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Oxidation of sludge from a wastewater treatment plant of food industry

B. Wassate[1], G. Bouabid[2], *K. El Falaki[1], Y. Karhat[1], B. El Amrani[1], M. Azzi[2]
[1] Laboratory of Geo-sciences applied to Development Engineering (G.A.I.A),
[2] Laboratory Interface, Materials and Environnement
Faculty of sciences Ain Chock, BP 5388 Maârif, Casablanca, Morocco.

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** Corresponding author. E mail: elfalaki_khadija@yahoo.fr Tel: (+212 663876505)*

Abstract
The treatment of domestic and industrial waste water generates big quantities of sludge. These residual sludge raise important environmental, economic and technological problems. The decrease of the quantity of produced sludge and the degradation of the organic matter are very important. A new Treatment process was finalized in order to oxidize the organic matter in sludge. This work studies the oxidation of sludge of a water-treatment plant of a dairy farming by the peroxide of hydrogen (H_2O_2). Several experimental laboratory tests were made under various conditions especially:

- Oxidation of sludge by H_2O_2, at ambient temperature and pressure
- Oxidation of sludge by H_2O_2, at ambient pressure high temperature (100°C)
- Oxidation of sludge by H_2O_2, at ambient temperature and pressure, in the presence of Fe^{2+} ions

The results showed that the ferrous ions can catalyse peroxide of hydrogen to promote of the organic matter degradation. The oxidation of sludge by peroxide of hydrogen H_2O_2 in the presence of iron salts, coupling H_2O_2/Fe^{2+} what we call reagent of Fenton, reduces in a significant way the organic matter of sludge and improves the quality of the product: the rate of the total organic carbon (TOC) was reduced from 423.5 g/kg to 36 g /kg.

Keywords **:** Sludge, oxidation, hydrogen peroxide, Fenton

1. Introduction
The treatment of residual sludge raises such problems as well as environmental, as economic and technological. Among the various sectors of treatment of sludge, the incineration offers certainly significant advantages with compared with the other ways [1]. It reduces to approximately 20% dry solids in sludge and eliminates some potential environmental problems, eliminating completely the pathogenic bodies and by degrading several toxic organic compounds. The incineration is a particularly expensive practice because the dehydration, the drying, the combustion and the purge of flue gases require important quantities of energy.
The agricultural valorization is the most attractive solution, because it is about a recycling of a source of fertilizing organic matter which allows can make substantial savings of fertilizer [2]. However the sludge reused as amendment have to fill a number of quality criteria : mechanical properties, stability, respect for the standards on heavy metals and micropolluants. If these pollutants turn out in too strong dose, sludge becomes a waste. This waste volume must be reduced as much as possible, by combustion, according to a heavy air pollution regulation. The elimination of the organic matter and the volume reduction of sludge can be obtained by oxidation of the organic matter, especially by the advanced oxidation processes (AOP) who allow the degradation of the organic matter and the decrease of the volume of sludge [3].
This study aims at using a simple, effective and less expensive process which allows to :

- Reduce the volumes of sludge and avoid their fermentation (smell) ;
- Oxidation of the organic matter in sludge
- Minimize the pathogenic risks ;

The aim of this work is the oxidation of sludge from a wastewater treatment plant of food industry by oxygen peroxide.

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2. Materials and Methods

2.1 The sludge used

The Sludge used in this study was obtained from a wastewater treatment plant of food industry. The thickened sludge is studied after a physico- chemical treatment.

2.2 Physico-chemical characterization

The study of physico- chemical characteristics involved several parameters. All analyzes were performed according to the AFNOR standards namely:

- The pH and electrical conductivity were measured in a sample of water-based mud (1g/10 ml) according to AFNOR NF T90- 008 method.
- Total organic carbon was determined by the method described by ANNE Aubert (1978).
- Kjeldhal total nitrogen (TKN) is determined by steam distillation according to the AFNOR T90 -110.
- Moisture (AFNOR X 31-102).
- Total Phosphorus (AFNOR T 90-023).
- The Heavy metal is determined by atomic absorption spectrophotometry (Schimadzu brand 2000)

2.3 Microbiological characterization

As our processing is done by hydrogen peroxide, we considered important to detect the presence of catalase bacteria. Catalase is an enzyme that allows the decomposition of hydrogen peroxide (oxygenated water) or water and oxygen. Then it is important to know the presence of catalase bacteria.

2.3.1 Isolation of strains from sludge samples

A sludge dilution 1/10 was carried out (Figure 1).

Then 10 µl of each dilution was carefully spread on Petri dishes containing 25 ml sterile nutrient agar and incubated in an oven at 37 ° C for 48 h.

The bacteria were subsequently isolated on nutrient agar according to the appearance of strains (colors, shapes).

After purification of the strains (Screening method), a catalase test was done as following:

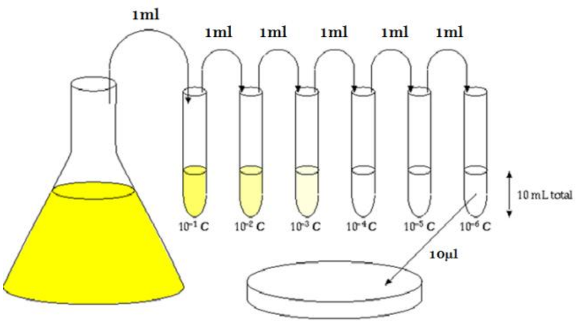


Figure 1: Seeding protocol

2.3.2 Catalase *test*

In the lid of a Petri dish ,we deposite biomass and put hydrogen peroxide (figure 2).

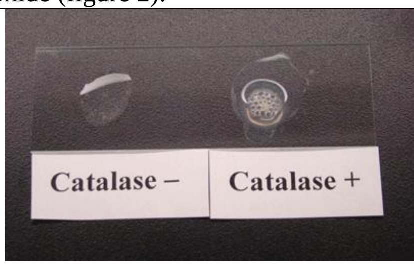
Bubble = catalase + No bubbles = catalase –	

Figure 2 : Catalase Test

2.4 Testing sludge treatment

The sludge oxidation tests were carried in a 500 ml reactor under mechanical stirring (Figure 3).
The reactor was charged with 5 g of sludge and 100 ml of distilled water.
The introduction of oxygen peroxide (30%) represents the zero time of the reaction which takes one hour.
Several oxidation tests were performed (table 1).

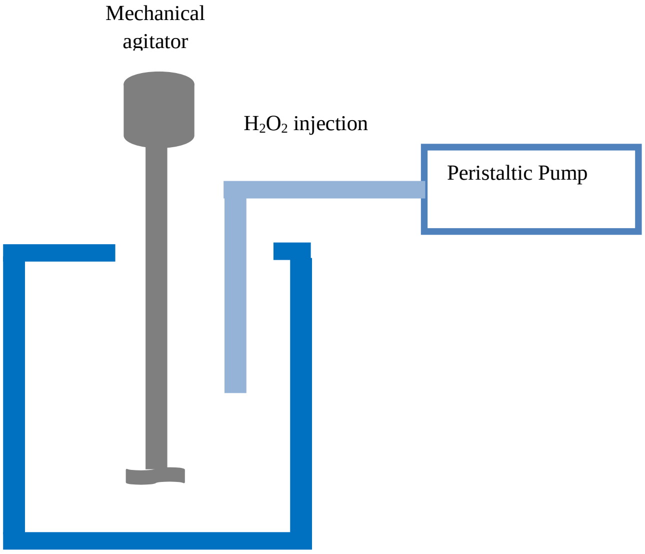


Figure 3: Schematic diagram of mounting sludge treatment

Table 1: Testing sludge treatment

Effect of oxidation by H_2O_2	Effect of oxidation by H_2O_2 at high temperature	Effect of oxidation by H_2O_2 in the presence of a catalyst (Fenton)
The addition of hydrogen peroxide (30%) using a peristaltic pump with a rate of 20 ml / h. the reaction lasted an hour.	The reactor is brought to 100°C. The hydrogen peroxide was injected at a rate of 20 ml / h to the reactor containing the sludge. The heating is maintained for 60 min.	The Fenton solution Fe^{2+} / H_2O_2 or Fe^{3+}/ H_2O_2 was then poured into sludge samples to start the process for 60 min.

*The Fenton solution was obtained by preparing a 100 ml solution containing Fe^{2+}, the initial pH was adjusted to 3 by the addition of H_2SO_4, the Fenton reaction is initiated after adding hydrogen peroxide.

The decomposition of hydrogen peroxide (H_2O_2) by ferrous ions generate radical species($OH°$, $HO_2°$, etc.) highly reactive with organic contaminants [4]. The decomposition of H_2O_2 by ferrous ions was first proposed by Haber and Weiss [5]. The reaction is radical type:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{2+} + OH^- + OH°$ Initiation (1)

$H_2O_2 + OH° \rightarrow H_2O + HO_2°$ Propagation (2)

$Fe^{2+} + OH° \rightarrow Fe^{3+} + OH^-$ Termination (3)

Given interference of H_2O_2 present in the sludge on the method of measurement of the TOC, the reduction of the organic matter was quantitated by measuring the total organic carbon (TOC). These analyses were carried out while following the protocole describes in figure 4.
We used the infrared spectroscopy (IR) to assess degradation and to determine the nature of the functional group which exists before and after each treatment.
Main transmission bands are given in Table (2).

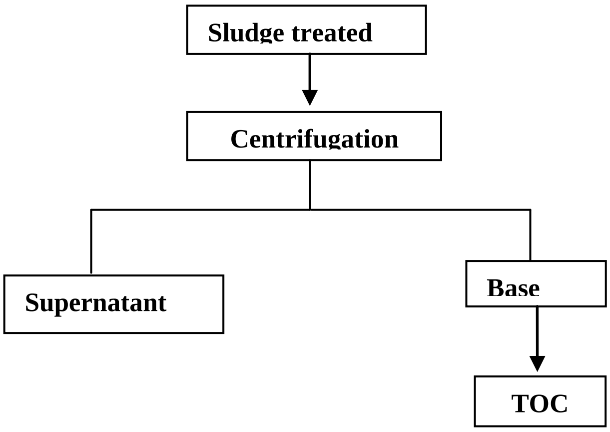


Figure 4: Analytical approach used for samples

Table 2: Transmission bands in the infrared spectra.

Wavelengths	Correspondance
3300-3500 cm^{-1}	Vibration H-OH (phenols, alcohols and carboxylic groups) N-H (amides and amines).
2925 cm^{-1}	Stretching vibration type C-H aliphatic structures (fatty acids, waxes and various aliphatic constituents).
2840 cm^{-1}	Symmetric stretch vibration CH in - CH_2 (alkanes and fatty acids)
1716 - 1740 cm^{-1}	Stretching vibration of C = O carboxyl groups COOH and ketones.
1620 - 1660 cm^{-1}	Stretching vibrations of C = O of primary amides Stretching vibrations of C = O ketone.
1200-1280 cm^{-1}	Vibrations of CH and OH deformation carboxyl groups, ethers CO cycle
700 et 900 cm^{-1}	Aromatic groups

3. Results and Discussion

3.1 Physico-chemical characterization

The sludge used in this study was obtained from the wastewater treatement plant of dairy industry. Results obtained after several series of analyzes are shown in Table 3.

Table 3 : Physico-chemical characterization of untreated sludge

	Untreated sludge	**Sludge refininge dible oils** [6].
Moisture %	77.7	75.86
pH	5.7	5.2
Conductivity (ms / cm)	3.61	4.1
Dry Matter %	22.3	24.14
Volatile Dry Matter %	96	-
Total Organic Carbon (g /kg)	423.5	359.1
Kjeldahl Nitrogen Total (g /kg)	14	11.5
Phosphorus (g /kg)	8.5	6.25
Fe (g/Kg)	26.2	-
Cr (g/Kg)	0.65	-
Zn (g/Kg)	0.68	-
Cd (g/Kg)	0	-
Cu (g/Kg)	0.21	-

Sludge analyzed are rich in organic matter and could compare them to sludge from a waste treatment of oil industry [5].
The presence of very high TOC concentrations in sludge is related to the activity of the industry.
The sludge is very lightly loaded of heavy metals.

3.2 Microbiological characterization:
We identified different bacteria (appearance, color), of negligible number.
The catalase tests are negatives, therefore the absence of catalase enzyme which allows the decomposition of hydrogen peroxide (oxygenated water) into water and oxygen.

3.3 Tests of sludge treatment with hydrogen peroxide.
The rates abatement of organic matter was quantified by measuring the total organic carbon (Figure 5).
We used the infrared spectroscopy (IR) to assess degradation and to determine the nature of the functional group which exists before and after each treatment.

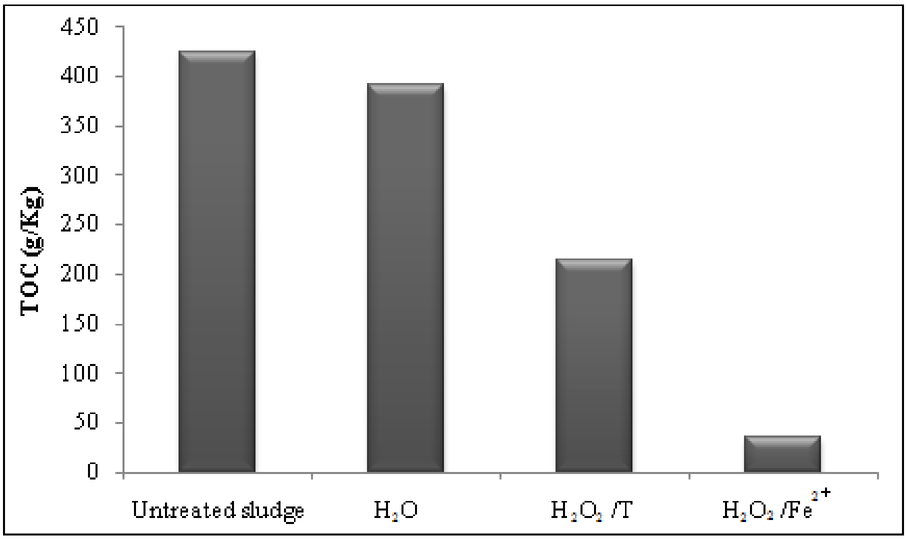


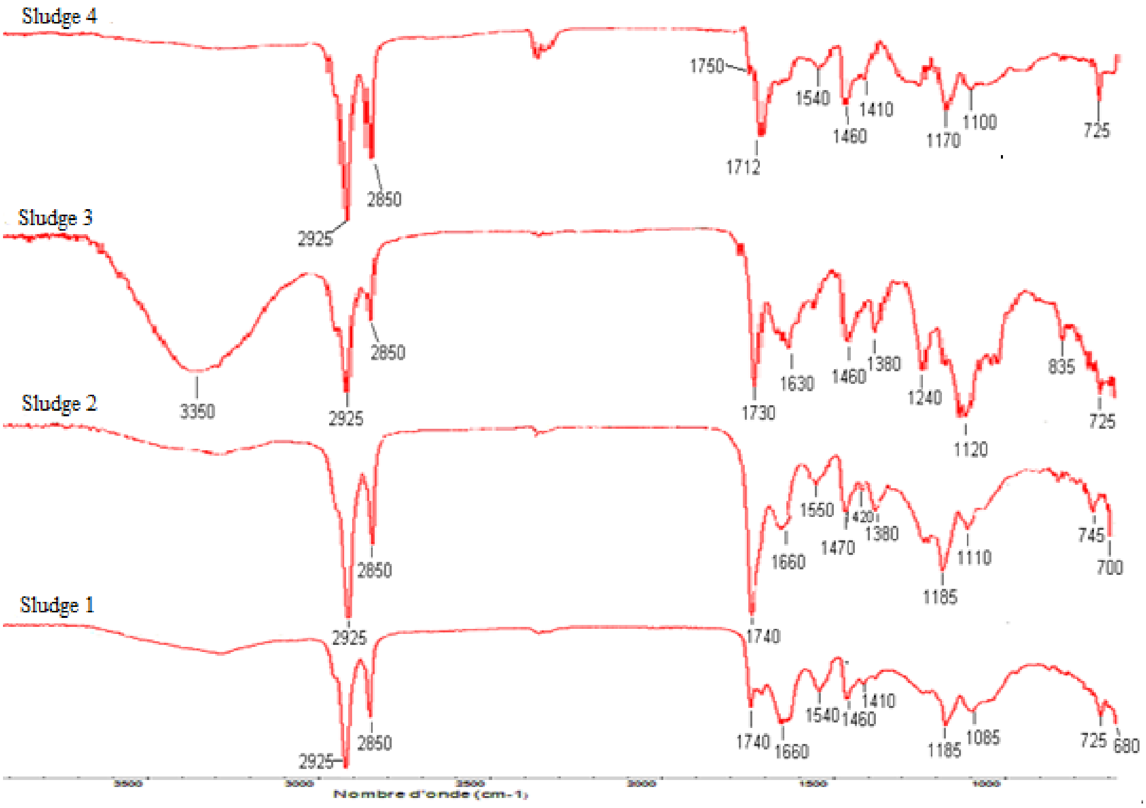
Figure 5: Comparison of rates TOC of different treatment trials

- *Effect of Oxidation sludge by H_2O_2:*

The oxidation of the sludge by H_2O_2 alone induced rates abatement of the COT 7,5 % (from 423.5 g/ kg to 391.5 g / kg) (Figure 5), this was confirmed by the results of infrared spectra. We notice that both of spectra (untreated sludge and sludge treated by peroxide alone) are similar. This can be explained by the ineffectiveness of this type of treatment (Figure 6). Although hydrogen peroxide is a strong oxidizing; several studies have shown that to use it alone is not sufficient for the removal of certain compounds.

- *Effect of Oxidation sludge by H_2O_2 at high temperature:*

The Sludge treatment by H_2O_2 at high temperature (100°C) induced a 50% reduction rate (from 423.5g/kg to 213.3g/kg) of total organic carbon (Figure 5); hydrogen peroxide is activated by the use of a relatively high temperature 100°C [7].
This activation by the temperature was also recorded by Rivas et al [8], Fang et al [9], Curreli et al [10], Trombotto et al [11].
If the temperature is increased, we generate both of the desorption of certain compounds initially adsorbed to the particles of sludge than the destruction of the solid organic materials (particles) of the components of the total solids [12].



Legend
Sludge 1: untreated sludge
Sludge 2: treated sludge by H_20_2
Sludge 3: treated sludge by H_20_2 /100°C
Sludge 4: treated sludge by H_20_2/Fe^{2+}

Figure 6: IR spectra of different types of sludge treatment

The study of the IR spectra of sludge treated with H_2O_2 at high temperature compared to raw sludge shows the disappearance of the peak 1660 cm^{-1} (Figure 6). This band corresponds to alkenes, which could be attributed to the reduction of functional groups alkene into functional group aliphatic according to Buxton et al [13].

We notice also the disappearance of the peaks 1235 and 1200 to1180 cm^{-1} corresponding to the CO bond and 1745 cm^{-1} corresponding to C = O. These bands correspond to the functional groups esters. Meanwhile, we notice the appearance of very broad and intense 3350 cm-1 band, this band corresponds to the functional alcohol group. This could be explained by the transformation of esters into alcohol.

- *The effect of Oxidation sludge by H_2O_2 in the presence of a catalyst (Fenton):*

The sludge treatment in the presence of H_2O_2 and ferrous ions at pH=3 called Fenton reagent H_2O_2/Fe^{2+} induces a reduction of more 91.5 % of the TOC levels (from 423.5 to 36g/kg). This was confirmed by analysis of the IR spectrum; the spectrum shows the disappearance of the peak 1660 cm^{-1} (Figure 6). This band corresponds to the functional groups C = C alkene, which could be explained by the reduction of functional groups alkene into alkanes.

According to Neyens et al [14], the addition of $OH^{\bullet}$ can open the unsaturated bonds of alkenes, and produce organic radicals $R^{\bullet}$ (Figure 7). They are highly reactive and may be further oxidized.

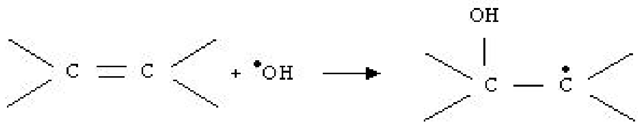


Figure 7: Addition of the OH • radical to a double bond

It is also to note the disappearance of the peaks 1235 and 1200 to 1180 cm^{-1} corresponding to the C-O bond and 1745 cm^{-1} corresponding to C = O, these bands correspond the Esters functional groups. Meanwhile, we notice the appearance of the bands between 1700-1725 cm^{-1} corresponding to carboxylic acids. This could be explained by the transformation of the esters to carboxylic acids.

We notice that for all types of sludge treatment, some aliphatic structures that absorb near 2925 and 2850 cm^{-1} are still abundant despite the treatment sludge. These aliphatic intermediates are difficult to oxidize [15].

The radical reacts faster on compounds with unsaturated double bonds (unsaturated). This reactivity decreases with saturated chain compounds (aliphatic) [16].

For compounds that contain double bonds (alkene, Ester ...), the radical attack is the double C = C bonds, followed by degradation [14]. Subsequent degradation by-products is quick, because these intermediates are also reactive with $HO^{\bullet}$ radicals [17].

According to Merz and Waters [18], oxidation of aromatic compounds almost never leads to CO_2, but at different intermediate oxidized. Among the oxidation of these intermediate products are the aliphatic groups, carboxylic acid ... , which are resistant to oxidation and easily converted to CO_2 [19].

Conclusion

The study of the oxidation of the sludge by H_2O_2 alone, at high temperature (100°C) and in the presence of metal ions (Fe^{2+}) showed that the use of hydrogen peroxide in the presence of Fe^{2+} ions induced rate significant reduction of more than 91.5% of total organic carbon, whereas the oxidation of sludge by hydrogen peroxide activated by heat induces a 50% reduction of total organic carbon. The action of H_2O_2 alone is almost ineffective for the oxidation of organic matter. The degradation of organic material with hydrogen peroxide depends strongly on the presence of Fe^{2+}/Fe^{3+}, and on the reaction temperature.

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