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Effect of Surfactant on Degradation of Polycyclic Aromatic Hydrocarbons (pahs) in Thermophilic Anaerobic Co-Digestion of Sludge from Kim-Ngưu River and Organic Waste

Cao Vũ Hưng[1,*], Bùi Duy Cam[1], Bạch Quang Dũng[2]

[1]*VNU University of Science, 334 Nguyễn Trãi, Hanoi, Vietnam*

[2]*Vietnam Institute of Meteorology, Hydrology and Environment*

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Abstract: The aim of this study was evaluate the effect of nonionic surfactant (Tween 80) on degradability of PAH compounds in thermophilic anaerobic co-digestion of sludge from Kim Nguu river and organic waste. The simulation on laboratory scale was use for testing with 3/1 ratio of organic waste and sludge. During experiment, the concentration of PAHs was measured by GC FID method and its variation was paid more attention to evaluate its degradability.

The results showed that removal efficiency of 2-3 rings, 4 rings, 5 rings, 6 rings and total PAHs compounds in the case of (Sludge + Organic waste) were 65.34%, 47.93%, 35.43%, 21.35% and 22.83% respectively. The degradability of 2-3 rings compounds was higher over two times than the 5 rings compounds and three times than the 6 rings compounds.

When using nonionic surfactant agent (Tween 80) with 0.5 g/l of concentration, the rate and degradability of PAHs compounds increased significantly except 4 rings of PAHs which had not identified in the influent of (SL + OW + Tween 80). Degradability of 2-3 rings PAHs compounds increased from 65.34% to 83.98%, 5 rings compounds increased from 35.43% to 53.71%, 6 rings compounds increased from 21.35% to 67.06% and total PAHs increased from 22.83% to 67.22%.

This result is basic for implement to study deeply enhancing degradability of PAHs compounds in the sludge of Kim Nguu river to remove them from initial substrate in effort applying end product for agricultural soil.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during the incomplete combustion of organic material or during pyrolysis processes. Though they may have natural origins, the main pollution sources for the PAHs are anthropic (combustion of fossil materials, motor vehicle, industrial combustion, smoke of cigarettes, etc.). This wide spectrum of sources allows explaining their ubiquity in the environment. They are carried out to wastewater treatment plants by effluent discharge and runoff waters. As they present low solubility in water and are highly lipophilic, they adsorb and accumulate in sludge throughout the wastewater treatment [1-5]. Moreover, the PAHs are highly toxic with carcinogenic and mutagenic properties. They

[*] Corresponding author. Tel: 84-904442426.
E-mail: hungcv@invitek.com.vn

are also persistent and are considered as priority pollutants in the US EPA and EU lists. The accumulation of polluted organic compounds and heavy metals is causes difficulties to use the municipal sewage sludge for agriculture [6, 7].

Currently, the research on anaerobic digestion of PAHs compounds are mainly focus on PAHs contaminated soil. It is not much the work to study PAHs in the municipal sewage sludge. In recent year, the anaerobic digestion of PAHs compounds in sewage sludge was paid more attention when the anaerobic method was applied like solution for recover energy from generated biogas.

Biodegradation of PAHs in sewage sludge has high rate of success, but the kinetics of this process is still not fully understood. According to (Haritash et al., 2009) [8] shown that the degradation of PAHs depended on their concentration in the sludge and strongly relative to partition-coefficient of PAHs between water phase and sludge phase. Therefore, sewage sludge is pre-treated by heat or ozone before anaerobic decomposition increases rate as well as degradability of PAHs.

Currently, using surfactant to enhance desorption and decomposition of PAHs from sewage sludge is an effective method. Surfactant agents effect on PAHs solubility and pull them from sludge particles into elute and enhance their decomposition. The surfactants were used mainly nonionic substances such as Tween 20, Tween 80, Triton X100 [9]. Investigation of (Zheng et al., 2007)[10] was shown that using Tween-80 to increase removal efficiency of total PAHs in sewage sludge from 54% to 60%.

Study the effect of nonionic surfactant (Tween 80) on decomposition of PAHs compounds in thermophilic anaerobic co-digestion of sludge from Kim Nguu river and organic waste was responsible for developing method to treat sludge from Kim Nguu river which one of the receiving urban wastewater river in Hanoi city. Results of this study will enhance developing treatment method for municipal sludge in Hanoi city as well as in overall system of urban waste management in Vietnam.

2. Materials and methods

2.1. Experimental set up

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

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 though valve in the bottom of reactor. The scheme of method was shown at fig. 1.

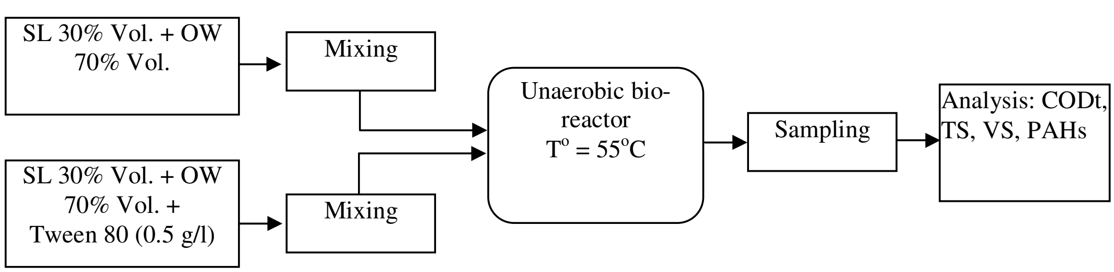

Fig. 1. Scheme of method.

2.2. Substrates characteristics

The anaerobic co-digestion included two different substrates, the sludge was collected from Kim Nguu River and the organic waste was selected from market with composition can be roughly estimated as 30% animal origin and 70% vegetable origin. The stones and inert substance were removed from sludge by sieving, organic waste was grinded and they were mixed with one part of sludge and three part of organic waste. According to (Cao & Bui., 2013) [11] this ratio is suitable for bio-degradation of Kim Nguu river sludge.

The composition influent substrate of two experiments was shown in table 1.

Table 1. Input substrates composition

Parameters	SL + OW	SL + OW + Tween 80
TS (%)	20.1	19.0
VS (% TS)	60.3	62.1
pH	7.33	7.54
EC	3530	3329
COD total	83590	79685
Tween 80 (g/l)	0	0.5
Heavy metals (mg/kg DS)		
As	25.3	20.7
Cd	3.10	2.15
Cr	146	139
Ni	74.8	75.9
Cu	124	115
Pb	71	59.7
Zn	571	535
PAHs (mg/kg DS)		
Naphthalene	0.55	0.67
Acenaphthylene	1.76	1.65
Acenaphthene	0	0.83
Fluorene	1.52	2.67
Anthracene	0	2.16
Fluoranthene	0.40	0
Pyrene	0.60	0
Benz[b]fluoranthene	0.61	0
Benzo[k]fluoranthene	2.47	0
Benzo[a]pyrene	1.69	8.12
Indeno[1,2,3-cd]pyrene	60.4	54.9
Dibenz[a,h]anthracene	49.4	27.1
Benzo[ghi]perylene	57.7	67.7
Σ PAHs	177	166

SL: sludge; OW: organic waste;

2.3. PAHs extraction and analysis

The sludge samples were dried at 60^{o}C, for 24 h, until it was completely dried. The exact weights of the samples were recorded. After grinding the sludge samples using a mortar, extraction process was performed. 50 µl of d_{10}-phenanthrene solution (10-mg d_{10}-phenanthrene in 50 ml dichloromethane) was added to the sample as a surrogate standard. The samples were extracted two times using 40 ml of CH_2Cl_2 in a tight Teflon tube under condition: temperature 80°C, maximum pressure 350 psi, retention time 20 minutes [12]. The supernatant were decanted after each cycle of extraction and then filtered through filter paper, sodium sulfate power added to remove excess water. The composite supernatants were evaporated using rotary vacuum evaporator at 40^{o}C, until sample volumes were smaller than 1 ml. The samples were fulfilled with dichloromethane to 2ml, filtered through a PP-housing 0.45 µm syringe filter (Minisart® RC 15) and stored in glass vials sealed with Teflon-butyl rubber caps. The samples were kept in refrigerator before GC injection.

Residual concentration of 16 PAHs compounds. PAHs samples were analyzed using YL 6100 series gas chromatograph using Agilent J&W Advanced Capillary GC column HP-5 (30 m x 0.32 mm i.d.; film thickness 0.25 µm) and flame ionization detector (FID). A 2µl aliquot of PAH sample was injected using an auto-sampler. Nitrogen was used as the carrier gas at a flow rate 2.5 ml/min. Inlet conditions are split ratio 5:1, split flow 10ml/min, heater 200^{o}C, pressure 11.5 psi. The starting temperature was 150^{o}C and the temperature was ramped to 190^{o}C at 8^{o}C/min with 5 min holding, ramped to 220^{o}C at 2^{o}C/min, ramped to 300^{o}C at 15^{o}C/min, and then ramped to

310°C at 2°C/min with 2 min holding. Detector conditions were heater 300°C, H_2 flow 36 ml/min, air flow 350 ml/min, and make up flow 30 ml/min.

2.4. Other analysis

COD total (CODt) was determined by dichromate method titration; Humidity is defined by drying at 105°C during 24 hours, volatile solid (VS) is determined by burning dry samples in ceramic cup at 550°C during 2 hours.

3. Results and discussions

Two experiments were implemented under thermophilic anaerobic condition during three months. The amount of CH_4 generated was determined to be 320 ml/g VS degraded. TS and VS removals were 15.4% and 18.2% respectively, in the case of (SL + OW). In the case of (SL +OW + Tween 80), CH_4 generated was 351 ml/g VS degraded, TS and VS removal were 13.51% and 18.3% respectively. This phenomenon indicated that the system active well in anaerobic condition and Tween 80 as well as heavy metals composition in initial substrate (table 1) do not effect on microbial activities.

3.1. Sludge + Organic waste treatment

The bio-degradation of PAHs in case of (SL + OW) was shown in fig. 2, 3. The removal efficiency of 2-3 rings, 4 rings, 5 rings, 6 rings and total PAHs compounds were 65.34 %, 47.93 %, 35.43 %, 21.35 % and 22.83 % respectively. The bio-degradability of 2-3 rings compounds was higher over two times than the 5 rings compounds and three times than the 6 rings compounds. Bio-degradation ability of 5, 6 rings compounds were lower than 2-3, 4 rings compounds due to their strong hydrophobicity which makes them less bioavailability [13]. The degradation rate of 2-3 rings, 4 rings compound more rapid during the first 18 days of decomposition process, this phenomenon is similar to the study of [10, 14, 15] which indicate that the bio-degradation kinetic of low molecular weight depends on their initial concentration.

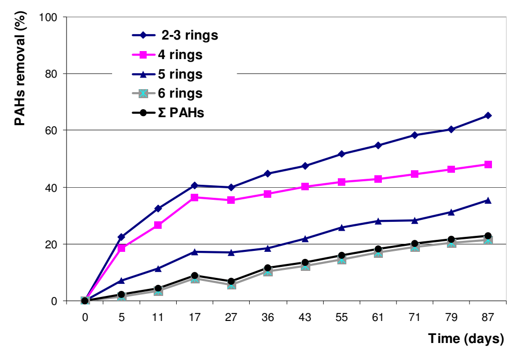

Fig. 2. Time variation of the PAH degradation in the case of (SL + OW).

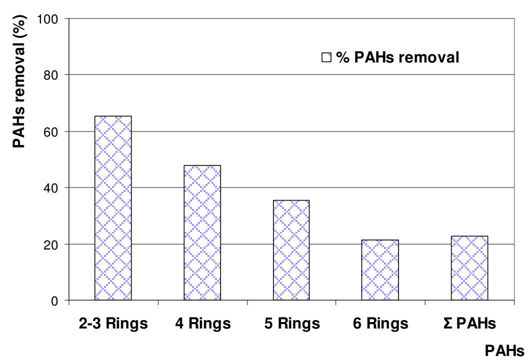

Fig. 3. PAHs removal yields in the case of (SL + OW) relation to the number of aromatic rings.

3.2. Sludge+Organic waste+Tween 80 treatment

In case of (SL + OW + Tween 80) is similar to the case of (SL + OW), degraded rate is rapid within the first 18 days (fig. 4). When using nonionic surfactant agent (Tween 80), the rate and degradability of PAHs compounds also increased significantly except 4 rings of PAHs which had not identified in the influent of (SL +

OW + Tween 80) (table 1). Degradability of 2-3 rings PAHs compounds increased from 65.34% to 83.98%, 5 rings compounds increased from 35.43% to 53.71%, 6 rings compounds increased from 21.35% to 67.06% and total PAHs increased from 22.83% to 67.22% (fig. 5).

As for the 5 rings PAHs compounds has differences between two experiments, the decomposition of 5 rings PAHs compounds was faster than 6 rings compounds in the case of (SL + OW) (fig. 2), this result is suitable to study of [13]. However, using Tween 80 in the case of (SL + OW + Tween 80) made degradability of 6 rings PAHs compounds increase more than 5 rings compounds (fig. 4), this phenomenon can be proved that the concentration of 5 rings compounds in influent was too lower than 6 rings compounds (table 1). The surfactant agent made 6 rings compounds dissolved more in the water phase which enhances their ability to decompose. In the study of [10], when used Tween 80 to enhanced decomposition of PAHs in sewage sludge has resulted in 2, 3, 4 rings of PAHs compound but 5, 6 ring compounds the results was unclear. However, in the case of this research, the experiment was carried out for long periods in high temperature with optimum agitation conditions which enhanced significantly the decomposition of 5, 6 ring PAH compounds.

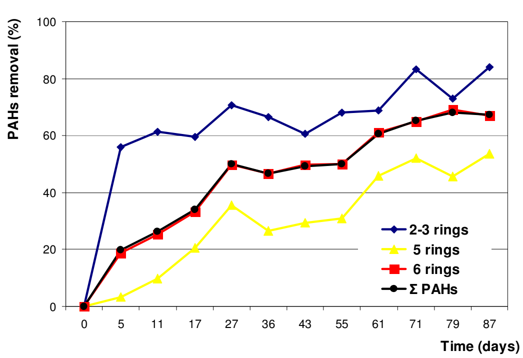

Fig. 4. Time variation of the PAHs degradation in the case of (SL + OW + Tween 80).

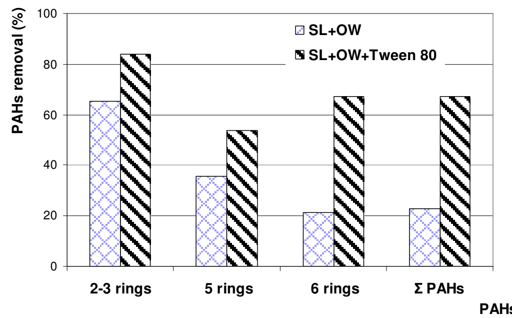

Fig. 5. Final PAHs removal yields after different thermophilic anaerobic treatments in relation to the number of aromatic rings.

4. Conclusions

The study showed the degradability of PAHs in thermophilic anaerobic co-digestion of sludge in Kim Nguu river and organic waste with three part of organic waste per one part of sludge ratio. The removal efficiency of 2-3 rings, 4 rings, 5 rings, 6 rings and total PAHs compounds were 65.34%, 47.93%, 35.43%, 21.35% and 22.83% respectively. The bio-degradability of 2-3 rings compounds was higher over two times than the 5 rings compounds and three times than the 6 rings compounds.

When using nonionic surfactant agent (Tween 80), the degradability of PAHs compounds also increased significantly except 4 rings of PAHs which had not identified in the influent of (SL + OW + Tween 80). Degradability of 2-3 rings PAHs compounds increased from 65.34% to 83.98%, 5 rings compounds increased from 35.43% to 53.71%, 6 rings compounds increased from 21.35% to 67.06% and total PAHs increased from 22.83% to 67.22%.

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Tác dụng của chất hoạt động bề mặt lên sự phân hủy hợp chất hữu cơ đa vòng thơm (PAHs) của bùn thải tại sông Kim Ngưu trong quá trình ổn định kết hợp rác hữu cơ bằng phương pháp lên men yếm khí nóng

Cao Vũ Hưng[1], Bùi Duy Cam[1], Bạch Quang Dũng[2]

[1]*Trường Đại học Khoa học Tự nhiên, ĐHQGHN, 334 Nguyễn Trãi, Hà Nội, Việt Nam*
[1]*Viện Khoa học Khí tượng Thủy văn và Môi trường*

Tóm tắt: Nghiên cứu nhằm đánh giá tác dụng của chất hoạt động bề mặt không phân cực Tween 80 lên sự phân hủy của một số hợp chất hữu cơ đa vòng thơm (PAHs) có trong bùn thải sông Kim Ngưu trong quá trình ổn định kết hợp với rác hữu cơ bằng phương pháp lên men yếm khí nóng. Nghiên cứu sử dụng mô hình qui mô phòng thí nghiệm để tiến hành ổn định bùn thải và rác hữu cơ với tỷ lệ theo thể tích 3 rác/1 bùn. Trong suốt thời gian thí nghiệm, mẫu hỗn hợp phản ứng được lấy định kỳ và hàm lượng PAHs trong sinh khối được xác định bằng phương pháp sắc ký khí kết hợp detector ngọn lửa (GC FID). Sự thay đổi của hàm lượng PAHs trong sinh khối theo thời gian là cơ sở để đánh giá khả năng phân hủy của các hợp chất PAHs.

Trong trường hợp không sử dụng chất hoạt động bề mặt, nghiên cứu đã chỉ ra rằng khả năng phân hủy của các hợp chất 2-3 vòng, 4 vòng, 5 vòng, 6 vòng và tổng PAHs lần lượt là 65.34%, 47.93%, 35.43%, 21.35% and 22.83%. Sự phân hủy của các hợp chất 2-3 vòng lớn hơn 2 lần so với các hợp chất 5 vòng và hơn 3 lần so với các hợp chất 6 vòng.

Khi sử dụng Tween 80 với hàm lượng 0,5 g/l, khả năng phân hủy các hợp chất PAHs đã tăng lên một cách rõ rệt. Ngoại trừ các hợp chất 4 vòng thơm không phát hiện trong nguyên liệu đầu vào, các hợp chất 2-3 vòng tăng khả năng phân hủy từ 65.34% lên đến 83.98%, các hợp chất 5 vòng tăng từ 35.43% lên 53.71%, hợp chất 6 vòng tăng từ 21.35% lên 67.06% và tổng PAHs tăng từ 22.83% lên 67.22%.

Kết quả nghiên cứu là cơ sở để tiến hành các nghiên cứu sâu hơn về sự phân hủy của các hợp chất PAHs trong bùn thải tại sông Kim Ngưu cũng như bùn thải đô thị nói chung nhằm loại bỏ các tác nhân ô nhiễm độc hại để có thể sử dụng sản phẩm sau xử lý trong cải tạo đất nông nghiệp.