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Accumulation and transpotation of selected heavy metals in thermophilic anaerobic co-digestion of municipal sewage sludge and organic waste

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Abstract. The aims of this research focus on accumulation and transportation of selected heavy metals in thermophilic anearobic co-digestion municipal sewage sludge and organic waste on the laboratory scale. Organic waste was collected from market and sewage sludge was collected from Kim Nguu River in Hanoi city. Organic waste and sewage sludge were mixed on optimal anaerobic digestion ratio. The influent substrate was put into experimental equipment. During experiment, some parameters such as pH, EC were measured daily, others parameters such as COD, heavy metals concentration were measured after 3 to 5 days. The heavy metals content in influent substrates and effluent substrates were paid more attention in this research.

This research discoved that the selected heavy metals content in effluent substrate which were increased with order Cd>Pb>Ni>Cr>Cu>Zn. The heavy metal content is lower in influent subtrate and higher in effluent substrate. The heavy metals were easily bleached in to eluted solution in 18 first days of themophilic anaerobic co-digestion process with order Ni>Cd>Cu>Cr>Zn.

The results of research provided data to help readers understand clearly about characteristics of municipal sewage sludge in Hanoi. Base on results of this research to develop sewage sludge treatment methods. Product after treatment could be used as fertilize for soil amendment.

Keywords: thermophilic anaerobic digestion, municipal sewage sludge, organic waste, heavy metals

1. Introduction

Heavy metals which are metals have private density rather than 5g/cm^3. From wastewater treatment processes, heavy metals were accumulated in sewage sludge. The content and characteristics of sewage sludge depend on properties of wastewater sources [2].

Urban area in Vietnam where still exist a lot small workshops in the city. Therefore, the properties of municipal wastewater are complicated which lead to complicated composition of municipal sewage sludge. Specialy, the heavy metals contents is very high in sewage sludge.

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Now a day, treating municipal sewage sludge is necessary in Vietnamese urban area. However, finding the suitable treatment method to orient reduces, reuses and recycles are difficult. In order to meet this requirement need to implement more investigation on municipal sewage sludge.

For example, in Japan where have high technology in development of municipal treatment method. After treatment, the municipal sewage sludge was used around 30% of mass as fertilize. This ratio will be raised in the future [5].

In this research, focus on accumulation and transportation of selected heavy metals in thermophilic anearobic co-digestion of municipal sewage sludge and organic waste. Results of research are provided data to develop treatment method with aim to use product as fertilizer for soil amendment [4].

2. Material and methods

2.1. Pilot equipment

The pilot equipment consists of single cylindrical reactor (diameter 0.6m, height 0.8m) made from stainless steel with available volume is 40 liters (fig. 1).

The out site is heat keeping layer. The reactor also is equipped with a thermal insulation and the temperature is kept constant at 55°C (thermophilic condition). Gas volumetric flow measurement is used to measure gas volume after 24 hour.

The effluent substrate was sampled daily though valve in the bottom of reactor and pH, EC were measured. Others parameters such as COD, heavy metals were measured after 3 days to 5 days follow experiment plan in order to assess the stabilization process.

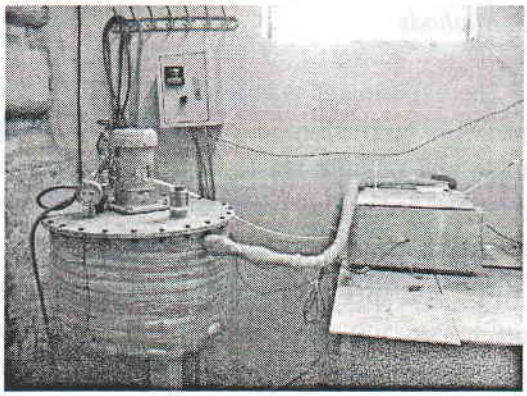

Fig.1. Photo of the pilot equipment.

2.2. Substrates characteristics

The anaerobic co-digestion involved two different substrates:

- The municipal sewage sludge was sampled from Kim Nguu River near from Lac Trung Bridge.

- The organic waste comes from market. Municipal sewage sludge was removed inert substances such as bridges, stones, special solid waste... after collection. The sewage sludge has to be smooth to avoid obstructed in reactor.

The organic fraction has quite variable characteristics however its average composition can be roughly estimated as 30% animal origin and 70% vegetable origin. It was grinded by grinding machine and mixed with municipal sewage sludge follow ratio three part of organic waste by volume and one part of municipal sewage sludge by volume before put into reactor.

Table 1. Input substrates composition

$V_{input\ Substrate}$ (L)	V_{MSS} (%)	V_{OW} (%)	D_{MSS} (g/ml)	D_{OW} (g/ml)
30	25	75	1.447	1.247

VMSS: Volume of municipal sewage sludge; VOW: Volume of organic waste; DMSS: density of municipal sewage sludge; DOW: density of organic waste.

2.3. Methods

The experiment was implemented in batch type with optimal ratio of municipal sewage sludge and organic waste is 1/3 for anaerobic digestion [6]. The component of influent substrate was shown in table 1.

EC and pH value were determined by Eutech Con 700 and Cyberscan pH 110. COD total was determined by titraction with $K_2Cr_2O_7$ method. Heavy metals were determined by ICP OES method.

Preparing solid samples for heavy metals determination

After sampling, samples were dryed at 60°C during 24 hours. After that, the samples were grinded and kept in anti-moisture vase. Each of samples was scaled one gram and put into Teflon tubes. Continuoustly put 9 ml HNO_3 acid 62% and 1 ml H_2O_2 30%. The heating mechanism of microway oven was divided two steps:

Step 1: the temperature need to reach 165°C around 2 minutes, the max pressure could be 350 psi, retention time is 4 minutes.

Step 2: The temperature need to reach 175°C around 3 minutes, the max pressure could be 350 psi retention time is 20 minutes.

The samples were cooled automatically to ambient temperature. After that they were determined by ICP OES.

Preparing eluted solution for heavy metals determination

Scale exactly 10g dry substrate and put into bottle 250 ml, add 100 ml distilled water and shake around 24 hours. After that, use spin filter to collect eluted solution and filled by filter paper before determination of heavy metals content by ICP OES method.

3. Results and discussions

3.1. Variations of pH and EC value

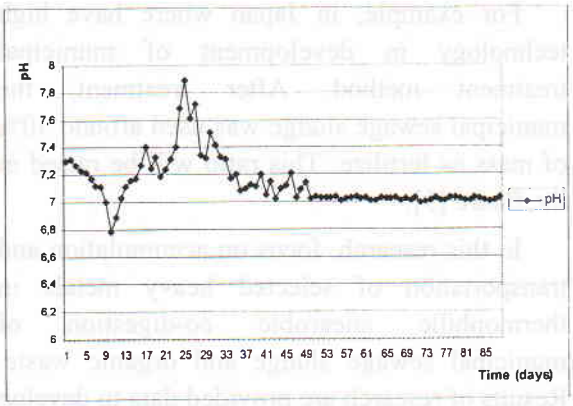

Fig. 2. Variation of pH value.

The variation of pH value was shown in fig.2. This variation is characteristic of anaerobic digestion. In the first phase, pH value has decreasing trend. It is suitable to organic compound digestion [3]. The lowest pH value in this experiment is 6.78 after 9 days. During digestion, pH value continoustly increases and stable at the stability phase of digestion process.

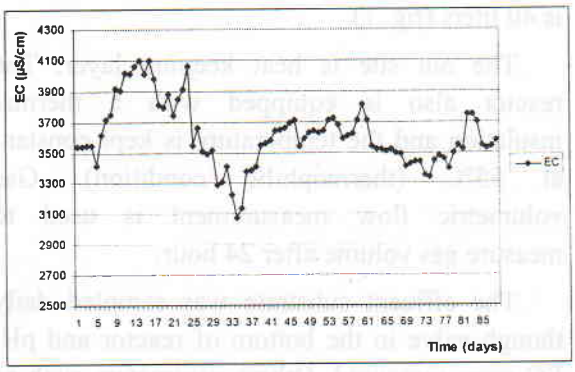

Fig. 3. Variation of EC value.

The variation of EC value is suitable rule of anaerobic digestion. Firstly, EC value usually increases. After that, it decreases and stable.

3.2. Variation of CODt

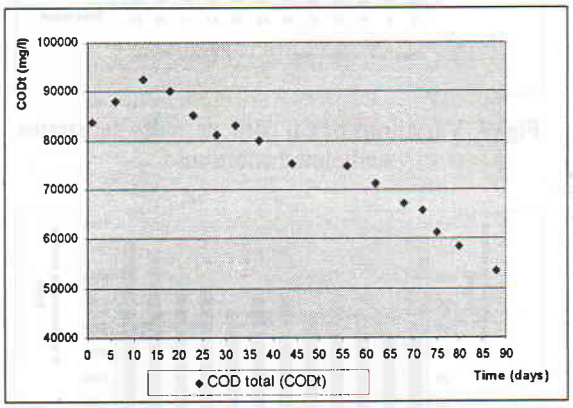

Fig. 4. Variation of CODt value.

Figure 4 shown variation of CODt depend on time. This variation is suitable to anaerobic digestion. In the first stage CODt increase in 5 to 10 days and decrease during anaerobic digestion take place.

The variations of pH, EC, CODt during digestion process affirm that the process take place in this experiment that is anaerobic digestion.

3.3. The accumulation and transportation of selected heavy metals

Accumulation of heavy metals in municipal sewage sludge

Municipal wastewater in Hanoi city not only contains household wastewater but also contains wastewater from small workshops. Therefore, the properties of municipal wastewater are very complicated.

Similar to popular wastewater treatment process, municipal wastewater though out sewage system that take place process such as physical processes, chemical processes and biological processes [1]. The accumulation of heavy metal in sewage sludge depends on characteristic of wastewater treatment plant system and its operation [2].

Therefore, the accumulation of heavy metals in municipal sewage sludge is different on each of zones as well as each of country.

The transportation of heavy metals

Transportation, biological characteristics or toxic behaviours of heavy metals mainly depend on chemical properties of each heavy metal as well as compound forms of heavy metal in sewage sludge [1]. It is difficult to determine a suitable method for treatment municipal sewage sludge with orient using product to soil amendment. Therefore, it is necessary to pay more attention to compound form of heavy metals in sewage sludge as well as its transportation during treatment process [1]. Efficiency of removing heavy metals from sewage sludge depends on compound form of heavy metals. Usually, heavy metals exist on a lot of compounds such as sunfide, hydroxide, silicate, coordinate form with organic legends.

There are a lot of mechanisms effect on transform of heavy metal compound in sewage sludge which are effect on transporting and bleaching of heavy metal from sewage sludge. In which, it is necessary to pay more attention to heavy metal mobilization mechanisms in sewage sludge treatment by anaerobic digestion. The microorganism activities oxidized sunfide compounds which promote bleaching of heavy metals into aqueous phase. Transportation mechanism follows equation:

Thio-oxidans

$$MeS + 2O_2 = MeSO_4$$

Though this mechanism, heavy metals exist on sunfide form in sewage sludge such as NiS, CuS, ZnS could be bleached [1].

However, the microorganism activities are affected by conditions of treatment process such as temperature, pH, and initial substrate component. Treatment process is implemented in thermophilic that have heavy metals bleaching rather than mesophilic condition. The pH value not only effect on heavy metals bleaching follow chemical mechanism but also indirectly effect on microorganism developing that cause to effect on transformation of heavy metals in substrate.

Thus, affirm that the accumulation and transportation of heavy metal in treatment process depends on initial substrate and technology conditions.

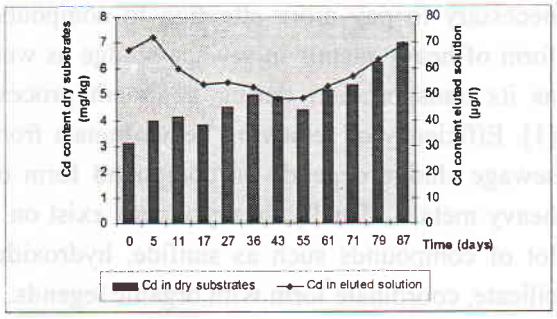

Fig. 5. Variations of Cadmium content in dry substrates and eluted solutions.

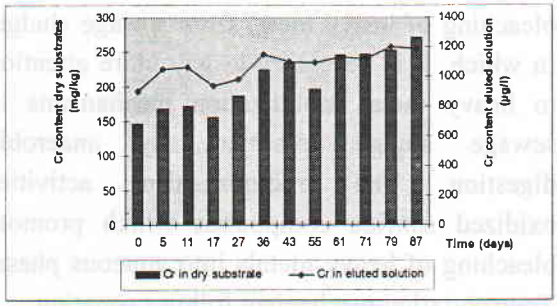

Fig. 6. Variations of Chromium content in dry substrates and eluted solutions.

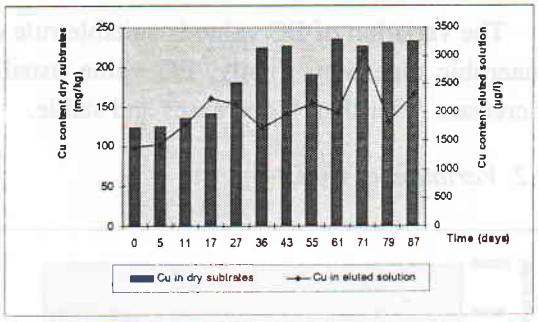

Fig. 7. Variations of Cu content in dry substrates and eluted solutions.

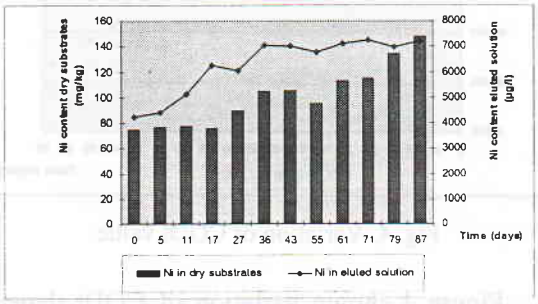

Fig. 8. Variations of Nickel content in dry substrates and eluted solutions.

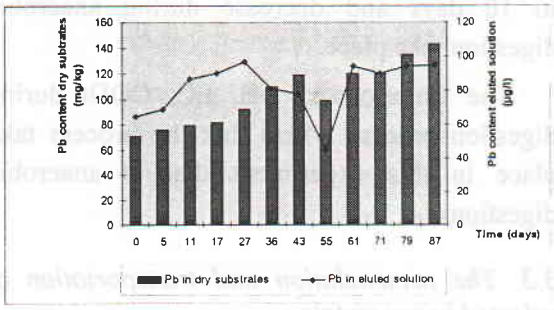

Fig. 9. Variations of Lead content in dry substrates and eluted solutions.

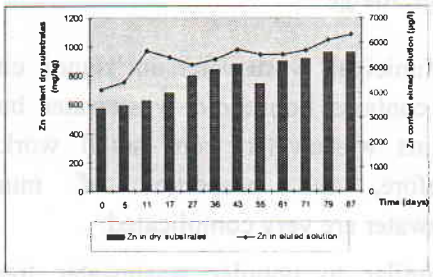

Fig. 10. Variations of Zinc content in dry substrates and eluted solutions.

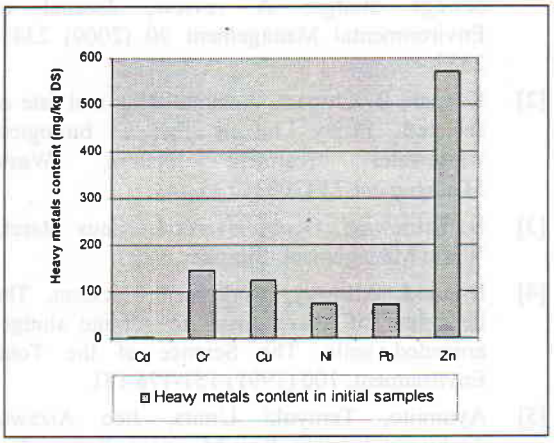

Fig. 11. Heavy metals content in initial substrate.

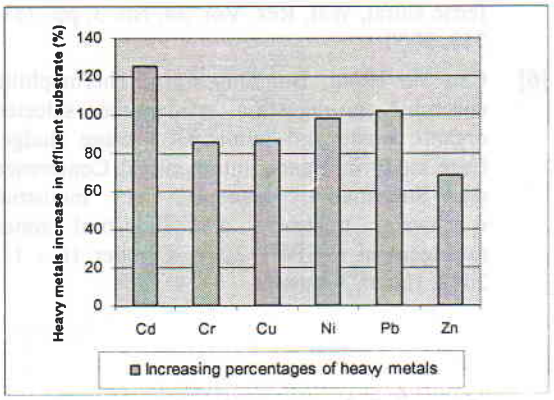

Fig. 12. Heavy metals increasing in effluent substrate.

This research shown that anaerobic digestion is the cause to increase heavy metals content in effluent substrate.

During anaerobic digestion, the biodegradation of organic compounds with the end products such as CH_4, CO_2, NH_3 also heavy metals are not biodegradable and negligible evapour. This is the main cause to make increase heavy metals content in dry effluent subtrate [2].

Fig.12 shown that the lower heavy metal content in initial substrate the higher heavy metal content in effluent substrate after treatment process.

The increasing percentages of heavy metals content follow the order Cd>Pb>Ni>Cr>Cu> Zn.

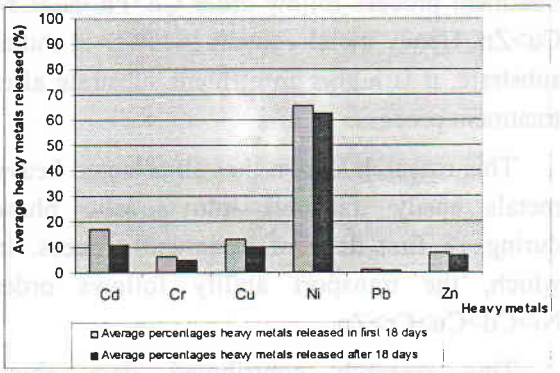

Fig.13. Average heavy metals released.

Fig. 13 descriped the average releasing of heavy metals in first 18 days is higher than after 18 days of treatment process. This phenomenon is quirely appreciate to decreasing of pH value in 18 first days of treatment process. In the first stage, the organic digestion creates organic acids and ammonium that have high coordinate abilities with heavy metals. pH value increases in after stage of treatment process but the releasing ability transporting into aquatic phase of heavy metals was lower than first stage. Therefore, this research shown that all selected heavy metals easily transporting into aquatic phase during 18 first days of treatment process. In which, the transporting ability follows order Ni>Cd>Cu>Cr>Zn.

4. Conclusions

Though researching results, we could conclude like that:

The accumulation and transportation of selected heavy metals in thermophilic anearobic co-digestion of municipal sewage sludge and organic waste depends on a lot of factors such as initial substrate characteristics, technology conditions, implement method...

Experiments shown that heavy metals content of effluent substrate increase after treatment process follow order Cd>Pb>Ni>Cr> Cu>Zn. Heavy metal content is lower in initial substrate, it is higher in effluent substrate after treatment process.

This research shown that all selected heavy metals easily transport into aquatic phase during 18 first days of treatment process. In which, the transport ability follows order Ni>Cd>Cu>Cr>Zn.

This research contributed data about characteristics of municipal sewage sludge. Base on collected data to build suitable releasing heavy metals method in treatment process. The product of treatment process could be used for soil amendment.

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Sự tích tụ và vận chuyển của một số kim loại nặng trong quá trình ổn định bùn thải kết hợp rác hữu cơ bằng phương pháp lên men nóng

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Trong nghiên cứu này tập trung nghiên cứu sự tích tụ và vận chuyển của một số kim loại nặng trong quá trình ổn định bùn thải kết hợp với rác hữu cơ bằng phương pháp lên men nóng trên qui mô phòng thí nghiệm. Rác thải hữu cơ được lựa chọn và bùn thải được lấy từ hệ thống sông thoát nước thành phố trên địa bàn thành phố Hà Nội. Rác hữu cơ và bùn thải được phối trộn với tỷ lệ thích hợp

theo hướng tối ưu quá trình phân hủy yếm khí. Hỗn hợp bùn thải và rác hữu cơ được đưa vào mô hình thí nghiệm hoạt động theo kiểu mẻ. Trong suốt quá trình tiến hành thí nghiệm các chỉ tiêu như pH, độ dẫn điện (EC), thể tích khí biogas (Vbiogas) được đo hàng ngày, các chỉ số khác như COD tổng, kim loại nặng được đo định kỳ theo kế hoạch thực nghiệm. Hàm lượng kim loại trong đầu vào và sản phẩm đầu ra của quá trình xử lý được đặc biệt quan tâm trong nghiên cứu.

Nghiên cứu đã chỉ ra được các kim loại nặng có hàm lượng tăng lên trong sản phẩm sau quá trình ổn định với thứ tự sau: Cd>Pb>Ni>Cr>Cu>Zn, kim loại càng có hàm lượng thấp trong nguyên liệu đầu vào, có phần trăm tăng càng cao trong sản phẩm sau ổn định. Nghiên cứu cũng đã chỉ ra các kim loại nặng dễ dàng vận chuyển vào pha nước hơn trong giai đoạn 18 ngày đầu của quá trình ổn định với thứ tự linh động của các kim loại như sau: Ni>Cd>Cu>Cr>Zn. Kết quả của nghiên cứu góp phần hiểu sâu hơn về bùn thải thoát nước điển hình tại Hà Nội trên cơ sở đó đề xuất phương án thích hợp cho việc loại bỏ kim loại nặng làm tiền đề sử dụng sản phẩm sau xử lý cho việc cải tạo đất nông nghiệp.