Catalysis Today 157 (2010) 420–424

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Performances of soluble metallic salts in the catalytic wet air oxidation of sewage sludge

Marco Bernardi [a], Didier Cretenot [b], Stéphane Deleris [c], Claude Descorme [a], Julien Chauzy [b], Michèle Besson [a,*]

[a] IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, UMR 5256 CNRS-Université Lyon 1, 2 Avenue Albert Einstein, 69626 Villeurbanne, France
[b] VEOLIA WATER, Technical Department, 94410 Saint Maurice, France
[c] ANJOU Recherche, Chemin de la Digue, 78603 Maisons Laffitte, France

ARTICLE INFO

Article history:
Available online 10 February 2010

Keywords:
Sewage sludge
Wastewater treatment
Wet air oxidation
Soluble catalysts
Batch reactor

ABSTRACT

Various soluble transition metal salts were compared in the wet air oxidation of industrial and municipal sewage sludges (2.5–25 g L^{-1} total organic carbon) at 200–250 °C under 4–15 bar O_2 partial pressure. The evolution of the TOC content in both the liquid and solid phases, and the overall TOC conversion were monitored. While copper sulphate prevented the dissolution of the suspended organic matter due to strong bounding of copper to a fraction of the organic matter in sludge, and showed high activity in the mineralization of the solubilized organic compounds (liquid phase), the implementation of iron sulphate resulted in a higher transfer of the organic matter to the liquid phase but in a moderate activity in the oxidation of solubilized molecules. When used in combination, a synergetic effect between these two salts was evidenced.

1. Introduction

Sewage sludge is the material which is generated upon conventional wastewater treatment processes. The sludge consists of a suspension containing non-degraded organics, the excess bacterial populations and some minerals. It possesses high moisture content (ca. 75–90 wt.%), and the dry matter contains 30–40 wt.% carbon. The management of sewage sludge is one of the most important and complex task to be addressed by the wastewater treatment sector, which accounts for about 50% of the total wastewater management costs [1]. Large volumes of sludge are produced every year. Furthermore, considering the promotion and the improvement of sewage water collection and the implementation of advanced wastewater treatment plants, the volume will undoubtedly continue to increase. In the same time, as the regulations concerning the waste management get more stringent, the most conventional disposal routes for sewage sludges (agricultural valorisation as fertilisers, landfilling and incineration) tend to be limited: (i) the use of sludge in the agriculture is a matter of controversial discussion, (ii) landfilling of waste with high organic content has been restricted in the recent years and the overall capacity is decreasing and (iii) the most serious environmental concerns related to incineration are the production of significant amounts of dioxin, furan and fly ash. In a near future, anyway, these management options will not be able to absorb the increasing sludge quantities. Subsequently, a growing attention has been paid to the development of suitable alternative solutions such as the energetic recovery through anaerobic treatment or gasification, or the oxidative treatments to reduce volumes [1].

One option which is currently gaining interest is the wet air oxidation (WAO) which consists in the oxidation of the organic pollutants in water using molecular oxygen at elevated temperature (150–330 °C) under high pressure (30–250 bar) [2–4]. Molecular oxygen dissolved in the wastewater reacts with the organic pollutants. A large fraction of the insoluble organic matters (proteins, lipids, carbohydrates, fibres, etc.) is transformed into simpler soluble organic compounds (sugars, aminoacids, fatty acids, etc.) which are in turn oxidized to intermediate easily biodegradable oxygenated products, carbon dioxide, inorganic salts and water after the complete oxidation.

The wet air oxidation of sludge was first implemented in the Zimpro process, with the objective of dewatering the sludge before landfilling [5]. Since then, different WAO processes have been developed and successfully commercialized [3]. The ATHOS® process, developed by Veolia Water, operates at 235 °C in the presence of 45 bar pure oxygen [2,6,7]. More than 80% of the total COD (chemical oxygen demand) is oxidized after a 1 h treatment.

Soluble transition metal salts, in particular copper sulphate, are known as effective catalysts in the wet air oxidation of model

---

[*] Corresponding author. Tel.: +33 472445358.
E-mail address: michele.besson@ircelyon.univ-lyon1.fr (M. Besson).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.01.030

pollutants and real wastewaters [2,4,8–16]. However, the use of metallic salts for the treatment of sewage sludge has not been studied in much details. Lendormi et al. [4] showed that the addition of copper sulphate in the continuous wet air oxidation of a sludge from an extended-aeration plant (1% Cu/COD) at 240 °C under 16.5 bar O_2 partial pressure increased the COD abatement from 71 to 86%. No explanation was proposed concerning the mechanism governing this process. Very little insights into the basics of the reactions are available in the literature. The aim of our study was then to investigate how copper sulphate and other transition metal salts may affect the WAO of sewage sludge upon batch experiments. As far as copper salts may cause heavy pollution, it appeared interesting to look for other salts such as iron salts.

2. Experimental

2.1. Materials

Most experiments were performed on a secondary sewage sludge obtained from an industrial plant treating effluents containing hydrocarbons, organic solvents, paintings and oily pollutants. Two batches collected at different periods of time were used. The first batch contained 21.4 wt.% dry solids, whereas the second batch was more diluted (10.9 wt.% dry solids). The elementary composition of the second batch was 32.3 wt.%C, 5 wt.%N, 4.6 wt.%H and 1 wt.%S on a dry basis. The inorganic part of the sludge was essentially composed of Ca (16%), Si (5.6%), Al (3.8%) and Fe (4.4%). After collection, the received sludge was centrifuged, the supernatant was eliminated and the received pasty sludge was divided into ca. 10 g homogeneous aliquots and frozen. Before any experiment, the pasty sludge was unfrozen and suspended in 150 mL water to reconstitute the sludge. Three municipal sludges, containing different volatile solid concentrations, were also tested.

The metallic salts $CuSO_4$ (copper II sulphate anhydrous) and $FeSO_4·7H_2O$ (iron II sulphate heptahydrate) were purchased from Merck.

2.2. Wet air oxidation treatment

Lab-scale experiments were performed in a 300 mL Hastelloy batch reactor equipped with a magnetically driven impeller and different control/measure tools such as a thermocouple, a rotameter and a pressure gauge. After loading the industrial sludge suspension (total organic carbon, $TOC_0 = 2.5–5.7\ g\ L^{-1}$) and the catalyst ($CuSO_4$ or/and $FeSO_4$, 0.063–6.3 mmol L^{-1} metal), the reactor was closed, purged using Ar and heated to the reaction temperature. The introduction of air was considered as time zero for the reaction. Different experiments were performed changing the reaction temperature (200 or 210 °C) and/or the air pressure (36 or 56 bar air).

Several experiments were also conducted in a 10 L semi-continuous reactor using 5 L of different more concentrated municipal sludge ($TOC_0 = 7.5–25\ g\ L^{-1}$) at 250 °C under 15 bar pure O_2 (oxygen flow rate 2.5 NL min^{-1}). The outlet gas phase was passed through different condensers and flasks containing sulphuric acid. Liquid samples were also withdrawn from the reactor through a sampling tube. The solid and liquid phases were further analyzed separately.

2.3. Analytical methods

After reaction, the whole suspension was recovered from the reactor and the TOC content of the supernatant and the solid, recovered after filtration, were measured using a Shimadzu 5050A TOC analyzer equipped with the solid SSM5000 module. The overall TOC conversion was then calculated. The oxidized liquors were further analyzed for the volatile fatty acids (VFAs) by gas chromatography using a Stabilwax-DA® capillary column (30 m × 0.53 mm) and a flame ionization detector. The transition metal concentrations in the supernatant and in the solid phase were measured by ICP-OES.

3. Results

3.1. Effect of copper and iron sulphates used separately upon batch experiments

The first series of experiments was carried out at 200 °C under 70 bar total pressure (56 bar of air, considering the water vapour pressure at 200 °C) using the sludge from batch 1. The oxygen stoichiometry for the total carbon mineralization was not achieved in that case.

Fig. 1 shows the TOC distribution between the solid and liquid phases as a function of the reaction time, upon independent experiments performed in the absence of catalyst or in the presence of $CuSO_4$ or $FeSO_4$ (6.3 mmol L^{-1}). Initially, the total organic matter in the suspension was in the insoluble form (TOC = 5775 mg L^{-1}). Upon heating under argon to the desired reaction temperature, some reactions took place resulting in the dissolution of part of the suspended organic matter. The TOC concentration in the liquid phase was 588 mg L^{-1} at time zero. After pressurization under air, the destruction of the sludge continued through (i) the thermal decomposition of the sludge, which resulted in the transfer of the organic substances from the solid to the aqueous phase, followed by (ii) the oxidation of the soluble organic compounds in the liquid phase. The results clearly show that the distribution was greatly affected by the addition of any metallic salt and clearly dependent on the nature of the catalyst.

In the absence of catalyst, the destruction of the particulate matter proceeded quickly and produced soluble organics which mainly remained unconverted in the aqueous phase. Indeed, the soluble TOC concentration only slowly decreased from a maximum of 2700 mg L^{-1} after 1 h to 2115 and 1835 mg L^{-1} after 8 and 24 h (not shown), respectively. The overall TOC conversion after 8 and 24 h were calculated to be 58.7 and 65%, respectively.

Upon the addition of copper sulphate (6.3 mmol L^{-1}, a concentration initially chosen to be close to those used in the literature for the degradation of model pollutants), the dissolution of the solid organic matter was greatly inhibited. After 1 h, solubilization was the same in both cases, but longer reaction times did not improve the transfer of the solid organic matter to the liquid phase in the presence of the metallic salt. Whereas a beneficial effect on the mineralization degree was clearly observed in the first 3 h, the overall TOC conversion after 8 h was lower compared to the uncatalyzed run, i.e. 46.4% vs. 58.7%. In reality, the TOC conversion decrease was mainly due to the higher amount of TOC remaining in the solid. Indeed, the TOC remaining in the solid was as high as 1642 mg L^{-1} after 24 h reaction compared to 184 mg L^{-1} in the uncatalyzed experiment. Nevertheless, the catalytic activity of copper in the mineralization of the solubilized compounds was clearly demonstrated. The beneficial effect of copper on the overall TOC conversion for reaction times shorter than 3 h is thus explained by the efficient mineralization of the soluble fraction in the presence of copper.

In contrast, when iron sulphate was used, the TOC content in the residual solid significantly and rapidly decreased compared to the uncatalyzed run. However, the mineralization activity (solubilized organics) was only moderate. The overall TOC conversion reached 64.8% after 8 h.

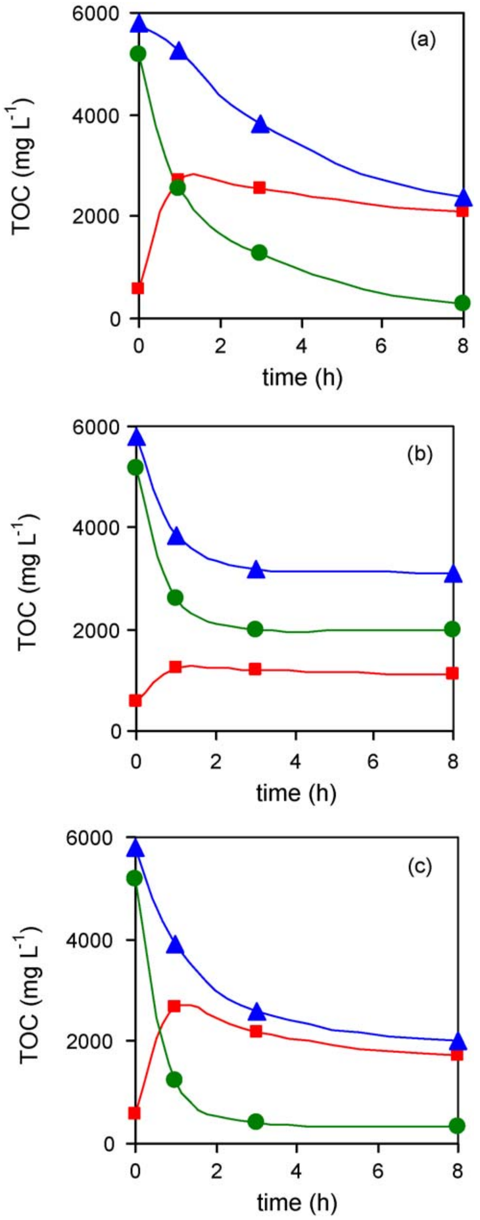

Fig. 1. CWAO of an industrial sewage sludge (batch 1, TOC_0 = 5775 mg L^{-1}) at 200 °C under 56 bar air in the absence (a) or in the presence of 6.3 mmol L^{-1} copper sulphate (b), and iron sulphate (c) catalyst: (▲) total TOC in the suspension, (■) soluble TOC and (●) solid TOC.

These results indicated that copper and iron sulphates (TOC:metal molar ratio = 75) influenced the solubilization of the solid phase differently. Iron sulphate seemed to improve the transfer of the organic compounds, initially present in the solid phase, to the liquid phase, while copper had some inhibiting effect. Furthermore, iron showed a limited mineralization capacity, much lower than copper.

Considering these results, the effect of copper sulphate was further studied by varying the copper concentration in the range 0.05–2 g L^{-1} (0.3–12.6 mmol L^{-1}). The results presented in Fig. 2 give the TOC concentrations in the solid and liquid phases after 8 h reaction. As the copper concentration increased, the TOC content in the residual solid significantly increased, while the TOC concentration in the liquid phase decreased. These data confirmed (i) the inhibiting effect of copper with respect to the solid matter solubilization and (ii) the high mineralization capacity of copper for the organic compounds in the liquid phase. Quite good results were obtained at a Cu dose as low as 0.1 g L^{-1}, yielding 65.2% overall TOC conversion. At such concentration, the inhibiting effect of the copper salt on the solubilization was largely compensated by the beneficial effect on the mineralization of soluble organic compounds in the liquid phase.

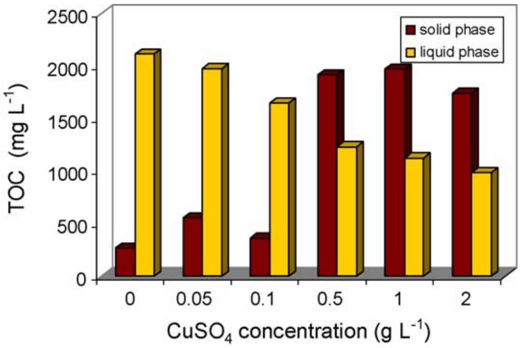

Fig. 2. Evolution of the TOC concentration in the solid and liquid phases as a function of the copper sulphate concentration upon CWAO of an industrial sludge (batch reactor): TOC_0 = 5775 mg L^{-1}, T = 200 °C, P_{air} = 56 bar and t = 8 h.

These results suggest a reduction in the solid solubilization efficiency with the addition of $CuSO_4$, whereas it was improved with the use of $FeSO_4$. The large amount of TOC retained in the solid phase after the addition of copper may be explained in the light of the studies on the sludge sorption affinity for metals. Sewage sludges from wastewater treatment plants are complex mixtures of particulate and colloidal organic matters, such as extra cellular polymer substances, humic acids, bacterial detritus, etc. These compounds may exhibit great affinity for the sorption of heavy metals due to their high organic matter content, polyfunctional character and reactive surface area. The uptake of heavy metals, and among them copper, has been the subject of numerous studies. Copper in activated sludges has been shown to be strongly bounded to the organic materials and to be associated with the extra cellular polymeric substances, which contain numerous complexing sites [17]. Surface binding and complexation at the negatively charged functional groups at the surface is the predominant mechanism which was identified to be responsible for the heavy metal uptake [18–20]. In particular, the stability of the Cu complexes was very high compared to Pb or Cd [17]. It appears that most of the copper is strongly bounded to this organic fraction in the sludge which is not readily degraded and solubilized.

On the other hand, copper may also form complexes with the soluble organic compounds, and the role of copper is then the degradation of soluble organic compounds. Indeed, the high oxidation capacity of the copper salts has been largely described in the literature [2,4,8–16]. The distribution of the Cu complexes may also vary during the reaction upon mineralization of the soluble products. At the beginning of the reaction, these dissolved organic molecules act as ligands towards the copper ions. Once they are efficiently oxidized, copper sorption on the sludge particulates occurs to a large extent. The analysis of the Cu distribution between the liquid and solid phases at the end of the reaction also confirms the complexing behaviour of copper. At low concentrations in copper sulphate (0.05 and 0.1 g L^{-1}) the metal was equally recovered in the liquid and solid phases. On the contrary, at higher concentrations, most of the copper was recovered in the solid (70–80%).

As for iron sulphate, an accelerating effect on the solubilization of the suspended solids was observed. Since iron is non-toxic, no data concerns the iron uptake by sludge, but other potentially toxic elements such as Zn, Cr, Cd, Ni, Pb, Hg, etc. have been investigated. One may note the poor retention of Ni on the solid phase [21,22]. However, this effect suggests that, on one hand, Fe binds less strongly to the solid fraction but, on the other hand, Fe readily reacts with some components in the sludge, through the hydrolysis and/or the depolymerization of polysaccharides or proteins. Furthermore, iron was totally recovered in the liquid phase.

More studies would be required to further explore and monitor the retention of copper and iron ions by the sludge as a function of the overall TOC conversion.

3.2. Synergetic effect between iron and copper upon batch experiments

Since iron sulphate improved the solubilization of the solid organic matter and copper sulphate acted favourably on the mineralization of organic intermediates in the liquid phase, a combination of both salts was tested. Sewage sludge from batch 2 was then used. Experiments were performed using a sludge suspension containing 2490 m g L^{-1} TOC initially. The temperature was set at 200 or 210 °C and the air pressure was fixed at 36 or 56 bar. Such air pressures corresponded to either a stoichiometric amount or an excess oxygen stoichiometry compared to the total mineralization of the suspension. Thus, the effect of the salts could be evaluated under harsh or middler operating conditions. The total metal concentration was fixed at 0.63 mmol L^{-1} in order to minimize the effect of copper on solubilization.

Transformations upon heating did not depend significantly on the reaction temperature. At time zero, 29.3% solubilization and 8.7% overall TOC conversion through thermolysis were measured at both temperatures. Table 1 compares the TOC concentrations in the solid and the liquid as well as the overall TOC conversion after 3 h of reaction in the absence of catalyst, or in the presence of $CuSO_4$, $FeSO_4$ or a mixture of both salts (Cu/Fe = 70/30 mol%). The total metal concentration was fixed at 0.6 mmol L^{-1}.

Further solubilization of the solid organic matter depended on both the temperature and the air pressure: the amount of residual TOC in the solid decreased as the temperature and/or the air pressure increased. Thus, in the absence of catalyst and under 36 bar air, the remaining TOC in the solid after 3 h decreased from 147 to 62 mg L^{-1}, going from 200 to 210 °C. The effect of pressure was as important: a decrease from 147 to 79 mg L^{-1} at 200 °C, and from 62 to 34 mg L^{-1} at 210 °C was observed by increasing the air pressure from 36 to 56 bar. Furthermore, in the presence of copper, the TOC in the solid decreased from 149 to 47 mg L^{-1} and from 103 to 32 mg L^{-1} at 200 and 210 °C, respectively, as the pressure increased from 36 to 56 bar.

Though lower amounts of metallic salts were used, the same effects as previously were observed for copper and iron, especially under less severe conditions. For instance, after 1 h reaction at 200 °C under 36 bar air, the TOC content in the solid upon the Cu-catalyzed run was the same as upon the uncatalyzed run (400 and 427 mg L^{-1}, respectively), while this value was lower in the presence of iron (225 mg L^{-1}). Upon oxidation, solubilization continued and the remaining TOC content in the solid after 3 h was 147 mg L^{-1} in the absence of catalyst, 149 mg L^{-1} in the presence of $CuSO_4$, and as low as 94 mg L^{-1} when $FeSO_4$ was used. At higher temperature (210 °C), the effect of the salts was observable at the lower air pressure, with a residual TOC content in the solid after 3 h reaction of 62 mg L^{-1} (no catalyst), 103 mg L^{-1} ($CuSO_4$) and 54 mg L^{-1} ($FeSO_4$), but much less visible at higher pressure since solubilization became predominant.

Once solubilized, the organic compounds were subsequently mineralized. The results again demonstrated the higher catalytic activity of copper sulphate for the mineralization of the soluble organic compounds at any operating conditions. The overall TOC conversion within a given period of time was calculated by subtracting the final TOC contents in the liquid and the solid from the initial TOC content in the suspension and compared. During the first hour under air, solubilization of the solid materials occurred to a very high extent: more than 2000 mg L^{-1} TOC. Among these accumulated soluble compounds, the most easily oxidized compounds were probably rapidly degraded at the early stages of the reaction. Consequently, the differences in the mineralization efficiencies for copper were moderate, though clearly noticeable since a systematic higher mineralization was calculated at any conditions in the presence of copper. After 1 h reaction, considering, on the one hand, an initial TOC concentration in the suspension of 2490 mg L^{-1} and on the other hand a TOC content of 152 and 1429 mg L^{-1} in the solid and liquid phase, respectively, after reaction at 210 °C under 36 bar air, 909 mg L^{-1} of carbon have been converted into carbon dioxide upon the uncatalyzed run. The corresponding value for the copper-catalyzed reaction was 1127 mg L^{-1}. Similarly, under 56 bar air and after 3 h reaction, 1533 and 1698 mg L^{-1} have been mineralized upon the uncatalyzed and copper-catalyzed runs, respectively. The improvement in the overall TOC conversion after

Table 1

Catalytic wet air oxidation of an industrial sewage sludge (batch 2, TOC_0 = 2490 mg L^{-1}) using 0.63 mmol L^{-1} metallic salt as a catalyst: TOC concentration in the solid (TOC_{sol}, mg L^{-1}) and the liquid (TOC_{liq}, mg L^{-1}) and overall TOC conversion (%) after 1 h or 3 h reaction at different *T* and *P* conditions.

	No catalyst		$CuSO_4$		$FeSO_4$		$CuSO_4 + FeSO_4$[a]	
	1 h	3 h	1 h	3 h	1 h	3 h	1 h	3 h
200 °C, 36 bar								
TOC_{sol}	427	147	400	149	257	94	225	64
TOC_{liq}	1180	1427	1152	1249	1544	1310	1429	1146
TOC conv	35.5	40.8	37.7	43.9	27.7	43.6	33.6	51.4
200 °C, 56 bar								
TOC_{sol}	192	79	223	47	154	51	200	24
TOC_{liq}	1562	1136	1307	1020	1549	1306	1436	1015
TOC conv	29.6	51.2	38.6	57.8	31.6	45.5	34.3	58.3
210 °C, 36 bar								
TOC_{sol}	152	62	179	103	100	35	151	0
TOC_{liq}	1429	1066	1184	948	1402	1225	1211	892
TOC conv	36.5	54.7	45.3	57.8	39.7	49.4	45.3	64.2
210 °C, 56 bar								
TOC_{sol}	82	34	116	32	34	46	80	7
TOC_{liq}	1309	923	1256	760	1308	1073	1161	718
TOC conv	44.2	61.6	44.9	68.5	46.1	55.1	50.2	70.7

[a] Cu/Fe molar ratio = 70/30.

3 h with the addition of copper was essentially due to the efficient mineralization of the soluble fraction. Iron sulphate, though very effective in the solubilization was only poorly active in the mineralization, therefore the overall TOC conversions were close to those upon the uncatalyzed runs.

At that stage, the results obtained in the two series of experiments (5775 or 2490 mg L^{-1} TOC) showed that both metallic salts exhibit different performances upon the treatment of the sludge suspension. Copper is a very good catalyst, leading high mineralization rates of the solubilized compounds. However, copper also tends to hinder the solubilization step. The latter effect might be minimized by operating at higher pressure and/or temperature. On the other hand, iron sulphate shows interesting performances in the solubilization of the solid organic matter, while it is only slightly active in the mineralization. A synergetic effect was clearly observed by combining both metallic salts. When used together in a 70/30 molar ratio, intermediate overall TOC conversions were achieved compared to each metallic salt taken alone. After 3 h, the TOC abatements were always higher. This effect was important at the higher temperature (210 °C), when solubilization reached high degrees and copper sulphate was able to act on the mineralization of the most recalcitrant organic compounds. After 3 h at 210 °C, the solid was nearly totally transferred to the liquid phase which contained no more than 0.7 g L^{-1} TOC. In conclusion, this synergetic effect could easily be explained by the combination of (i) the easier solubilization of the suspended solids in the presence of iron and (ii) the higher mineralization activity of copper in solution.

3.3. Semi-continuous reactor

These conclusions were further confirmed during the oxidation of three different municipal sewage sludges in a semi-continuous pilot-scale reactor under more severe conditions (250 °C, 15 bar O_2). Sludge A ($TOC_0 = 25$ g L^{-1}) was obtained from a municipal wastewater treatment plant and contained a high volatile solid content (65.9%). Sludge B ($TOC_0 = 7.5$ g L^{-1}) and Sludge C ($TOC_0 = 21.5$ g L^{-1}) were taken from an anaerobic digester, without or with a lysis pre-treatment, and contained 47.5 and 33.4% volatile solid. The TOC in the liquid phase was analyzed as previously mentioned. Furthermore, since the formation of carboxylic acids, mainly acetic acid, is systematically observed in addition to carbon dioxide and water, the oxidized liquors were also analyzed for the volatile fatty acids (VFAs, C2–C6 carboxylic acids) by gas chromatography. The results are summarized in Table 2. $CuSO_4$ and the ($CuSO_4 + FeSO_4$) mixture gave similar TOC conversions after 2 or 3 h treatment. However, at similar TOC conversions, the mixture gave higher yields in volatile fatty acids (VFA). As an example, the TOC remaining in the liquid phase after 2 h treatment of Sludge A, consisted in only 54% VFA in the presence of copper, whereas this value reached 83% in the presence of the mixture. Similarly, the percentage of acetic acid was higher than in the presence of $CuSO_4$. The use of both salts significantly increased the concentration in carboxylic acids in the oxidized liquors, especially acetic acid.

Table 2
CWAO of municipal sludges in a 10 L semi-continuous reactor at 250 °C under 15 bar O_2 for 2 h (Sludge A) or 3 h (Sludges B and C) in the presence of $CuSO_4$ or ($CuSO_4 + FeSO_4$) mixture, as catalyst.

Sludge	Catalyst	TOC conv. (%)	VFA (%)	Acetic acid (%)
Sludge A	$CuSO_4$	83.0	53.7	39.8
$TOC_0 = 25$ g L^{-1}	$CuSO_4 + FeSO_4$	79.0	83.1	56.5
Sludge B	$CuSO_4$	70.3	29.2	27.2
$TOC_0 = 7.5$ g L^{-1}	$CuSO_4 + FeSO_4$	73.0	43.8	40.7
Sludge C	$CuSO_4$	82.8	63	20
$TOC_0 = 21.5$ g L^{-1}	$CuSO_4 + FeSO_4$	82.1	69	31

4. Conclusions

The performances of copper and iron salts, used either separately or in combination, were compared in the catalytic wet air oxidation of different sewage sludges. The influence of the reaction temperature, pressure and oxidant pressure was evaluated. In this preliminary study, although the relative importance and evolution of the metallic salts complexation by the dissolved and particulate organic matters remain to be elucidated, a number of conclusions might be clearly drawn. Soluble metallic salts act as efficient catalysts, but in different ways. Iron favours the solubilization of the solid organic matter, while copper improves the mineralization of the organic compounds in the liquid phase. The performances of the ($CuSO_4 + FeSO_4$) mixture were at least similar to those of $CuSO_4$ in terms of TOC overall conversion. However, the mixture gave an increased amount of carboxylic acids (especially acetic acid) in the oxidized liquor, suggesting that both salts act in synergy.

References

[1] D. Fytili, A. Zabaniotou, Renew. Sustain. Energy Rev. 12 (2008) 116–140.
[2] M. Djafer, F. Luck, M.M. Bourbigot, in: Proceedings of the 1st International Conference on Advanced Oxidation Technologies, London, Ontario, (1994), p. 207.
[3] F. Luck, Catal. Today 53 (1999) 81.
[4] T. Lendormi, C. Prevot, F. Doppenberg, J.N. Foussard, H. Debellefontaine, Water Sci. Technol. 44 (2001) 161.
[5] F.J. Zimmermann, Chem. Eng. 56 (1958) 117.
[6] M. Belkhodja, J.-P. Levasseur, D. Cretenot, in: Proceedings of the Annual International Conference On Incineration and Thermal Treatment Technologies 22nd, Orlando, USA, May 12–16, (2003), p. 74.
[7] E. Guibelin, Water Sci. Technol. 49 (2004) 209.
[8] F. Luck, M. Djafer, M.M. Bourbigot, Catal. Today 24 (1995) 73.
[9] C.J. Chang, J.-C. Lin, C.-K. Chen, J. Chem. Technol. Biotechnol. 57 (1993) 355.
[11] S. Imamura, T. Sakai, T. Ikuyama, Ind. Eng. Chem. Res. 38 (1999) 1473.
[12] R.V. Shende, V.V. Mahajani, Ind. Eng. Chem. Res. 33 (1994) 3125.
[13] S.H. Lin, S.J. Ho, Appl. Catal. B: Environ. 9 (1996) 133;
L. Lei, G. Chen, X. Hu, P.-L. Yue, Water Environ. Res. 72 (2000) 147.
[14] A. Garg, S. Saha, V. Rastogi, S. Chand, Indian J. Chem. Technol. 10 (2003) 305.
[15] Y. Kaçar, E. Alpay, V.K. Ceylan, Water Res. 37 (2003) 1170.
[16] B. Kayan, A.M. Gizir, React. Kinet. Catal. Lett. 84 (2005) 189.
[17] D.L. Lake, P.W.W. Kirk, J.N. Lester, Water Res. 23 (1989) 285.
[18] G. Guibaud, N. Tixier, A. Bouju, M. Boudu, Chemosphere 42 (2003) 1701.
[19] G. Guibaud, S. Comte, F. Bordas, S. Dupuy, M. Baudu, Chemosphere 59 (2005) 629.
[20] A.H. Hawari, C.N. Mulligan, Process. Biochem. 41 (2006) 187.
[21] R.J. Oake, C.S. Brooker, R.D. Davis, Water Sci. Technol. 17 (1984) 587.
[22] D.J. Ashworth, B.J. Alloway, Environ. Pollut. 27 (2004) 137.