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

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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.

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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

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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 $FeSO_4 \cdot 7H_2O$ (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.