

New process of catalytic oxidation of organic pollutants from water in soft conditions in presence of sulfonated cobalt phthalocyanines supported on activated carbon

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ABSTRACT

In the field of water treatment, catalytic oxidation has been developed around the Fenton reagent (hydrogen peroxide coupled with ferrous iron salt) but this oxidative system has drawbacks. In effect, this system only works in acidic pH. In addition, the Fenton reagent used at room temperature generally offers a partial oxidation of pollutants and is not accompanied by a significant removal of total organic carbon.

The WPO process (Wet Peroxide Oxidation) that uses the catalytic activation of peroxide hydrogen at high temperature accelerates the kinetic of degradation reactions. But this method poses problems of cost due to the use of high temperatures reaching 140°C.

In clean water, the oxygen is found mainly in the processes WAO (Wet Air Oxidation) which generates a huge investment because of high temperature and pressure (250 to 320 °C - 50 to 150 bar). This represents a major drawback in the industry.

The catalytic oxidation reactions in the presence of métallophthalocyanines described in the literature involve KHSO_5 or H_2O_2 which presents a disadvantage in a field of water depollution. Indeed, for the oxidation of trichlorophenol, adding an organic co-solvent is necessary: The reactions present the inconvenient to be conducted in a mixture acetonitrile / buffer (1 / 3, V / V) and not in an aqueous medium. Therefore, it appears that finding a method for oxidation catalysis involving transition metals and using oxygen under mild conditions of temperature and pressure is a particularly important challenge.

During this work, we showed that the synthesis of a catalyst: phthalocyanine cobalt sulfonated fixed on activated carbon is a simple process that takes place at room temperature. The action of these catalysts has been studied in the oxidation of hexanoic acid by oxygen in normal conditions (20 °C, 1 atm.).

We studied the reaction using two catalysts supported on activated carbon as grains, containing respectively 12 and 50 $\mu\text{mol} / \text{g}$ cobalt. We showed that:

- the acid mineralization increases with the degree of grafting. In all cases, 97% of hexanoic acid is removed after 6h.
- the behavior of catalysts has been studied through recycling. The catalyst with the lowest content in cobalt showed an increase of activity during the first four cycles. Such activity is stabilised with apparent values of the fall of total organic carbon (TOC) and chemical demand of oxygen (COD) of about 90 %. The increase of cobalt concentration enhances the rate of mineralization (expressed in relation to TOC eliminate d) from 45 % in the first cycle to 62 % at the third cycle.

The loss of cobalt is very low. It is below 0,57 % after six cycles.

We have also tested the catalytic action of this system in the succinic acid oxidation, oxalic acid and trichlorophenol. We obtain a quasi total fall of TOC and COD and an important rate of mineralization. All these consistent results, can validate this catalytic system. Especially since the catalyst is inexpensive.

KEYWORDS

Water treatment ; catalytic oxidation ; phthalocyanines ; activated carbon ; oxygen.

1 INTRODUCTION

In front of the toxicity of industrial discharges which represent a threat for the balance of the ecosystem, the regulations on dumpings and on standards of discharges evolve ceaselessly towards a bigger severity.

So, as soon as it is about organic and toxic or with difficulty biodegradable aqueous organic waste, the processes of oxidation have a place of choice.

In the field of the water treatment, the catalytic oxidation especially developed around the reagent of Fenton [1] but this oxidizing system works only in pH acid. Besides, the reagent of Fenton used at room temperature allows generally a partial oxidation of pollutants and is not accompanied by an important elimination of the total organic carbon.

The WPO process allows to accelerate the kinetics of degradation reactions. But this process raises problems of cost due to the use of high temperatures reaching 140 °C [2].

In the cleanup of water, we find dioxygen especially in WAO process (Wet Air Oxidation) [3]. Oxidation in aqueous phase by the molecular oxygen with temperature and pressure raised (250 - 320 °C - 50 in 150 bars) allows to answer problems posed by the toxic aqueous waste which cannot be treated by biological way. In spite of the process efficiency, the binding conditions of functioning (temperature and pressure raised) engender a heavy investment and constitute a brake in the development of this treatment method .

Phthalocyanine complexes of transition metals are attractive as potential oxidation catalysts because of their rather cheap and facile preparation in a large scale and their chemical and thermal stability.

Metallophthalocyanines are well known as electrocatalysts for oxidation of variety of analytes including chlorophenols [4, 5].

All the reactions of catalytic oxidation in presence of metallophthalocyanines described in literature involve KHSO_5 or H_2O_2 as oxidizing agent and do not enter within the framework of water cleanup. The addition of a co-organic solvent in the reactional medium is indispensable; the authors do not work in an aqueous medium but in a mixture acetonitrile / buffer (1 / 3, V / V) or in a solution phosphates buffer / ethanol (80 / 20) or in a solution phosphates buffer / acetone 80 / 20 [6, 7, 8].

Concerning the stability of metallophthalocyanines in the presence of H_2O_2 or KHSO_5 , certain authors are discreet about this stability [9, 10] while the others show the fast degradation of catalyst in presence of these oxidizing agents whether it is in solution or supported [11].

As regards the reactions of oxidation involving the dioxygen as the oxidizer, we find especially in the literature the use of cobalt phthalocyanine supported in oxidation of thiols to disulfides in oil distillates [12, 13].

A phthalocyanine complex with eight triethoxysilyl substituents which can be directly anchored to silica without any modification of silica support shows good catalytic activity in epoxidation of olefins by dioxygen in the presence of isobutyraldehyde. The same catalytic system is also active in the oxidation of phenols to biphenols [14].

Thus it seems that to find a catalysis oxidation process involving metallophthalocyanines and using the dioxygen in soft conditions constitutes a particularly important challenge.

2 Grafting of metallophthalocyanines on activated carbon :

The activated carbon used as catalyst support should be extremely pure to prevent inhibition of chemical reaction. In particular, the presence of ashes would make a low yield. It should also be mechanically resistant to prevent formation of tiny particles through attrition of particles which would generate a loss of material as well as a fall of yield.

Then we have chosen two types of activated carbon used in catalysis, characterised by a good resistance and their rate of very low impurities.

- the activated carbon Acticarbone CECA (grains)
- the activated carbon AC 35 CECA (extruded)

The grafting reaction on activated carbon takes place at an ambient temperature by a simple addition of sulfonated cobalt phthalocyanine CoPcS solution with sufficient concentration to make an aqueous suspension of activated carbon in the presence of NH_4OH .

We obtain a black material whose graft rate has been calculated and which is characterised by IR spectroscopy by diffused reflection.

The graft rate has been calculated through two different manners : by atomic absorption dosing the supported Co(II) and by UV-visible spectroscopy dosing the quantity of CoPcS getting in the filtrate and into the washing solutions.

The stability of the activated carbon grafted by CoPcS has been studied.

It remains stable for pH between 2 and 10. In fact, no relargage has been observed by UV – visible spectroscopy after 6 - hour agitation in water for pH between 2 and 10.

This synthesis seems to be suitable for an eventual adaptation at an industrial level. In fact, the operatory method is simple and the obtained results are correct, the graft rates vary from 1 to 4,5.10⁻⁵ mol/g with rates also varying from 60 % to 99% for the most important grafts.

We have also been able to show the role of NH₄OH. In fact, we realized that the pH had an important role in the fixation on activated carbon which is optimal for pH between 8,5 and 10.

3 catalytic Oxidation of the hexanoic acid:

These oxidation reactions were carried out in an engine into which we introduce the catalyst (with a concentration of 100 g/l) and 525 ml of water in which we solubilized 182 µl of hexanoic acid what corresponds respectively to an initial TOC and an initial COD due to the hexanoic acid of 200 mg/l and 680 mg/l. All the oxidation reactions have a duration of 6 hours with a gas flow of 25 l/h and a gas pressure at the entry of the engine of 0,38 bars. The catalysts were tested in the oxidation of the hexanoic acid by dioxygen.

3-1 Variation of grafting rate:

Two catalysts grafted on activated carbon Acticarbone (grains) prepared with different grafting rates (12 µmol / g and 45 µmol / g), were tested in the hexanoic acid oxidation by oxygen. The results are presented in the following table:

Catalyst	CoPcS / CA Acticarbone (grains) (I)	CoPcS / CA Acticarbone (grains) (II)
Temperature (°C)	20	20
Grafting rate	12 µmol / g	45 µmol / g
[catalyst] g/l	100	100
[metal] g/l	0,07	0,3
pH _i *	4,13	4,52
TOC _i (mg/L)	173	206
COD _i (mg/L)	627	662
ΔTOC (mg/L)	116	142
ΔTOC %	67	69
ΔCOD (mg/L)	456	513
ΔCOD %	73	77
pH _f	9,41	9,47
ΔIC (mg/L)	30	64
Mineralization rate %	17	45
[AH] _i mg/l	315	335
[AH] _f mg/l	10	10
Eq TOC (mg/L)	6	6
% TOC _f	11	9
Δ[AH] %	97	97

* pH_i is the pH of hexanoic acid solutions without material

Table 1.

Whatever is the grafting rate, the falls of TOC and COD are relatively invariant and respectively of the order of 70 % and 77 %. Simultaneously, the disappearance of the hexanoic acid is almost total in 6 hours (97 %).

We also notice that the rate of mineralization increases with the rate of grafting.

Balance sheet in carbon:

The balance sheet in carbon is established for both catalysts (with two grafting rates: 12 $\mu\text{mol} / \text{g}$ and 45 $\mu\text{mol} / \text{g}$)

The lack in the carbon balance sheet = $[(\text{TOC}_i - \text{TOC}_f - \Delta\text{IC}) / \text{TOC}_i] * 100$.

Catalyst	CoPcS / activated carbon (grains)	CoPcS / activated carbon (grains)
Grafting rate ($\mu\text{mol}/\text{g}$)	12	45
TOC_i (mg / L)	173	206
TOC_f (mg / L)	57	64
ΔIC (mg / L)	30	63
lack in the carbon balance sheet	50	38
% COT_i		

Table 2.

The lack in the balance sheet in carbon decreases when the rate of grafting increases. Indeed, more the rate of grafting increases, more the liberation of CO_2 is important sign of a more advanced reaction. The lack in the carbon balance sheet is due to organic compounds adsorbed at the end of reaction.

3-2 Effect of the adsorption of organic compounds on the activity of the catalyst with a grafting rate of 12 $\mu\text{mol} / \text{g}$:

This catalyst is used in six successive oxidation essays to oxidize in every essay during 6 hours, 200 mg / l of TOC due to the hexanoic acid.

The catalyst underwent no wash and no drying between the oxidation essays: the catalyst is just filtered and reintroduced in a new solution.

The obtained results are summarized in the table 3

Oxidation essays	1 st essay	2 nd essay	3 rd essay	4 th essay	5 th essay	6 th essay
Duration	6 h	6 h	6 h	6 h	6 h	6 h
[catalyst] g/l	100	100	100	100	100	100
[metal] g/l	0,07	0,07	0,07	0,07	0,07	0,07
pH _i	4,13	4,16	4,00	4,32	4,38	4,43
TOC _i (mg/L)	173	205	185	184	194	199
DOD _i (mg/L)	627	665	656	669	649	659
ΔTOC (mg/L)	116	156	143	161	178	179
ΔTOC %	67	76	77	87	91	90
ΔCOD (mg/L)	456	504	551	611	602	602
ΔCOD %	73	76	84	91	93	91
pH _f	9,41	9,18	8,87	8,39	8,36	8,27
ΔIC (mg/L)	30	18	17	57	76	70
mineralization rate%	17	12	12	35	43	40
[AH] _i mg/l	315	314	314	304	329	347
[AH] _f mg/l	10	19	29	11	16	22
Eq TOC (mg/L)	6	12	18	7	10	14
%TOC _f	11	24	43	30	59	72
Δ[AH] %	97	94	91	96	95	93

Table 3.

The apparent rate of mineralization, is close to 15 % on the first three essays, passes then to 40 % and this corresponds to a pH of the reactional medium stabilized at 8,3.

During the dosage of the hexanoic acid by CIHP, we detected in addition to residual acid new products among which two were identified thanks to:

.their retention time

.the comparison with stallion compounds

They are the maleic acid: $C_4H_4O_4$ and the malonic acid: $C_3H_4O_4$

Essay	TOC _f	Identified Products	retention time(min)	c.(mg/L)	TOC equivalent (mg/L)	% TOC _f	ΣC of identified products (mg / L)
1	57	maleic acid	16,47	102	42	74	48
		hexanoic Acid	10,90	10	6	11	
2	49	malonic acid	15,72	8	3	6	26
		maleic acid	16,53	27	11	22	
		hexanoic acid	10,90	19	12	24	
3	42	malonic acid	15,73	5	2	4	23
		maleic acid	16,53	8	3	8	
4	23	hexanoic acid	10,90	29	18	43	10
		malonic acid	15,68	9	3	14	
5	16	hexanoic acid	10,90	11	7	30	13
		Malonic acid	15,48	10	3	20	
6	20	hexanoic acid	10,90	16	10	59	16
		malonic acid	15,60	7	2	12	
		hexanoic acid	10,90	22	14	72	
		malonic acid	15,60	7	2	12	

Table 4.

However, the other peaks, corresponding to not identified products, were detected by CIHP.

The quantity of maleic acid with regard to the final TOC decreases when the catalyst activity increases according to the oxidation essays and the quantity of malonic acid with regard to the final TOC increases. The hexanoic acid seems to be transformed into maleic acid then in malonic acid then in CO_2 .

Loss in active agent:

The dissolved cobalt is measured by atomic absorption in the final sample of every essay of recycling:

oxidation Essays	1 st essay	2 nd essay	3 rd essay	4 th essay	5 th essay	6 th essay
dissolved Co (mg / L)	0,04	<0,03	<0,03	0,1	0,1	0,1
%	0,057	<0,043	<0,043	0,142	0,142	0,142

Table 5.

We notice that the cobalt relegate in the solution is very low, lower than 0,57 % after six recycling essays.

3-3 Effect of organic compounds adsorption on the catalyst activity with high rate of metallophthalocyanines :

The catalyst CoPcS 806 fixed to activated carbon Acticarbhone CECA (grains) according with a rate of grafting of 45 $\mu\text{mol} / \text{g}$ is used in four successive oxidation essays of solutions of 200 mg C / L of hexanoic acid.

The catalyst underwent no wash and no drying between the various essays of oxidation.

The obtained results are given in the table below:

Oxidation essays	1 st essay	2 nd essay	3 th essay	4 th essay
Duration	6 h	6 h	6 h	6 h
[catalyst] g/l	100	100	100	100
[metal] g/l	0,3	0,3	0,3	0,3
pH _i *	4,52	4,54	4,52	4,58
TOC _i (mg/L)	206	204	207	196
COD _i (mg/L)	662	643	670	637
ΔTOC (mg/L)	142	185	191	182
ΔTOC %	67	76	77	87
ΔCOD (mg/L)	513	587	652	599
ΔCOD %	69	90	92	94
pH _f	4,95	4,13	4,26	4,15
ΔIC (mg/L)	63	103	119	113
mineralization rate%	45	56	62	62
[AH] _i (mg/L)	335	322	331	314
[AH] _f (mg/L)	10	8	8	8
Eq TOC (mg/L)	6	5	5	5

%CTOC _f	9	25	31	36
Δ[AH] %	97	94	98	97

* pH_i is the pH of hexanoic acid solutions without material.

Table 6.

The activity of the oxidizing system increases during the use of the catalyst. With this catalyst, presenting a grafting rate of 45 μmol / g, two oxidation essays of six hours each seem sufficient to produce reproducible results in term of rate of total organic carbon fall and transformation in carbon dioxide against three essays of six hours each for the catalyst presenting a grafting rate of 12 μmol / g. By increasing the rate of grafting, we end more quickly in a better activity of the catalyst.

During the dosage of the hexanoic acid by CIHP, we detected, as previously the maleic acid C₄H₄O₄ and the malonic acid C₃H₄O₄ besides the residual hexanoic acid.

Essays	TOC _f	Identified Products	Retention time (min)	c.(mg/L)	TOC equivalent (mg/L)	% TOC _f	ΣC of identified products (mg / L)
1 st essay	64	malonic acid	15,62	16	6	9	23
		maleic acid	16,43	26	11	17	
		hexanoic acid	10,90	10	6	9	
2 nd essay	19	malonic acid	15,67	16	5	27	10
		hexanoic acid	10,90	8	5	25	
3 rd essay	16	malonic acid	15,70	14	5	31	10
		hexanoic acid	10,90	8	5	31	
4 th essay	14	malonic acid	15,75	10	3	24	8
		hexanoic acid	10,90	8	5	36	

Table 7.

The quantity of maleïc acid ($C_4H_4O_4$) with regard to the final TOC decreases when the activity of the catalyst increases according to the essays of oxidation, while the quantity of malonic acid ($C_3H_4O_4$) increases. The hexanoïc acid seems to be transformed into maleïc acid (C4) then in acid malonic (C3) then in CO_2 .

3-4 Variation of the characteristics of the activated carbon:

The table below summarizes the results obtained with the catalyst supported on the activated carbon (extruded) and the catalyst fixed on the activated carbon (grains) obtained with two different rates of grafting:

activated carbon type	AC 35 CECA 3 mm (extruded)	Acticarbone CECA (grains)	Acticarbone CECA (grains)
Catalyst	Co 806 / activated carbon (extruded)	Co 806 / activated carbon (grains)	Co 806 / activated carbon (grains)
[catalyst] g/l	100	100	100
[metal] g/l	0,05	0,07	0,3
pH _i	4,29	4,13	4,52
TOC _i (mg/L)	191	173	206
COD _i (mg/L)	697	627	662
ΔTOC (mg/L)	188	116	142
ΔTOC %	98	67	67
ΔCOD (mg/L)	688	456	513
ΔCOD %	99	73	69
pH _f	8,01	9,41	9,47
ΔIC (mg/L)	28	30	63
mineralization rate %	15	17	45

Table 8.

With the catalyst [Co806 / activated carbon AC 35 CECA (extruded)], we obtain a very important fall of TOC and COD of the order of 98 % while two other catalysts fixed on the activated carbon (grains) lead to a fall of TOC and in OCD of the order of 70 %.

The catalyst [Co806 / activated carbon AC 35 CECA (extruded)] seems more active than the catalyst Co 806 / activated carbon Acticarbone CECA (grains) in spite of lower grafting rate.

On the other hand, the rate of mineralization is sharply more important for the catalyst [Co 806 / activated carbon Acticarbone CECA (grains)] in 0,3 % in Co.

4 Validation of the catalyst:

To validate the catalyst, we applied the same oxidation system to recalcitrant model molecules, others than the hexanoic acid which are the succinic acid, the oxalic acid and the trichlorophenol.

4-1 Oxidation of the succinic acid ($\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$) :

We made the essays of oxidation in the same conditions as with the hexanoic acid.

The catalyst tested in the oxidation of the succinic acid by the dioxygen is [Co 806 / Activated carbon AC 35CECA (extruded)] obtained with a grafting rate of 0,05 % of Co.

We realized an oxidation test of the succinic acid by the dioxygen in absence of catalyst. We so verified that the succinic acid is inert towards dioxygen.

During the oxidation of the succinic acid by the dioxygen without catalyst, we observe a very light variation of the pH as well as an unimportant TOC fall (of 8 %).

In the presence of the catalyst, we observe a net rise of the pH, a very important TOC fall (of 87 %) and a significant rate of mineralization (expressed with regard to the eliminated TOC) of the order of 30 %.

Effect of the adsorption of organic compounds on the activity of the catalyst:

The catalyst is six times used for six successive oxidation essays to oxidize in every essay during 6h, 200 mg / l of TOC due to the succinic acid. The catalyst underwent no wash and no drying between the various oxidation essays but just a filtration.

The obtained results appear in the table which follows:

oxidation essays	1 st essay	2 nd essay	3 rd essay	4 th essay	5 th essay	6 th essay
Duration	6 h	6 h	6 h	6 h	6 h	6 h
[catalyst] g / l	100	100	100	100	100	100
[metal] g / l	0,05	0,05	0,05	0,05	0,05	0,05
pH _i	4,8	4,8	5,0	4,7	4,7	4,8
TOC _i (mg/L)	179	161	190	180	165	183
COD _i (mg/L)	485	471	452	455	485	442
ΔTOC (mg/L)	156	142	187	154	141	151
ΔTOC %	87	88	98	86	85	83
ΔCOD (mg/L)	413	407	442	427	429	394
ΔCOD %	85	86	98	94	88	89
pH _f	7,9	6,9	7,3	7,0	7,0	6,9
ΔIC (mg/L)	45	49	39	56	45	66
mineralization rate %	29	35	21	36	32	43
[AS] _i mg/l	557	481	546	505	556	543
[AS] _f mg/l	58	44	0	62	60	72
Eq TOC (mg/L)	23,5	17,9	0	25	24	29

% TOC _f	100	91,2	0	98	100	94
Δ[AS] %	89,6	90,8	100	88	88	87

Table 9.

During six oxidation essays, the rate of disappearance of the succinic acid is of about 90 %. During the essays, we observe a light increase of the apparent rate of mineralization. This mineralization rate is of 29 % in the first oxidation essay, reaches 43 % at the end of 6th essay of recycling.

During the dosage of the succinic acid by CIHP, we detected, as previously, the maleïc acid, C₄H₄O₄ and the malonic acid C₃H₄O₄ besides the succinic acid, identified thanks to their retention time and compared with stallion compounds.

Essay	TOC _f	identified Products	retention time (min)	c.(mg/L)	TOC equivalent (mg/L)	% TOC _f	ΣC of identified products (mg/L)
1	23	Succinic acid	17,8	58	23	100	23
2	19	malonic acid	16,0	4	1	8	19
		Succinic acid	17,8	44	18	91	
3	3	malonic acid	16,0	28	3	90	3
4	26	Succinic acid	17,8	62	25	98	25
5	24	Succinic acid	17,8	60	24	100	24
6	32	Succinic acid	17,8	72	29	94	29

Table 10.

For six oxidation essays of the succinic acid, in the experimental errors near, the final TOC is equal to the sum in carbon of the identified products. All the products of the reaction are then known.

4-2 Oxidation of the oxalic acid (HO₂CCO₂H)

Having studied the oxidation of the hexanoïc acid (acid in C6) and that the succinic acid (diacid in C4) by the dioxygen in the presence of the catalyst [CoPcS / activated carbon (extruded)] with a cobalt grafting rate of 0,05 %, in soft conditions of temperature and pressure, we applied the same oxidation system to a diacid (in C2) considered too refractory: the oxalic acid.

We made the oxidation essays in the same conditions operating as with the hexanoïc acid and the succinic acid.

Two essays were realized in absence and in the presence of the catalyst.

During the not catalytic oxidation of the oxalic acid by the dioxygen, we observe a very light variation of the pH as well as TOC and OCD falls (respectively of 3 % and 4 %). The oxalic acid is inert towards the dioxygen.

However, in the presence of the catalyst, we see a net rise of the pH, a quasi total TOC and OCD fall (of 92 %) and an important rate of mineralization of 55 % from the first essay of oxidation.

In the table which follows, we compare the activity of the catalyst in the first essay of oxidation of the hexanoïc acid, the succinic acid and the oxalic acid in term of TOC, OCD and rate of mineralization (calculated with regard to the eliminated TOC):

Oxydised Acid	ΔTOC %	ΔCOD %	mineralization rate%
hexanoïc acid	98	99	15
Succinic acid	87	85	30
Oxalic acid	92	91	55

Table 11.

The fall of total organic carbon and in chemical demand in oxygen is quasi total for the three studied acids. However, the rate of mineralization, calculated with regard to the eliminated TOC, increases sharply when the studied acid possesses fewer atoms of carbon. The ability to react increases when the carbon chain of the acid to be oxidized is shorter.

4-3 Oxidation of trichlorophenol :

Having made a success in the oxidation of several carboxylic acids (the hexanoïc acid, the succinic acid and the oxalic acid) considered being all as recalcitrant organic molecules, we have been interested in the oxidation of another family of compounds: the trichlorophenol.

The oxidation by the dioxygen was realized in the same conditions operating as precedely in the presence of the catalyst [CoPcS / activated carbon (extruded)] with a cobalt grafting rate of 0,05 % in soft conditions of temperature and pressure. We come to total TOC and COD falls and at an important rate of mineralization of 46 % from the first essay of oxidation.

5 CONCLUSIONS

We showed that the synthesis of catalysts supported on activated carbon is a simple process which is made in the ambient temperature. According to the nature of supports (extruded or grains) the rates of fixation of the sulfonated cobalt phthalocyanine are different.

The activity of these catalysts was studied in the oxidation of the hexanoic acid by the dioxygen in the normal conditions (20°C, 1 atm.).

In every case, the catalyst is active. We studied the reaction by means of two catalysts, containing respectively 12 and 45 $\mu\text{mol} / \text{g}$ of cobalt. We showed that:

- these catalysts are responsible for the acid mineralization which increases with the rate of grafting. In every case, 97 % of the hexanoic acid disappears at the end of 6 hours but the apparent rate of mineralization, calculated with regard to the eliminated TOC, nearby of 17 % at the beginning of the reaction and about 40 % to the fourth cycle, indicates a lack to the balance sheet in carbon which is attributed to the adsorption of the inorganic carbon on the surface of the catalyst. Indeed the basic pH of the reactional medium is convenient to the stabilization in solution of the carbon dioxide released in the form of bicarbonate.

- The behavior of catalysts was studied through their recycling. For the catalyst the least rich in cobalt, an increase of activity is observed during the first four cycles. It stabilizes then with apparent values of TOC and COD falls of the order of 90 %. The increase of the concentration in cobalt (45 $\mu\text{mol} / \text{g}$) has no significant effect on the TOC and COD falls but increases the rate of mineralization expressed with regard to the eliminated TOC, from 45 % during the first cycle to 62 % in the third.

- The loss in cobalt is very low. It is lower than 0,57 % after six cycles.

Both catalytic systems were used, it seems that the system on extruded support is more active than the system on activated carbon (grains) with lower concentration of cobalt and it is the one which was used to study the oxidation of the succinic and oxalic acids and of the trichlorophenol. On the other hand, the system on activated carbon (grains) containing 0,3 % of cobalt gives a more important rate of mineralization of the acid.

In the case of the oxidation of the succinic acid, made in the same experimental conditions, we observe a TOC fall of 87 % and a rate of mineralization about 30 %. From the first oxidation essay, the succinic acid disappears totally from the middle, with a rate of mineralization (expressed with regard to the TOC eliminated) of 43 %.

In the same conditions and with the same catalyst, the oxidation of the oxalic acid is translated by a TOC fall of 92 % and an important rate of mineralization, (expressed with regard to the eliminated TOC) of 55 % from the first cycle. The catalyst is thus particularly effective.

It's the same for the oxidation of the trichlorophenol. The TOC and COD falls are total and the mineralization rate, expressed with regard to the eliminated TOC, of 46 %. The ability to react observed on carboxylic acids is verified with the trichlorophenol.

Every these consistent results, very corresponding, allow to validate the catalytic system. Especially since the catalyst is inexpensive.

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