Optimization of the degradation of sewage sludge by wet air oxidation. Study of the reaction mechanism on a cellulose model compound

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Abstract. The aim of this work is to optimize the degradation yield of an activated sludge and to study the reaction mechanism on a cellulose model compound. This optimization is performed with a Simplex design with four parameters: reaction temperature (280-350 °C), injected air pressure (40-60 MPa), reaction time (10-45 minutes) and COD concentration (0.5-5 g L^{-1}). The better yield obtained on TOC concentration is 82 5% at 330 °C. Over this temperature, the yield substantially decreases. The use of cellulose as a model compound for activated sludge confirms optimization results and leads to the identification of by-products and free radical species participating in the reaction. Two major organic compounds have been detected: 4-oxo pentanoïc acid and 3-oxo butanoïc acid, and three types of radicals: HO°, $CO_2^{°-}$ and °CH(OH)CH$_3$.

Keywords. Wet air oxidation – sewage sludge – optimization – by-products – free radicals.

Introduction

Because of the improvement of drainage systems, the amount of sludge is in constant increase and the current treatments like incineration or agricultural disposal will become insufficient in a near future. Landfilling of sewage sludge will be prohibited in a few years because of tighter environmental laws. Therefore, it is more and more necessary to put forward some other ways of treating those wastes, and wet air oxidation should be a well-adapted process for this aim. It consists in mineralizing organic matter in water with an oxidizing mixture. This technology works at relatively high temperature and pressure and leads mainly to clean gaseous effluents and liquid effluents, which can be further treated by a biological process [1,2]. Other advantages of the technology are lower operating costs than those of incineration, and the possibility to recover energy with diluted substrates [3].

Numerous previous studies have dealt with wet air oxidation of sewage sludge. With rather low temperature and pressure conditions (between 150 °C and 260 °C, and under 7 MPa), this technology represents an excellent pretreatment to sterilize the sludge and to enhance further dewatering and settling [2,4-6]. It allows the production of a final sludge with a higher dry solid content than with a classical way of treatment. But it implies further sludge treatment and doesn't resolve the problem of disposal. Most of industrial Wet Air Oxidation (WAO) plants work in these conditions [6,7]. But WAO can also be considered as a destructive process: with hard temperature and pressure conditions (between 260 °C and 350 °C, and higher than 7 MPa), the organic matter can

be completely oxidized leading to a substantial volume reduction of the solid part and consequently to an important decrease of disposal costs [8-10]. Few studies have dealt with the oxidation of activated sludge in that temperature range and, to our knowledge, no-one has tried to optimize the degradation yield [11-14].

The aim of the present work is to use the experimental research methodology to determine the best conditions for the highest degradation yield. Another part of this work will try to bring back information on the reaction mechanism by studying by-products and free radical species. To achieve this second purpose, cellulose is used for the modeling of sewage sludge.

Experimental

WAO apparatus

WAO experiments were carried out in a laboratory batch reactor which has been previously described [15]. The 500 mL autoclave is equipped with an agitator, a thermocouple, a liquid and a gas sample lines and a safety system. The oxidizing mixture used is enriched air (50 % O$_2$/50 % N$_2$) and a low pressure nitrogen line allows the purge of the system before experiment.

300 mL of sewage sludge were introduced in the reactor vessel. The autoclave was closed hermetically, purged with nitrogen and stirred at 500 rounds per minute. It was then heated up to the desired reaction temperature and the

oxidizing mixture was introduced only at this stage. This injection was considered as the starting point of the experiment. When the reaction time was passed, the reactor was rapidly cooled down and liquid and solid effluents were then recovered for further analyses.

Analytical methods

- Global parameters used to characterize the sludge (COD, TKN, dry solid, cellulose concentration) were performed according to AFNOR standard methods.

- The total organic carbon content was measured on the initial substrate and on the liquid effluent after treatment, using a Shimadzu TOC 5050A analyser. The degradation yield was calculated on TOC and COD concentration by the following expressions:

$$\Delta COD = \frac{COD_{initial} - COD_{final}}{COD_{initial}} * 100$$

$$\Delta TOC = \frac{TOC_{initial} - TOC_{final}}{TOC_{initial}} * 100$$

- The detection of low weight organic acids was carried out using HPLC and UV-absorption detection at 204 nm, equipped with an ORH 801 International Chromatography column (6.5 mm i. d., 300 mm length), and a Varian 9050 detector. The eluant was a 0.03 N sulfuric acid solution eluted at 0.8 mL min^{-1} with a Shimadzu LC-10AT VP pump.

- Organic by-products were also analyzed by a HP 5890 gas chromatograph equipped with a HP Inno-WAX column (0.25 mm i. d., 15 m length) and a FID detector. We have set up a temperature gradient for the oven: 50 °C for 5 min, 10 °C per minute between 50 and 250 °C, and 250 °C for 5 min.

- A GC/MS system composed of a HP 5890 chromatograph equipped with a HP Carbo-WAX 20 M (50 m length, 0.2 mm i. d.), connected to a HP 5971A mass spectrometer fitted with a quadrupolar separator, was used to identify organic by-products. The temperature conditions for the oven were: 60 °C for 4 min, 10 °C per minute between 60 and 220 °C, and 220 °C for 30 min.

- ESR spectroscopy allowed us to detect and identify free radical species. We used the spin trapping technique to trap the radicals before the ESR analysis [16,17]. The trapping solution used was DMPO (5,5-dimethyl-1-pyrroline *N*-oxide, 0.4 M) in a phosphate buffer (0.1 M, pH 6.8). 100 µL of samples collected from the WAO reactor were rapidly mixed with 100 µL of this trapping solution and frozen in liquid nitrogen to stop reactions. ESR analysis were preformed at room temperature. A Bruker EMX spectrometer was used (X-band, TM$_{110}$ cavity), with the following conditions: microwave power, 10 mW; modulation frequency, 100 kHz; modulation amplitude, 0.1 mT; receiver gain, 6.0 10^5; time constant, 10 ms; scan range, 12.0 mT; scan time, 355 s. The P.E.S.T. software by Duling was used to analyze ESR spectra in order to determine ESR parameters which lead to the identification of the adducts.

Results and discussion

Optimization of the degradation yield

Characterization of the substrate

Tests concerning the optimization of the degradation yield were carried out on an activated sewage sludge issued from a biological treatment plant producing 100 m^3 day^{-1} of this kind of sludge. Samples were taken every week and kept in a cold place to avoid any significant alteration. Table I shows characteristics of the sludge.

Simplex design

Experimental research methodology has recently shown its efficiency on reducing the number of experiments using a simultaneous variation of parameters [18-20]. A Simplex design has been used to achieve the optimization. This concept is particularly adapted to this aim and is rather simple to carry out. Four parameters and two responses have been chosen. The four parameters are given in table II with the center and the variation pace. Stirring speed was not held as a parameter because it has no effect on the yield over 500 rounds per minute in our experiments. The COD measurement has been chosen to indicate the concentration of the substrate. This parameter is currently used in the environmental field and it proved the easiest to obtain.

One of the calculated responses was ΔCOD but it was not used to make the Simplex progress: the normalized method used to measure COD concentration of the effluents is not

Table I. Characteristics of the activated sludge.

Parameter	Value
pH	6.7 ± 0.2
Dry solid (%)	0.4 ± 0.1 %
Organic matter (%)	75 ± 1 %
COD	5.5 ± 0.4 g L^{-1}
TOC	1.7 ± 0.2 g L^{-1}

Table II. Center and variation pace of parameters.

		Center C	Variation pace P
Reaction temperature (°C)	X1	280	43
Air injected pressure (MPa)	X2	4.0	2.2
Reaction time (min)	X3	10	22
Initial COD concentration (g L^{-1})	X4	5	– 4.9

accurate enough to lead to a correct yield. For two different experiments performed in the same conditions, a 3 % difference has sometimes been observed between the two ΔCOD. As for ΔTOC, the difference was always less than 0.8 %. This is why the ΔTOC yield was chosen to organize the progression of the Simplex method.

It was also necessary to set the limits of the experimental area. The maximum temperature was 350 °C as our reactor cannot work over this. Experiments must be conducted in excess of oxygen and the minimum injected air pressure was set to 4 MPa. This corresponds to an excess of at least 20 % compared with stoichiometric conditions. As the maximum COD concentration of sludge samples was 5 g L^{-1}, this value was chosen as the upper limit of the concentration parameter. In case the calculation of parameter value exceeded those limits, the closer possible value was arbitrary affected to the parameter concerned.

Numerous calculation matrix exist and are adapted to different cases. A two parameters matrix which is described in table III has been chosen. Following transfer formula was used to obtain coordinates of experimental matrix.

$$\text{Transfer formula}: X_{ij} = C + k_{ij} * P.$$

Tests were carried out and led to the optimization of the degradation yield. The experimental matrix and corresponding responses are given in table IV. The gray tone line corresponds to the optimal conditions: 330 °C, 4.3 MPa, 35 min, 3.0 g L^{-1}, and the ΔTOC yield reaches 82.5 %, showing the good efficiency of the process. The residual TOC (and COD) represents also a good indication of the efficiency: it is of 202 ± 6 ppm (respectively 520 ± 22 ppm).

Furthermore, one can notice that the injected air pressure has no significant effect on the yield: it do not vary much in all experiments and stays close to the minimum value. The optimal reaction time shows that it is not necessary to apply a longer time because it will not provide a noticeable increase of the yield. The concentration seems to have a negative effect on the degradation yield: a higher concentration leads to a lower yield. The temperature appears as the most influent factor: the more it increases, the better the yield. But the interesting result is that this is true only under 330 °C. Over this temperature, the yield substantially decreases. With a reaction temperature of 345 °C, the yield only reaches

74.9 %. This phenomenon has never been described in the literature and needs further explanation.

Study of the mechanisms

Experimental conditions

As it was commonly assumed that temperature was the predominant factor for the improvement of the yield [15], the reaction mechanism was studied to try to understand why the yield was lower for a reaction temperature over 330 °C. It was difficult to work directly on such a complex substrate, because the detailed composition of the sludge was not known. Therefore, it was decided to work on a model compound. We chose cellulose because it usually represents the major part of the activated sludge organic matter.

In order to follow the yield as a function of reaction temperature, experiments were carried out during the heating up of the reactor, before air injection. In our experiments, it was always considered that the reaction time started when the oxidizing mixture was injected. But at high temperature, it is obvious that degradation starts far earlier.

Cellulose concentration was set at 10 g L^{-1} for all experiments (2 g in 200 mL). The temperature varied from 25 °C to 350 °C (upper limit of the apparatus). Reaction times were not considered because the aim was only to assess the substrate degradation according to temperature, within air injection. Cellulose and deionized water were introduced in the reactor and the gaseous phase was purged with nitrogen, as for a classical experiment. During the heating up period, liquid samples were taken every fifteen minutes and analyzed them with a TOC analyzer, HPLC, GC and GC/MS systems.

Reaction by-products

The dissolved TOC concentration as a function of temperature is described in figure 1. Under 250 °C, the dissolved

Table III. Calculation matrix k_{ij}.

X1	X2	X3	X4	
0	0	0	0	
p	q	q	q	$p = \dfrac{1}{n\sqrt{2}}\left[\sqrt{n+1}+n-1\right]$
q	p	q	q	
q	q	p	q	$q = \dfrac{1}{n\sqrt{2}}\left[\sqrt{n+1}-1\right]$
q	q	q	p	
				with $n = 4$

Table IV. Experimental matrix and responses.

	X1 (°C)	X2 (MPa)	X3 (min)	X4 (g L^{-1})	ΔTOC (%)	ΔCOD (%)[*]
1	280	4.0	10	5.0	62.2	67
2	320	4.5	15	3.9	73.3	75
3	289	6.0	15	3.9	67.3	64
4	289	4.5	30	3.9	74.6	78
5	289	4.5	15	0.5	65.6	66
6	313	5.7	27	1.1	67.6	74
7	317	5.9	28	5.0	76.8	82
8	330	4.3	35	3.0	82.5	82
9	315	4.0	27	5.0	80.9	82
10	306	4.8	45	4.6	80.5	78
11	345	5.0	38	4.9	74.9	66
12	303	4.0	32	3.3	78.9	79
13	338	4.1	44	4.0	76.8	80
14	313	4.0	35	3.0	76.1	80

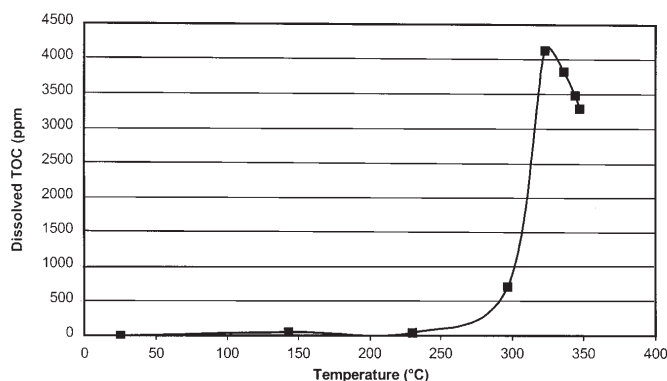[*]ΔCOD yields have been indicated for mere information.

Figure 1. Dissolved TOC evolution according to temperature during the heating up period.

TOC is very low and stable. This indicates that during this first step, solid cellulose is not yet degraded into soluble compounds. The second step appears between 250 °C and 330 °C. TOC concentration greatly increases in this field of temperature and reaches a maximum at 330 °C. This optimal temperature is in very good agreement with the optimal temperature determined on sewage sludge degradation. During this step, cellulose is transformed into soluble compounds and when the temperature reaches 330 °C, almost all of the solid substrate is degraded into soluble fractions. The last step corresponds to temperatures over 330 °C. At these high temperatures, soluble fractions are destroyed and transformed into low weight compounds, some of them in gaseous phase, and refractory by-products. This can explain the decrease of dissolved TOC concentration during this step.

One can observe here a very good correlation between the degradation yield of activated sludge and the evolution of the dissolved TOC. One knows that the wet air oxidation occurs preferentially in the liquid phase, and the soluble compounds concentration is maximum at 330 °C. This can explain why when the oxidant is injected at this temperature, the degradation yield is better. Over this temperature, a part of the by-products is probably in gaseous phase and so is unattainable for the oxidation, leading to a lower degradation yield.

Experiments in these conditions lead to a partial degradation of the substrate. Thus, a lot of by-products were formed and only a few of them could have been identified. Low weight organic acids and alcohols were not produced in these tests. They need the presence of oxygen to be formed. On the contrary, acetone was detected in non negligible

concentration (about 100 ppm) indicating that in absence of oxygen, this by-product is not transformed into carboxylic acids as for wet air oxidation [21] (see Fig. 2). An unknown refractory compound appeared in HPLC analysis at 10.9 min and its concentration increased up to 350 °C. This peak was also observed in the treated effluent during WAO of sewage sludge. This confirms that over 330 °C, refractory by-products are formed before the oxidant injection and limit the degradation yield.

Other by-products were found using GC/MS technique on the sample taken at 330 °C. Two major by-products have been detected and identified: 4-oxo pentanoïc acid and 3-oxo butanoïc acid. This is an important result because those compounds have never been reported in the literature before. On the contrary, many authors have reported the production of sugars during cellulose hydrolysis [22-25]. But here, those species do not appear. Only heavier compounds with higher retention times were observed. Operating pressure was there half that found in those previous studies, and this could explain the formation of heavy soluble fractions of cellulose instead of monomer fractions.

Free radicals identification

The intervention of free radicals in wet air oxidation mechanism has been admitted by many authors [21,26,27] and our purpose is to identify them and try to understand their role in the degradation reaction.

The samples taken during the heating up of the reactor between 150 and 330 °C were rapidly added to the trapping solution and then frozen in liquid nitrogen to be preserved before analysis. ESR spectra are given in figure 3. Spectrum A corresponds to the control sample and confirms the absence of interfering signal. Spectrum B shows a characteristic quartet which corresponds to the DMPO/HO° adduct. This signal can be observed at 150 °C and 330 °C (spectra B and E) with a high intensity. It also seems to be present on spectrum C but with a very feeble intensity. It has virtually disappeared on spectrum D: the signal is not significant compared with the background noise. It means that HO° radicals play a part during hydrolysis of cellulose without any oxidant. But compared with the evolution of TOC concentration, the formation of HO° radicals appears in the first step, when the TOC is low, and they are not detected during the second step. It is possible that HO° radicals step in the initial phase of the reaction to transform the substrate into insoluble fractions, which, in turn, are degraded in soluble compounds at higher temperature and without the help of radical species. When the temperature reaches 330 °C, the ESR spectra of the sample reveals the simultaneous presence of three signals.
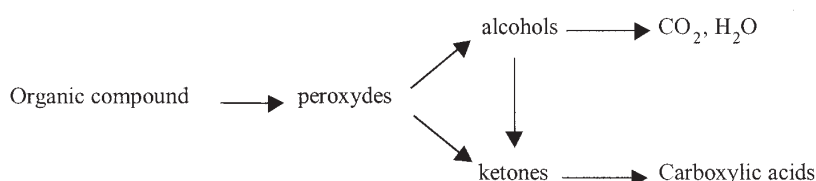

Figure 2. Wet air oxidation scheme of an organic compound[21].
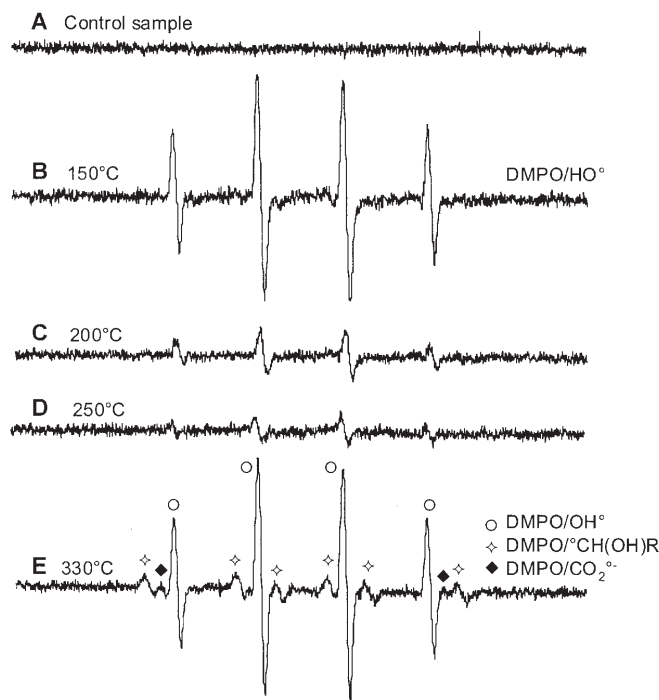
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Figure 3. ESR spectra of samples – A) Control sample; B) Sample collected at 150°C; C) Sample collected at 200°C; D) Sample collected at 250°C; E) Sample collected at 330°C.

The first one, which is the major one, corresponds to DMPO/HO° signal. The other two can be attributed to carbon centered adducts. The compiled data base of Buettner [28] helps us to identify those two adducts, and their hyperfine coupling constants correspond to DMPO/CO_2^{o-} and DMPO/°CH(OH)R spin adducts. In these conditions, three major compounds have been previously highlighted: acetone, 4-oxo pentanoïc acid and 3-oxo butanoïc acid. The
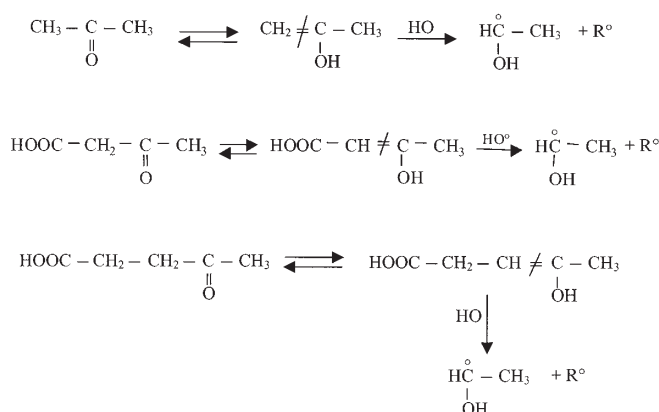

Figure 4. °CH(OH)CH$_3$ radicals production scheme.

production of CO_2^{o-} and °CH(OH)R radicals could be explained by the degradation of these compounds. If the two acid compounds are broken at their acidic function, it can lead to the formation of CO_2^{o-} radicals. °CH(OH)CH$_3$ radicals may be formed after the action of HO° radicals on organic compounds, following reaction scheme indicated in figure 4. Consequently the C-centered radicals may be attributed to CO_2^{o-} and °CH(OH)CH$_3$ radicals.

Once again those ESR results confirm the interest of working at the optimal temperature. At 330 °C, three different kinds of radical species have been observed and their action is essential for the enhancement of the degradation yield.

Conclusion

The study of the degradation of an activated sludge using a Simplex design led to an optimal yield of 82.5 % *versus* TOC concentration. This show the very good efficiency of the process. The optimal working conditions are 330 °C, 4.3 MPa for oxidant partial pressure, 35 min and an initial COD concentration of 3.0 g L^{-1}. The Simplex design has also shown an interesting phenomenon: over the optimal temperature, the yield decreases and this has not been previously described.

Working on cellulose model compound, it was noticed that the optimal temperature coincides with the highest dissolved TOC. Thus, injecting the oxidant at the time when the solid substrate is almost completely degraded into soluble compounds is the condition for a high degradation yield. Moreover, at this temperature three different kinds of radical species have been identified: HO°, CO_2^{o-} and °CH(OH)CH$_3$. Those species are essential in the initial phase of the reaction and consequently enhance the yield at this temperature.

Finally, the study of reaction by-products allowed the identification of two major compounds: 4-oxo pentanoïc acid and 3-oxo butanoïc acid which may play a part in the free radical production.

Thus, the simultaneous action of temperature, oxidant and radical species is essential to lead to the best degradation yield.

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