Development of an industrial wet air oxidation for waste treatment: a success story

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1. Introduction

Industrial effluents have variable compositions depending on the industry: refineries, pharmaceuticals, distilleries, food processing, paper mill… Legislations regulate more and more severely the management of these wastes and favor the development of alternative processes allowing to treat effectively particular pollutions, as in pre-treatment before a biological process or for a complete degradation of organic matters in carbon dioxide and in water. Wet Air Oxidation (WAO) processes answer very efficiently these constraints, especially for wastewaters that contains high chemical oxygen demand.

WAO aims at oxidizing the organic fraction of an aqueous effluent by contacting organic pollutants with an oxidizing agent, in conditions of temperature ranging from 100 to 340°C and a total pressure (of air or pure oxygen, according to the choice of the oxidizer) of 0,5 to 20MPa [1-2]. The oxidation yield is about 70 to 95 % with a residence time of 30 minutes to several hours [3]. The residual liquid phase contains mainly acetic acid, formic acid and other volatile fatty acids. In these operating conditions, the solubility of oxygen in water is more important than in the ambient conditions and favors degradation kinetics of the organic fraction in carbon dioxide and water. Lefèvre and al. [4] suggest that this technology is the most adapted solution for the aqueous effluents having a COD included between 20 and 200 $g.L^{-1}$, thanks to exothermicity of the oxidation reaction for its functioning. Beyond 200 $g.L^{-1}$, the amount of oxidizer becomes too important and generate higher costs that makes incineration more attractive.

Since 2011, CTTEi, INOVERTIS-A3i and Aix-Marseille University have been working together on R&D projects and industrial feasibility studies on hydrothermal processes for specific effluents: lagoon sludge, highly chlorinated wastewater, hospital effluents, leachates, frigate waste ... the partners have thus acquired multi-scale equipments to develop their technical skills and prepare for the industrialization of the process.

2. Materials and Methods

The recent scientific literature is dense as regards the experimental studies in laboratory on WAO of simple organic compounds or more complex effluents, in particular on the use of catalysts allowing to lower the conditions of pressure and temperature. However, all these studies do not supply enough information to design this process to industrial scale. On reaction aspects, the experimental work of the partners consists to run experiments with oxygen concentration conditions suitable for designing an industrial treatment unit, up to70% excess of oxygen, that is realistic contrary to 1000–2000% of excess found in literature [5]. The batch reactors used for these studies are made of stainless steel 316L or specific alloys (Inconel) for corrosion constraints. The autoclaves have the following characteristics: 30 MPa maximum pressure, 350°C maximum temperature. The temperature in the cell is kept stable by a hot (electric power)/cold (double jacket with air or water) regulating system. The stirring devices are Rushton type mixers and a dip tube at the bottom of the reactor allows to take samples at regular intervals during the experiments. Continuous units have the same temperature/pressure specifications and are equipped with heat exchangers, and maximum instrumentation to collect sizing data. The bubble column reactors, at the heart of the process, were the subject of in-depth work. The results have shown the importance to study this gas liquid systems at high pressure and temperature, the evolution being significantly different from the evolution obtained at ambient conditions. As no results existed before in literature, our studies allow to propose correlations and design parameters of bubble column functioning at high pressure and temperature. Therefore, a patent [6-7] has been elaborated for the design of bubble columns for wet air oxidation applications. These dimensioning parameters are currently used to build our continuous reactors for WAO.

Figure 1. Multi-scale equipment: A-200mL batch[b], B-1L batch[a], C-10 kg/h unit[a], D-1 kg/h unit[b], E-100 kg/h unit[c]

3. Results and discussion

The following table presents the results obtained by the teams of the partners on various deposits and under operating conditions sweeping the subcritical field of water.

Table 1. TOC reduction and operating conditions for WAO experiments

Waste	Partner	Temperature (°C)	Pressure (MPa)	Reaction time (min)	Maximum TOC or COD reduction (%)
Lagoon sludge	CTTEi	200-260	10-15	15	87
Frigate waste (paper, cardboard, plastics, bilge & wastewater)	AMU/INOVERTIS	200-300	15-20	60	97
Paper mill sludge	All	200-260	10-15	15	75
Landfill leachates	AMU/INOVERTIS	250-340	15-20	60	99
Chorinated wastewater	All	325	19	60	98
Radioactive wastewater & solvents	INOVERTIS	300-340	30	60-120	98

The results shows that TOC or COD reduction is temperature dependent, as it is generally observed in oxidation reaction. The yields obtained in batch reactors are confirmed or even improved on continuous systems, with lower oxygen/waste stoichiometries in connection with the optimization of the exchange surface in bubble column reactors (and therefore of the volumetric mass transfer coefficient k_La). The experimental data obtained at lab-scale (kinetic models, degradation yields, gas holdup and volumetric mass transfer coefficient k_La correlations) were used to design and manufacture the two last continuous units (C and D on Figure 1) which are the last step before the stage of a first industrial realization (scale of m^3/h).

4. Conclusions

The results obtained show that WAO is a high-performance alternative for the destruction of organic solid wastes and wastewater. The experimental data obtained will be used to carry out engineering studies for the implantation of optimized WAO unit at industrial scale or containerized compact units for autarkic sites, with an environmental comparison (done by life cycle analysis methodology) with the conventional solutions. Thus, depending on the performance to be achieved and the specific limitations of implantation, it may be preferred a milder temperature with a longer processing time (larger capacity reactor) or fast treatment at 300°C or more, with a more compact system. The scientific and technological aspects presented in this paper show an efficient collaboration between academic and non academic partners to propose an optimized solution for different industrial wastes treatment.

References

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