

Wet electrolytic oxidation of organic sludge

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Abstract

Electrolysis of an aqueous solution at subcritical water conditions, referred here as wet electrolytic oxidation (WEO), results in a completely different reaction product compared to that from usual water electrolysis. Oxygen, hydrogen and chlorine evolution is almost completely suppressed when carrying out the electrolysis of aqueous NaCl solution at temperatures higher than 250 °C. Chemical oxygen demand (COD) compounds can be completely mineralized by this electrolytic reaction, but this work focused in partial oxidation of organic sludge and combining with biological process. The treatment of organic sludge by WEO increased the biodegradability of organic sludge due to the formation of organic acids. The electrochemical reaction of WEO suppressed the evolution of color that often appears in subcritical water treatment of organic waste.

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1. Introduction

The disposal of huge amounts of organics sludge produced such as in sewage and wastewater treatment has always been a concern. The ocean was an option for disposal of the huge amount of the organic sludge and the amount reached 1.2 M tonnes in Japan alone in 2002. The London Convention 1972 basically prohibits the disposal of waste in the ocean, but permits the sewage sludge and other wastes of natural origin in the list of material that may be considered for ocean dumping. The 1996 London protocol places more emphasis on the progressive reduction of dumping at sea and gives guidelines for assessment of waste to be dumped. The national authorities are charged to accept dumping only under certain circumstances, imposing obligation to make further efforts to reduce the waste.

The wet oxidation is a land treatment of organic sludge using subcritical water conditions. The process was invented nearly 50 years ago by Zimmerman and sometimes bears his name. The process uses high temperature and high-pressure conditions and can be operated autothermally, by injecting air as oxidizer and using the organic waste as the fuel to keep the reaction temperature.

The wet electrolytic oxidation (WEO) referred in this work is a wet oxidation coupled with electrochemical reaction. This

work describes the peculiar electrochemical reaction that takes place at subcritical water conditions and the application of WEO for treatment of organic sludge. The investigation was made using organic sludge from a methane fermentation facility in combining the WEO with biological treatment. The main objective of WEO in this work is not to completely remove the chemical oxygen demand (COD) but to transform refractory sludge to a biodegradable water stream, allowing further biological treatment.

2. Methods and apparatus

Three apparatuses were used in this work. Fig. 1 illustrates the batch apparatus that was used for WEO of sludge and electrolyte solutions. The HC-276 made 300 mL autoclave has inside a magnetic driven mixer and an iridium cylindrical anode (25 mm in diameter and 30 mm in length). The autoclave wall was used as the cathode. Half of autoclave's inner volume was charged with the sludge or electrolyte solution. After sealing the autoclave, the air inside of the autoclave was purged with argon gas. The headspace of autoclave was pressurized up to 3 MPa with argon gas or oxygen balanced with argon. The sealed autoclave was then heated by the surrounding electrical heater. After achieving the intended temperature, the WEO experiments were carried out charging a DC current between the electrodes. The autoclave was stirred during all the WEO experiments.

Fig. 2 illustrates the autoclave used for voltammetric investigations. The inner volume of an Inco-625 made autoclave is

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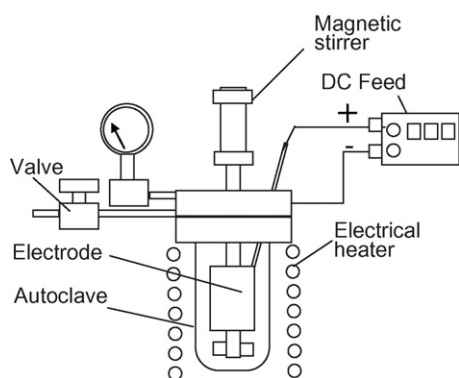


Fig. 1. Schematic illustration of batch autoclave.

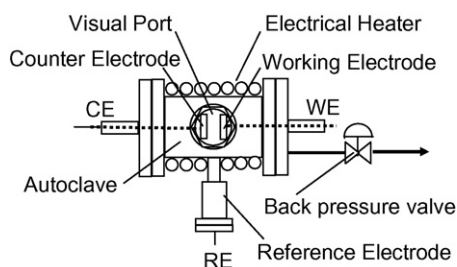


Fig. 2. Schematic illustration of autoclave for voltametric investigation.

300 mL and has inside two disk electrodes (20 mm diameter) that are used as a working electrode and counter electrode. A high pressure resistant Ag/AgCl reference electrode from Tokyo-Kooki, Japan was coupled at the bottom of the autoclave. The electrodes were connected to a potentiostat (Hokuto Denko, Japan). The maximum working condition of reference electrode was up to 15 MPa and 300 °C. This autoclave has also a sapphire visual port for optical access of the electrode during the voltametric investigation. This autoclave was filled with electrolyte solution and heated by the surrounding electrical heater. Cyclic voltametry was collected at different temperatures. A backpressure valve (Tescon, USA) was connected to the autoclave to work as a cushion for thermal expansion of electrolyte solution at high temperatures.

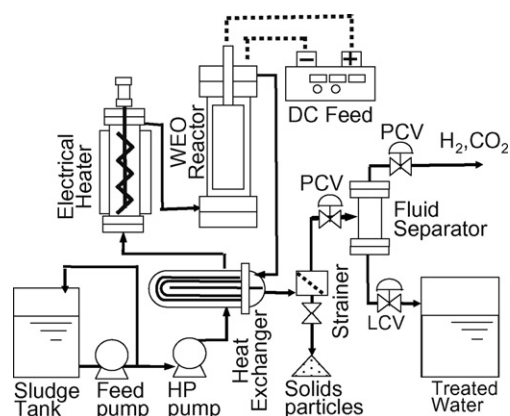


Fig. 3. Schematic illustrations WEO bench facility for continuous sludge treatment.

Fig. 3 illustrates the bench facility for continuous WEO treatment of organic sludge. The capacity of bench facility is 10 L-sludge per hour. The effective inner volume of the reactor is 5 L and has inside an anode with 0.5 m² total area. The anode material was tantalum coated with iridium by thermal decomposition. The steel reactor has inner walls lined with titanium, which are used as the cathode. A mono pump circulates the organic sludge in the tank, for the purposes of stirring the sludge as well as to supply the sludge to the high-pressure pump. The sludge was pressurized up to 15 MPa by the high-pressure pump and supplied to the heat exchanger. The sludge was preheated at the heat exchanger followed by a temperature adjustment at the electrical heater. The temperature of sludge exiting the electrical heater was adjusted to the temperature of the reactor. At the reactor, the sludge moves in an up flow stream being thermo/electro-chemically processed. The reaction products are introduced to the heat exchanger and cooled to 40–50 °C. The cooled products are filtered at the strainer in which the solid particles are removed. The gaseous and liquid products are then separated in the fluid separator and depressurized to the atmospheric pressure.

Table 1 shows the property of organic sludge used in this work. The organic sludge was collected from a commercial methane facility treating garbage and night-soil.

3. Results and discussion

3.1. Electrochemical peculiarity of subcritical water

Fig. 4 shows the phase diagram of the water and the regions that are referred to as subcritical water. Subcritical water is a high-temperature water, but not higher than the critical temperature of water (374 °C), kept at liquid state applying a pressure higher than the saturation pressure. At super-critical condition, the water behaves as a high-density gas and most of inorganic salts such as sodium chloride are insoluble. However, at subcritical condition, the water can still dissolve the inorganic salts allowing the use of an electrolyte solution. Furthermore, the ionic product of water at subcritical condition is two orders of magnitude higher than at room temperature. The large quantity of dissociated water molecules at this condition can promote electrochemical reaction.

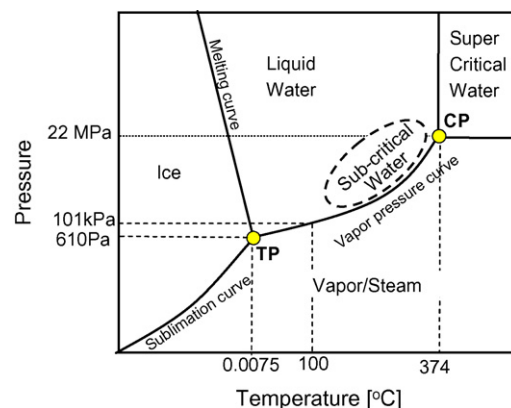


Fig. 4. Phase diagram of the water and subcritical water region.

Table 1
Water quality analysis of methane fermentation sludge

Total analysis	MLSS (mg/L) 34,000	MLVSS (mg/L) 23,000	T-COD _{Cr} (mg/L) 45,000	T-BOD (mg/L) 2,600	T-sugar (mg/L) 5,700	EC (mS/cm) 8.2
Soluble analysis	pH- 7.7	Color- 2,400	S-COD _{Cr} (mg/L) 5,900	S-BOD (mg/L) 450	S-Sugar (mg/L) 760	VFA (mg/L) 25

The thermodynamic conditions of subcritical water can allow the progress of an electrochemical reaction that does not happen at room temperature. One peculiar electrochemical reaction at subcritical water condition is the electrolysis of aqueous chloride solution. Fig. 5 shows the electrolysis product of 2 wt % aqueous NaCl solution inside batch autoclave as a function of reaction temperature. Hydrogen, oxygen and chlorine (measured as free residual chlorine) evolution are strongly suppressed at

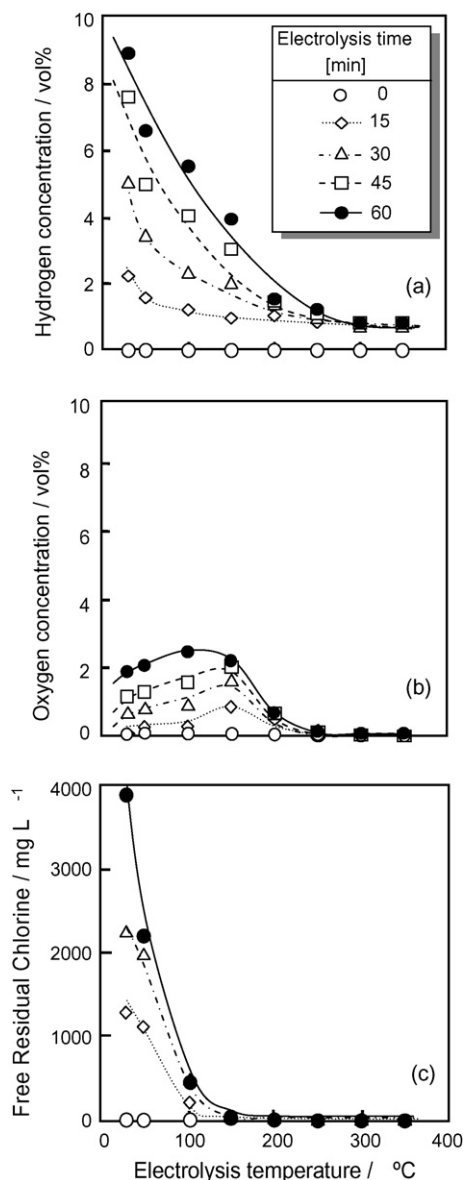


Fig. 5. Temperature influence on the product of aqueous NaCl electrolysis (2A-DC).

temperature higher than 200 °C. These data show that electrolysis of water can take place at subcritical water condition without hydrogen or oxygen production. The mechanism for suppression of these usual electrolysis products of water at subcritical condition is not fully understood. Cyclic voltammetry investigation using a chloride solution (Fig. 6) clearly shows the anodic and cathodic peak currents even at 250 °C. This indicates that some anodic and cathodic reaction is in progress at subcritical water. Possible mechanism for explanation of hydrogen and oxygen gas disappearance inside the electrolytic autoclave is the reduction of oxidizer at the cathode or oxidation of hydrogen at the anode. Direct chemical reaction of oxygen with hydrogen is unlikely because hydrogen gas is known to be difficult to oxidise at subcritical water condition. Nevertheless, some catalytic effect of the electrode or autoclave material is possible but a more likely explanation of disappearance of free residual chlorine at subcritical water electrolysis is thermal degradation.

The voltammetry investigation in Fig. 6 also shows that the thermodynamic windows become narrow with increase in the temperature. This means that, subcritical water decreases the electrode over-voltage and works in favour of an electrochemical reaction.

The production of hydrogen, oxygen and chlorine are highly suppressed in the electrolysis of aqueous sodium chloride solution at subcritical water condition. When some reducing compound is present in this reaction media, an efficient oxidation reaction can be observed. Fig. 7 shows the WEO of ammonia at 250 °C and the respective reaction products. This experiment was conducted in the batch autoclave, charging an electrolyte solution with 3,000 mg/L ammonia and 2 wt % NaCl. Faster degradation of ammonia was obtained for higher currents. The

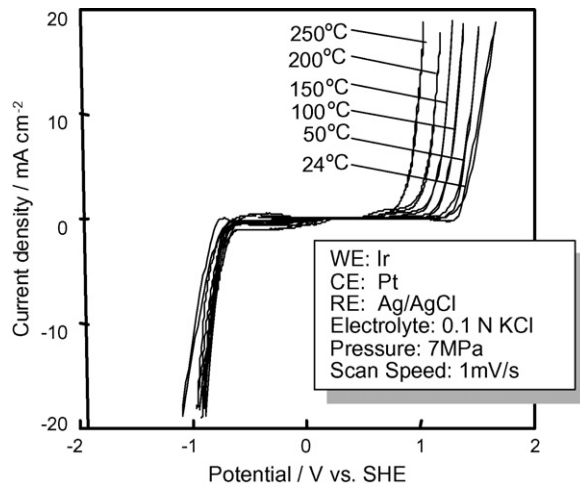


Fig. 6. Temperature influence on the thermodynamic windows.

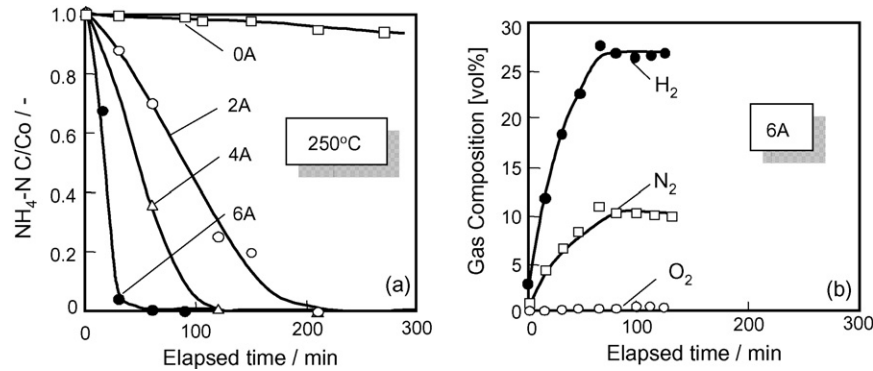


Fig. 7. WEO of ammonia (a) and the reaction product (b).

reaction products were nitrogen gas and hydrogen according to the following overall reaction: $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$. Please note that the degradation of ammonia is not due to the break-point reaction by free residual chlorine. The break point reaction does not produce hydrogen. Furthermore, as shown in Fig. 5, there is no free residual chlorine available for break-point reaction at 250°C. Ammonia is known to be extremely refractory compound in wet oxidation reaction, but was easily degraded by WEO. Other COD compounds present in aqueous solution can be completely mineralized by the WEO [1].

3.2. Sludge behaviour at subcritical water condition

The current technology trends of organic sludge treatment using ozone, ultra-sonic or thermal processes focus mainly on the solubilization of sludge and not on the complete COD removal. Once the COD compounds in the sludge are transformed to a biodegradable form, the biological process will remove the COD. The WEO in this work also aims to improve the biodegradability of sludge residue and achieve a complete treatment in combination with biological process.

The influence of temperature on the sludge product behaviour was investigated, prior to the WEO investigation. Fig. 8 show the results of sludge treatment when 150 mL of sludge listed in Table 1 was charged into the batch autoclave and kept at each temperature for 30 min. Electrical current was not applied here, nor was oxygen pressurized in the autoclave. The organ-

ics in the form of suspended solids (VSS) start to decrease at temperature higher than 100°C by the thermal solubilization. The first compound that appears as the result of this solubilization is the soluble sugar (S-Sugar), due to the hydrolysis of organic compound in the sludge. The origin of soluble sugar is attributed to the polymeric sugars composing the cell wall of methanogenic microorganisms. The soluble sugar achieves a maximum yield at 180°C. Though not illustrated in this figure, there is also a production of amino acids at similar temperature, due to the hydrolysis of proteins. Further increase in the temperature causes the degradation of S-Sugars and appearance of colour compounds that achieves a maximum concentration at 200°C. These colour compounds often appears when treating organic wastes at subcritical water condition and are extremely problematic. These colour compounds dye the treated water in a dark black colour and usually cannot be removed by biological process. The production of colour compounds at subcritical water is attributed to the progress of melanoidin reaction of amino acids and S-Sugars. Further increase in the reaction temperature to higher than 250°C; causes a decrease of colours and increase in the production of volatile fatty acids (VFA). The VFA are composed of acetic acid, lactic acid, formic acid and propionic acid (Fig. 9). Among the VFA, acetic acid is very stable at subcritical water condition. The production of VFA is due to the partial oxidation of organic compounds in the sludge. For a combined process with biological system, it is interesting to convert the sludge, as much as possible, to VFAs. The VFA provide a good

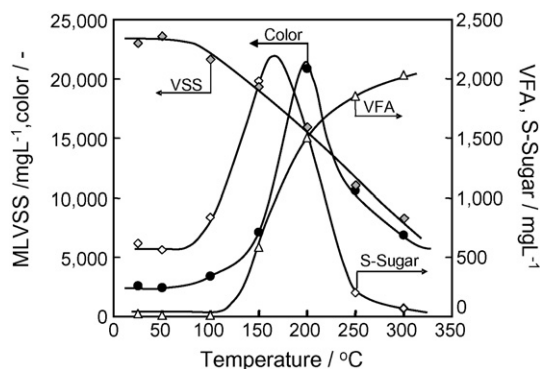


Fig. 8. Influence of temperature on the hydrothermal treatment of organic sludge.

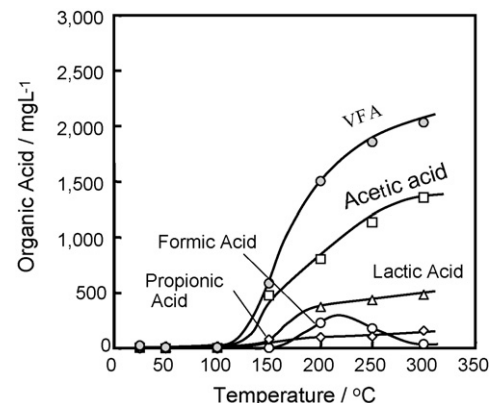


Fig. 9. VFA products from the hydrothermal treatment of organic sludge.

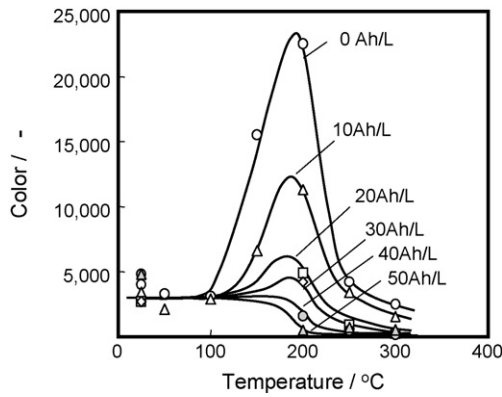


Fig. 10. Colour behaviour during WEO treatment of organic sludge.

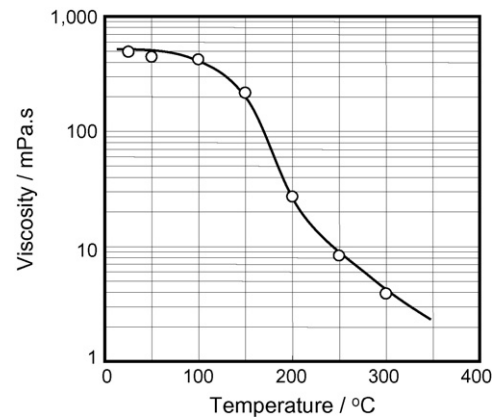


Fig. 12. Viscosity behaviour of sludge in WEO treatment.

substrate for the biological process and can be readily treated in anaerobic or aerobic processes.

3.3. Sludge treatment by WEO

As described in the previous section, when submitting the organic sludge to a subcritical water treatment there is a production of problematic colour compounds at 200 °C. In the WEO, the colour is erased by the electrochemical reaction. Fig. 10 shows the colour behaviour of WEO treated water as a function of electrical charge. The colour that appears at 200 °C clearly decreases with increase of electrical charge applied to the sludge. Although the colour disappears in WEO, the VFA are not degraded. On contrary, the VFA amount in WEO treatment can be increased in function of applied electrical charge (Fig. 11).

Another relevant aspect of sludge treatment by WEO that should be considered is related to the dewatering properties of organic sludge. Larger part of the water in the organics sludge is located inside or strongly attached to the microorganism cells. The gel like compound that surrounds microorganism cells retains huge amounts of water and increases the viscosity of the sludge. Usually, dewatering of organic sludge by filtration is difficult to accomplish due to this viscosity and requires a precipitation procedure using huge amount of chemical coagulants. However, WEO can degrade these viscous compounds, decreasing drastically the viscosity of sludge. Fig. 12 illustrates

the viscosity behaviour of organic sludge during the WEO treatment. There is a clear decrease of sludge viscosity with increase in the reaction temperature. Furthermore, rupture of the cell wall of the microorganism occurs due to the thermal effects releasing the inside water. Part of the thermally degraded cell walls is transformed to small particles of char like products in WEO. These char particles naturally precipitate and can be easily removed from the treated water by filtration. The filtrate after WEO treatment is transparent and almost colourless. However, it still contains dissolved COD compounds. These remaining COD compounds in the filtrate should be removed by biological processing. Complete COD removal of sludge by WEO is possible but no longer recommended. The initial T-COD concentration of this sludge was 45 g per litter. According to the Faradays Law's, electrical charge of 151 kWh per cubic meter of sludge will be required for complete COD removal. Considering that the voltage between the electrodes in the WEO is around 5 V, an electrical power of 755 kWh per cubic meter of sludge will be required for total COD removal. This level of electrical power consumption is usually prohibitive for a commercial treatment of organic sludge suggesting the necessity in coupling WEO with biological process.

The WEO product filtrate should have an improved biodegradability if it is to be treated by biological process. One reference for this biodegradability is the BOD/COD ratio. Fig. 13 shows the BOD/COD ratio of the filtrate in function of electrical

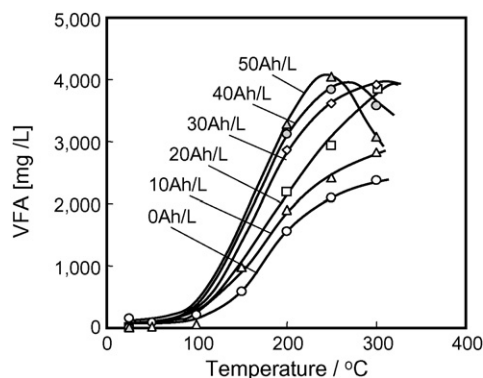


Fig. 11. VFA yield during WEO treatment of organic sludge.

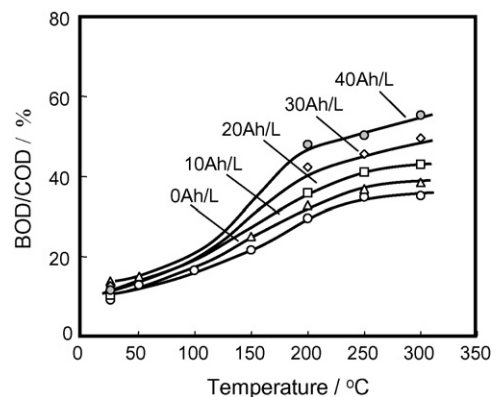


Fig. 13. BOD/COD ratio of WEO filtrate.

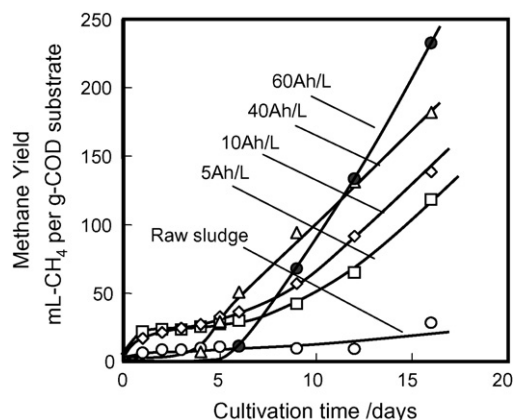


Fig. 14. Methane fermentation test of WEO filtrate (250 °C).

charge and reaction temperature. The BOD/COD ratio of original sludge was 6–15% but after the WEO treatment, this value could be increased to higher than 50%. The BOD/COD ratio increased with increase in temperature and electrical charge, and that was attributed to the formation of VFA.

The BOD/COD ratio is an indicator of biodegradability for an aerobic process but the WEO was also found to increase the biodegradability for anaerobic treatment. The filtrate from WEO treatment of organic sludge at 250 °C was submitted to a methane fermentation test. Fig. 14 shows the methane yield for the filtrate of WEO, in which different electrical charges were applied. A clear increase in the methane yield was observed with increase in the electrical charge of WEO. The methane yield from raw sludge was very low because the residue had already been treated by methane fermentation. The aqueous product from the WEO treatment has a good biodegradability in aerobic and anaerobic biological processes.

3.4. Continuous WEO sludge treatment in the bench facility

Continuous treatment of organic sludge were carried out in the WEO bench facility. This bench facility was equipped with a heat exchanger which allowed recovery of energy to maintain the reaction temperature. The experiment in the bench facility was conducted to establish the total energy required for processing the sludge by WEO and the optimal operation conditions. The basic behaviour of treated water quality in the continuous systems was similar to batch experiments. The VFA concentration and BOD/COD ratio of treated water increased with increasing the applied electrical charge. 98% of the moisture liquor suspended solids (MLSS) of raw sludge was removed in the bench facility, part being retained at strainer in form of char products. The use of compressed air as a cooxidizer during

Table 2

Total power consumption of WEO system for the treatment of organic sludge

Sludge MLSS (mg/L)	10,000	20,000	30,000	40,000
Total power consumption (kWh/m ³)	58.8	64.6	70.3	76.0

the WEO, was found to promote the colour suppression in the treated water and also reduced the required electrical charge. Wet oxidation experiments, in which air was introduced to the reactor without applying electrical charge, were also carried out in the bench facility and compared with results of WEO. For the case of wet oxidation, the biodegradability of treated water was found to be low compared to WEO. The optimum condition for treating the organic sludge in the bench facility were found to be 250 °C, 7 MPa, electrical charge of 10 Ah/L and using air ratio of 0.5. At these operation conditions, the treated water showed a BOD/COD ratio higher than 50% and was almost colourless (300°). The COD removal rate of the sludge was 80% and the MLSS removal rate was 98%. The power consumption, including the heating energy, electrolysis energy and compressing energy, was found to depend on the MLSS concentration of sludge. Table 2 lists the power consumption data obtained in the WEO bench facility as a function of sludge MLSS. The power consumption increased with increase in the sludge MLSS, because MLSS was directly proportional to COD concentration. Once the air ratio was kept at 0.5, higher COD required higher amounts of air used as the cooxidizer and consequently increasing the energy for compressing the air.

4. Conclusions

Wet electrolytic oxidation was investigated for the treatment of organic sludges. The electrochemical reactions of WEO contributed to decreasing the color, increasing the VFA yield and consequently improving the biodegradability of treated water. Cost calculations suggest that this system should be used in combination with biological treatment. WEO is a modified wet oxidation process which permits better control of the sludge reaction and the quality of treated water.

Acknowledgements

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