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Catalytic wet air oxidation of biosolids in a monolithic reactor

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Abstract

Wet air oxidation (WAO) was studied as an alternative to wastewater treatment solids (biosolids) incineration. WAO of biosolids was performed in the presence of a monolithic copper/titania catalyst. The total pressures were in the range 4.0–4.7 MPa, and the temperature was 508 K. The flow pattern in the horizontal tube reactor was plug flow. Compared to non-catalytic runs, the presence of the catalyst increased the oxidation of biosolids significantly.

1. Introduction

Sludge management is an essential part of the wastewater treatment process. The volume of sewage sludge (biosolids) is steadily growing in Europe, due to the implementation of the 1991 EU Wastewater Directive. Simultaneously, increased environmental constraints and an unfavorable public opinion challenge the application of existing biosolids disposal routes (agricultural use, landfill and incineration). This context presses for novel effective and acceptable sludge management processes.

Destruction of organic matter of biosolids and large reduction in biosolid volume are achieved either by incineration or by wet air oxidation (WAO) which needs no fuel and generates minimal air pollution problems. The aim of this study was to explore less aggressive process conditions for WAO by using a combination of molecular oxygen with catalysts. The current paper describes the use of a copper/titania monolith catalyst which should provide optimal transfer properties because of its unique geometry.

2. Wet air oxidation

Wet air oxidation is an attractive destruction method for the treatment of waste streams which are too dilute to incinerate and too concentrated for biological treatment. It can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures. Typical conditions for wet air oxidation range from 440 K and 2 MPa to 600 K and 14 MPa. Residence times may range from 15 to 120 min, and the chemical oxygen demand (COD) removal may typically be about 75 to 90%. Insoluble organic matter is converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water, without emissions of NO_x, SO_2, HCl, dioxins, furans, fly ash, etc. The last residual organic compounds are fatty acids, especially acetic acid.

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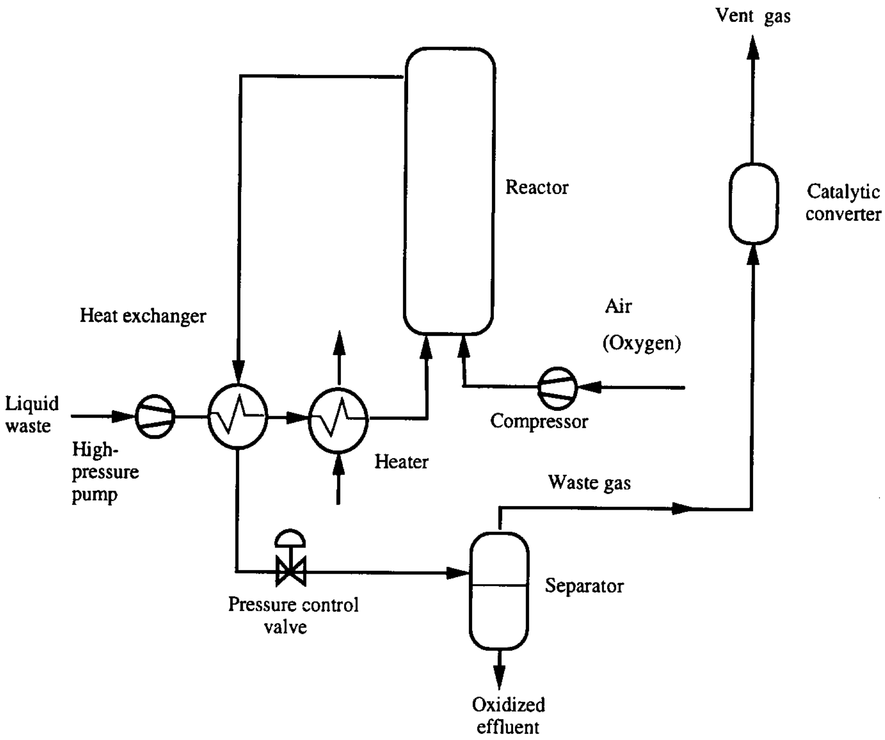

Fig. 1. Flow diagram of a wet air oxidation plant.

Fig. 1 shows a basic WAO flow diagram. The plant consists of only a few elements: a high-pressure pump, an air or oxygen compressor, a heat-exchanger as well as a reactor with a relief valve and a downstream separator. The waste is retained in the reactor for a sufficient period of time to achieve the desired chemical oxidation. The oxidized effluent is cooled down by heat exchange with the feed before pressure release through a control valve. The simplest reactor design is usually a concurrent vertical bubble column with a height-to-diameter ratio in the range of 5–20. Some design aspects of WAO reactors have been reported [1–3].

WAO was developed in the mid-40s as a process to recover vanillin from spent pulping liquor and has been used as early as 1962 to oxidize sewage sludge [1]. However, drastic temperature and pressure conditions (i.e. 543 K, 12.5 MPa in [1]) entailed high capital and operating costs preventing extensive development of WAO for biosolid application. The challenging operating conditions of WAO provided a strong driving force to investigate catalysts which would allow substantial gains on temperature, pressure and residence time. Thus, several types of heterogeneous catalysts were studied in the last decades, mostly based on supported or unsupported base metal oxides [4–20] (Table 1).

For some applications, as it would be the case for biosolids, the presence of suspended solids requires a monolithic catalyst reactor to minimize bed plugging. Two-phase flow in vertical monoliths gives in a broad range of G–L velocities a very beneficial flow pattern, the slug flow (segmented gas–liquid flow). Since each liquid plug is sandwiched between two gas plugs, a recirculation pattern is developed within each liquid plug, which improves mass transfer significantly [21] and could also in our case prevent solid deposition. In addition, a thin liquid film is formed between the gas and the channel wall which allows high mass-transfer rates while keeping the catalyst continuously wetted.

Table 1
Summary of reported heterogeneous catalytic WAO research

Catalyst		Application	Ref.
Active phase	Carrier		
Cu	Alumina	Phenol	[4]
Cu	Alumina	Phenol	[5]
Cu	Alumina	*p*-Cresol	[6]
Cu	Alumina, silica	Chlorophenols	[7]
Cu–Zn	Alumina, silica	Phenol compounds	[8]
Cu–Mg–La	Zn aluminate	Acetic acid	[9,10]
Mn	Alumina	Phenol	[4]
Mn	SR 115	Chlorophenols	[7]
Mn–Ce	None	Poly(ethyleneglycol)	[11]
Mn–Zn–Cr	None	Industrial wastes	[12]
Cu–Co–Ti–Al	Cement	Phenol	[13]
Co	None	Alcohols, amines, etc.	[14]
Co–Bi	None	Acetic acid	[15]
Co–Ce	None	Ammonia	[16]
Fe	Silica	Chlorophenols	[7]
Ru	Cerium oxide	Alcohols, phenol, etc.	[17]
Ru–Rh	Alumina	Spacecraft wastewater	[18]
Pt–Pd	Titania–zirconia	Industrial wastes	[19]
Ru	Titania–zirconia	Industrial wastes, sludge	[20]

This type of three-phase reactor is already used commercially for hydrogenation of anthraquinone in hydrogen peroxide production [22] and two catalytic WAO processes based on a precious metal/TiO_2–ZrO_2 honeycomb catalysts have been developed in Japan [19,20]. To our best knowledge only one academic study of catalytic WAO involving a monolithic reactor has been previously published [5]. From this background and the results obtained with biosolids oxidation in presence of Cu^{2+} in solution [23], a supported copper honeycomb catalyst was evaluated in this study.

3. Experimental

3.1. Characteristics of the monolithic copper catalyst

The monolith catalyst used in this study was extruded titania doped with several metal oxides by the manufacturer (Siemens). The honeycomb structure consisted of 1225 vertical parallel channels with a height of 465 mm (cross-sectional edge length 150 × 150 mm). The square channels had a width of 3.56 mm, with a wall thickness of 0.65 mm. The density of the catalyst was 620 kg/m^3 with a bed porosity of 87%. The total volumetric liquid–solid mass transfer area of the catalyst was 775 m^{-1}.

The monolithic catalyst was doped with copper by soaking in a copper nitrate hexahydrate solution with a concentration suited to achieve 5 wt.-% CuO in the calcined catalyst. It was then successively carefully drained, dried overnight at 328 K and calcined in an electric oven during 20 h with temperature ranging from 423 to 723 K. Prior to use, the honeycomb was cut into a cylindrical form 45 mm in diameter (81 cells), to fit into the flow reactor.

3.2. Reactors

The wet oxidation of biosolids was studied in a continuous flow single coiled horizontal tubular reactor with high effluent recycle, not originally designed for heterogeneous catalytic reactions. The reactor was an electrically heated 316 L stainless steel tube of about 6 m long, with an internal diameter of 50 mm. The raw material was a mixture of primary and secondary sludge containing 5% solids before dilution and a chemical oxygen demand (COD) value of 70 g/l. Biosolids diluted with water to COD in the range 5–10 g/l were fed through a positive displacement pump (Hydra-Cell) with a flow rate of 0.13 dm^3/min. Pure oxygen was used as the oxidizing gas (Alphagaz gas cylinders) and was injected at a constant flow rate based on stoichiometric demand through the use of a gas mass flow controller (typical flow rate of 0.70 dm^3/min (NTP, 273 K and 1 atm)). A recycling pump (Caster) circulated the gas–liquid mixture in the reactor with a total flow rate of 133 dm^3/min, inducing CSTR behavior.

The total catalyst load was 0.92 kg, in form of 3 pieces (length 465 mm, diameter 45 mm) inserted in the upper horizontal tube. An electronically controlled back pressure regulator controlled the pressure in the entire reactor system.

The time required to reach steady state with the reactor initially filled with pressurized water at reaction temperature was about 100 min. Typical operating conditions were 4.5 MPa total pressure, temperature 508 K and 1 h residence time.

Comparative tests were carried out in a 1-l stainless steel electrically heated batch autoclave (Autoclave Engineers) filled with 100 ml biosolid samples and the oxygen pressure corresponding to O_2/COD = 1.0. Stirrer speed was set at 1500 rpm for all runs and switched only when the reactor reached reaction temperature. The impeller was designed to draw gas continuously from above the liquid and redisperse it in the aqueous phase to ensure high gas–liquid mass transfer capabilities.

3.3. Chemical analysis

The change in liquid-phase composition was followed by COD analysis on samples collected from the flow reactor exit every 20 min. In selected cases the solutions were analyzed for metal content, to determine the extent of any dissolution of catalyst under reaction conditions. Some samples were also submitted to a quantitative analysis of nitrogen species and carboxylic acids.

4. Results and discussion

4.1. COD abatement

Compared to blank tests without catalyst in which COD removal was 58%, the presence of the titania-based catalyst increases the COD removal up to 72–74% (Fig. 2). Most of the residual COD consisted of carboxylic acids, 50–60 wt.-% of these being acetic acid, which is known to be refractory to oxidation [24]. Organic nitrogen compounds were converted into ammonium (85%), dinitrogen (10%) and nitrate (5%). Eight 5 h-runs were performed with the same catalyst load without any activity decrease. However, traces of copper (2–10 mg/l) leached from the catalyst were detected in the supernatant after reaction. These values are approximately two orders of magnitude lower than those reported in a recent WAO study with a different copper catalyst [25].

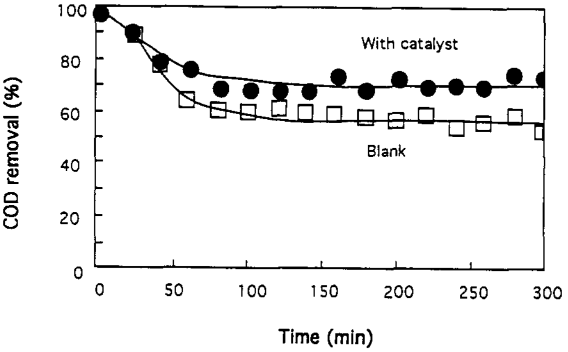

Fig. 2. Effect of a monolith catalyst on wet air oxidation of biosolids. Operating conditions: temperature 508 K, total pressure 4.0 MPa, O_2/COD 0.96.

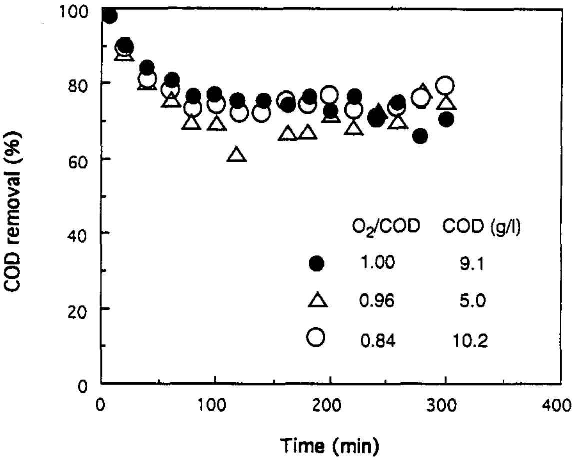

Fig. 3. Effect of initial COD and O_2/COD ratio on catalyzed wet air oxidation of biosolids. Operating conditions: temperature 508 K, pressure 4.0–4.7 MPa.

Fig. 3 shows biosolid oxidation curves obtained in the flow reactor in presence of the monolith catalyst at 508 K and about 4.5 MPa total pressure. In these runs, the initial COD loading as well as the oxygen/COD ratio were varied, without any clear influence on the COD abatement. This behavior is in agreement with the frequent observation of a first-order reaction for organic compounds and a zero-order reaction for oxygen [24]. In CSTR conditions with refractory compounds, the reaction mainly takes place in the bulk of the liquid with oxygen concentration in the liquid approaching saturation concentration [2].

A comparative test was performed in the stirred batch autoclave reactor, in which the monolith catalyst (3.4 g) was placed in form of small fragments (6–12 mm). The catalyst/biosolid suspension weight ratio was in that case only 37% of the ratio used in the flow reactor. However, at the end of the run the catalyst was broken down in a fine powder due to the stirring of the reaction mixture. In the autoclave tests, COD removal at 508 K reached 78% compared to 70% without catalyst. The improved oxidation observed in both catalyzed and uncatalyzed batch autoclave runs is in agreement with the higher conversions obtained in batch vs. continuous stirred tank reactors. Yet the presence of the catalyst allows a significant improvement of organic matter oxidation whatever the reactor type.

4.2. Flow patterns

In order to characterize the flow pattern in the tube reactor without catalyst, a flow pattern map published in the literature for concurrent flow with constant liquid–gas ratio in a horizontal pipe was used (Fig. 4) [26]. This map proposes transition boundaries in a two-dimensional coordinate system as determined from the experiment. The conditions required to use the map are:

- isothermal phases, which should be the case in this study involving oxidation of rather dilute solutions in a perfectly mixed reactor;
- identical velocities for both phases, which were obtained by the circulation pump;
- turbulent flows.

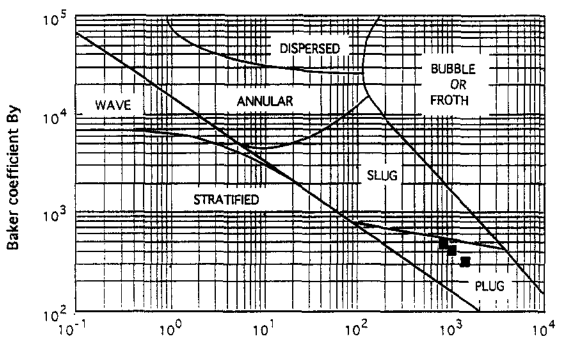

Fig. 4. Flow-pattern regions in concurrent liquid–gas flow through horizontal pipes (from Ref. [26]). Experimental results from the present study are indicated.

Reynolds numbers for gas and liquid flows were calculated with the approximation of likening the liquid phase (0.5 wt.-% ammonium acetate solution) to pure water and the gas phase to oxygen. For the liquid phase N_{Re} ranged from $1.6 \cdot 10^5$ to $1.7 \cdot 10^5$ and for the gas phase between 3200 and 5200. Therefore, turbulent flows existed in the reactor for both phases, validating the use of the map proposed by Baker for the horizontal flow system, with the proviso that the limited amount of suspended solids (0.20–0.50 wt.-% at outlet conditions) did not radically alter the flow regime.

The flow system was identified on this map through calculation of B_x and B_y coefficients, given by the relations,

$$B_x = 2.1 \frac{G_l}{G_v} \times \frac{1}{\sigma} \times \left(\frac{\mu_l}{\rho_l^2}\right)^{1/3} \times (\rho_l \rho_v)^{1/2}$$

$$B_y = 25.513 \cdot 10^3 \times G_v (\rho_l \rho_v)^{-1/2}$$

where G_v = gas mass velocity, G_l = liquid mass velocity, ρ_v = gas density, ρ_l = liquid density, σ = liquid surface tension and μ_l = liquid dynamic viscosity.

Located on the map (Fig. 4), the experimental points indicate plug flow. In this pattern alternate plugs of liquid and gas move along the top side of the pipe while water flows on the bottom side.

After a series of runs totalling 30 h, the catalyst was removed from the reactor for inspection. While no visible damage to the catalyst could be evidenced, a non-adherent light-brown powder was observed on the three monolith pieces, except on the upper third of the cross section of each piece. Precipitation of scale made of calcium carbonate and calcium sulfate (anhydrite) is documented in WAO conditions [27]. This observation of an asymmetric deposit tends to confirm the plug flow regime, in which the upper part of the catalyst is less wetted by the liquid due to the horizontal position of the catalyst.

Concerning the flow regime within the honeycomb channels, the map proposed by Kukano and Kariyasaki for gas–liquid two-phase flow in horizontal capillary tubes was used [28]. According to this map valid for water at ambient temperature and pressure, the gas and liquid velocities of about 1 m/s in the present experiments correspond to an intermittent (or slug) flow regime. This segmented two-phase flow beneficial to catalytic activity [29] affected probably most of the catalyst cross section apart from the bottom side less or not in contact with the gas plugs.

5. Conclusions

Catalytic wet air oxidation offers a new method for disposal of biosolids. The use of a copper/titania honeycomb catalyst allows significant process improvements in terms of temperature and pressure conditions. The catalyst was submitted to an intermittent two-phase flow regime without any significant loss of material. However, additional experiments are needed to ascertain catalyst lifetime.

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