Anaerobic fermentation of maize (Zea mays) contaminated with cadmium

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Abstract: Maize (CE 220 hybrid) was chosen as a phytoremediation plant for Cd decontamination. A solution combining $CdCl_2$ and EDTA was added into the nutrient solution during the growing phase of the maize plants cultivated hydroponically. The contaminated maize plants were harvested and fed into model biogas plant reactors. Inoculum sourced from agricultural biogas plant operations was applied into these 3-litre reactors, with the addition of Cd-contaminated maize plants. Subsequently, there was an analysis of the quantity and quality of the biogas produced in the reactors. The addition of maize plants increased production of both biogas and methane compared with control samples without the addition. Cd-contaminated maize can therefore be biotechnologically processed in biogas plant reactors, in a mesophilic, anaerobic environment. Analyses of Cd concentration in fermentation residues and grown contaminated plants confirmed the presence of Cd while providing the evidence of the fact that at such concentrations Cd presence in maize plants does not form an element inhibiting biogas production. Fermentation residues may however be not suitable, given the content of Cd, for application to agricultural land. Recommended measures involve analysis of the cadmium concentration and then disposal of the fermentation residue in compliance with applicable legislation.

Key words: phytoremediation, anaerobic fermentation, contamination, methane

Introduction

The use of toxic metals by the society still represents a real threat to the environment. 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. [6] 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 23-25^{o}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. The temperature inside the laboratory ranged between 25 and 26^{o}C. After thirteen days of cultivating under these conditions, a contaminant ($CdCl_2$, the concentration being 10 μMl^{-1}) 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, while two tanks were left uncontaminated as controls. The contamination phase was underway for 17 days. Subsequently, 107 plants contaminated with cadmium and 53 uncontaminated plants were harvested and cut manually cut to form 0.5 cm long sections for easier application into the fermenters. The cutting length roughly equals the ensilaged maize particle size. 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^{0}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 (25 g and 50 g of plants) and two units contained 25 g of contaminated plants along with the inoculum. Finally, two reactors contained 50 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^{0}C, the humidity was 55% and pressure was 101,735 Pa.

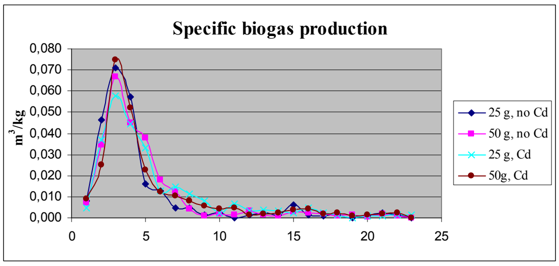
The determination of cadmic metal concentration in the maize plants and in fermentation residues was conducted electrochemically by differential pulse voltammetry with the conventional tri-electrode system. There was a working (mercury - HMDE) electrode, auxiliary (platinum - Pt) electrode, and reference (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

Out of a total of 173 plants of full-grown maize plants (CE 220 hybrid), 107 plants contaminated with cadmium and 53 uncontaminated plants were harvested after 17 days of contamination. The total weight of the harvested contaminated plants was 609.68 g. The total weight of uncontaminated plants was 326.46 g.

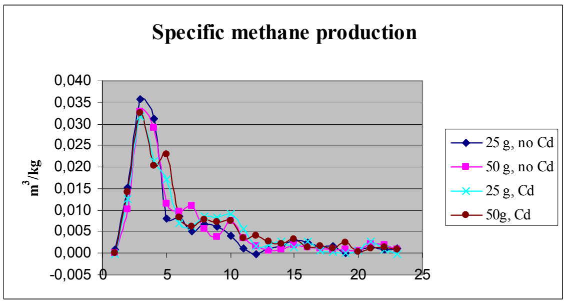
The total biogas production in the samples with applied plants was higher than in control samples without the addition of plants. Adding the biological material thus caused the biogas production to increase. The daily specific biogas production from the fermenters is shown in Fig. 1.

Fig. 1 Daily specific biogas production



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. Daily specific methane production is illustrated in Fig. 2.

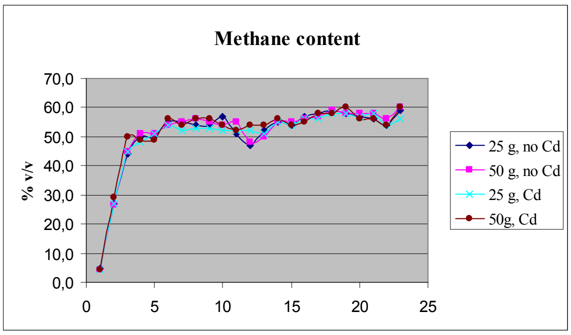
Fig. 2 Daily specific methane production



After feeding the system of model reactors, the air present is consumed by aerobic processes in the first two days to produce carbon dioxide.

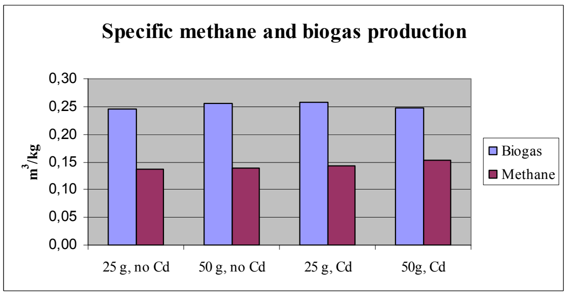
Subsequently, there is an increase in methane concentration, thus a higher daily specific production of methane. Daily specific methane production for each of the test samples is comparable. Production of methane, as the main combustible component of biogas, is essential for energy utilisation. Important, however, is its concentration in biogas. Cogeneration units burning biogas to produce electricity and heat require the methane concentration to be above 50%.

Fig. 3 Methane content in biogas



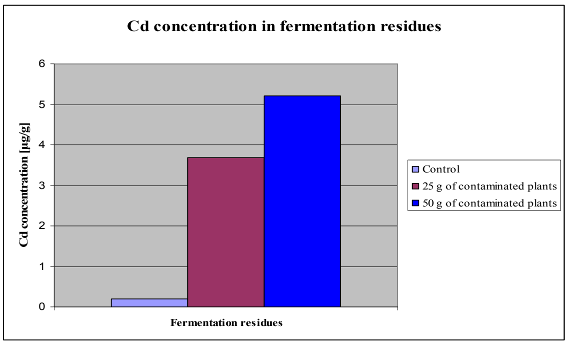
After balancing the methane concentration in the biogas at the beginning of the test, the methane content was above 50%. All tested samples thus show the methane concentration suitable for direct combustion of biogas in cogeneration units. Co-fermentation with other materials is not required in terms of methane content in biogas.

Fig. 4 Total specific production of biogas and methane



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 $m^3 \cdot kg^{-1}$. [1] The tests achieved the production to range between 0.229 and 0.254 $m^3 \cdot kg^{-1}$. 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 $m^3 \cdot kg^{-1}$. 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%. [1] This difference is due to the launch of the system and application of maize before the growth of cobs.

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 III can be used at a concentration to 4 $\mu g \cdot g^{-1}$ on the surface of a terrain being generated by reclamation layers of secured landfills according to ČSN 83 8035.

Conclusion

During the tests, a total of 107 plants of maize (CE 220 hybrid) contaminated by cadmium were grown and harvested, along with 53 plants without contamination. Subsequently, anaerobic fermentation tests were carried out. Analyses 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 0.229 and 0.254 $m^3 \cdot kg^{-1}$. 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. As the dosage of cadmium-contaminated plants increases, the concentration of cadmium in the fermentation residue grows. Subsequently, the fermentation residue becomes waste the concentration of which could also theoretically reach the limit values for hazardous waste.

Acknowledgement

The research was conducted with the support of the project Postdoktorské pozice v technických a ekonomických oborech na MENDELU CZ.1.07/2.3.00/30.0031.

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