

# AN INTEGRATED APPROACH TO ASSESS THE BIODEGRADABILITY OF A WASTEWATER CONTAINING CHROMIUM BY USING CHEMICAL AND BIOLOGICAL METHODS

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## Abstract

The Water Company of the North Alentejo (Águas do Norte Alentejano) (Portugal) has decided to implement a treatment plant to treat an urban wastewater with a significant influence of tannery effluents. The design of the wastewater treatment plant was attributed to a consortium coordinated by Sisaqua Company. Since the levels of the biodegradability and toxicity of the wastewater to be treated were unknown, Sisaqua Company asked the New University of Lisboa to develop and execute a monitoring plan to define the chemical composition and the levels of the biodegradability and toxicity of the wastewater.

A composite sampling procedure of the wastewater was performed during a daily working cycle of the tanneries. The composite sample was characterized for 19 chemical parameters. Five of these parameters were total Cr, Cr (VI), Zn, Cu and Al, which were determined in the dissolved and suspended fractions. The composite sample was also submitted to a biological test to assess its biodegradability degree. This assay was performed according to the methodology indicated in the test 301E of OECD [1], taking into account the amendment of 1992. A respirometric assay was carried out, to assess the toxic effect of the composite sample on the biological populations involved in the biological stabilization of organic compounds. This assay followed the “Sapromat” methodology developed by Brabander and Vandeputte [2]. Finally, the composite sample was submitted to a coagulation-flocculation process according to the methodologies proposed by Eckenfelder [3, 4] and Pereira [5]. The supernatants were characterized for the same chemical and biological parameters as it was described for the composite sample.

It was possible to conclude that the high levels of Cr present in the composite wastewater were mainly in the trivalent oxidation state. Since this oxidation state is less toxic for biological populations than the Cr (VI) and this metal was mainly in the suspended fraction, it was possible to obtain a biodegradability of the organic compounds quite similar to those observed for domestic wastewaters. The toxicity determined by the “Sapromat” method was slightly higher than those determined for domestic wastewaters. Nevertheless, this toxicity did not affect significantly the wastewater biodegradability. The Cr (III) was easily removed by a chemical coagulation-flocculation process.

## Introduction

Terrugem is a small county with about 1300 inhabitants. It makes part of Elvas municipality, in North Alentejo (Portugal), near the Spanish border. The major part of the population is concentrated in the main village, with the same name, where there is no kind of municipal wastewater treatment system. The village wastewaters are collected by a mixed sewer system and discharged, without treatment, in a small creek, affluent to the Guadiana River, in the North of the Alqueva dam basin. The main activities in the drainage basin are agriculture, cattle breeding (mainly sheep breeding) and tanning. Tourism and traditional workmanship have also some representation. Depending on the time of the day and on the day of the week, the wastewater flow shows a clear influence of the discharges of sheep corrals and tanneries effluents.

In order to solve this problem, the Water Company of North Alentejo (Águas do Norte Alentejano) has decided to install a wastewater treatment plant in Terrugem. The project design was attributed to a consortium coordinated by Sisaqua Company. Sisaqua aims to develop the best economic and environmentally sound solution. Therefore, the project makers need to have the most complete information about the problem.

Tannery effluents are known to adversely affect the biological treatment of domestic wastewaters, mainly due to salinity and Cr content. So, it was possible that a standard treatment solution would not fit in this specific situation. Since the composition and the levels of the biodegradability and toxicity of the mixed wastewater to be treated were unknown, Sisaqua asked the New University of Lisboa to develop a monitoring plan that could define the chemical composition and the levels of the biodegradability and toxicity of the wastewaters.

## Experimental Details

### Sampling

Type of Sample Analyzed: The sample analyzed was of a domestic wastewater with a significant contribution of tannery effluents. During the sampling period, it was also detected the discharge of another type of wastewater characterized by an intensive odor of ammonia. This effluent was associated to the sheep breeding. Therefore, the sample collected was named, in this paper, as mixed wastewater.

Collection Site: The sample of the mixed wastewater was collected in the Terrugem county. The sample was collected according to a composite methodology, during a period of 8.0 hours. The collection site was located in a discharging channel, which is an affluent of the main small creek that crosses the Terrugem county. The collection site was located 40 m upstream of the confluence between the discharging channel and the main creek. In this place, it was not detected any influence of the creek water on the quality of the effluent running in the discharging channel. Downstream to this point, no other type of wastewater discharge was identified.

Sampling Procedure: The sample of the mixed wastewater was obtained through a composite sampling methodology without considering the wastewater flows at the moments of the collection of the sub-samples. The composite sample was constructed through the collection of nine sub-samples, each with a volume of four liters. The collection period has started at 11:00 and it was

finished at 19:00. All sub-samples were collected with an interval of one hour. The nine sub-samples were stored in glass bottles with PTFE caps (Schott) previously rinsed with nitric acid (1:10) (Riedel-de-Häen) and deionised water (Elix 5, Millipore). During the sampling period, the sub-samples were kept at 4°C. The composite sample was obtained through the mixing of the nine sub-samples in a polyethylene reservoir of 60 liters. This reservoir was previously rinsed with detergent, tap water, nitric acid (1:10) and deionised water. The composite sample was maintained in this reservoir all over the study, at 4°C.

### Chemical Assays

Parameters Analyzed on Site: During the sampling period, the instant water flows were estimated based on the following parameters: water depth in the channel, slope of the channel walls, slope of the channel, factor of concrete roughness. It was also measured the pH, conductivity, temperature and turbidity of the mixed wastewater. These parameters were determined by using a multiparametric probe (Horiba).

Chemical Characterization of the Composite Sample: The composite sample was characterized for the following chemical parameters: pH (electrometric method by using of a specific probe (Orion)), Conductivity (electrometric method by using a Pt probe (Orion)), Turbidity (nephelometric method), Total alkalinity (volumetric method by using H<sub>2</sub>SO<sub>4</sub> and a solution of bromocresol green), COD (volumetric method after a previous oxidation with potassium dichromate in an open-reflux, at 160°C, in an acidic environment, for 110 min), BOD<sub>5</sub> (dilution method and determination of the DO by using a specific probe (G. Vittadini)), True color (colorimetric method by using a Pt-Co standard solution), TSS (gravimetric method after a filtration over 0.45 µm membrane filters and drying at 105°C), Dissolved organic carbon (DOC) (combustion in excess air and infra-red detection (Shimadzu TOC Analyzer), after filtration over 0.45 µm membrane filters), Kjeldahl nitrogen (volumetric method after a digestion with H<sub>2</sub>SO<sub>4</sub> and distillation with vapor flow (Kjeltec Distiller)), Nitrates (specific probe method (Orion)), Nitrites (spectrophotometric method by using sulfanilamide reagent and NED reagent), Total phosphorous (colorimetric method by using ascorbic acid and ammonium molybdate reagent, after a H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> digestion), Total Cr, Zn, Cu and Al (AAS method after a HNO<sub>3</sub> microwave digestion (Ethos-Milestone Microwave)), Dissolved Cr, Zn, Cu and Al (AAS after a filtration over 0.45 µm membrane filters) [6]. Cr (VI) was determined through the spectrophotometric method by using the 1,5-diphenylcarbazide reagent [7].

Coagulation-Flocculation Assay: In order to assess the removal efficiency of color and Cr from the composite sample of the wastewater through a chemical process, a coagulation-flocculation assay was carried on in a JAR-test system (G. Vittadini). The coagulant used was the alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O) and the analytical methodology followed the technical protocols of Eckenfelder [3, 4] and Pereira [5] All alum dosages reported hereafter are expressed as Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The coagulation-flocculation assay was developed in the following four different levels:

**a) First level** – An incremental addition of alum to a sample of the composite wastewater at its natural pH (7.5) and to a sample at a pH value corrected for 6.0 (iso-electric point of the alum) was done. The pH correction was performed with HCl 0.5 M (Riedel-de-Häen). The addition of the alum was made at 100 rpm, during 1 min. The coagulation-flocculation periods were of 15 min, at 40 rpm. The settling periods were of 30 min, without mechanical agitation. After each cycle of coagulation-flocculation-sedimentation, a supernatant sample was taken and

characterized for the following parameters: true color, DOC and Cr after the digestion of the samples. The analytical methodologies were as referred above;

- b) **Second level** – Five samples of the composite wastewater, at its natural pH (7.5), were submitted to one cycle of coagulation-flocculation-sedimentation with the following alum additions: 0, 160, 190, 220 and 250 mg.L<sup>-1</sup>. The supernatant samples were characterized for the same parameters as referred in the first level and for Al after the digestion of the samples. The analytical methodologies were as referred above;
- c) **Third level** – Four samples of the composite wastewater were submitted to a pH correction with either HCl 0.5 M or NaOH 1.0 M (Riedel-de-Häen). The final pH values were the following: 5.3, 6.2, 8.6 and 9.6. A sample at its natural pH was also tested. The five samples were submitted to a coagulation-flocculation-sedimentation cycle with the optimum dosage defined in the second level of this methodology (200 mg.L<sup>-1</sup>). The supernatant samples were characterized for the same parameters as defined in the second level of the coagulation-flocculation assay;
- d) **Fourth level** – The optimum dosage of alum and the optimum pH value determined in the previous levels were used to perform a final assay over an enlarged sample of the composite wastewater. The supernatant was characterized for the same parameters referred in the chemical characterization of the composite sample.

### Biological Assays

Biodegradability Assay: The composite sample was submitted to the intrinsic biodegradability assay defined in the method 301E of OECD [1]. Three reservoirs were prepared as follows:

- a) **Reservoir B1** – containing 5 L of the composite sample. The main aim of this assay was to assess the intrinsic biological degradation of the composite wastewater;
- b) **Reservoir B2** – containing 5 L of a sodium acetate solution inoculated with 23 mL of the sludge from the composite wastewater. This sludge was obtained through the settlement of 1 L of the composite wastewater, during 1 h. The main aim of this assay was to assess the biological activity of the microorganisms present in the composite sample of the wastewater;
- c) **Reservoir B3** – containing 5 L of a sodium acetate solution, without inoculation. This assay was the blank test for the assay in the reservoir B2.

The mixed liquors in each reservoir were continuously aerated through the injection of non-sterilised air. The air injection has also maintained the contents in each reservoir completely mixed. The biodegradability assay took place in a laboratory with a controlled temperature of 20°C. During 28 days, the COD, TSS, total Cr, dissolved Cr and dissolved Cr (VI) were measured in the contents of each reservoir. These parameters were determined according to the methodologies described above.

Inhibition of the Peptone Biodegradation (Respirometric Assay): A respirometric assay was done to assess the biodegradability of the composite wastewater and to assess its potential toxic effect in the biodegradation of an easily biodegradable substrate. The easily biodegradable organic substrate was the peptone from bacteria digests (Bacto-peptone from Difco). This assay was performed according to the “Sapromat” method [2]. Three experimental respirometers (Hach) were prepared as follows:

- a) **Respirometer S** – containing 160 mL of the composite sample of the wastewater, 660 µL of four micro-nutrient solutions and 3.3 mL of deionised water. The main aim of this assay was to establish the curve of the biological oxygen consumption (BOD) for the composite sample;

- b) **Respirometer *P*** – containing 3.3 mL of a peptone solution ( $10 \text{ g.L}^{-1}$ ), 159 mL of deionised water, 1 mL of the sludge from the composite wastewater and 660  $\mu\text{L}$  of four micro-nutrient solutions. This assay allowed to establish the curve of the BOD for peptone solution;
- c) **Respirometer *S+P exp*** – containing 3.3 mL of the peptone solution, 160 mL of the composite sample and 660  $\mu\text{L}$  of four micro-nutrient solutions. The main aim of this assay was to establish the curve of the BOD for the peptone solution in the presence of the wastewater composite sample.

The incubation of the respirometers was done in a dark chamber with a constant temperature of  $20^\circ\text{C}$ . During the assay, multiple measures of the BOD were done. All BOD curves were then determined, based on the method of the least squares. The BOD curves obtained for the composite sample (*S*) and for the peptone (*P*) allowed to calculate the theoretical curve for peptone in the presence of the composite sample (*S+P th*). The comparison between the curves *S+P exp* and *S+P th* allowed to determine the effect of the composite sample on the biological degradation of the peptone. This effect was calculated based on the ratio of the areas below both curves for the last 24 hours of assay.

## Results and Discussion

### Field determinations

Fig. 1 shows the variation of the temperature, pH, conductivity, turbidity and estimated flow, during the sampling period of the nine fractions of the mixed wastewater.

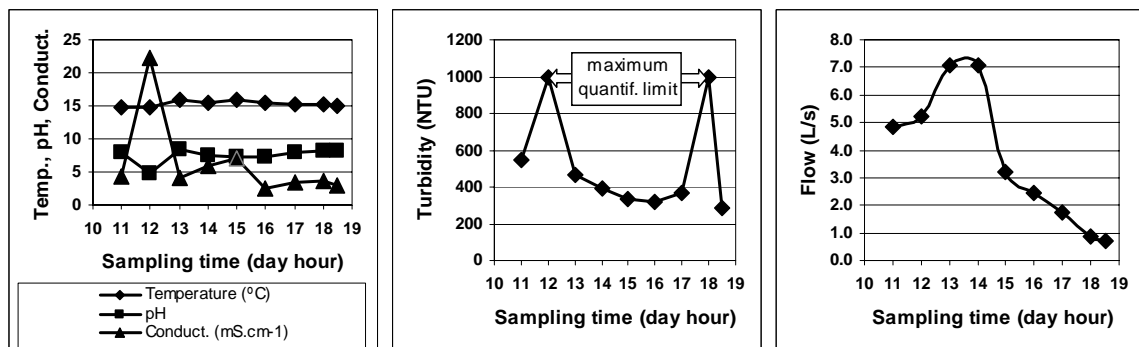


Figure 1: Variation of temperature, pH, conductivity, turbidity and estimated flow along the sampling period.

It was observed an increase of the wastewater flow between 11:00 and 14:30. During this period, it was detected a discharge of wastewaters characterized by blue color at 12:00 and 14:00. The fraction collected at 12:00 was characterized by a low pH value (4.7) and high values of conductivity ( $22.3 \text{ mS.cm}^{-1}$ ) and turbidity ( $>999 \text{ NTU}$ ). This fraction has presented well-developed flocs with a high settling velocity and a high chemical activity. After 1 to 2 min of retention in the glass bottle, the flocs were settled and the color had changed for brown. The fraction collected at 14:00 has also shown a slightly increase of the conductivity and a decrease of pH. Nevertheless, this fraction was not so different from the background wastewater as it was the 12:00 fraction. This fraction had no flocs and no change in the blue color was noticed. From the set of the other fractions collected, it has also to be referred the 18:00 fraction. This was characterized by a brownish color, a high value of turbidity ( $>999 \text{ NTU}$ ), an intensive odor of

ammonia and a high amount of straws in suspension. These characteristics were related with the discharge of wastewaters coming from sheep breeding installations.

### Composite Sample Characterization

The results obtained in the chemical characterization of the composite sample of the wastewater are shown in Table I. The chemical characterization of the supernatant of the composite sample, obtained after the third level of the coagulation-flocculation assay, is also shown in this Table. These results will be discussed later on in this paper.

**Table I. Results of Composite Sample Characterization, before and after the coagulation-flocculation assay. ‘Total’ stands for dissolved plus suspended. n. a. – not applicable; i. c. – impossible to calculate.**

Parameter (Unit or scale)	Before	After	Removal (%)
pH (Sorensen scale)	7.5	6.39	n. a.
Conductivity (mS.cm <sup>-1</sup> )	6.33	3.02	n. a.
Turbidity (NTU)	782	39	95.0
Alkalinity (mg CaCO <sub>3</sub> .L <sup>-1</sup> )	276	153	44.6
Chemical Oxygen Demand (COD) (mg O <sub>2</sub> .L <sup>-1</sup> )	873	240	72.5
BOD <sub>5</sub> (20) (mg O <sub>2</sub> .L <sup>-1</sup> )	407	185	54.5
Color (Hazen)	67	7	89.6
TSS (mg.L <sup>-1</sup> )	456	55	87.9
DOC (mg.L <sup>-1</sup> )	120	71	40.8
Dissolved Cr (mg.L <sup>-1</sup> )	1.2	0.04	96.7
Dissolved Cr (VI) (mg.L <sup>-1</sup> )	<0.1	<0.1	i. c.
Dissolved Zn (mg.L <sup>-1</sup> )	0.14	<0.005	>96.4
Dissolved Cu (mg.L <sup>-1</sup> )	<0.01	<0.01	i. c.
Dissolved Al (mg.L <sup>-1</sup> )	<0.1	<0.1	i. c.
Total Cr (mg.L <sup>-1</sup> )	34.0	0.47	98.6
Total Cr (VI) (mg.L <sup>-1</sup> )	<0.1	<0.1	i. c.
Total Zn (mg.L <sup>-1</sup> )	0.37	0.21	43.2
Total Cu (mg.L <sup>-1</sup> )	0.02	<0.01	>50.0
Total Al (mg.L <sup>-1</sup> )	11.2	0.53	95.3
Kjeldahl Nitrogen (mg N.L <sup>-1</sup> ) (a)	41.4	23.8	42.5
Nitrate (mg N.L <sup>-1</sup> ) (b)	4.1	0.02	99.5
Nitrite (mg N.L <sup>-1</sup> ) (c)	4.3	<0.01	>99.8
Total Nitrogen (mg N.L <sup>-1</sup> ) (a+b+c)	49.8	23.8	52.2
Total Phosphorus (mg P.L <sup>-1</sup> )	0.6	0.04	93.3

In this set of results, it is important to stress the high concentrations of alkalinity, COD, BOD<sub>5</sub>, TSS, nitrates, nitrites and total Cr. The comparison of these concentrations, except the total Cr, with the average values usually observed in domestic wastewaters [8, 9] allows concluding that the composite sample has shown characteristics similar to a heavy concentrated domestic wastewater. In what concerns the total Cr, the concentration determined was significantly higher than the values usually obtained in domestic wastewaters. This is possible due to the influence of the tannery wastewaters discharged into the channel in which the composite sample was collected. The Cr was found to be mainly in the suspended fraction (96.5%) and the main oxidation form was the trivalent state. Although this oxidation state is less toxic than the hexavalent state, its

concentration in the dissolved fraction ( $1.2 \text{ mg.L}^{-1}$ ) was significantly high to promote a certain toxicity level in biological populations. For example, according to Munkittrick e Power [10], the  $EC_{50}$  (24 h) of Cr (III) for the microcrustacean *Daphnia magna* is of  $0.71 \text{ mg.L}^{-1}$ . These authors stress the high sensitivity of this organism to chromium.

The Cr (VI) was below the quantification limit ( $0.1 \text{ mg.L}^{-1}$ ) of the analytical method used. Therefore, it is not foreseen that this level of Cr (VI) could originate any significant toxicity level.

### Biodegradability Assay

The evolutions of the DOC and TSS in the reservoirs B1, B2 and B3 of the intrinsic biodegradability assay are shown in Fig. 2.

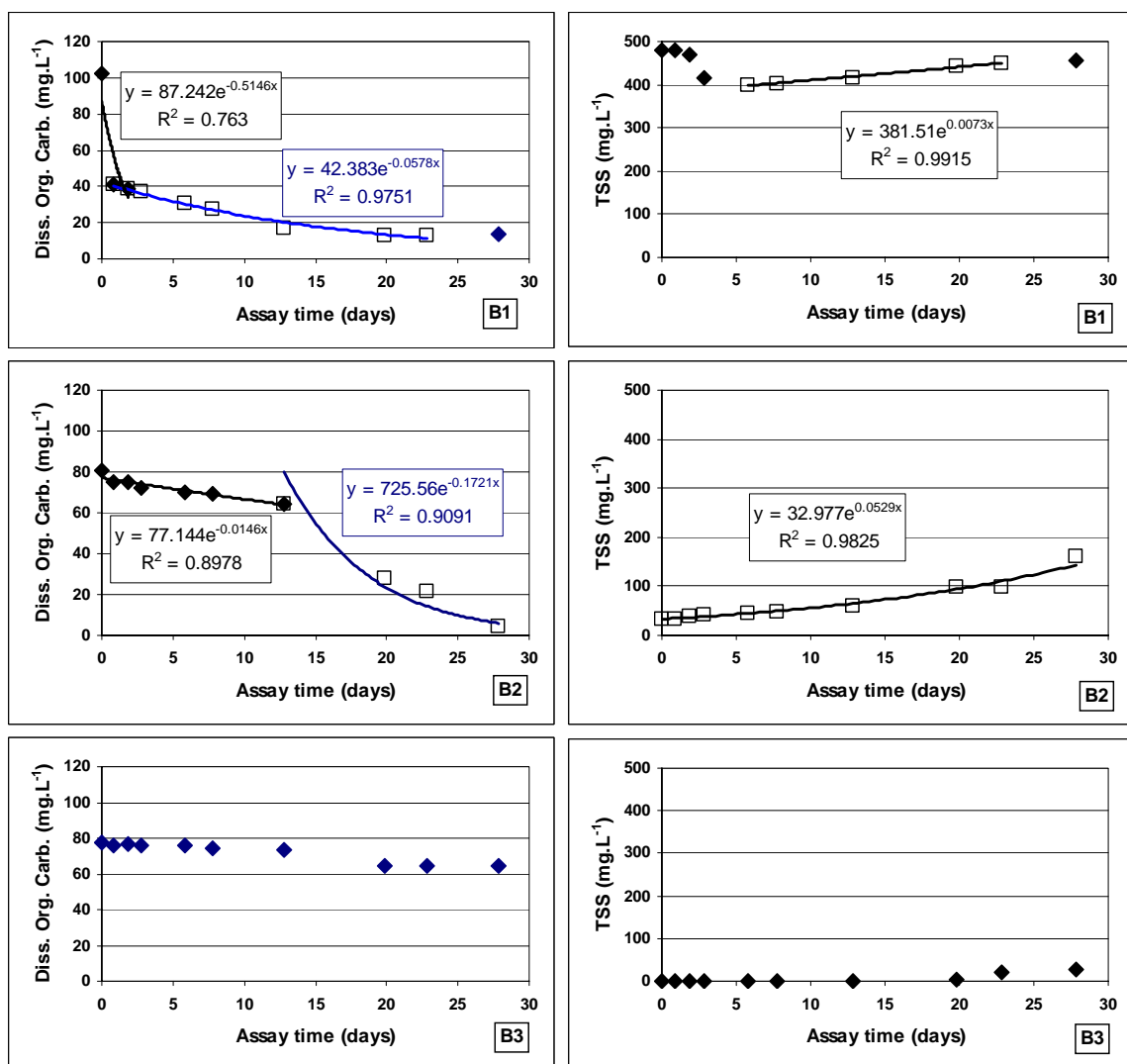


Figure 2: Variation of DOC and TSS along the biodegradability assay.

The TSS has shown an evolution in two different phases in the reservoir B1. For the first days of the assay, it was observed a decrease in this parameter, possibly due to the dissolution of some

inorganic suspended solids induced by the modification of the redox conditions. The second phase of the TSS evolution was characterized by an increase of this parameter, probably related with the increase of the biological populations. This increase followed a first-order kinetic with a constant of  $0.0073 \text{ d}^{-1}$  ( $r^2=0.9915$ ). In this same reservoir, the removal of DOC followed a two-phase first-order kinetic. In the first 24 h of the assay, it was determined a percentage removal higher than 60% of the initial concentration ( $k=0.5146 \text{ d}^{-1}$ ,  $r^2 =0.7630$ ). The second phase was comprised between the day 1 and the day 23 of the assay with a much lower constant rate ( $k=0.0578 \text{ d}^{-1}$ ,  $r^2 =0.9751$ ). This type of carbon oxidation makes possible to foresee the presence of different organic substrates in the composite wastewater, which are characterized by different rates of biodegradability. The biological oxidation takes place first over the easiest biodegradable substrates and then over the more difficult biodegradable substances after the exhaustion of the former.

In the reservoir B2, the evolution of the TSS followed a first order kinetic all over the time of the assay ( $k=0.0529 \text{ d}^{-1}$ ,  $r^2 =0.9825$ ). The evolution observed was typical of the microbiological growth under batch conditions in the presence of an easily biodegradable substrate. The removal of the DOC in this reservoir was also characterized by a two-phase evolution, which was represented by two first order kinetics. Nevertheless, in this case, the higher constant rate was determined in the second phase of the DOC removal. The delay observed in the oxidation of the DOC can be explained by the adaptation of the microbial populations to the sodium acetate substrate. Both results of TSS and DOC have proved the existence of an active microbial population in the sludge of the composite wastewater.

In the reservoir B3, neither the TSS nor the DOC have shown a significant modification of their initial concentrations. The slight decrease in the DOC and the slight increase in the TSS can be attributed to the development of microbial populations due to the contamination induced by the non-sterilized compressed air pumped into the sodium acetate solution. The conversion of the DOC evolution in the reservoir B1 to the removal percentage allowed classifying the composite sample as biodegradable, according to the OECD principle. In fact, the removal percentage was higher than 70% ten days after the removal percentage of 10% has been registered.

#### Inhibition of Peptone Biodegradation (Respirometric Assay)

Fig. 3 shows the BOD evolution in the three respirometers prepared for this assay. The points were obtained experimentally and the curves were defined by the method of the least squares. The theoretical curve of the peptone in the presence of the composite sample (*S+P th*) is also shown. The points of this curve were obtained by the sum of the experimental points determined for the peptone (*P*) and for the composite sample (*S*).

In the composite sample (*S*), it was observed a high oxygen consumption rate during the first 24 h of the assay. This is compatible with the high DOC oxidation observed in the intrinsic biodegradability assay. The results obtained in the respirometric assay have demonstrated a slightly degree of toxicity of the composite sample over the biological degradation of the peptone. This effect was detected because the experimental BOD values obtained for the peptone degradation in the presence of the wastewater (*S+P exp*) were lower than the expected theoretical values for this curve (*S+P th*). The estimated reduction of the  $\text{BOD}_5$  was of 16.6% and the estimated inhibition of the ultimate BOD was of 16.7%. As it was foreseen in the intrinsic



biodegradability assay, the composite sample has shown toxicity over the microbial populations involved in the degradation of soluble organic substrates, although the inhibition levels determined were low.

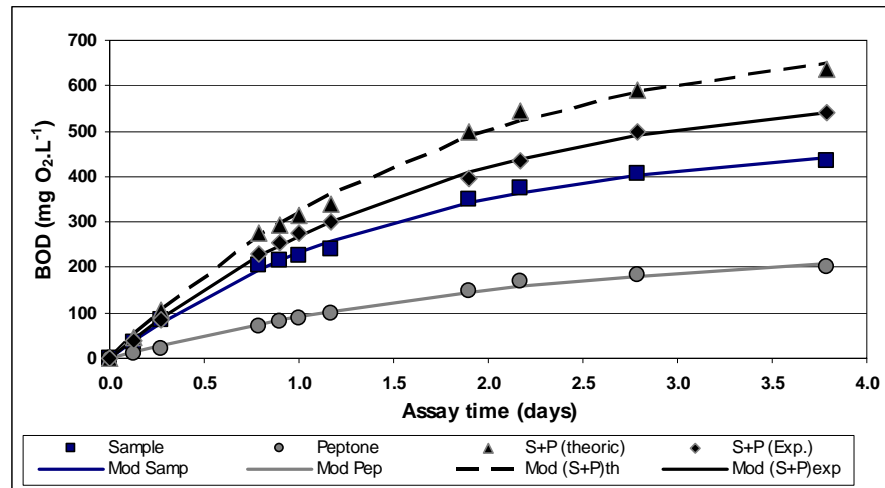


Figure 3: BOD evolution in the respirometric assay.

### Coagulation-Flocculation Assay

In Fig. 4 it is shown the removal percentages of the DOC, true color and total Cr as a function of the incremental dosages of alum to the composite sample, for its natural pH (7.5) and for the iso-electric point of alum (pH=6.0).

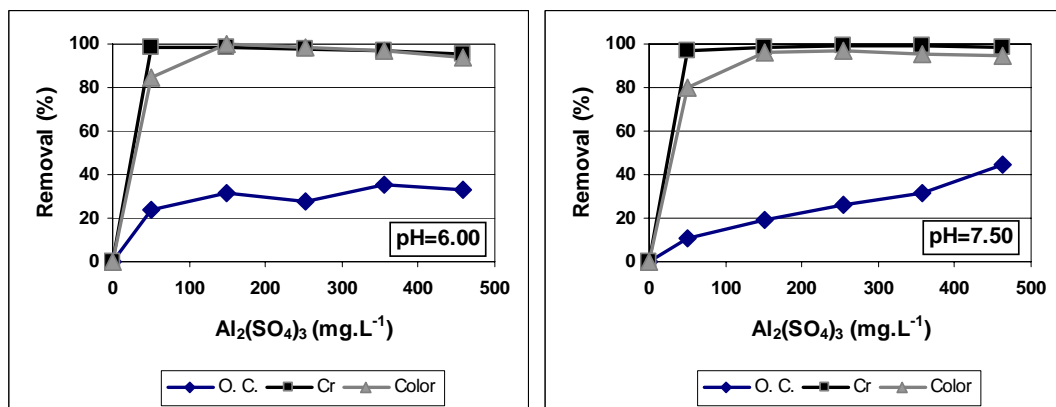


Figure 4: Coagulation-flocculation assay. Dissolved Organic Carbon (O.C.), total Cr and true color removal efficiencies for different initial pH, as a function of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosages (incremental additions).

The removal percentages of Cr were considerably high for all dosages of alum and for both initial pH values. The removal percentages have varied between 97.1% and 99.4% for the initial pH of 7.5, and between 95.6% and 98.7% for the initial pH of 6.0. The highest removal percentages of color were obtained for the dosages of alum higher than 150 mg.L<sup>-1</sup>, for both initial pH values.

Only the DOC has shown a different behavior for both initial pH values and removal percentages much lower than those determined for Cr and color. For the initial pH value of 6.0, all dosages of alum have induced similar removal percentages of DOC, which have varied between 23.8% and 35.2%. For the pH value of 7.5, the incremental dosages of alum have promoted a linear removal of DOC. The highest removal percentage was found at the alum dosage of 459 mg.L<sup>-1</sup> (44.9%). At this level of the coagulation-flocculation assay, the optimum interval for the Cr and color removal was defined to be from 150 up to 250 mg.L<sup>-1</sup>. In the second level of the coagulation-flocculation assay, the following dosages of alum were tested, for the natural pH of the composite wastewater (7.5): 0, 160, 190, 220 and 250 mg.L<sup>-1</sup>.

Fig. 5 shows the removal percentages of DOC, total Cr, true color and total Al determined in the supernatants of the second level of the coagulation-flocculation assay.

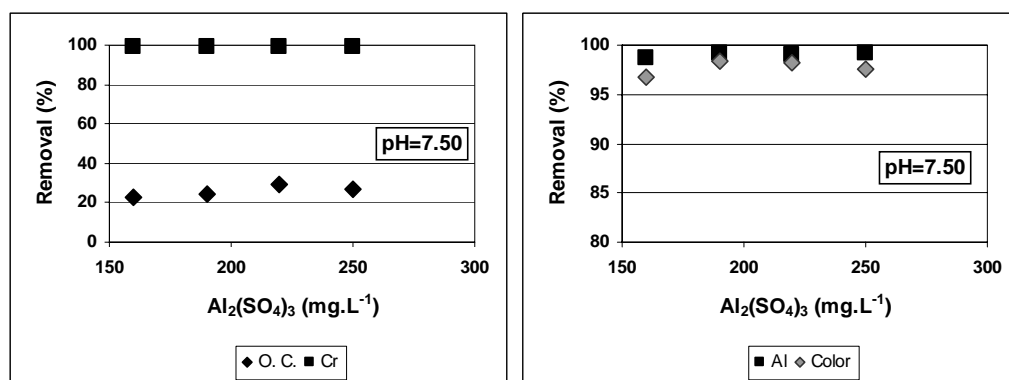


Figure 5: Coagulation-flocculation assay. Dissolved Organic Carbon (O.C.), total Cr, total Al and true color removal efficiencies for fixed initial pH=7.5, as function of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosage (independent tests).

The removal percentages of total Cr, total Al and true color were high for all dosages of alum. The lowest removal percentage for this set of chemical parameters was obtained for true color and for the alum dosage of 160 mg.L<sup>-1</sup>. Even for this dosage, the removal percentage of color was of about 96.7%. As it was found in the first level of the coagulation-flocculation assay, the removal percentages of DOC were the lowest ones of the four chemical parameters analyzed in the supernatants. Nevertheless, this parameter was not considered as a major parameter in the definition of the optimum dosage of alum. In the second level of the coagulation-flocculation assay, the addition of 200 mg.L<sup>-1</sup> of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was considered to be the optimum dosage of alum for the removal of total Cr and true color.

Fig. 6 shows the removal of DOC, total Cr, true color and total Al for different initial pH values of the composite wastewater and for the alum dosage of 200 mg.L<sup>-1</sup>. The lowest removal percentages of the total Cr, total Al and color were obtained for the initial pH of 5.3. For all the other initial pH values, the removal percentages for these parameters were high and quite similar to each other. The removal of DOC has presented the lowest removal percentages from all the four chemical parameters analyzed. These percentages were similar to those ones determined in the previous levels of the coagulation-flocculation assay (between 30 and 40%).

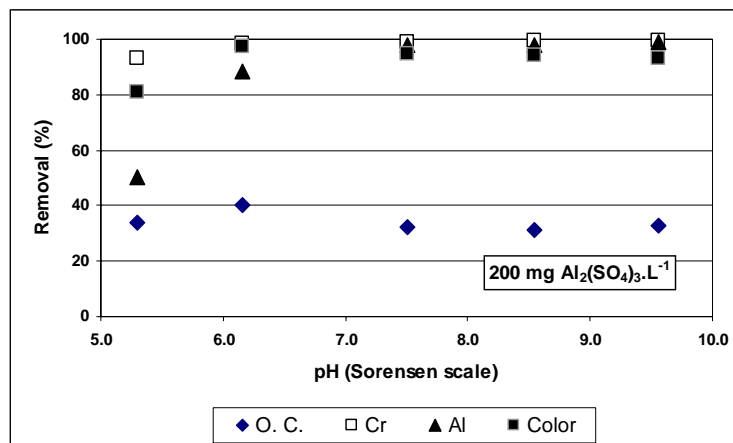


Figure 6: Coagulation-flocculation assay. Dissolved Organic Carbon (O.C.), total Cr, total Al and true color removal efficiencies for fixed  $\text{Al}_2(\text{SO}_4)_3$  concentration =  $200 \text{ mg.L}^{-1}$ , as function of initial pH (independent tests).

In order to reduce the amount of reagents used in the coagulation-flocculation process, it was defined that the most adequate pH to which the composite sample should be tested in the last level of the coagulation-flocculation assay would be its natural pH value. Therefore, the composite sample was finally submitted to an enlarged coagulation-flocculation assay with the dosage of  $200 \text{ mg.L}^{-1}$  of alum at the pH of 7.5. The chemical results obtained in the supernatant of this last assay were shown in Table I. The comparison of these chemical results with the average values defined in the literature for domestic wastewaters [8, 9] allowed to conclude that the effluent resulting from this assay could be classified as a domestic wastewater with low to medium load. From the set of parameters with the highest load contribution, it is possible to stress the  $\text{BOD}_5$ , total nitrogen and alkalinity.  $\text{BOD}_5$  and total nitrogen have shown low to medium concentrations, and alkalinity has shown a heavy concentration. In the crude composite sample, the ratio  $\text{BOD}_5/\text{COD}$  was of 0.47. After the coagulation-flocculation process, the supernatant has shown a ratio  $\text{BOD}_5/\text{COD}$  of 0.77. The coagulation-flocculation process has also promoted a decrease in the total phosphorus concentration. Therefore, the assessment of the phosphorus needed for the biological treatment and its availability in the coagulation-flocculation effluent has to be made in order to avoid that it can become a limiting factor for the biological activity.

## Conclusions

The monitoring plan allowed to confirm the existence of industrial wastewaters discharges on the selected sewer channel. These discharges were responsible for the increase of the flows and for the variability of the wastewater colors along the day. The presence of Cr in a concentration much higher than the average values for a domestic wastewater was also attributed to those discharges.

The comparison of the results obtained in the crude and in filtered composite sample allowed to conclude that the major part of Cr was present in the suspended fraction, at the trivalent oxidation state.

In what concerns the biodegradability, the 28-days assay has shown that the composite sample had the same behavior as a biodegradable wastewater. The microbial community of the

wastewater was metabolically active and a significant fraction of organic matter underwent degradation in the first 24 h of the assay. Anyway, it must be referred that the respirometric assay revealed the existence of some toxicity, shown by a little inhibition of peptone biodegradation.

The coagulation-flocculation assay confirmed the easiness of Cr removal by this method, as it was foreseen after the chemical characterization of the crude wastewater. The addition of 200 mg.L<sup>-1</sup> of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> at a pH of 7.5 resulted in removal rates higher than 95% for Cr (dissolved and suspended) and close to 90% for color. It was proved that the pH correction to 6.0 is useless.

Other parameters whose concentrations were significantly reduced with the coagulation-flocculation treatment were TSS, suspended Al and total phosphorus. This efficiency in phosphorus removal may affect adversely the biological treatment of this wastewater. So, it must be evaluated if the remaining phosphorus in the supernatant liquid is enough to assure an adequate level of biodegradability. Anyway, the ratio BOD<sub>5</sub>(20)/COD increased after this treatment. This means that the success of a biological treatment can probably be enhanced by a previous coagulation-flocculation treatment of the wastewater.

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