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Sewage sludge digestion at increased micropollutant content

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ABSTRACT

Research was conducted, which aim was to evaluate quantitative and qualitative PCB changes in sewage sludge during mesophilic digestion, and the influence of those compound concentration above acceptable level (1.9 mg kg^{-1} of sludge dry matter), also nickel and cadmium ions, on mesophilic digestion process. Before and after the digestion, concentration of seven PCB congeners, Ni and Cd in particular chemical fractions of the sludge was analyzed.

During mesophilic digestion it was stated that increased PCB and heavy metal ions content in sewage sludge, did not disturb correct progress of the process. Last days of digestion were important for intensive degradation of higher chlorinated PCB to congeners containing less chlorine atoms in particle. In liquid of sludge with increased PCB content, up until the 14th day of mesophilic digestion process, gradual increase in amount and sorts of indicator PCB congeners was observed. First LCB were released into sludge liquid. Total amount of PCB in sludge after digestion was decreased significantly, which indicate that biological degradation of those compounds under anaerobic conditions, and/or biosorption of those compounds, proceeded. It has been proved that the digestion of sludge excessively loaded with nickel ions can lead to an adverse accumulation of this metal in the exchangeable and carbonate fraction of stabilized sludge.

Keywords: Digestion; Sewage sludge; PCB; High concentration; Heavy metals; Biogas

1. Introduction

One of the methods of sewage sludge treatment is digestion, which result in decomposition of complex large molecule organic compounds, leading to sludge stabilization. Hydrolysis is considered to be the stage limiting velocity of sludge digestion (Khalid et al., 2011). Acceleration of sludge organic compound transformation into soluble forms, results in significant improvement of efficiency of following digestion stages progress. Increase in process temperature can act as an accelerator. Therefore apart from mesophilic sludge digestion, thermophilic-mesophilic systems are also used (Oles et al., 1997). Optimal temperature range for mesophilic digestion is between 30 and 38 °C, whereas for thermophilic digestion 49 and 57 °C.

Inhibiting substances are a threat for correct digestion progress, they can be either incorporated in the biomass, or emerge as products of substrate decomposition. Those include: ammonia, sulfide, heavy metal ions, chlorophenols, nitrobenzenes, halogenated aliphatics, LCFAs (Chen et al., 2008), and PCBs (Chang et al., 1999). Under certain conditions, PCBs are capable of abiotic and biotic transitions. The studies have shown that, under suitable conditions, PCBs can be biodegraded with participation of microorganisms under aerobic and anaerobic conditions. During above mentioned processes, changes of PCBs result in decrease of their content in sludge. According to earlier reported data, under anaerobic conditions, the reductive dechlorination of higher chlorinated PCB (HCB) occurs, forming lower chlorinated PCB (LCB). During anaerobic degradation, microorganisms cause selective elimination of substituted chlorine, especially in meta- and para-positions. As a result of the process, a decline in toxicity of PCB is obtained (Borja et al., 2005; Fava et al., 2003; Master et al., 2002; Wu et al., 1996). In literature it is reported that in sewage sludge with higher PCB concentration, rate and velocity of dechlorination were low. Data was regarding sludge with

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PCB concentration of: 1.5 and 10 mg L^{-1} (Chang et al., 1999).

Metal toxicity depends on concentration and chemical form, which can change under anaerobic conditions during digestion, and also on pH, Eh, temperature, and presence of other cations. Soluble metal compounds are easier absorbed by organisms, therefore they are more toxic than insoluble metal salts. Concentration of heavy metals in sludge, which cause decrease in efficiency or complete inhibition of digestion process, is defined by many authors in very wide range from a few up to several hundred mg in L. Amongst others, Malina and Pohland (1992), Appels et al. (2008), stated that inhibiting or toxic concentration of zinc, copper, nickel, lead, and cadmium in sludge liquid amounted respectively to: 3–100; 5–100; 30–200; 5–30; 70 mg L^{-1}.

A subject which is not yet well known, is the influence of increased PCB content on sewage sludge digestion progress. In this studies, research was conducted, which aim was to evaluate quantitative and qualitative PCB changes in sewage sludge, and the influence of those compound concentration above acceptable level, also nickel and cadmium ions, on mesophilic digestion process. Seven chosen PCB congeners were analyzed, marked with codes 28, 52, 101, 118, 138, 153, and 180, identification of which is recommended by EPA, moreover The Sludge Directive introduces the allowable value of total concentration of seven above mentioned congeners in sewage sludge intended for agricultural purposes (Working Document, 2000). Metal speciation analysis was performed, which revealed some changes in chemical forms of the metals during sludge stabilization process.

2. Materials and methods

2.1. Experimental setup

For the experiment the following types of sludge was used: a mixture of primary and excess sludge (with ratio of ca. 3:1), and digesting sludge. Sewage sludge was sampled from a municipal, mechanical–biological wastewater treatment plant in Czestochowa (Poland). The treated wastewater contains approximately 20 vol% of industrial wastewater. In the WWTP, purification process is performed with the use of activated sludge method, which covers nitrification, denitrification, and chemical/biological removal of phosphorus. Mesophilic digestion of sludge from settling tank is carried out in closed digesters (temperature 37 ± 2 °C).

The first stage of the performed experiment was the hydrolysis of the mixture of primary and excess sludge (P + E) at 55 °C in closed, 1000 mL bioreactors for 4 days. The bioreactors filled with 650 mL of the sludge mixture were placed in a thermostat, facilitating proper temperature.

Hydrolyzed sludge mixture (P + E) was inoculated with mesophilic digesting sludge (D) in volumetric ratio of 1:2. Sludge mixture (P + E + D) was obtained, which was placed into 30 bioreactors. Next, the sludge in 10 bioreactors was enriched with standard mixture PCB-mix3, which consists of congeners with codes: 28, 52, 101, 118, 138, 153, and 180. Sludge samples marked with symbol (P + E + D)p were obtained. The amount of added standard was selected in a way providing total PCB concentration to be higher than acceptable level stipulated in Sludge Directive, for sludge designated for agricultural applications (Aparcio et al., 2009; Working Document, 2000). The quantity of introduced PCB standard amounted to 1.9 mg kg^{-1} of sludge dry matter. For further 10 reactors, marked as (P + E + D)m, 1 mL of solution containing nickel and cadmium ions was added, which was prepared out of salts: $NiCl_2 \cdot 6H_2O$ and $Cd(NO)_3 \cdot 4H_2O$. Concentration of introduced nickel and cadmium ions amounted respectively to 20 and 5 mg L^{-1} of sludge. Sludge in remaining 10 bioreactors was used as a reference setup (P + E + D)c. Sludge (P + E + D)p, (P + E + D)m, and (P + E + D)c, were placed into thermostat at temperature of 37 °C ± 1 °C, and mesophilic digestion process was carried out for 21 days.

Before and during the mesophilic digestion at a specified time intervals the following parameters of the sludge were determined: hydration, total solids, volatile solids. Alkalinity, pH, volatile fatty acids (VFA), total organic carbon (TOC), and heavy metals (Ni, Cd) were determined for the sludge liquid separated in a centrifuge (rotary speed – 6000 rpm, duration – 10 min). Three samples were measured, and commonly accepted methodology was used (APHA, 1998).

Analysis of PCBs was also carried out for sewage sludge and sludge liquid before, during and after the process of mesophilic digestion. Before and after the digestion, concentration of Ni and Cd in the particular chemical fractions of the sludge was analyzed.

2.2. Biogas

During digestion, pressure and biogas composition were monitored. Pressure measurement was conducted every 24 h. The composition of biogas (content of CH_4 and CO_2) was measured every 72 h with the use of GC (model Agilent GC 6890N made by Agilent Technologies).

2.3. PCB analysis

Methodology of sample preparation was described elsewhere (Dąbrowska and Rosińska, 2012). The extract was compacted in vacuum and then subject to qualitative and quantitative analysis by means of gas CGC chromatography. Separation was conducted on a DB-5 column (30 m × 32 mm × 1 μm). A quadrupole mass spectrometer MS 800, working in a selective mode of ion monitoring was used for detection. Determination was performed for each sample and each four injection of the obtained extract. In order to evaluate the procedure for determination of PCBs in sewage sludge, the recovery values were also determined. Sewage sludge was enriched with Ehrenstorfer's PCB MIX3 at the concentration of 10 ng μL^{-1}. Then biphenyls determination was carried out using the abovementioned procedure. The obtained values of recovery ranged from 65% to 93% and were within the range typical of the references (Berset and Holzer, 1996). The precision of the determination was expressed with the values of standard deviation.

2.4. Fractionation of Ni and Cd in sewage sludge

Sequential extraction was carried out according to the BCR procedure in order to quantify the occurrence forms of Ni and Cd in the sludge. The preparation of necessary reagents and the extraction procedure were carried out according to (Rauret et al., 2000).

In first stage, in order to extract exchangeable metals and metals bound to carbonates, 0.11 M CH_3COOH was used; in second stage (extraction of metals bound to hydrated iron and manganese oxides) 0.5 M NH_2OH HCl (pH 2) was used. In next stage, in order to extract metals bound to organic matter and sulfides, 8.8 M H_2O_2 (pH 2–3) and 1 M CH_3COONH_4