiological treatment of the plant effluents. Thus, effluent streams need a special treatment before being discharged into other streams arising from other production units of the industry.

Logically, the *dilution* idea of the streams with other plant effluents and municipal wastes (Fig. 11) was investigated, but besides being technically practicable, it wasn't feasible economically.

For this reason, the feasibility of the ozonization process in the detoxification of these two effluent streams from the trifluraline production was first investigated (Fig. 12). In the beginning, our ozone generator was a domestic one, for water purification, and was transformed and adapted for our purposes. Our reactor was a 3 L-borossilicate vessel. We also developed a FIA-method for the *on line* measurement of ozonizated gas flows, which facilitate the material balance of the process.

Samples → / Parameters ↓	Neutralization Water	Amination Water	FEPAM Values
COD (mg $O_2 \cdot L^{-1}$)	9000	14000	320
TOC (mg C $\cdot L^{-1}$)	4000	4500	-
BOD_5 (mg $O_2 \cdot L^{-1}$)	-	-	108
Cl^- (mg $\cdot L^{-1}$)	4280	150000	4000
F^- (mg $\cdot L^{-1}$)	60	40	<10
pH	7	11	6 - 8,5
Trifluraline	-	traces	ND
Nitrophenols	traces	traces	ND

Fig. 10 Effluent streams characterization.

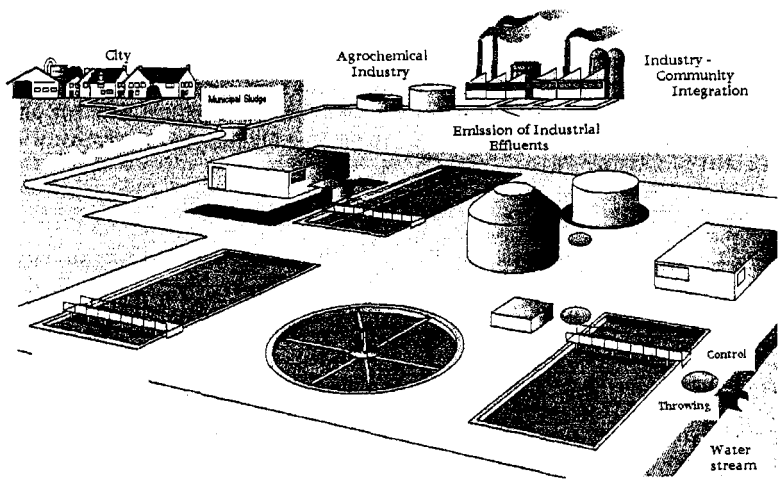
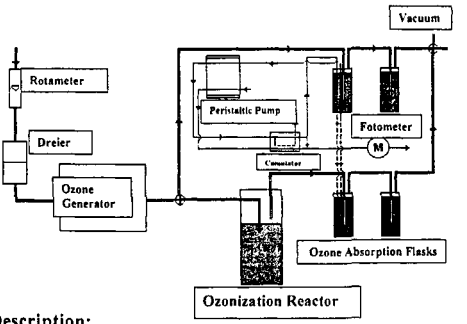


Fig. 11 Integrated effluent treatment.

Many combinations were tested. From these we demonstrate the most significant ones: ozonization in acidic pH, ozonization/peroxidation in basic pH, and ozonization in basic pH. The latter gave the best results for both streams. Among other results, a desirable TOC reduction of 35 and 45%, respectively, for both streams, and a significant increase in the respiratory activity was obtained. Therefore, when tested in pilot scale at the industry, the ozonization processes demonstrated their high operational cost: they were declared economically unpracticable. Additionally, the corrosion problems on the ozonization pilot unit were very serious.

At bench scale we also made photooxidation tests and the best results are shown in Fig. 13 and 14 a. The photoperoxidation was the best, and the industry took advantage of this, constructing a primary unit for the treatment of "Amination Water" effluent stream, as we can see in Fig. 15. A combination of photoperoxidation, dilution with other effluent streams, microbiological plus active carbon treatment, successively, gave raise to a final effluent with satisfactory characteristics for disposal into the Taquarí river (which correspond to the FEPAM norms).

Ozonization Unit Scheme

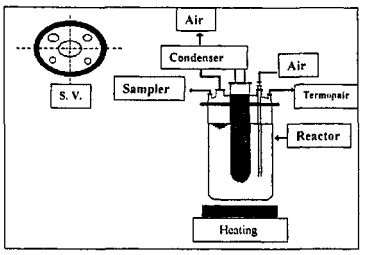


Description:
Combinations: O_3; $O_3 + HO^-$; $O_3 + H_2O_2$; Conditions: Flow: 15 mg $O_3.h^{-1}.L^{-1}$; Reactor (semi-batch, 3 L); pH 5-11; Time: 16 horas; Rate H_2O_2/O_3: 0,5.

Results: (Color reduction: ~80%)

Process ⇨		O_3 pH = 5		$O_3 + H_2O_2$ pH = 11		$O_3 + HO^-$ pH = 11	
Sample ⇩	%	TOC Red.	Resp. Activ.	TOC Red.	Resp. Activ.	TOC Red.	Resp. Activ.
NW		30	-	28	-	35	45
AW		35	-	35	-	45	55

Fig. 12 AOP's: treatment of effluents from an agrochemical industry.



Combinations: UV/H_2O_2; UV/TiO_2; $UV/H_2O_2/TiO_2$; $UV/H_2O_2/ZnO$; $UV/H_2O_2/Fe^{2+}$

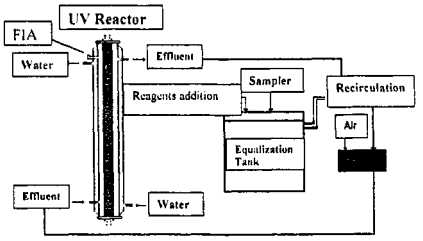
Operational Conditions: UV (λ = <360 nm); semi-batch Reactor (3 L); pH 7-11; Fotooxidation time: 3 h; H_2O_2 concentration: 16 $g.L^{-1}$; Irradiated Power: 20 $W.L^{-1}$; Temperature: 60-70 °C; Catalyst: 0,1-0,5 % m/v

Results:

Process ⇨ Sample		UV/H_2O_2		UV/TiO_2		$UV/H_2O_2/TiO_2$		$UV/H_2O_2/ZnO$		$UV/H_2O_2/Fe^{++}$	
⇩	%	TOC Red.	R. A.	Red. COT	R. A.	TOC Red.	R. A.	TOC Red.	R. A.	TOC Red.	R. A.
NW		20	35	-	-	15	20	12	10	-	-
AW		35	55	-	-	20	25	19	15	-	-

Fig. 13 AOP's: treatment of effluent from an agrochemical industry: photooxidation and microbiological oxidation of effluent streams from the trifluraline production.

And finally, I'll show you, the partial results recently obtained from a combined system using airing and scrap iron at bench scale (Fig. 16). We were really surprised with the high color and chloride reduction by this simple process, which makes it adequate to a pre-treatment, before photooxidation and microbiological stages. The industry has taken immediately advantage of this fact, and is now investigating the possibility to use this treatment in its most problematic effluent streams.



Combinations: UV/H_2O_2; UV/TiO_2; $UV/H_2O_2/TiO_2$; $UV/H_2O_2/ZnO$; $UV/H_2O_2/Fe^{++}$

Operational conditions: UV (λ = 254 nm); semi-batch Reactor (10 L); pH 7-11; Fotooxidation time: 3 h; H_2O_2 Concentration: 16 $g.L^{-1}$; Irradiated Power: 24 $W.L^{-1}$; Temperature 60-70 °C; Catalysts: 0,1-0,5 % m/v; Recirculation rate: 120 $L.h^{-1}$.

Results:

Process ⇨ Sample		UV/H_2O_2		UV/TiO_2		$UV/H_2O_2/TiO_2$		$UV/H_2O_2/ZnO$		$UV/H_2O_2/Fe^{++}$	
⇩	%	TOC Red.	R. A.	TOC Red.	R. A.	TOC Red.	R. A.	TOC Red.	R. A.	TOC Red.	R. A.
NW		14	35	-	-	10	18	12	9	-	-
AW		25	45	-	-	18	22	19	12	-	-

Fig. 14 Photooxidation unit scheme.

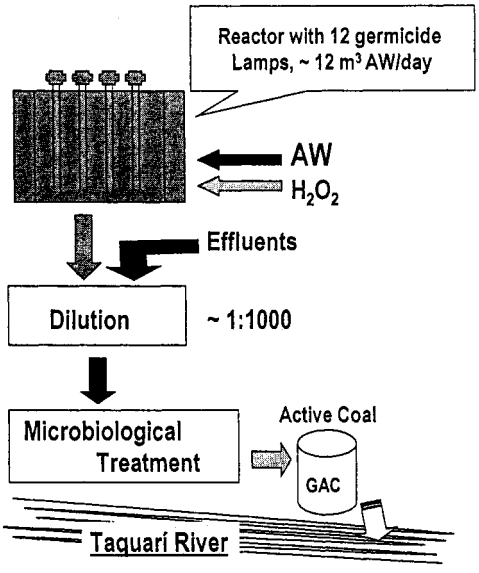
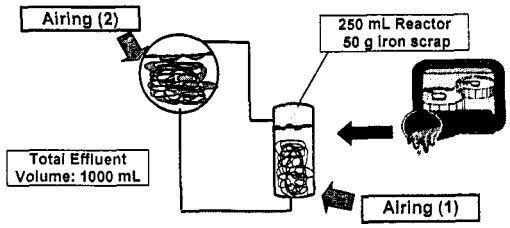


Fig. 15 Adopted solution by the agrochemical industry.



✓Description:

- Airing: Air Pumps (1) e (2)
- Recirculation rate: 12 $L.h^{-1}$
- Air flow: 720 $L.h^{-1}$
- Operation time: 4 h / batch

Results:

pH	Dilution (%) (v/v)	Reduction Cl^- (%)	Reduction Color (%)	Reduction DQO (%)	Biodegradability (% raise)
4	1	80	97	15	10
	5	80	98	5	5
	10	90	98	5	5
7	1	91	97	15	10
	5	91	97	10	10
	10	89	97	10	5
11	1	81	92	10	(*)
	5	85	83	5	(*)
	10	59	65	5	(*)

Color Reduction (λ = 420 nm); Fe_{res} < 0,02 $mg.L^{-1}$ (FAAS); Biodegradability parameter: DBO_5; (*) not detected.

Fig. 16 Combined system iron scrap-airing.