



Removal of polycyclic aromatic hydrocarbons (PAH) during anaerobic digestion with recirculation of ozonated digested sludge

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ABSTRACT

PAH are particularly monitored because of their carcinogenic properties and their ubiquity in the environment. Their presence in municipal sewage sludge is a major problem due to the environmental risks associated with the sludge spreading on agricultural soils. The objective of this work was to assess the removal of PAH naturally present in sludge by continuous anaerobic digestion with recirculation of ozonated sludge. Recirculation of ozonated digested sludge allowed to enhance PAH removals, the highest efficiency was obtained with the highest ozone dose (0.11 g O₃/g_{TS}). In order to study the effect of recirculation, a reactor was operated without recirculation but was fed with a mixture of raw and ozonated digested sludge. This process led to the best performances in terms of PAH and solid removals. This pointed out some accumulation of nonbiodegradable or recalcitrant compounds during recirculation assay. Smallest and most soluble compounds presented the highest biodegradation efficiencies.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are related to incomplete oxidation and combustion of organic compounds. They are thus produced during industrial pyrolysis and combustion processes, by residential heating, motor vehicles, ... As they are ubiquitous in the environment, they cause contamination of soil and groundwater. Due to their transport by runoff waters, they converge to wastewater treatment plants. During wastewater treatment, they adsorb and concentrate in the sludge solid phase because of their high hydrophobicity and recalcitrance. Thus, the presence of PAH in municipal sewage sludge is a major problem due to the risks associated with the agricultural application of sludge and potential risk of transfer to waters, plants and animals. Many of PAH are known to be carcinogenic and mutagenic. They are absorbed by the respiratory tracts (the inhalation of contaminated atmospheric particles or cigarette smokes), the digestive system (ingestion of contaminated foodstuffs, in particular the roasted or smoked products) and the skin [1,2]. Environmental Protection Agency included 16 of them in the list of priority pollutants (naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene,

benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. Some of them are also listed in the EU Water framework directive (2000/60/EC). The European Commission [3] 2000) has proposed a limit value of 6 mg/kg_{TS} for the sum of 11 PAH from acenaphthene to indeno(1,2,3-cd)pyrene as the limit to allow sludge spreading.

Beside, ozone is known to have high reactivity with PAH in liquid media. Ozone is a very strong oxidant ($E^\circ = +2.07\text{ V}$) that has been used successfully in wastewater treatment for the oxidation of organic contaminants. It oxidizes organic compounds either by direct oxidation or through the generation of hydroxyl radicals, or both. Organic compounds treated with ozone are transformed

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to oxygenated intermediates which are more soluble and more biodegradable [8]. Trapido et al. [9] investigated the ozonation of seven PAH. All compounds were degraded by ozone in few minutes. Due to a higher reaction rate in neutral and acidic media than in basic one, and a slower degradation using advanced oxidation processes, they concluded that the reaction proceeds mostly by molecular ozone. PAHs ozonation has also been investigated in dodecane/water emulsions [10], kerosene films [11], sediments [12] or soils [13–15]. The high potentiality of combining ozonation with biological aerobic treatment of PAH has been shown in the case of remediation of sediments [12] or soils [14,15].

But no study was focussed on the fate of PAH in processes combining ozonation and anaerobic digestions although such processes are investigated with the aim of reducing sludge amount during their stabilisation [16,17]. In previous works, we showed that ozonation was efficient to remove PAHs in digested sludge and we selected an optimum dose equal to $1.5 \text{ g O}_3/\text{L}$ corresponding to $0.11 \text{ g O}_3/\text{g}_{\text{Total Solid}}$ [18]. We also showed that PAH degradation by anaerobic digestion could be improved by ozone pre-treatment [19].

The objective of this work was to assess the removal of PAH naturally present in sludge by continuous anaerobic digestion with recirculation of ozonated sludge. Two combined processes with 100% recirculation ratio were carried out. One was operated with the optimal ozone dose of $0.11 \text{ g O}_3/\text{g}_{\text{TS}}$ and the other one was run with a dose of $0.055 \text{ g O}_3/\text{g}_{\text{TS}}$ to investigate the impact of ozone dose. Finally, in order to assess the impact of sludge recirculation, a cascade configuration was also tested with the $0.11 \text{ g O}_3/\text{g}_{\text{TS}}$ dose.

2. Material and methods

2.1. Sludge

Sludge were collected from a wastewater plant in an industrial area. They were long term naturally contaminated with PAH. It was a mixture of primary sludge and excess waste activated sludge (50/50, v/v). They were stored at -20°C . Anaerobic inoculum was collected from the same wastewater plant, it was thus long term acclimated.

2.2. Continuous anaerobic reactors

Four laboratory-scale reactors of anaerobic digestion (Fig. 1) were run during 176 days. They were started up with anaerobic inoculum acclimated to the contaminated sludge. The first reactor R1, with a working volume of 20 L, was fed with a primary and secondary sludge mixture. This reactor was considered as the anaerobic digestion control reactor. The second reactor R2 had a working volume of 5 L. It was operated without recirculation, it was fed with 50% of fresh sludge and 50% of the ozonated sludge ($1.5 \text{ g O}_3/\text{L}$) from R1. The third and fourth reactors R3 and R4 had volume of 5 L, they were operated with recirculation of ozonated sludge, the recirculation ratio was 100%. They were fed with 50% of fresh sludge and 50% of digested ozonated sludge. Hydraulic retention time (HRT) was 40 days in anaerobic reactors. Such high HRT was chosen in order to have no kinetics limitation for PAH biodegradation. If the combined processes are considered, retention time was equal to 80 days for R3 and R4 configurations (Table 1).

Ozone dose was the optimum one ($0.11 \text{ g O}_3/\text{g}_{\text{TS}}$) for R2 and R3 as determined by Bernal-Martinez et al. [18] and was $0.055 \text{ g O}_3/\text{g}_{\text{TS}}$ for R4. pH was not regulated but did not evolve significantly; it ranged from 7.8 to 8.0 in R1 and R2, from 8.0 to 8.2 in R3 and from 7.9 to 8.1 in R4. Biogas outlet was cooled to avoid water or PAH losses. Produced biogas volume was measured by a gas counter. Temperature

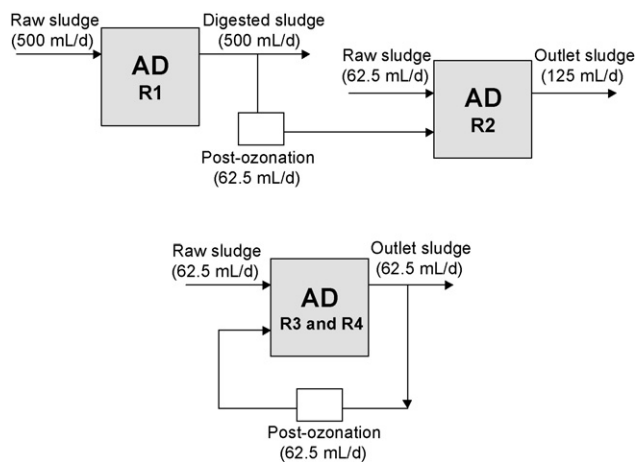


Fig. 1. Process configurations. AD, Anaerobic digestion. Configuration R1: anaerobic digester fed with raw sludge. Configuration R2: anaerobic digester fed with raw sludge and ozonated digested sludge from R1. Configuration R3: anaerobic digester fed with raw sludge and recirculation of and ozonated digested sludge, ozone dose: $0.11 \text{ g O}_3/\text{g}_{\text{TS}}$. Configuration R4: anaerobic digester fed with raw sludge and recirculation of and ozonated digested sludge, ozone dose: $0.055 \text{ g O}_3/\text{g}_{\text{TS}}$.

was maintained at 35° with a water bath. In the substrate storage tank, microbial degradation was limited by cooling the substrate at 4°C until its entrance in the reactor. After reaching steady state, PAH removal efficiencies were calculated by the average of 5 outlet samples.

2.3. Ozonation

The digested sludge was ozonated in a 2 L fed batch reactor. 0.45 L of sludge was introduced in the reactor and ozone was fed continuously. The ozone was generated from pure oxygen by an Ozat CFSI generator (1425 Hz) and injected into the bottom of the reactor through a thin bubble diffuser. The reactor was mixed by a Rushton-type stirrer. The gas flow rate was $1 \text{ L}/\text{min}$, O_3 concentration in oxygen varied from 50 to $60 \text{ mg}/\text{L}$ in the produced gas. The ozone concentrations in gas phase (before and after the reaction with sludge) were determined each 30 s during the oxidation (with UV BMT 963 analysers) in order to calculate the ozone consumption thanks to a computer.

Ozonated sludge samples were bubbled with nitrogen before their introduction in the anaerobic digestors in order to remove dissolved oxygen.

2.4. PAH analysis

Analytical methods were previously tested and validated in the laboratory by the use of certified sludge [20]. The minimum volume of sample for PAH analysis was about 350 ml. Total solids were determined by drying 20 ml of the sludge sample in an oven at 110°C for 24 h. The remaining other 300 ml of the sludge sample were first centrifuged ($20,000 \times g$, 25 min). Aqueous phases were stored at -20°C for further Solid-Phase Extraction on PAH-affinity column (Supelco ENVI-18TM) according to the Supelco recommendations. Solid pellets were grounded with glass beads (diameter 4 mm) and were dried in ventilated oven (60 h, 40°C). Dry samples were sieved on grid (diameter 2 mm) and were stored at -20°C for further Accelerated Solvent Extraction with an ASE-200 system (DIONEXTM). Extraction conditions are reported in Trably et al. [20]. Extracts were then softly evaporated under nitrogen flow to dryness. Residues were dissolved in acetonitrile and analyzed by reverse phase-high

Table 1
Process parameters

	Feeding sludge		Anaerobic digester			Combined system	
	Characteristics	Ozone dose (g O ₃ /g _{TS})	Volume (L)	HRT (days)	OL (g VS/L/d)	HRT (days)	OL (g VS/L/d)
R1	Raw sludge (RS)		20	40	0.48		
R2	RS + ozonated DS (50/50)	0.11	5	40	0.34		
R3	RS + recirculation ozonated DS (50/50)	0.11	5	40	0.33	80	0.25
R4	RS + recirculation ozonated DS (50/50)	0.055	5	40	0.34	80	0.25

RS, Raw sludge; DS, digested sludge; HRT, hydraulic retention time; OL, organic loading.

performance liquid chromatography [20]. Standard solution of PAH (PAH-mix 9) was purchased from Cluzeau Info Labo. 12 PAH were considered: phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenzo(*a,h*)anthracene, benzo(*g,h,i*)perylene, indeno(1,2,3-*cd*)pyrene. Concentration and properties of the 12 PAH are shown in Table 2.

2.5. Other analysis

Anaerobic digestion and ozonation performances were evaluated through total solids (TS) and volatile solids (VS). They were measured in accordance with standard methods [21].

Ratios of CH₄ and CO₂ in biogas were determined by gas chromatography (Shimadzu) equipped with two columns (molecular

Table 2
Molecular structure, properties and initial concentration of PAH considered in this study

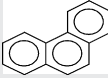
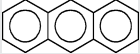
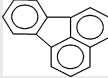

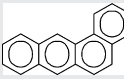
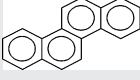
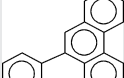
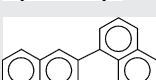
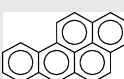
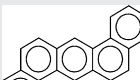
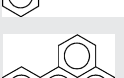

Compounds	Structure	<i>M</i> (g mol ⁻¹)	Water solubility at 25 °C (mg L ⁻¹)	Concentration in raw sludge (μg L ⁻¹)
Phenanthrene		178	1.0	44 ± 3
Anthracene		178	0.045	13 ± 7
Fluoranthene		202	0.206	163 ± 2
Pyrene		202	0.132	135 ± 1
Benzo(<i>a</i>)anthracene		228	0.0094	45 ± 7
Chrysene		228	0.0018	75 ± 1
Benzo(<i>b</i>)fluoranthene		252	0.0015	93 ± 1
Benzo(<i>k</i>)fluoranthene		252	0.0080	48 ± 5
Benzo(<i>a</i>)pyrene		252	0.0016	90 ± 2
Dibenzo(<i>a,h</i>)anthracene		278	0.0050	12 ± 1
Benzo(<i>g,h,i</i>)perylene		276	0.0007	68 ± 2
Indeno(1,2,3- <i>cd</i>)pyrene		276	0.0002	77 ± 4

Table 3

Total and volatile solids and PAH (sum of 12 PAH) concentrations in raw sludge, in digested and ozonated sludge and in the outlet of anaerobic reactors

	TS (g/L)	VS (g/L)	PAH extracted from solids		Removal (%)		
			$\mu\text{g/L}$	$\mu\text{g/g}_{\text{TS}}$	TS	VS	PAH
Raw sludge	28.1 \pm 1.2	19.3 \pm 1.7	863 \pm 9	30.7 \pm 2			
Ozonated sludge ^a	12 \pm 1	8 \pm 0.2	270 \pm 5	22 \pm 0.5			
R1	14 \pm 0.7	7.9 \pm 0.4	420 \pm 11	29.6 \pm 2	50 \pm 3	59 \pm 3	52 \pm 1
R2	12.2 \pm 0.5	6.3 \pm 0.3	292 \pm 9	23.4 \pm 2	57 \pm 3	67 \pm 2	66 \pm 1
R3	13.8 \pm 0.5	7.5 \pm 0.5	322 \pm 10	23.6 \pm 1	51 \pm 2	61 \pm 2	63 \pm 1
R4	14.3 \pm 0.5	7.4 \pm 0.1	405 \pm 10	28.6 \pm 1	49 \pm 2	61 \pm 2	53 \pm 1

Removal efficiencies by combined processes calculated towards raw sludge (mean value \pm standard deviation value on 5 points).^a Digested (from R1) and ozonated sludge, ozone dose: 0.11 g O₃/g_{TS}

sieved and Hays sep Q) and catharometric detection. Columns and injector temperatures were maintained at 30, 100 °C, respectively. Detector current was maintained at 80 mA. Argon was used as a carrier gas at 2.6 bars.

2.6. Calculation methods

Removals were defined as the difference between inlet and outlet concentrations divided by the inlet concentration. They were calculated after reactors stabilisation (after 160 days of operations which corresponded to 4 hydraulic retention times). Results were the average of 5 points, corresponding to 5 weeks of operation. Series of results were compared two by two using a *t*-test under a Student law at 5% assuming the variance equality, normality and independence of repetitions. Confidence interval was fixed at 95%, thus probability to reject the null hypothesis was equal to 5%.

3. Results and discussion

3.1. Feeding sludge characteristics

Table 3 shows the characteristics of the raw sludge and the ozonated digested sludge, which were the main feeding sludge for configuration R2. Such analysis could not be carried out for configurations R3 and R4 because the volume of samples which were withdrawn from the digester was just enough for recirculation and analysis of outlet sludge. Removals were thus calculated from raw sludge. PAH biodegradation by anaerobic digestion (R1, 40 days sludge retention time) was 52% and was correlated to total solids removal (50%) in agreement with results of Trably et al. [6]. Consequently, PAH concentration per amount of total solids remained the same after anaerobic digestion. Ozonation, after anaerobic digestion, led mainly to sludge solubilisation and partial PAH elimination. Ozonation at 0.11 g O₃/g_{TS} dose led 36% PAH removal.

3.2. Volatile and total solids removal efficiencies

Table 3 shows the concentrations and removal efficiencies of total and volatile solids in the different combined processes: R1, the control reactor; R2, reactor fed with ozonated digested sludge and raw sludge; R3 and R4, reactors with recirculation of ozonated sludge (0.11 and 0.055 g O₃/g_{TS}, respectively). In the case of the control reactor, the concentration of total solids at the inlet was 28.1 and 14 g/L after the anaerobic digestion, which means a 50% removal.

In the reactor fed with a mixture of digested ozonated (R2, 0.11 g O₃/g_{TS}) a 57% removal of total solids from the raw sludge was obtained. For reactors with recirculation, R3 and R4, the TS removals were 51 and 48% removal, respectively. On the other hand, anaerobic digestion (R1) led to a 59% decrease in volatile solids, whereas with the addition of ozone, a 67% removal was achieved. For configurations, R3 and R4, a 61% removal was obtained.

If we compare combined processes with recirculation (R3 and R4) with the reference one (R1), we can conclude that total and volatile solids removal rates were not significantly different. In other words, recirculation of ozonated digested sludge did not improve the sludge elimination rate, whatever the ozone dose. This can be explained by the high value of sludge retention time which was equal to 40 days. Indeed, when ozonation is combined to anaerobic digestion, it is used to disintegrate and solubilize sludge cells [22] in order to accelerate sludge biological hydrolysis which is the first and limiting-rate step of sludge anaerobic digestion. Thus, the aim of ozonation is rather to accelerate anaerobic digestion. This acceleration of anaerobic digestion performance could not be seen (or was very low in R2 configuration) at such high sludge retention time.

The influence of sludge retention time in the digester on the impact of ozonation on digestion performance was confirmed by Goel et al. [16]. They used ozone (0.05 g O₃/g_{TS}) as pretreatment of anaerobic digestion. At a 7 days sludge retention time, ozonation led to an improvement of 170% in VS removal (from 17% without ozone to 46% with ozone) and to an improvement of only 68% (from 35 to 59%) at 28 days sludge retention time.

Comparison of configurations R2 and R3 (which were operated with the same ozone dose) allows to assess the impact of ozonated sludge recirculation. Solids removal rates were slightly higher in the configuration without recirculation (R2). That means that recirculation or successive digestion of ozonated sludge was useless. Everything that was biodegradable was digested within one or two passages through the digester because of high sludge retention time. Moreover sludge recirculation had a negative impact on anaerobic digestion performance, which may be explained by some production and accumulation of recalcitrant compounds.

Methane yields reported to the amount of introduced or removed volatile solids are shown in Table 4. Methane production per amount of removed volatile solids are of course almost the same in all reactors, which shows correct working of anaerobic digestors. But, if we consider methane productions per amount of introduced volatile solids, they are in agreement with VS removals in anaerobic reactors (which are different from the ones obtained with the combined process in Table 3). Reactor R1 led to the highest methane yield. Indeed, all sludge introduced in this reactor was raw sludge whereas sludge introduced in other ones was a mixture of raw and ozonated digested sludge, and volatile solids present in the digested sludge were not easily biodegradable. Beside, methane

Table 4

Methane yields in anaerobic reactors, calculated towards the feeding of anaerobic reactors

Methane yield	R1	R2	R3	R4
mL CH ₄ /g VS _{introduced}	233 \pm 21	187 \pm 8	162 \pm 6	167 \pm 7
mL CH ₄ /g VS _{removed}	398 \pm 53	358 \pm 24	388 \pm 31	387 \pm 14
VS removal (AD reactors)	59% \pm 3	54 \pm 2	44 \pm 3	45 \pm 1

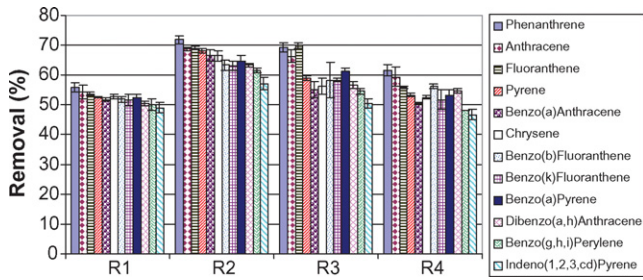


Fig. 2. Process removal efficiency of different PAH in the 4 configurations (mean value ± standard deviation value on 5 points).

yields obtained with recirculation reactors were equivalent and slightly inferior to the one obtained in configuration R2.

3.3. PAH removal efficiencies

The initial concentration of PAH in raw sludge was 863 µg/L and after anaerobic digestion, it decreased to 420 µg/L (52% removal) in the control reactor (R1). With the combination of ozonation (R2) a 66% removal was obtained compared to the raw sludge. For reactors R3 and R4, the removals were 63 and 53%, respectively. Thus, except in the case of configuration R4 with the low ozone dose, ozonation improved the degradation of PAH, even if solids removal rates were not improved by ozonation (Table 3). This point has to be underlined because it shows the action of ozonation on PAH and not on total and volatile solids, whereas COD due to PAH was less than 0.01% of total COD (12 g/L) of digested sludge. Indeed the concentration of PAH present in digested sludge was equivalent to about 1.1 mg COD/L. This confirms the high affinity of ozone towards PAH. In consequence, whereas anaerobic digestion did not reduce PAH concentration per amount of total solids, combination with ozonation allowed to reduce this concentration. However, this reduction was not enough to lower PAH concentration under the limit of 6 µg/g_{TS} required to allow land application of sludge.

When tested on recirculation processes, the highest ozone doses led to a higher PAH removals than the other dose. Moreover, configuration R2 led to higher PAH removal rates than the processes with recirculation and the same ozone dose. This confirms that one passage of digested ozonated sludge through the digester was more favourable than several ones because of production and accumulation of refractory compounds that may affect anaerobic digestion and PAH bioavailability or degrading activity.

Fig. 2 shows removal efficiency of each PAH in the four configurations. In simple anaerobic digestion (R1) and in anaerobic digestion fed by the mixture of raw sludge and digested and ozonated sludge (R2), removal efficiencies seem to be linked to molecular mass of PAH (Fig. 3) and to their solubility in water (Fig. 4). Indeed, the smallest and most soluble compounds presented the highest biodegradation yield. This was already observed in the case of anaerobic digestors without recycling fed with digested sludge or

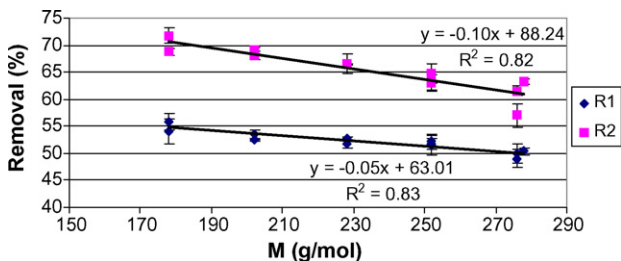


Fig. 3. PAH removal efficiency vs. PAH molecular mass in configurations 1 and 2.

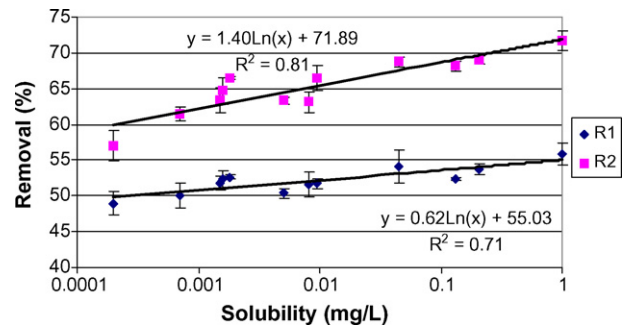


Fig. 4. PAH removal efficiency vs. PAH solubility in water in configurations 1 and 2.

digested and ozonated sludge [19]. This result was also observed by El-Hadj et al. [7] who indicated a removal efficiency of low molecular weight PAH ranging from 52.6 to 57% whereas total PAH removal was ranging from 36.5 and 43%. This results is also often reported in studies of PAH degradation in soils mainly under aerobic conditions [13,23–25]. The low biodegradability of high molecular weight (PAH) is often explained by low solubilities of PAH in water which in turn reduces the accessibility of PAHs for metabolism by microbial cells in soils [4,26].

Moreover, the slopes of regression lines in Figs. 3 and 4 are higher for the digester fed by ozonated sludge (R2) than for control anaerobic digestion (R1), this means that ozonation had more impact on the smallest and most soluble PAH (phenanthrene, fluoranthene, pyrene and anthracene). A detailed study on ozonation of sludge contaminated by PAH [27] showed that, at a given ozone dose, PAH removal efficiency was primarily determined by the solubility of PAH in water and the number of 5-carbon rings: their presence had a negative effect on ozone reactivity which was higher for totally aromatic PAH. This may partially explain the low removal efficiency (57%) obtained for indeno(1,2,3-cd)pyrene.

On the other hand, removal efficiencies obtained in digestors with recirculation could not be properly linked to PAH molecular mass or solubility. Fig. 5 shows however the improvement of PAH removal due to ozonation and recycling towards simple anaerobic digestion. Configurations with ozone allowed to improve PAH removals except in the case of low ozone dose (R4) for which Student test showed that pyrene, benzo(a)pyrene, chrysene and benzo(k)fluoranthene removals were not significantly different from R1 control. Moreover, benzo(a)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene removals were lower than removals obtained in R1 control.

If the two processes with recirculation (R3 and R4) are considered, it is clear that the 0.11 g O₃/g_{TS} dose was more efficient than the 0.055 g O₃/g_{TS} dose for each PAH. It has to be reminded that the 0.11 g O₃/g_{TS} (or 1.5 g O₃/L) was considered as the optimum dose for

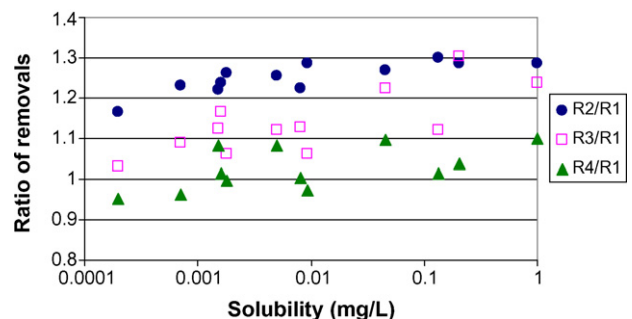


Fig. 5. PAH removal efficiency of processes with ozonation (R2, R3, R4) divided by removal efficiency of anaerobic digestion control (R1).

removal of PAH during ozonation of digested sludge [18]. It does not seem advantageous to operate the continuous combined process with a lower ozone dose.

If we compare configurations R2 and R3 carried out with the same ozone dose, removals obtained in the process without recycling (R2) are significantly higher for all PAH except for phenanthrene, anthracene and fluoranthene. In the case of these PAH which present 3 aromatic rings, the difference between the 2 processes was lower than 4%. We can thus conclude that recirculation penalised the removal of PAH with 4 and more aromatic rings but not of smallest PAH. This may be due to partial inhibition observed through solids removals. Indeed, it is commonly assumed that biodegradation of aromatic compounds requires syntrophic microbial populations to occur under methanogenic conditions [28]. This syntrophy may be reduced due to the partial inhibition in configurations with recirculation.

4. Conclusion

In this study, continuous anaerobic digestion reactors with and without combined ozonation and recirculation were run with a high sludge retention time (40 days). Thus, sludge digestion was almost complete and processes with partial recirculation ozonated digested sludge did not improve solids removal rates. But, in the configurations where anaerobic digestion was combined with ozonation at 0.11 g O₃/g_{TS}, ozonation allowed to enhance PAH removal rates. This indicates that, in the combined processes, PAH removal was not linked to total solids removal, as it was for classic anaerobic digestion. Smallest and most soluble compounds presented the highest biodegradation efficiencies.

Nevertheless, the highest PAH and solid removal rates were obtained with the combined process without recirculation, which pointed out some accumulation of nonbiodegradable or recalcitrant compounds during recirculation.

References

- [1] P. Boffeta, N. Jourenkova, P. Gustavsson, Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons, *Cancer Causes Control* 8 (1997) 444–472.
- [2] M. Wornat, E. Ledesma, A. Sandrowitz, Polycyclic aromatic hydrocarbons identified in soot extracts from domestic coal-burning stoves of Henan provinces, China, *Appl. Environ. Microbiol.* 62 (2001) 4174–4179.
- [3] CEC, Working Document on Sludge (3rd Draft), Commission of the European Communities Directorate-General Environment, ENV.E.3/LM, Brussels, 27 April 2000.
- [4] S.M. Bamforth, I. Singleton, Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions, *J. Chem. Technol. Biot.* 80 (2005) 723–736.
- [5] B.V. Chang, S.W. Chang, S.Y. Yuan, Anaerobic degradation of polycyclic aromatic hydrocarbons in sludge, *Adv. Environ. Res.* 7 (2003) 623–628.
- [6] E. Trably, D. Patureau, J.P. Delgenes, Enhancement of polycyclic aromatic hydrocarbons (PAH) removal during anaerobic treatment of urban sludges, *Water Sci. Technol.* 48 (4) (2003) 53–60.
- [7] T.B. El-Hadj, J. Dosta, J. Mata-Alvarez, Biodegradation of PAH and DEHP micro-pollutants in mesophilic and thermophilic anaerobic sewage sludge digestion, *Water Sci. Technol.* 53 (8) (2006) 99–107.
- [8] E. Gilbert, Investigations on the changes of biological degradability of single substances induced by ozonation, *Ozone Sci. Eng.* 5 (1983) 137–149.
- [9] M. Trapido, Y. Veressina, R. Munter, Ozonation and advanced oxidation processes of polycyclic aromatic hydrocarbons in aqueous solutions—a kinetic study, *Environ. Technol.* 16 (1995) 729–740.
- [10] A. Kornmüller, M. Cuno, U. Wiesmann, Selective ozonation of polycyclic aromatic hydrocarbons in oil/water-emulsions, *Water Sci. Technol.* 35 (4) (1997) 57–64.
- [11] A.K. Marley, A.R. Larson, L.P. Stapleton, J.W. Garrison, M.C. Klodnyoky, Ozonolysis of naphthalene derivatives in water and in kerosene films, *Ozone Sci. Eng.* 9 (1987) 23–36.
- [12] Y. Zeng, P.K.A. Hong, Slurry phase ozonation for remediation of sediments contaminated by polycyclic aromatic hydrocarbons, *J. Air Waste Manage. Assoc.* 52 (2002) 58–68.
- [13] A. Goi, M. Trapido, Degradation of polycyclic aromatic hydrocarbons in soil: the Fenton reagent versus ozonation, *Environ. Technol.* 25 (2004) 155–164.
- [14] K. Nam, J.J. Kukor, Combined ozonation and biodegradation for remediation of mixtures of polycyclic aromatic hydrocarbons in soil, *Biodegradation* 11 (2000) 1–9.
- [15] P. Haapea, T. Tuhkanen, Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment, *J. Hazard. Mater.* 136 (2006) 244–250.
- [16] R. Goel, T. Tokutomi, H. Yasui, Anaerobic digestion of excess activated sludge with ozone pre-treatment, *Water Sci. Technol.* 47 (12) (2003) 207–214.
- [17] C. Bougrier, A. Battimelli, J.P. Delgenes, H. Carrère, Biological sludge pretreatment by ozone for solubilisation and enhancement of biogas production, *Ozone Sci. Eng.* 29 (2007) 201–206.
- [18] A. Bernal-Martinez, H. Carrère, D. Patureau, J.P. Delgenes, Combining ozonation and anaerobic digestion to remove PAH from urban sludge, *Process Biochem.* 40 (2005) 3244–3250.
- [19] A. Bernal-Martinez, H. Carrère, D. Patureau, J.P. Delgenes, Ozone pre-treatment as improver of PAH removal during anaerobic digestion of urban sludge, *Chemosphere* 68 (2007) 1013–1019.
- [20] E. Trably, N. Delgenes, D. Patureau, J.P. Delgenes, Statistical tools for the optimization of a highly reproducible method for the analysis of polycyclic aromatic hydrocarbons in sludge samples, *Int. J. Environ. Anal. Chem.* 84 (2004) 995–1008.
- [21] APHA, American Public Health Association, in: L.S. Clesceri, A.E. Greenberg, R.R. Trussel (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Water Works Association, Water Pollution Control Federation, 1992.
- [22] J. Muller, G. Lehne, J. Schwedes, S. Battenberg, R. Naveke, J. Kopp, N. Dichtl, A. Scheminski, R. Krull, D.C. Hempel, Disintegration of sewage sludge and influence on anaerobic digestion, *Water Sci. Technol.* 18 (8) (1998) 425–433.
- [23] K. Nam, W. Rodriguez, J.J. Kukor, Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction, *Chemosphere* 45 (2001) 11–20.
- [24] H. Aichberger, A.P. Loibner, R. Celis, C. Bertrand, F. Ottner, H. Rost, Assessment of factors governing biodegradability of PAHs in three soils aged under field conditions, *Soil Sediment Contam.* 15 (2006) 73–85.
- [25] X.J. Zheng, J.F. Blais, G. Mercier, M. Bergeron, P. Drogui, PAH removal from spiked municipal wastewater sewage sludge using biological, chemical and electrochemical treatments, *Chemosphere* 68 (2007) 1143–1152.
- [26] W.L. Straube, J. Jones-Meehan, P.H. Pritchard, W.R. Jones, Bench-scale optimization of bioaugmentation strategies for treatment of soils contaminated with high molecular weight polyaromatic hydrocarbons, *Resour. Conserv. Recycl.* 27 (1999) 27–37.
- [27] H. Carrère, A. Bernal-Martinez, D. Patureau, J.P. Delgenes, Parameters explaining PAHs removal from sewage sludge by ozonation, *AIChE J.* 52 (2006) 3612–3620.
- [28] R. Kleerebezem, L.W. Hulshoff Pol, G. Lettinga, Anaerobic degradation of phthalate isomers by methanogenic consortia, *Appl. Environ. Microbiol.* 65 (1999) 1152–1160.