# Biogas production of phytoremediation plants contaminated with cadmium

#### Martin Šotnar, Jan Mareček, Pavel Máchal, Tomáš Koutný, Milan Geršl, Eva Krčálová, Maroš Korenko

**Abstract:** This work is about biogas production of phytoremediation plants contaminated with cadmium. As the phytoremediation plant was chosen maize (Zea mays). For growing of corn sown (HYBRID): CE 220 was used hydroponic method. Subsequently corn was contaminated with cadmium addition to the nutrient solution. This text also discusses aplication growed, contaminated corn into models of fermentors biogas station. Next there are evaluation of analyzes quantify and quality of biogas. Concentration of cadmium was determinated in green plants and in fermentation residues. During the anaerobic fermentation wasn't discovered inhibitory effects of contaminated corn by cadmium. Anaerobic fermentation of these plants is therefore possible to use for energy production.

Key words: Biogas, phytoremediation, anaerobic fermentation, contamination of cadmium, methane production.

#### INTRODUCTION

Use of heavy metals is associated with the development of technology. Transport and industry represents a threat to the environment. Soil contaminated by heavy metals in history was reflected several times. Cadmium is a naturally occurring element in the earth's crust. Contamination of the environment is becoming a range of natural effects and anthropogenic activities. Cadmium contamination can cause by mining, processing of zinclead ores. Cadmium is also in batteries. Elevated concentrations of cadmium are mainly in the USA and in Asia on flood plain the rice fields. Attention has been paid very recently to the methods of environmental decontamination, these including phytoremediation. Maize is a commonly grown field crop. In addition to it being a phytoremediation plant, it is also the most widely used substrate today - in the form of silage - for biogas production in agricultural biogas plants, where it is typically applied in association with liquid manure from livestock farms. If processing is needed in phytoremediation plants, combustion is an option. For large areas with the possibility of utilising the contaminant, extraction of heavy metals from phytoremediation plants is another alternative. Local contaminations, however, do not provide sufficient quantities for economic plans of the extraction method. [3] Making use of one of the biotechnological plant processing methods is thus possible. Utilising phytoremediation plants to obtain biogas and energy released by the combustion of biogas is therefore another option.

## MATERIAL AND METHODS

Seeds of maize (CE 220 hybrid) were placed on a filter paper moistened with potable water, without any other chemical treatment. After six days at a temperature of 24-25 °C, 216 pre-germinated plants were placed in plastic tanks subjected to a periodic, 12-hour light regimen. Maize plants were grown locally by hydroponic method on the Richter solution. After fourteen days of cultivating under these conditions, a contaminant (CdCl<sub>2</sub>, the concentration being 10  $\mu$ Ml<sup>-1</sup>) and a complexing agent (ethylenediaminetetraacetic acid, EDTA) were added into the nutrient solution. A total of four tanks were contaminated out of the six tanks containing maize plants. The contamination phase was underway for 19 days. Subsequently, plants were harvested and cut manually cut to form 0.5 cm long sections for easier application into the fermenters.

Dry matter and loss on ignition was also determined in plants, as well as dry matter and loss on ignition of the inoculum as the basic input substrate. The inoculum was transported from the operations of the biogas plant in Čejč, Czech Republic. Subsequently, the inoculum was applied into model biogas plant reactors, the volume being 3 litres per each. The reactors were maintained in a water bath at a constant temperature of 42 <sup>0</sup>C. A total of eight model reactors were filled of which two units contained only the inoculum without the addition of maize and served as control samples of the process of anaerobic fermentation, two units contained the inoculum with the addition of uncontaminated maize plants (50 g and 75 g of plants) and two units contained 50 g of contaminated plants along with the inoculum. Finally, two reactors contained 75 g of contaminated plants along with the inoculum. This was followed by analysis of the quantity and quality of the biogas produced. Biogas quantity measurements were using the BK G4 gas meter. The biogas composition was analysed by means of the device Combimas GA-m with columns for measuring  $CH_4$ ,  $CO_2$ ,  $O_2$ ,  $H_2S$  and  $H_2$ . The average laboratory temperature was 20  $^{\circ}C$ , the humidity was 55 % and pressure was 101,735 Pa.

The determination of cadmic metal concentration in the maize plants and in fermentation residues was conducted electrochemically by differential pulse voltammetry with the conventional tri-electrode system. There was a working (mercury - HMDE) electrode, auxiliary (platinum - Pt) electrode, and reference (argentchloride - Ag/AgCl/3M/KCl) electrode. Measurements were carried out using the devices 813 Compact Autosampler + 797 VA Computrace (Metrohm, CH). Dosage consisted of 100 ml of sample and 1,900 ml of acetate buffer (pH 5.0). When carrying out the cadmic metal determination method, the potential range was (-1.3) to (+0.2) V, potential step was 0.005 V, the accumulation time was 120 seconds, the accumulation potential was -1.15 V, the bubbling of the sample with argon took place for 90 seconds and equilibration time was 5 seconds. Acetate buffer (pH 5.0) was used as electrolyte.

#### **RESULTS AND DISCUSSION**

The quantity and quality of the biogas is development on the addition of biodegradable material. Microorganisms thereby increasing its activity and leads to increased production of biogas. Contamination of the environment, however, could cause a problem. The total biogas production in samples with applied plants is higher than in control samples without the addition of plants.

Out of a total of 216 plants of full-grown maize plants (CE 220 hybrid), 121 plants contaminated with cadmium and 64 uncontaminated plants were harvested after 19 days of contamination. The total weight of the harvested contaminated plants was 683.51 g. The total weight of uncontaminated plants was 341.74 g.

The daily specific biogas production from the fermenters is shown in Fig. 1.

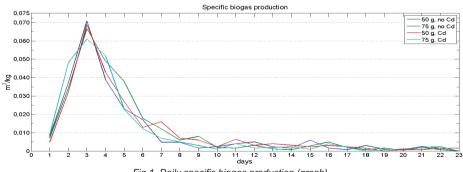
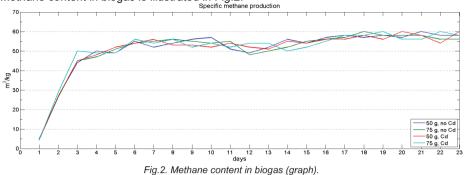


Fig.1. Daily specific biogas production (graph).

The production of applied samples was obtained by deducting the average biogas production in controls from biogas production of test samples. The increased production in the first five days is determined by an increase in activity of microorganisms caused by the addition of the biodegradable material. The daily specific production of biogas does not show any noticeable difference between the samples with the cadmium content and those with no cadmium. Energy assessment of biogas however requires sufficient methane content in the substance. Methane production is thus critical as regards energy utilisation. Methane content in biogas is illustrated in Fig.2.



After balancing the methane concentration in the biogas at the beginning of the test. the methane content was above 50 %. All tested samples thus show the methane concentration suitable for direct combustion of biogas in cogeneration units. Cofermentation with other materials is not required in terms of methane content in biogas. Daily specific methane production is illustrated in Fig. 3.

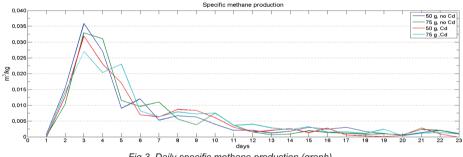
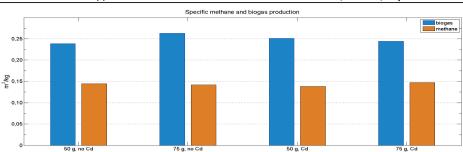


Fig.3. Daily specific methane production (graph).

Begin the process of anaerobic fermentation is problematic. When metering system will the entry of air and thus oxygenation process. Next, the aerobic processes to oxygen depletion. Suppression of methane and methane production levelling is visible on the graph No. 2. Daily specific methane production at various test samples is comparable. The production of methane, as the main combustible component of biogas is for energy recovery basis. Important is, however, its concentration in the biogas. Cogeneration units burring biogas to produce electricity and heat demand methane concentration above 50 %.

Ensilaged maize and liquid manure present the commonly used substrates for biogas production in agricultural biogas plants. Fresh maize reaches the production volume of  $0.52 \text{ m}^3 \cdot \text{kg}^{-1}$ . [5] The tests achieved the production to range between 0.239 and 0.263 m<sup>3</sup>·kg<sup>-1</sup>. The decreased production results from harvesting the maize plants before the growth of cobs and from the cultivation method. For ensilaged maize, the normal production of biogas is 0.55 m<sup>3</sup>·kg<sup>-1</sup>. The average methane content in the biogas made from the tested samples is around 55 %. Typically, the methane concentration in the biogas produced from fresh maize is 65 %. [5] This difference is due to the launch of the system and application of maize before the growth of cobs.



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Fig.4. Total specific production of biogas and methane.

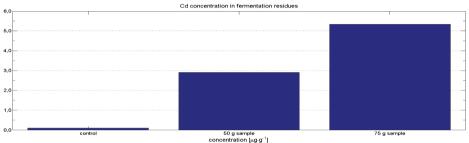


Fig.5. Cadmium concentration in fermentation residues.

In the real life, the fermentation residues are applied to agricultural land. Any cadmium concentration in the fermentation residues is therefore undesirable. At a concentration above 5  $\mu g \cdot g^{-1}$ , the biological material is considered to be beyond the permitted concentration for category 3 pursuant to the Czech legislation (Regulation 341/2008 Coll.), and is therefore considered to be non-degradable waste intended for disposal. Group 2, class II can be used at a concentration to 3  $\mu g \cdot g^{-1}$  can be used on the surface of the ground used or intended for urban green, green parks and forest parks, the creation of reclamation layers in the industrial zones.

#### CONCLUSIONS AND FUTURE WORK

For the analysis was grown total of 121 plants of maize (CE 220 hybrid) contaminated by cadmium were grown and harvested, along with 64 plants without contamination. Analyses of biogas production showed no difference as regards production of biogas and methane contained in the substance between the samples with the addition of contaminated plants and those containing uncontaminated plants. The total specific production during 23 days ranged between 0.239 and 0.263 m<sup>3</sup>·kg<sup>-1</sup>. The methane concentration (50-60 %) demonstrates the possibility of energy utilisation for the biogas generated by direct combustion in the cogeneration unit. Energy utilisation in phytoremediation plants of maize contaminated with cadmium is thus possible. The problem consists of cadmium concentration in the fermentation residues that achieved during the test  $5.34 \mu g \cdot g^{-1}$ .

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