

## **Methane production of crop residue from heavy metal-contaminated soils with different OLRs in lab-scale test**

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### **ABSTRACT**

In order to finalize the phytoremediation as a feasible remediation technology highly contaminated crop residues (i.e., plant biomass) should be properly disposed. Anaerobic digestion for contaminated crop residues disposal was focused in this study. According to the previous studies, anaerobic digestion has been suggested as an alternative for the management of crop residues containing heavy metals. Anaerobic digestion was operated without serious problems and heavy metals in biomass can be also efficiently extracted as a form of sludge. A series of laboratory anaerobic digestion test were conducted to evaluate the effect of organic loading rates (OLRs) on the methane production using sunflower (i.e., *Helianthus annuus*) grown in heavy metals-contaminated soils. The OLR of reactor was raised gradually from 1.0 to 1.5 g-VS/L/day. The specific methane yields obtained were 0.04, 0.04, and 0.05 m<sup>3</sup>/kg added volatile solids (VS<sub>added</sub>) for OLRs 1.0, 1.25, and 1.5 g-VS/L/day, respectively. According to the results, the methane production was stable up to 1.5 g-VS/L/day of OLRs for the sunflowers harvested in the heavy metal contaminated sites.

### **1. INTRODUCTION**

Phytoremediation is an emerging technology that uses the plants, known as hyperaccumulators which adsorb large amounts of contaminants in comparison of the other plants, to clean up contaminated areas for the as a cost-effective green technology (Lone 2008). Especially, the use of plants to uptake and concentrate metals from the soil into the biomass of plants, has gained widespread attention alternative to traditional physicochemical remediation methods. After phytoremediation, the shoot (i.e., stem, leaf, and flower) of the plant are harvested, removed, followed by proper

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disposal. Conventionally, highly contaminated byproducts were disposed by appropriate technology including composting, incineration, ashing, pyrolysis, direct dispose, and anaerobic digestion. Many researchers suggest that the incineration of harvested plant biomass, either to reduce the volume of the material requiring disposal dramatically or recover energy (Pasad 2003). However, some metals are extremely volatile (Hg and Cd), and can lead to the toxic metal oxide. Metal containing ash that results from the incineration must be controlled. Thus, we focused the anaerobic digestion, producing the energy in the form of biogas and reducing the volume of byproducts, for highly contaminated crop residues disposal after phytoremediation in this study. The main objective of this study was to observe the methane production with different OLRs for verifying the stable anaerobic digestion operation.

## **2. MATERIALS AND METHODS**

### *2.1 Inoculum and substrate*

The Inoculum was taken from the anaerobic digester of a municipal sewage treatment plant in Seoul, Republic of Korea. The sludge had a pH of 7.22 and contained on average 2.19% total solid and 1.41% volatile solid. The sunflowers were cultivated in a contaminated field under natural condition and plants were harvested after 114 days. The concentration of heavy metals in crop residues were 3.21, 13.13, 56.02, 1.45, and 127.75 mg/kg (dry basis) for Cd, Pb, Zn, Ni, and Cu, respectively.

### *2.2 Reactor operation*

In this experiment, an 8 L continuous stirred tank reactor (CSTR) (working volume of 5 L) was operated under 0.25-0.75 g-VS/L/day feeding rate with daily feeding pattern for 3 months to reach the steady state conditions with sunflower substrate. The organic loading rates (OLRs) were increased gradually from 1.0 to 1.5 g-VS/L/day in order to minimize the organic loading shock on microorganism and allow sufficient time for adaptation to the changing conditions. The reactor was operated under mesophilic conditions at  $35\pm 1^\circ\text{C}$ . Reactors were constantly mixed using mechanical stirrers to ensure the homogeneity of the liquid phase. The substrate was injected manually with 50 mL plastic syringe and samples of sludge were taken before feeding for analysis. Biogas generated was collected in gas sampling bags.

### *2.3 Analytical methods*

The methane content in the biogas was measured by gas chromatography (Younglin, Korea) with a thermal conductivity detector (TCD) operated at  $120^\circ\text{C}$ , with injector and oven temperatures of 120 and  $35^\circ\text{C}$ , respectively. The biogas volume was measured with a wet-type gas flow meter. The volume was converted into standard temperature and pressure conditions (272.15 K, 1013.25 hPa). The helium was used as the carrier gas. The heavy metal mass was measured by inductively coupled plasma optical emission spectrometer (Thermo, U.S.A.).

### 3. RESULTS AND DISCUSSION

#### 3.1 Reactor performance

The OLR was gradually increased over time from 1.0 g-VS/L/day to 1.5 g-VS/L/day to avoid the shock on microorganisms. The methane content in biogas was maintained to constant during the anaerobic digester operation, indicating that the digester operation might be stable (Peter 2001) (Fig. 1). This meant that the heavy metals contained in the crop residues would not significantly adverse effect anaerobic digester performance up to 1.5 g-VS/L/day of OLR.

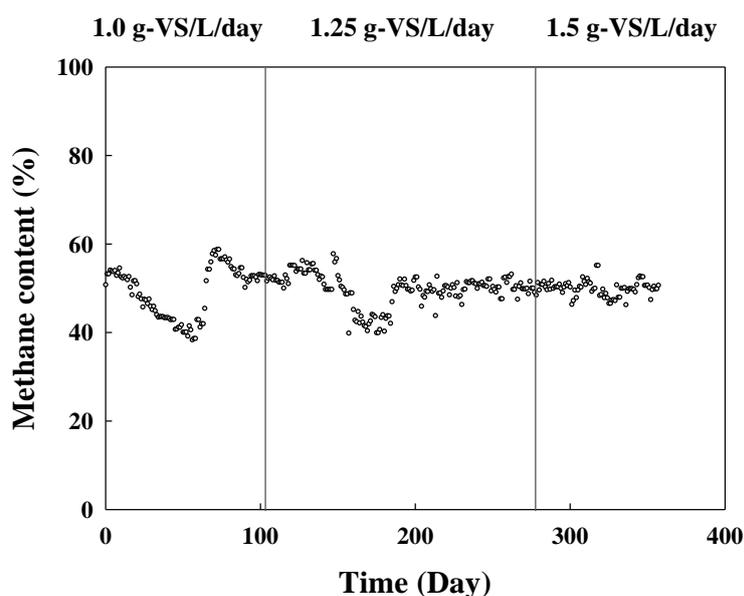


Fig. 1. Methane composition of biogas with different OLRs

#### 3.2 Heavy metals accumulation in reactor

As anaerobic digester operation continues, released heavy metal mass to reactor was increased, thus subsequently accumulated in reactor (Table 1). The heavy metals accumulation showed that released heavy metals from substrate remained in reactor, probably due to non-homogeneous flow. Thus, the accumulation of heavy metals should be considered when anaerobic digester operates for long periods.

Table 1. Changes of heavy metals mass in reactor

Day		5	45	338	358
Cd	mg-heavy metal	0.08	0.18	0.27	0.27
Pb		0.33	0.73	1.13	1.13
Zn		1.14	2.54	4.14	4.09
Ni		0.00	0.06	0.11	0.11
Cu		0.24	0.55	0.99	1.01

Biodegradability for accumulating of heavy metals in reactor was calculated in Table 2. Above these ranges, heavy metals can be accumulated in reactor considering 9.23% of the theoretical biodegradability of substrate in reactor.

Table 2. Calculated biodegradability for accumulating of heavy metals in reactor

	<b>Cd</b>	<b>Pb</b>	<b>Zn</b>	<b>Ni</b>	<b>Cu</b>
Biodegradability (%)	>2.6-5.5	>4.3-6.5	>13.0-18.9	>4.1-50.9	>8.0-22.5

#### **4. CONCLUSION**

This study aimed to propose a potential application of anaerobic digestion for disposal of crop residues grown in heavy metal contaminated soil. The methane production was stable up to 1.5 g-VS/L/day of OLRs for the sunflowers from heavy metal contaminated sites. However, accumulation of released heavy metals from substrate was observed. Thus, heavy metals accumulation should be considered according to the long-term anaerobic digester operation.

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