Non-Catalytic Subcritical Wet Oxidation of a Wastewater Treatment Sludge

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Abstract— Among the treatment and conversion technologies used for organic solid waste, wet oxidation has become an important process due to the fascinating characteristics of water as a reaction medium at elevated temperatures and pressure. Wet oxidation is able to degrade and remove organic compounds and thus reduce the mass and volume of solid wastes. Recovering valuable compounds and enhancement of anaerobic fermentation are the other advantages. Wet oxidation of soluble compounds such as phenol, aromatic alcohols and carboxylic acids has been well studied. However, behaviour of wet oxidation of wastewater treatment sludges has not been studied completely due to their complex structure. The current work was aimed at investigating non-catalytic wet oxidation of wastewater treatment sludge and studying degradation of solids, organic compounds and nutrients. A fermented mixed sludge which consisted of primary and secondary sludges was subjected to wet oxidation at temperature ranging 220-240 °C, oxygen to biomass ratio of 1:1-2:1 and stirring speed of 300-500 rpm. Wet oxidation was effective at degrading the organic solids, with approximately 90 % degradation within 60 minutes. It was found that reaction temperature has the most significant impact on sludge oxidation. The results also showed production of acetic acid under wet oxidation treatment.

Keywords- Sludge; wastewater treatment; wet oxidation; hydrothermal processing

I. INTRODUCTION

Sewage sludge is the solid residue of municipal wastewater treatment process, is a suspension produced by separating solids from wastewater. The treated liquor is disposed of separately while solids are removed for disposal. In a world of increasing demand for sustainable waste management, the drivers for reducing sewage sludge volumes to landfills have become critical, and regulations are becoming more restrictive [1].

Therefore technologies for sludge diversion from landfills, i.e. composting, anaerobic fermentation, thermal processing (incineration, gasification and pyrolysis) and hydrothermal processing (thermal hydrolysis and wet oxidation) are attracting the attention of the public and governments. However, the incapability of conventional techniques to eliminate organic material from municipal sludge has made it evident that more advanced and effective processes are required. The wet oxidation process is known to have great potential for the treatment of effluents such as municipal sludges which contain a high content of organic matter or toxic contaminants for which direct biological purification is unfeasible [2].

Wet oxidation involves the liquid phase oxidation of organic or oxidisable inorganic compounds at elevated temperatures and pressures using oxygen (applied as air or pure oxygen). Typical conditions for wet oxidation are 150-320 °C under 20-150 bar of pressure for 15-120 minutes [3]. The reactions are completed in the water phase, thus eliminating the need for water removal prior to treatment. This is an advantage over thermal technologies such as incineration, gasification and pyrolysis. Wet oxidation of municipal sludge has four major objectives based on subsequent application: (I) enhancement of fermentation, (II) degradation and removal of organic compounds, (III) reduction of mass and volume [4] and (IV) recovery of valuable compounds [5, 6].

Wet oxidation of soluble compounds such as phenol, aromatic alcohols and carboxylic acids in a two-phase reaction environment has been well studied [7-13]. However, the behaviour of wet oxidation of municipal sludge has not been studied completely due to the complex sludge structure and reaction mechanism.

The current study was designed to address this gap and to investigate degradation of municipal sludge by a non-catalytic wet oxidation.

II. EXPERIMENTAL

A. Material

Municipal sludge, which was a mixture of primary (40 %) and secondary (60 %) sludge, was obtained from the Rotorua District Council wastewater treatment plant, Rotorua, New Zealand. It was fermented at the plant using a 2000 litre anaerobic fermentator at 35 °C and under controlled pH (5.5-6.2). The fermented sludge was frozen until required.

Oxygen (>99.5 %) and nitrogen (>99.7 %) gas were obtained from BOC Limited (New Zealand).
B. Wet Oxidation

The sludge slurry was stored at 4 °C and homogenised by means of a magnetic stirrer at the start of each experiment. Wet oxidation was carried out in a high temperature high pressure Parr reactor (Model 4540 high pressure reactor equipped with a 4848 controller, Parr Instrument Company, US). The reactor (Figure 1) was equipped with a pre-heated feed tank in which 150 ml sludge was heated to 90 °C for 5 minutes with stirring to minimise the temperature gradient on transfer to the main reactor.

The reactor was initially charged with 250 ml water and pressurized to 20-40 bar with pure oxygen. It was then heated to 220 °C before the pre-heated material was injected under pressure (using pure nitrogen). The initial concentration of solids in the reactor was approximately 1.5 wt%.

The sampling tube was flushed with water followed by nitrogen before each sample was collected. Using a manual system 20 ml samples were taken and cooled immediately to stop further reaction.

C. Analysis

Total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to standard methods recommended by the American Public Health Association [14]. Well-mixed samples were filtered through a weighed glass fibre filter paper and the residues retained on the filter paper were dried 105 °C. The increase in weight of the filter paper represented TSS. The residues were then ignited at 500 °C and the weight lost represented VSS.

Soluble Chemical Oxygen Demand (COD) was determined using an in-house micro scale method similar to Standard Methods 5220D [14]. Samples were filtered and digested with an excess of acidic potassium dichromate solution and COD was determined by colorimetric estimation of the reduced dichromate.

Volatile fatty acids were determined using a gas chromatograph (Hewlett Packard, 5890A, U.S.A.) equipped with an FID detector containing a fused silica capillary column (Nukol 30 m, 0.53 μm ID, 30 m, 0.5 μm).

III. RESULTS AND DISCUSSIONS

A. Solid Degradation

Degradation of sludge TSS and VSS during 60 minute wet oxidation at different operational conditions are shown in Figures 2 and 3, respectively. Increasing reaction temperature and mixing intensity resulted in a greater solid degradation. The results showed that by increasing oxygen to biomass ratio the sludge TSS and VSS concentrations decreased.
**B. Changes in sCOD**

The effect of temperature, oxygen ratio and mixing intensity was studied on the sludge COD reduction. Wet oxidation decreased soluble COD yield by oxidising organic matter to carbon dioxide (Figure 4). Temperature was found to have a significant impact on the COD degradation. Higher COD reduction was achieved at higher temperatures due to a higher degree of solubilisation and faster oxidation rate.

**C. Acetic Acid Production**

Production of C1-C6 organic acids during wet oxidation treatment is highly desirable because these compounds consist of low molecular weight, readily degradable carbon compounds that form a suitable substrate for methanogenesis. Acetic acid is an important intermediate in biological methane production and its formation enhances the effects of hydrothermal processing during pre-treatment of sludge [4]. In this study, acetic acid was the main VFA produced during wet oxidation of sludge.

Production of acetic acid from municipal sludge under different conditions of wet oxidation process is shown in Figure 5. As can be seen, increasing process variables resulted in greater acetic acid formation. However, at reaction temperatures higher than 230 °C, less acetic acid was formed. This can be explained by the fact that acetic acid is a stable intermediate and a high reaction temperature is required for its complete degradation [15].
CONCLUSIONS

Wet oxidation was found to be an effective method at degrading organic solids from municipal wastewater treatment plant. Approximately 90% solids degradation was occurred within 60 minutes of non-catalytic processing. The results indicate that higher temperature favours higher sludge degradation. The substantial amount of acetic acid formation indicates a favourable potential for anaerobic biogas production in a subsequent downstream process.

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REFERENCES