PROJECT:
Ozonolysis and Photocatalytic Oxidation Treatment of Effluents with Organic Contamination
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Project:

Ozonolysis and Photocatalytic Oxidation Treatment of Effluents with Organic Contamination

Abstract:

The work carried out was aimed at assisting oxidative processes, for the treatment of water effluents with organic substances contamination. The methodology employed was consistent with a primary oxidation by the action of ozone (ozonolysis), followed by a photocatalytic oxidation, by the action of photocatalysts activated by ultraviolet radiation.

Executive Summary:

Considering that the use of solar energy with photoactive catalysts in combination with oxygen in the air, could generate an oxidation process in fluid systems with a load of organic substances, it was decided to approach this issue, complementing the oxidation with a very proactive agent such as ozone. To check the efficacy of the proposal, an experimental pilot plant was designed to test and evaluate the process under scale conditions, providing as an advance the specificity of the photoactive catalysts by ultraviolet light, in conjunction with an ozone producer as a coadjuvant of the process.

The equipment used was made by coupling an ozone generator to an existing laboratory equipment used to test photoactive catalysts by ultraviolet light action.

The technological development was verified through a simulation in the prototype with a river effluent with high organic pollution, testing the progress of the process through Chemical Oxygen Demand (COD) measurements.

The results obtained showed a high degradation rate of organic matter, above 70%, with a 3rd order reaction kinetics. These values give us an optimistic expectation when it comes to choose a viable treatment for this type of effluent.

Ozonolysis and Photocatalytic Oxidation Treatment of Effluents with Organic Contamination

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THEORETICAL FRAMEWORK

a) About the processes involved: HETEROGENEOUS PHOTOCATALYSIS

Data extracted from: Eliminación de Contaminantes por Fotocatálisis Heterogénea - Collective text elaborated by CYTED Network VIII-G, Edited by Miguel A. Blesa (for CYTED - and CNEA) - ISBN: 987-43-3809-1 Ed. 2001.

HETEROGENEOUS PHOTOCATALYSIS

b) About: Ozonolysis

Data extracted from: CINÉTICA Y MECANISMOS DE LAS REACCIONES DE OZONÓLISIS... - Thesis submitted to the Faculty of Exact and Natural Sciences, National University of Asunción - Paraguay- Author: ELIZABETH GAONA COLMÁN - Ed- June 2013.

REFERENTIAL MOTIVATION:

The problems caused by organic waste from urban or industrial effluents, discharged into water sources such as rivers, streams or lakes, which compromise the sustainability of obtaining drinking water in the future, and the background of institutional work with significant contributions in the area of oxidation treatment by heterogeneous cyanide photocatalysis, motivated the team to contribute advances in a technological solution to the treatment of effluents where oxidation-reduction processes are needed, taking advantage of the experience in the use of photoactive catalysts.

PROBLEM SITUATION:

To provide technological solutions by using ozonolysis and complementary heterogeneous photocatalysis in the treatment of effluents with high organic pollution loads.

WORKING HYPOTHESIS:

Urban and industrial effluents with organic pollutants can be treated by ozonolysis oxidation processes and heterogeneous catalysis of oxygen in the air, using technological equipment with advances in the specificity of some photoactive materials.

DEVELOPMENT OF THE WORK:

Materials and methodology:

Design of the redox process to be achieved

The process was designed considering:

Removal of pollutants by ozonolysis: by oxidative mineralisation of organic matter, by the action of atomic oxygen generated by the decomposition of ozone

$$O_3 \rightleftharpoons O^o + O_2$$

Ozone **atomic oxygen** **molecular oxygen**

Removal of pollutants by heterogeneous photocatalysis: by oxidative mineralisation of organic matter

Choice of inducing oxidant: As the generation of ozone by corona effect is done from air (composition approx. 21% molecular oxygen and 79% nitrogen) and the yield of the ozone formation reaction is very low (60% at CNPT).

Air (21% O2 +79% N2) + corona effect ⟶ (12,6 % O3 + 8,4 % O2 + 79% N2)

The availability of this energetic oxidant is scarce, therefore the application of a method by which the oxygen in the air can be activated by formation into atomic oxygen or free radicals would assist the oxidation of organic matter.

Choice of the activation reaction of oxygen from air: Knowing that heterogeneous photocatalysis using broadband semiconducting metal oxides, such as TiO_2, are able to **adsorb** gases on their surface and go to an excited state by **absorption** of radiant energy (visible or UV) and transfer this energy in the interfacial region to the **adsorbed** gas, such as oxygen in the air, it can be inferred that oxygen can go to an excited radical state or transform into atomic oxygen, with the potential to oxidise organic compounds. It would be possible to infer that oxygen can go to an excited radical state or transform into atomic oxygen, with the potential to oxidise organic compounds.

Possible ozone-forming reaction:

$$3O_2 \rightleftharpoons 2O_3$$

Oxygen *Ozone*

Possible photocatalytic activation reactions:

$$TiO_2 + h\nu \rightleftharpoons TiO_2^*$$

Titanium dioxide — Photon Energy — Activated Titanium dioxide

$$O_2 + TiO_2^* \rightleftharpoons 2\,O^o + TiO_2$$

Oxygen from the air — Titanium dioxide — Activated atomic Oxygen — Titanium dioxide

Possible oxidation reactions of organic substances:

$$O_3 \rightleftharpoons O^o + O_2$$ ***Ozone decomposition***

Ozone **atomic oxygen** **molecular oxygen**

$$Organic\ Matter + O^o \longrightarrow Oxidised\ (mineralised)\ Organic\ Matter + n\,e^-$$

Atomic oxygen

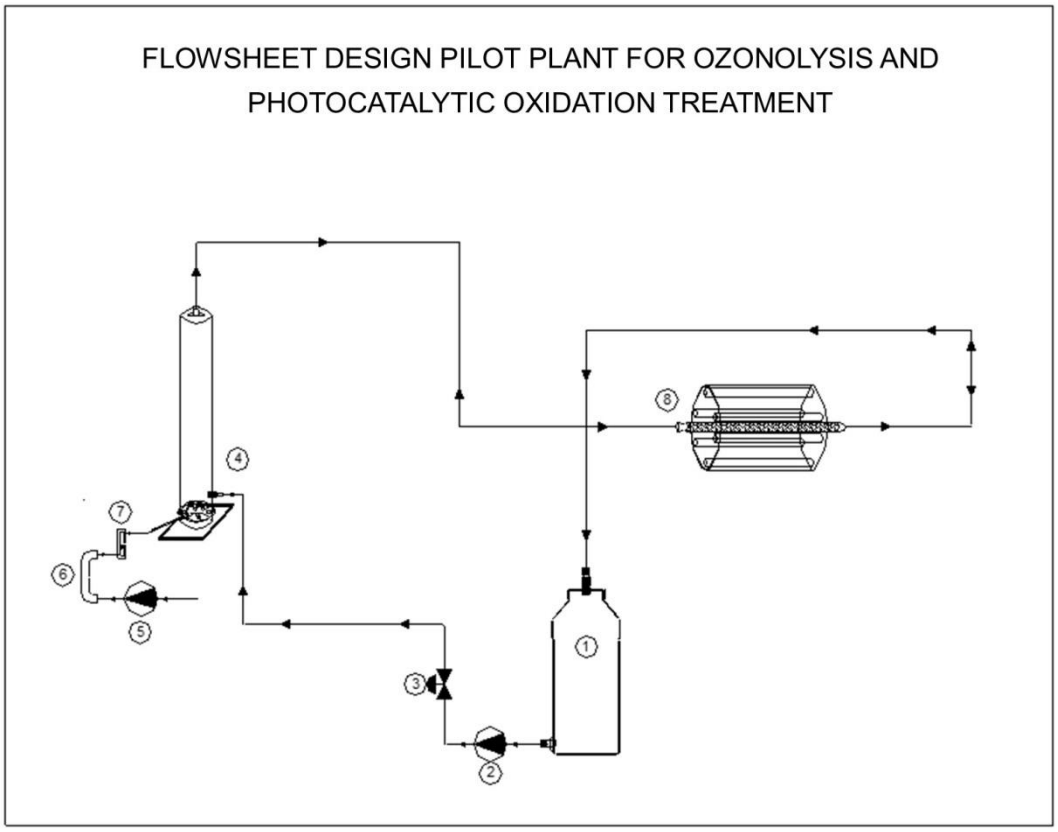
<u>Evaluation of organic effluents that cover the expectations of the ozonolysis and photocatalytic oxidation process</u>

Some of the effluents with high loads of organic substances that meet the conditions to be treated by oxidative mineralisation include:

- Urban sewage and storm sewer effluents.
- Industrial effluents from food-related industries.
- Industrial effluents from washing or cleaning processes.
- Water from rivers and/or streams receiving urban and industrial waste.
- Water from stagnant artificial lagoons.
- Water from piped rivers and/or streamsEfluentes urbanos cloacales y pluviales de alcantarillado.

Design of the pilot prototype for simulation

In order to test the treatment of the proposed process for the remediation of water contaminated with organic substances, an experimental prototype was designed, which could incorporate, in addition to the process equipment, a treatment monitoring methodology to follow its performance.



References:

(1) Pumping well where the liquid with organic matter load is recirculated

(2) Fluid circulation pump

(3) Flow control valve

(4) Ozonation chamber, with microporous diffusers

(5) Air compressor

(6) Ozone generator

(7) Ozone flowmeter

(8) Photoreactor with UV lamps and TiO_2 columns supported on borosilicate glass

Development and construction

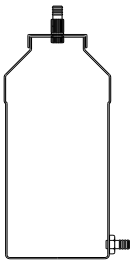
The development and construction of the experimental pilot plant involved a series of activities such as:

- - Choice and economic evaluation of materials for the construction of the pilot plant
- - Development and construction of the device in accordance with the design conditions
- - Stability, tightness and hydraulic circulation tests
- - Calibration of measuring instruments

Activities:

A standard 220v washing machine discharge pump with a flow rate of 1200 dm3 /hour (20 dm3/minute) for a static head of 1m was used for fluid delivery.

Pumping Well



For the construction of the pumping well, the feasibility of building it with PVC sanitary elements was evaluated, due to its cost and/or performance, or using a shaped polypropylene container from the ENPA line (a company that manufactures and sells this type of container). In its sizing, it was considered that with a liquid circulation pump with a maximum flow rate of 20 dm3/minute, working at an average flow rate of 10 dm3/minute and considering that the residence time of the system was 1 minute, the pumping well should have a volume of 10 dm3. A standard 220v washing machine discharge pump with a flow rate of 1200 dm3 /hour (20 dm3/minute) for a static head of 1m was used to pump the fluids.

With this required value, a polypropylene container supplied by ENPA was used as a distilled water reservoir for laboratory use, with a ½" threaded tap outlet, which was adapted to the needs of the pumping well for this pilot prototype.

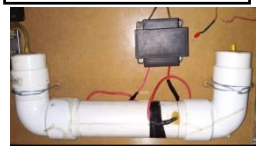
A standard 220v washing machine discharge pump with a flow rate of 1200 dm3 /hour (20 dm3/minute) for a static head of 1m was used for fluid delivery, and a 1/2" brass ball valve was incorporated between the pump and the ozonation chamber in order to regulate the flow rate of the fluid.

Pump and Valve

The flow rate was measured during operation, taking the loading time of a 250 cm3 test tube with water, in the recirculation by return to the pumping well, corresponding to a flow rate of 7.35 dm3/minute.

To provide the equipment with a source of ozone, a corona generator was built, produced by a high voltage source from a FlyBack, coupled with a mini-compressor to inject the ozone produced into the ozonolysis oxidation chamber.

O3 generator



The ozone generator supply flow rate was measured with a ball-type floatameter flow meter, which in operation worked at a rate of 4.5 dm3/minute.

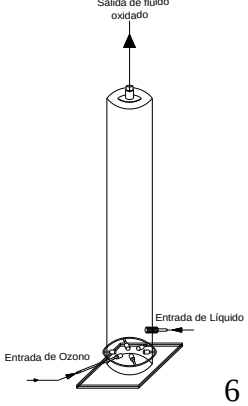
Compressor and Flow Meter

For the ozonolysis oxidation chamber, a polymethacrylate (transparent acrylic) tube 4 mm thick and 100 mm in diameter was used. The head was sized by estimating a fluid flow rate of 7 dm3/minute and a residence time of 1 minute to fully load the tube.

Calculating a height of:

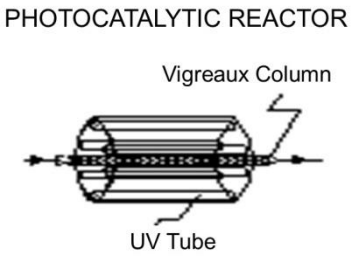
$H = 4Vol/\pi.Ø^2 = 891$ mm

Ozonolysis chamber



As air diffusers, the equipment was provided with 6 sintered glass fish tank micro-diffusers to achieve a higher injection of micro-bubbles.

The heterogeneous photocatalysis reactor was designed as a collector reactor of ultraviolet radiation by direct radial incidence and reflection, generated by low-pressure gas tubes capable of emitting Uv radiation in a radiation spectrum with wavelengths between 380 nm and 440 nm. The tubes, which are 600 mm long, have a power of 18 W each.

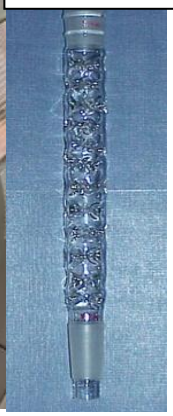


They were arranged with their capacitors and inductive reactors radially every 60º, using a 200 mm diameter PVC tube, internally coated with reflective aluminium foil.

The collector that will conduct the photoactive catalyst together with the effluent, was arranged centrally on the axis of the PVC pipe with support brackets and as the characteristics required for this collector had to meet the following conditions: a) Transparent to UV light; b) High contact surface; c) High radiation collecting surface; d) Chemical and radiation resistance.

One element that met these conditions was the use of VIGREAUX columns used for fractional distillation in the laboratory, made of high-strength borosilicate glass with a large contact surface.

Vigreaux Column



The photocatalysis reactor was formed by using two vigreaux columns with ground-glass coupling ports, fixed at their ends. The contact surface of both columns was calculated by geometric measurements considering the cones, their diameters and generatrices, with a total surface area of 59690 mm^2 (0.0597 m^2) and their volume measured with a test tube with water was 260 cm3.

These were internally coated with a suspension of TiO_2 (rich in the anatase variety) in sodium metasilicate and subjected to a heat treatment of 250°C for 30 minutes to effect the setting of the metasilicate, forming a glassy support surface for the photoactive semiconductor.

All the elements that make up this installation were assembled in the laboratory using rigid and flexible PVC connectors, sealed with butyl rubber adhesives, teflon tapes and clamps on the dowelled mixed joints. The mounting bases of the photoreactor and the pumping well were made of wire mesh and rods conveniently welded to support the elements that were coupled and the electrical installation conveniently insulated and protected with a differential circuit breaker.

Circulation and water tightness tests were determined empirically. The internal volume of the equipment was measured to have the parameter of the total circulation volume, calculated by difference of heights at full pumping well with 10 dm3 of water at fully closed valve and then at open valve in steady state circulation, giving a volume of 7.35 dm3.

Note: TiO_2 catalyst

The TiO_2 used corresponds to a Degussa product called P-25 with a TiO_2concentration of 99% under the crystalline forms of anatase and rutile (in a ratio of 70:30), non-porous, with a specific surface area of 55±15 m^2 /g and an average particle size of 30 nm.

Evaluation of the proposed processes:

Methodology used in the trial:

To test and see the performance of the process, we proceeded to simulate the treatment with a sample of the effluent from the Reconquista River (local river with high organic pollution loads) and to extract samples in the pumping well at different working times of the equipment.

The extracted samples were tested with a marker parameter that characterises the progress of the process, that is, the COD (chemical oxygen demand) analysis, which expresses the amount of oxygen necessary to oxidise the organic compounds, by quantitative equivalence with another more energetic oxidant such as dichromate ion in an acid medium, catalysed with silver ion and acting on the organic sample for 2 hours at 148ºC.

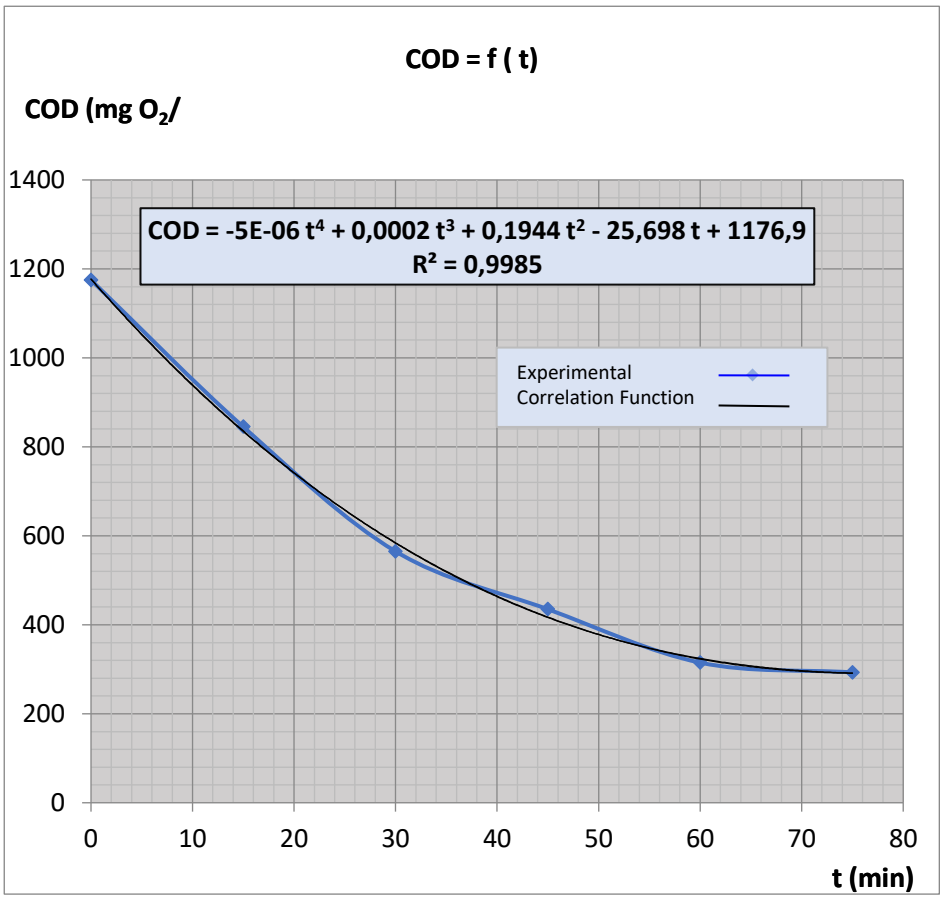
For these tests, COD vials of 500 mg O_2 / dm^3, an automatic temperature digester and a spectrophotometer at λ= 475 nm optimum wavelength of dichromate were used.

Data collection and evaluation of the results obtained:

Operating the equipment with a river effluent with a flow rate of 7.35 dm^3/min and a flow rate of 4.5 dm^3/min of ozone injected into the ozonolysis oxidation chamber and recirculation through the pumping well. Samples were extracted every 15 minutes and subjected to COD analysis, with the following results:

If the COD values of organic matter are plotted as a function of time, the following results are obtained:

Time (min)	COD (mgO_2/ dm^3)
0	1175
15	845
30	565
45	435
60	315
75	293



Since the quadratic correlation coefficient is very close to R2= 1 (R2= 0,9985)

From an analysis of the empirical mathematical expression, it can be seen that it is representative for determining the expression of the reaction kinetics. It follows that the independent term corresponds to the initial COD (COD_0), therefore the general expression would have the following format:

$$\mathbf{COD = -5.10^{-6}\ t^4 + 2.10^{-4}\ t^3 + 0{,}19\ t^2 - 25{,}70\ t + 1177}$$

$$\mathbf{COD = -5.10^{-6}\ t^4 + 2.10^{-4}\ t^3 + 0{,}19\ t^2 - 25{,}70\ t + COD_0}$$

Equation expressing how COD varies as a function of time.

If this expression is derived to give the reaction rate: v= -d(COD)/dt

$$\mathbf{v= -d(COD)/dt= 2.10^{-5}\ t^3 - 6.10^{-4}\ t^2 - 0{,}38\ t + 25{,}70}$$

It can be seen that it is a cubic function, corresponding to a 3rd order kinetic equation, which governs the oxidation reaction of mineralisation of organic matter by ozonolysis, combined with oxidation by heterogeneous photocatalysis. Expression showing the remediation of polluted waters with organic load as a function of time, very useful to develop a process of oxidation of organic matter, evaluate the time and efficiency of the process.

Analysing the percentage of organic matter degradation during the simulation time (75 minutes), a COD decrease of 75.1 % process efficiency is obtained.

Conclusions on the process of oxidation by ozonolysis and photocatalysis in organic effluents

It can be seen that in the pilot experiment, carried out on simulated effluents with organic pollutants, by means of a batch process of ozonolysis combined with heterogeneous photocatalysis with specific ultraviolet light irradiation, the organic matter loads were reduced by oxidation by up to 75% in a period of 75 minutes and it is concluded that the reaction kinetics are viable for the proposed treatment.

The values obtained give rise to encouraging expectations when choosing a feasible treatment for this type of effluent.

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Annexes:

Feasibility assessment of scaling up from pilot plant to industrial plant

From the conclusions it can be seen that the process has defined kinetics for the treatment of industrial effluents proposed with this pilot plant design, i.e. the method is defined for the process parameters that were used. If this process were to be adopted for an industrial plant with similar characteristics to this pilot plant, a dimensional and dynamic scale-up would have to be made to maintain the constancy of the process parameters.

To achieve this leap, the pi or Buckingham Theorem can be applied, that from a set of **dimensional variables that influence the process**, a linearly independent combination of **dimensionless monomials of these variables that govern the process** can be found, whereby the leap in scale can be made taking into account the values that these dimensionless variables take in the pilot experience.

Dimensional analysis:

Variables affecting the process	Dimensions
E (radiant energy)	$M^1 T^{-2}$
Sc (collector area)	L^2
Se (catalyst specific surface area)	$L^2 M^{-1}$
Qc (flow rate)	$L^3 T^{-1}$
Qo (ozone flow rate)	$L^3 T^{-1}$
C (organic load concentration)	$M^1 L^{-3}$
Vc (control volume)	L^3
t (time)	T^1

n= number of variables = 8

r= dimensional range = 3-(-3)= 6

m= number of linearly independent dimensionless π monomials = n-r= 8-6= 2

dimensionless monomials shall have the following format:

$\pi = f (E^a.Sc^b.Se^c.Qc^d.Qo^e.C^f.Vc^g.t^h) = 0$

Forming the dimensional matrix:

	a	b	c	d	e	f	g	h
	E	Sc	Se	Qc	Qo	C	Vc	t
M	1	0	-1	0	0	1	0	0
L	0	2	2	3	3	-3	3	0
T	-2	0	0	-1	-1	0	0	1

The dimensionally homogeneous equations:

$$\begin{cases} a - c + f = 0 \\ 2b + 2c + 3d + 3e - 3f + 3g = 0 \\ -2a - d - e + h = 0 \end{cases}$$

Possible linearly independent solutions:

a	b	c	d	e	f	g	h
1	0	0	0	-1	-1	0	1
0	-1	1	-1	0	1	2	-1

$\pi_1 = E.t / C.Q_a$ Dimensionless photocatalytic and redox process

Calculating each dimensionless monomer with the parameters used in the pilot plant, we obtain:

$\pi_1 = E.t / C.Q_a$

E= (radiant power / Collector area)= 108 W / 0,0597 m^2 = 1809,04 w/m^2

t= 75 min. 60s= 4500 s

C= (1175mg/ dm^3 . 10^{-6} Kg/mg)/ $10^{-3}m^3/dm^3$ = 1,175 kg/m3

Qo= (4,5 dm^3/min. $10^{-3}m^3/dm^3$)/ (60 s/min) = 7,5. 10^{-5} m^3/ s

$$\boldsymbol{\pi_1 = E.t / C.Q_o = 9,24.\ 10^{13}}$$

$\pi_2 = S_e.C.V^2_c / S_c.Q_c.t$

S_e= (55 m^2/g) /10^{-3}kg/g = 55000 m^2/kg

C= (1175mg/ dm^3 . 10^{-6} Kg/mg)/ $10^{-3}m^3/dm^3$ = 1,175 kg/m3

V_c= 7,35 dm^3 = 7,35. 10^{-3} m^3

S_c= 0,0597 m^2

Q_c=7,35 dm^3/ min=1,225.10^{-4} m^3/s

t= 4500 s

$\pi_2 = S_e.C.V^2_c / S_c.Q_c.tc$

π_2 = 55000 m^2/kg . 1,175 kg/m^3 . 5,40. 10^{-5} m^6 / 0,0597 m^2 . 1,225.10^{-4} m^3/s . 4500 s = 106,04

$$\pi_2 = S_e.C.V^2_c / S_c.Q_c.tc = 106,04$$

Conclusion of the leap in scale:

The values adopted by the three dimensionless monomials, by linking the variables, which experimentally in pilot plant, complied with the proposed treatment, will be used as a basis for sizing a plant at industrial level, which complies with the same scale performance, maintaining the 3rd order kinetics found for the oxidation treatment.