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Comprehensive Study of Organic and Inorganic Compounds Released by Animal and Pineapple Fruits Wastes

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Abstract In developping countries, fruits and farm wastes are usually abandonned in the nature or used for soil amendements ordisposed in landfill. The pollution occured by such wastes is generaly unquantified and uncknown. So, the aim of this study was to provide a detailed overview of the characteristic and evolution of organic matter leached from farm wastes and pineapple fruits wastes. Therefore a leaching test with solution renewal procedure on a total period of 192h divided into three steps 0-24h, 24-72h and 72 -192h was developped. The results showed that the organic carbon of the solid wastes released in the liquid phase varied from 1.8 to 3.4 % for animal wastes and 70 to 99 % for fruits wastes while the TKN of the solid waste released in the liquid phase varied from 57 to 79.5 % and 11.6 to 17.6 % for animal and fruits wastes respectively. Animal wastes released a DOC between 5 to 15 $g_C.kg^{-1}_{DM}$ while that of pineapple fruits wastes was at least 20 times higher during the 192h of leaching test ; whatever the wastes, the DOC released in the first 24h was 77 ± 3 % and decreased over the time. Animal wastes released a TN between 5 to 20 $g_N.kg^{-1}_{DM}$ while that of pineapple fruits wastes was at least 7 times lower on a total period of 192 h ; the TN released during the first 24 h was 91 ± 2 and 63 ± 6 % for animal wastes and fruits wastes respectively. The mobilization of TP by animal wastes was constant (33 ± 4 %) during the three step of leaching test with solution renewal while that of fruits wastes fluctuate. Animal wastes were characterized by organic carbon fractions AH*+HPO* ≥ HPI* while on pineapple fruits wastes AH*+HPO*+TPH* < HPI* showing that animal wastes were composed of more aromatic compounds than pineapple fruits wastes. The SUVA index were correlated with the hydrophobic fractionation. The biogas produced by animal wastes and pineapple wastes was less than 0.5 $m^3_{biogas}.kg^{-1}_{VS}$ and about 0.78 ± 0.02 $m^3_{biogas}.kg^{-1}_{VS}$.The study helped to quantify the pollution generated by fruits and animal wastes and the evolution of organic carbon over time.

Keywords Organic, Inorganic, Animal, Pineapple, Fruits Wastes

1. Introduction

Animal and fruits wastes production has a great potential for environmental pollution. As a result of this activity, a huge volume of gases, leachedorganic material and bacteria are generated, posing a risk factor for air, soil, and water pollution [1]. Animal wastes are usually applied as organic manure by population and remain a relative source of re-usesof nutrients in agriculture while most of fruits wastes and pineapple wastes particulary which represents 20 % of fruits production because of their acidity are disposed in landfill [2]. For instance, in Republic of Togo, wastes management are guided by many legislations, standards and programs. But the application of such measures are very low and the majority of the wastes ends up as municipal solid waste and disposed in landfill where pollution can leach. This way of wastes disposal generates through the world hundred thousand cubic meters of effluents highly toxic and billions liters of toxic gases every year [3,4]. So, solid wastes behavior in contact with waterin aerobic or anaerobic conditions is one of the critical problemthat need to be well understood.Therefore, there is a need to go through waste characterizationin order to evaluate the amount of organic and inorganic compound that could be released in the environment during rainfall or biodegradation and the fraction implied in the production of gas such ascarbon dioxide (CO_2), nitrogen (N_2), methane (CH_4).In this perspective, leaching test with solution renewal and biochemical potential tests could be applied as useful tools to highlithed the released of pollutants, the evolution of the organic matter fraction and the production of gas.Many standards of countries requires a total period of 24 h of leaching for municipal solid waste. According to several authors, a period of 24 h could not extract a sufficient and representative information [5,6]. So, [7] proposed a leaching test varying from 24 to 336hwhich allow the establishment of a chemical equilibrium. Same information could probably be obtained by reducing the time and varying it from 0 to 192 h. Therefore, the aim of this study isto provide a detailed overview of the characteristic and evolution of organic matter leached from farm wastes and pineapple fruits wastes.

2. Materials and Methods

2.1. Wastes collection and solid characterization

Two different type of wastes (animal and fruits wastes) were considered in this study. The animal wastes were composed of i) cattle maure (A_1), ii) goat and cheap slaughterhouses wastes stored (A_2) and iii) goat and cheap slaughterhouses wastes not stored (A_3);the fruits wastes were divided into i) pineapple peel (F_1) and ii) pineapple core wastes (F_2). Slaughterhouses wastes were collected in a slaughterhouse; cattle maure were sampled in a cattle market and pineapple wastes in a fruit company. All the wastes were sampled by quatering method in Republic of Togo. The solid characterization was performed for organic carbon (C_{org}) and total kjedhal nitogen (TKN) according to international standards [8,9].

2.2. Leaching test with solution renewal procedure and solution analysis

The leaching test with solution renewal (LTR) was developped to determine the maximum mobilisation of nutrients and to evaluate the type of organic carbon fractions released over time. The LTR consisted in a mixing of distilled water with substrate in a ratio of 10 on a total period of 192h. The renewal of the solution was divided into three tranches 0-24 h, 24-72 h and 72-192 h. The solution extracted was at every step analyzed. The experimental protocol is shown Figure 1.

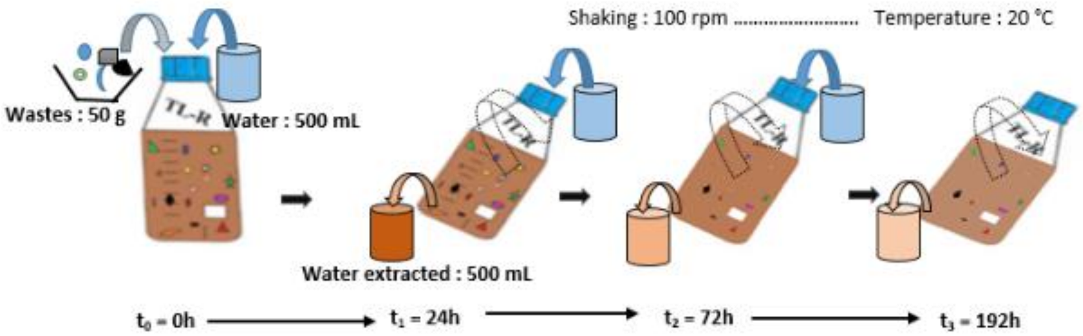

Figure 1: Experimental protocol of leaching test with solution renewal

pH was measured using Multi 9430 Inolab-IDS-WTW calibrated every day with pH 4, 7and 10 buffer solutions according to [10]. The VFA and alkalinitywere analyzed using titimetric method(H_2SO_4 and NaOH 1N and 0.1N) [11].Total nitogen, ammonium and total phosphorous were performed by Dr Lange LCK method using DR-2800 spectrophotometer. Dissolved organic carbon content on the liquid phase were determined using a SHIMADZU carbon analyzer. The principle is based on the acidifiction of the liquid sample with HCl 1M; the liquid is then sparged with high purity air to removed inorganic carbon and volatile organic compounds. Non-volatile organic carbon was combusted in an furnace at 720 °C producing CO_2 which was then was quantified by infrared spectroscopy. The SUVA index is define as the ratio of the ultraviolet absorbance measured at 254 nm and the DOC. This index help to estimate the aromatic character of the organic molecules. The higher the

SUVA index the higher the aromatic character of the molecules. The absorbance 254 nm was measured with a SHIMADZU spectrophotometer (model 1700 PharmasPec) and a 1 cm long quartz cell.

2.3. Organic carbon fractionation according to its hydrophobic character

Organic carbon was quantified on the liquid phase after the leaching test with solution renewal procedure and fractionated according to its hydrophobic character to highlighted the different fractions of carbon in each wastes and its evolution during the solution renewal. The hydrophobic fractionation technic (Figure 2) separates organic carbon into four fractions of decreasing aromaticity: humic like acids (AH*), hydrophobic like compounds (HPO*), transphilic like compounds (TPH*) and hydrophilic like compounds (HPI*) [12,13,14].This fractionation belong from the method used for natural water and was transformed to applied on leachate [12,13]. Two kind of non-ionic resins ared used. The DAX-8, which is slightly polar with an acrylic nature, and XAD-4, a non-polar and styrenedivinylbenzene type. The fractionnation start with the filtration of the sample through a 0.45 µmcellulose nitrate filter to eliminate humins compounds which are insoluble at any pH. The solution obtained is then acidified at pH 2 with 37% HCl and filtrated on 0.45 µm membrane in order to provoque the precipitation and the removal of humic acids respectively.The liquid phase is then percolated on the resins DAX-8 to adsorb HPO* fractions and XAD-4 to retain TPH*. The HPI* fractions remain in the solution. The content of each fraction is determined after the measurements of DOC.

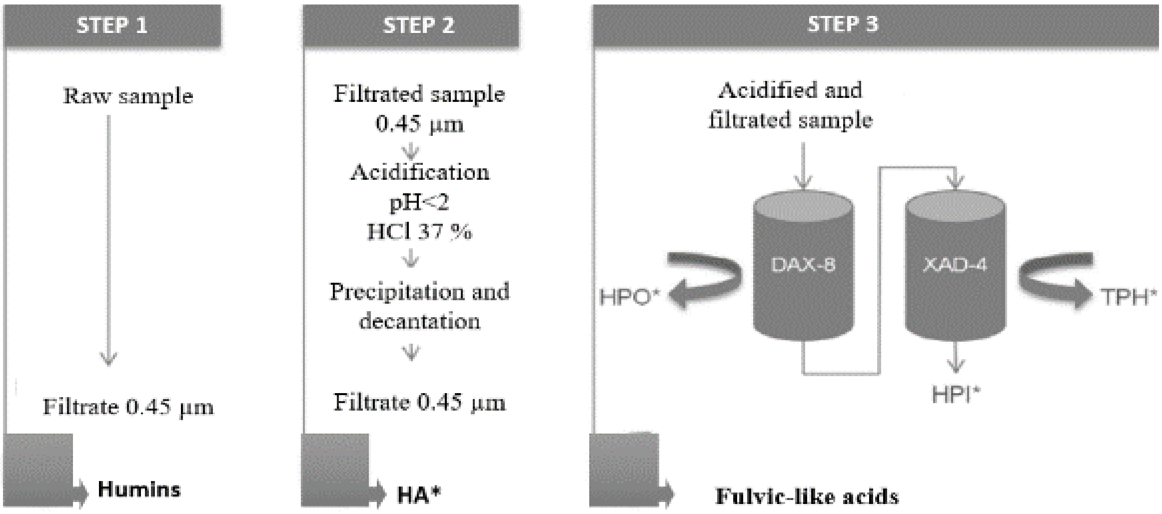

Figure 2: Protocol of fractionation of the dissolved organic carbon according to it hydrophobic character

2.4. Biochemical Methane potential

The BMP test were developped according to [15,16,17].Dry matter (DM) and volatile solids (VS) were determined for all wastes at 105 and 550 °C rspectively and helped to fixed the ratio inoculum to substrate to 2 [16]. The working volume of the used bottles was 120 mL corresponding to 80 % of the total volume. The inoculum used was an anaerobic digested sludge sampled in the municipal wastewater treatment plant. This inoculum was fasten for 8 days in order to reduce its organic load. The volumic production of the inoculum was 0.158 $m^3_{biogas}.kg^{-1}VS_{sludge}$ with 39 % of methane. The inoculum of the present study was thus rich in methane and the absence of a stationary phase was characteristic of an appropriate inoculum for BMP tests [18]. Although the inoculum used had a high buffer capacity, $NaHCO_3$ (0.3 $g.g^{-1}$ of substrate) was added to avoid any pH fluctuation. A mineral medium following ISO standards [17] was added to increase the content in nutrients. N_2 was used to flush the headspace of the bottles which were then incubated at 35 ± 2 °C and shaked manually once a day during 55 days. The biogas production was quantified by the volumetric method using a solution of distilled water acidified at pH 2. The biogas composition was determined with Micro GC Agilent gas chromatography coupled with a thermal conductivity detector. A positive control using fibrous cellulose was realised to ensure that bacteria in the inoculum were able to digest substrate. Its volumic production was 0.75 $m^3_{biogas}.kg^{-1}VS_{cellulose}$ and 0.32 $m^3_{methane}.kg^{-1}VS_{cellulose}$ as [18] (from 0.54 to 0.71 $m^3_{biogas}.kg^{-1}VS_{cellulose}$ and from 0.34 to 0.45 $m^3_{methane}.kg^{-1}VS_{cellulose}$). A negative control using only inoculum was performed to follow the production of pure inoculum.

3. Results and Discussion

3.1. pH and alkalinity

Fig. 3 presents pH and alkalinity evolution during the leaching test with solution renewal. Fig. 3a shows that pH of animal wastes was more higher than pH of fruits wastes. The slaughterhouses wastes not stored and cattle manure wastes (A_1, A_2) pH is sligthly basic, the stored one (A_3) pH is neutral and the pineapple fruits wastes (F_1, F_2) presenteda very acidic pH less than 5.

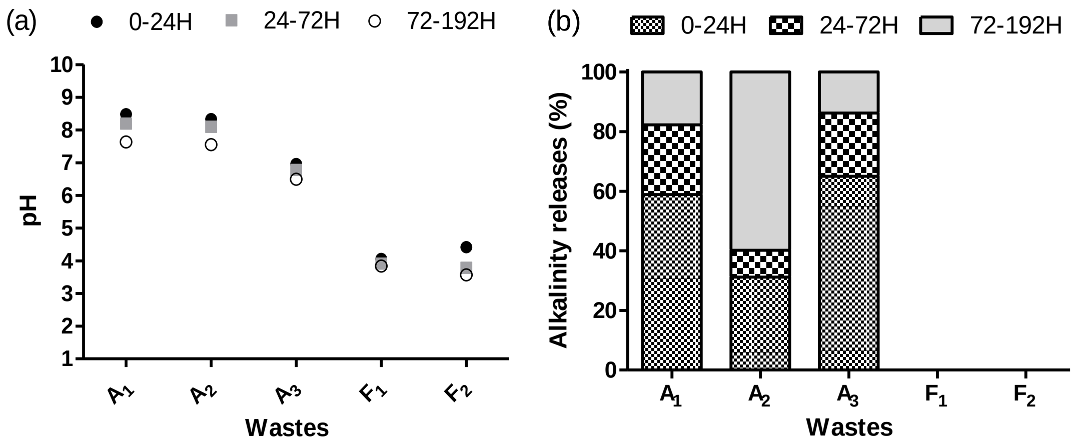

Figure 3: Evolution of pH (a) and alkalinity (b) during leaching test with solution renewal

The pH of A_3 and F_1 did not varied significantly during the three steps of leaching test with solution renewal. In opposite, the pH of A_1, A_2 and F_2 decreased by 0.2 and 0.8 unit pH between 0-24h to 24-72h and 24-72h to 72-192h respectively. The decrease of pH in the case of animal wastes is logic because it moves towards the pH of distilled water which pH was around 5.8±0.2. In contrary, the decrease of pH in the case of pineapple fruits wastes showed that it had a high reserve of acidity. The alkalinity of animal wastes was 0.28 ± 0.02 $g_{CaCO3}.kg^{-1}_{DM}$. It was highly released during the first step of leaching test except in the case of A_3. The alkalinity of pineapple wastes have a value of nil and is well correlated with the acidic pH.

3.2. Total nitrogen released and ammonia generation

The mineral compounds especially nitrates and nitrites were not measured because of their very low content in the wastes and the short time of the leaching test which don't help their generation [6]. The animal wastes released a total nitrogen(TN) of 9.8 ± 0.2; 15.5 ± 0.2 and 7.2 ± 0.2 $gN.kg^{-1}_{DM}$ for A_1, A_2 and A_3 respectively during the192 h of leaching test. The TN released by fruits wastes was at least 7 times lower and estimated to 1.09 ± 0.01 and 0.46 ± 0.01 $gN.kg^{-1}_{DM}$for F_1 and F_2 respectively. The TN released during the first 24 h of leaching test with solution renewal was 91 ± 2 and 63 ± 6 % for animal wastes and fruits wastes respectively (Figure 4a).

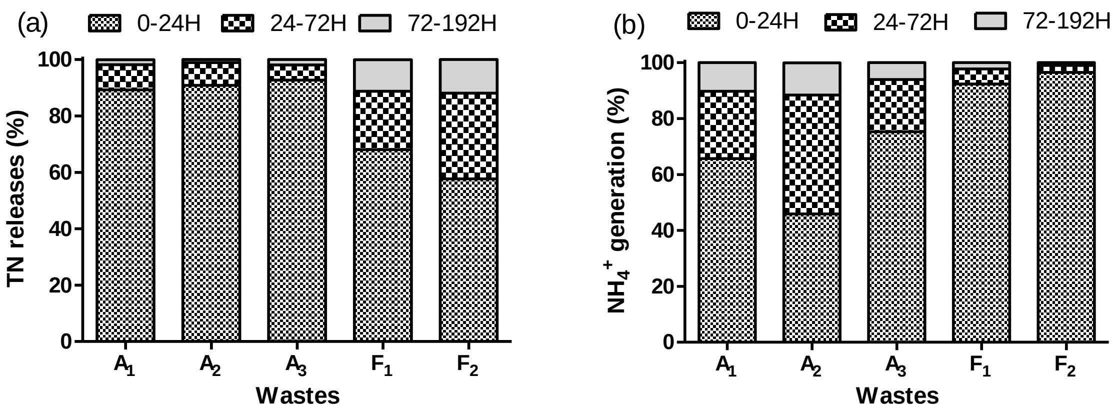

Figure 4: Evolution of TN (a) and NH_4^+(b) during leaching test with solution renewal

Generally, the ammonium (NH_4^+) is not released by the wastes, it belong from the biotransformation of total nitrogen releases in the liquid phase by ammonification process. The ammonium generated by animal wastes and fruits wastes is 1 ± 0.2 and 0.12 ± 0.03$g_N.kg^{-1}_{DM}$ respectively. The ammonium generated during the first 24h is 94 ± 4 % for fruits wastes and varied from 40 to 70 % for animal wastes (Figure 4b).

The ratio NH_4^+/TN increased from 6 to 70 % from 24 to 192 h in the case of animal wastes and decreased from 40 to 0.5 % on fruits wastes. In 24h, the ammonium generated represented less than 10 % of TN on animal wastes and more than 15 % on fruits wastes.

3.3. Phosphorus behavior under leaching test

The total phosphorus (TP) released during 192h was higher and lower than 1 $gPO_4^{3-}.kg^{-1}_{DM}$ for animal wastes and fruits wastes respectively. It was1.13 ± 0.02 ; 2.47 ± 0.00 and 2.31 ± 0.02 $gPO_4^{3-}.kg^{-1}_{DM}$ for A_1, A_2 and A_3 respectively. For fruits wastes, TP was at least 2 times higher and estimated to 0.071±0.002 and 0.002 $gPO_4^{3-}.kg^{-1}_{DM}$for F_1 and F_2 respectively. The mobilization of TP by animal wastes was constant (33 ± 4 %) during the three step of leaching test with solution renewal (Figure 5). For fruits wastes, the mobilization of TP was higher during the third step (72 – 192h) of leaching test in the case of F_1 (pineapple peel) and higher during the first step (0-24h) in the case of F_2 (pineapple core).

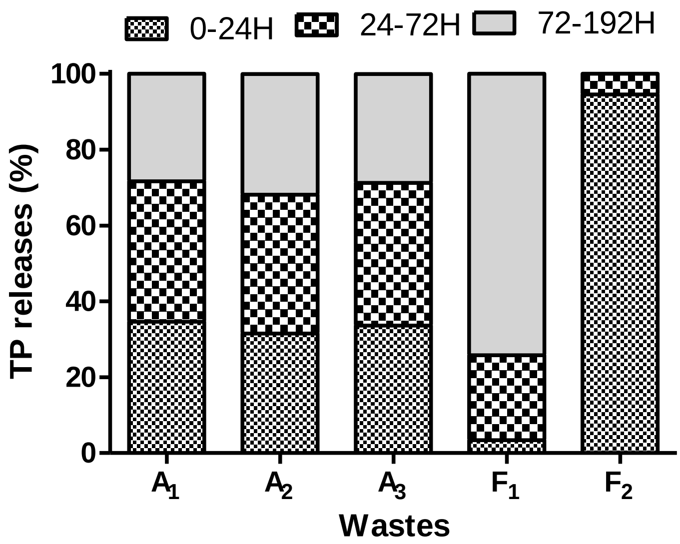

Figure 5: Evolution of phosphorus during leaching test with solution renewal

The low releases of TP by pineapple fruits wastes could be due to the low content of TP in the solid phase. In the case of animal wastes, studies underlined that, the fresh wastes released more phosphorus than the old wastes [7,19,20]. This conclusion is in line with our results showing that, the cattle manure wastes (A_1) which were more digested released a content of phosphorus two times lower than slaughterhouses wastes (A_2, A_3) which belonged from animals stomach. Some studies revealed that phosphorous exist in the form of solid precipitate in animal wastes. This state of phosphorus is helped by the high presence of calcium and magnesium. Such ions could be fixed the released phosphorus in the liquid phase to make struvite (NH_4MgPO_4, $6H_2O$). This could be the reason why the mobilization of phosphorus was constant during the three step of the leaching test with solution renewal in the case of animal wastes [21]. The decrease of pH could have also contributed to the constant release of phosphorous during the solution renewal.

3.4. Carbon mobilization (DOC) and volatile fatty acids (VFA) generation

The animal wastes released a DOC of 9.6 ± 0.1 ; 11.4 ± 0.3 and 6.01 ± 0.04 $g_C.kg^{-1}_{DM}$ for A_1, A_2 and A_3 respectively during the192h of leaching test. The DOC released by fruits wastes was 20 times higher and estimated to 235 ± 2 and 367 ± 4 $g_C.kg^{-1}_{DM}$ for F_1 and F_2 respectively. Whatever the wastes, the dissolved organic carbon released in the first 24h on a total of 192h was 77 ± 3 % during the leaching test with solution renewal while the second step (24 -72h) released 15.6 ± 0.4 % (Figure 6a).

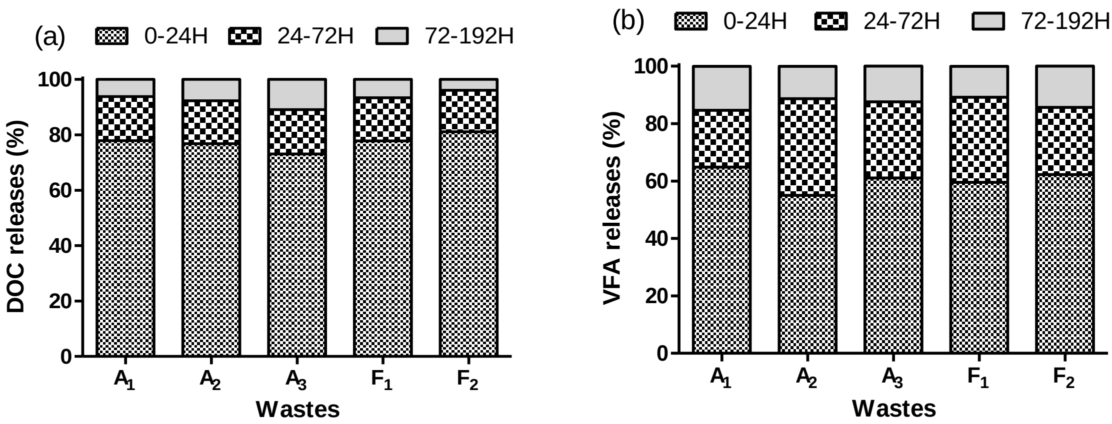

Figure 6: Evolution of DOC (a) and VFA (b) during leaching test with solution renewal

In the case of VFA, the animal wastes released 4.55 ± 0.02 ;9.9 ± 0.1 and 5.7 ± 0.0 $g_{CH3COOH}.kg^{-1}{}_{DM}$ for A_1, A_2 and A_3 respectively during the 192 h of leaching test. The VFA released by fruits wastes was at least 2 times higher and estimated to 53 ± 1 and 17.4 ± 0.3$g_{CH3COOH}.kg^{-1}{}_{DM}$ for F_1 and F_2 respectively. Whatever the wastes, the VFA released was 61 ± 3 ; 27 ± 5 and 13 ± 2 % during0-24h, 24-72h and 72-192h respectively (Figure 6b).So, at least 50 % of DOC and VFA are released during the first 24 h of contact between distilled water and the solid wastes. Fruits wastes released more DOC and VFA than animal wastes. This could be explained by the fact that, animal wastes were already digested and seemed to be more stabilized in opposite to fruits wastes which are more fresh. The total content of VFA released by animal wastes are far from the inhibiting concentration in biogas production process in opposite to pineapple fruits wastes [22]. So, animal wastes are adequate for biogas production while pineapple wastes could required a co-digestion process or a pretreatment.

The ratio VFA/DOC is essential as a high value state a high transformation of DOC into VFA, precursors of biogas production. Table 1 shows that VFA represented less than 15 % of DOC whatever the wastes. On animal wastes, VFA accounted for 6 to 12 and 0.6 to 2.7 % on pineapple fruits wastes.The ratio VFA/DOC decreased with the solution renewal whatever the wastes. The decrease informed about the the fall down of VFA generation during the solution renewal.

Table 1: Ratios VFA/DOC and HPI*/VFA of different types of wastes during leaching test with solution renewal

	VFA/DOC (%)					**HPI*/VFA (%)**				
	A_1	**A_2**	**A_3**	**F_1**	**F_2**	**A_1**	**A_2**	**A_3**	**F_1**	**F_2**
0-24h	6,1	9,5	11,6	2,7	0,6	11,4	6,1	6,8	51,5	ND
24-72h	1,9	5,8	5,1	1,3	0,2	4,6	2,9	1,5	8,4	ND
72-192h	1,5	2	2,4	0,5	0,14	2,8	1,4	2	20,5	ND

3.5. Hydrophobic fractionation of organic carbon and its evolution during leaching test

The fractionation of organic carbon was made on the liquid phase collected during the three steps of leaching test with solution renewal. It help to highlightened the type of organic carbon released over time. Whatever the substrate, the released of both AH*+HPO* fractions did not exceeded 70 % of the total mass of carbon released (Figure 7). The HPI* fraction varied between 70 and 90 % on pineapple fruits wastes during all the leaching test steps except the second step 24-72h where AH* fraction was higher and was the consequence of a precipitation phenomenon because of the low pH of 3 to 4 (Figure 7d,e). After 24h, AH* and HPO* fractions seemed to be more extracted on animal wastes (A_1, A_2), while HPI* fraction remained highly released on pineapple fruits wastes. On the animal waste (A_3), AH* fraction was highly released during the first step and AH*+HPO* decreased sharply over the time. This could be due to the fact that, this waste during it storage and because of the raining, lost easily the HPI* fraction and the AH* fraction was ready to be released when the sampling was made. HPO* and TPH* fractions known as precursors of methane production were higher than 40 % on animal wastes during the three steps of leaching test and lower than 25 % on pineapple wastes.

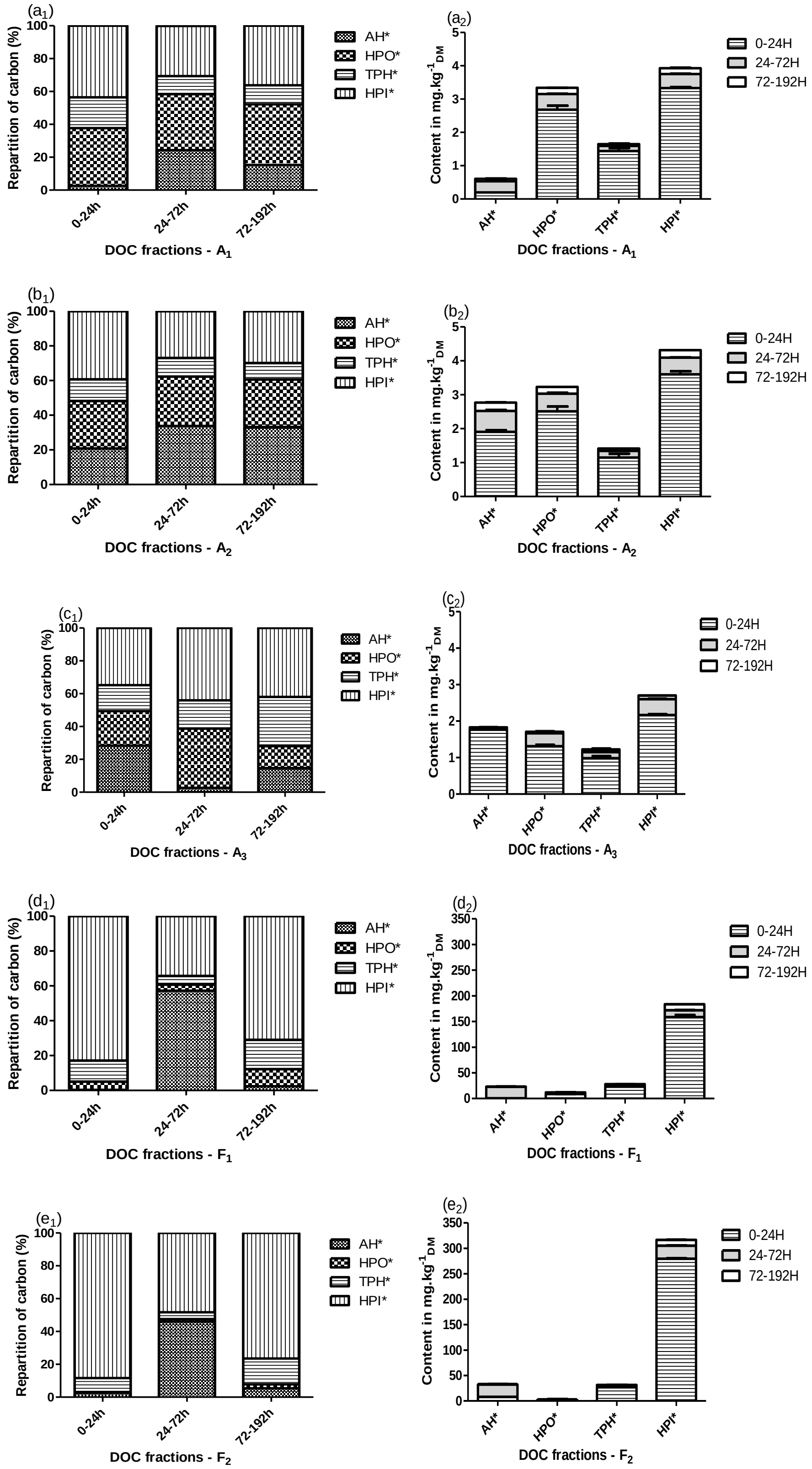

Figure 7: Qualitative (a_1, b_1, c_1, d_1, c_1) and quantitative (a_2, b_2, c_2, d_2, c_2) evaluation of organic carbon fractions during leaching test with solution renewal

So, on the animal wastes, AH*+HPO* ≥ HPI* while on pineapple fruits wastes AH*+HPO*+TPH* < HPI*. The animal wastes are characterized by more aromatic compounds than pineapple fruits wastes.

As, VFA are assimilated to small compounds as HPI* fractions, a relation was underlined between the two type of compounds toward the ratio HPI*/VFA (**Table 1**). The fraction HPI* represented less than 15 % of VFA released on animal wastes while it represented more than 50 % in the case of pineapple fruits wastes during the first 24h. The ratio decreased with the solution renewal.

3.6. Evolution of SUVA index

The SUVA index is generally correlated with the organic carbon fractionation according to its hydrophobic character [6,19,23]. The SUVA of A_1 did not vary significantly (35 ± 2 $L.g^{-1}.cm^{-1}$) during the three steps of leaching test (Figure 8a). In contrary, the SUVA of A_2 increased from 40 to 60 $L.g^{-1}.cm^{-1}$ while that of A_3 fluctuated between 10 and 20 $L.g^{-1}.cm^{-1}$. For pineapple fruits wastes (Figure 8b), the SUVA of F_1 (pineapple peel) was 10.3 and decreased to 1.5 ± 0.2 $L.g^{-1}.cm^{-1}$ while for pineapple core (F_2), it was 0.23 ± 0.08 $L.g^{-1}.cm^{-1}$ during the three steps of leaching test with solution renewal. The SUVA of animal wastes is higher than the SUVA of pineapple fruits wastes. The low SUVA of pineapple fruits wastes is therefore correlated with its high content in HPI* fractions. So, animal wastes are characterized by more aromatic compounds than pineapple fruits wastes.

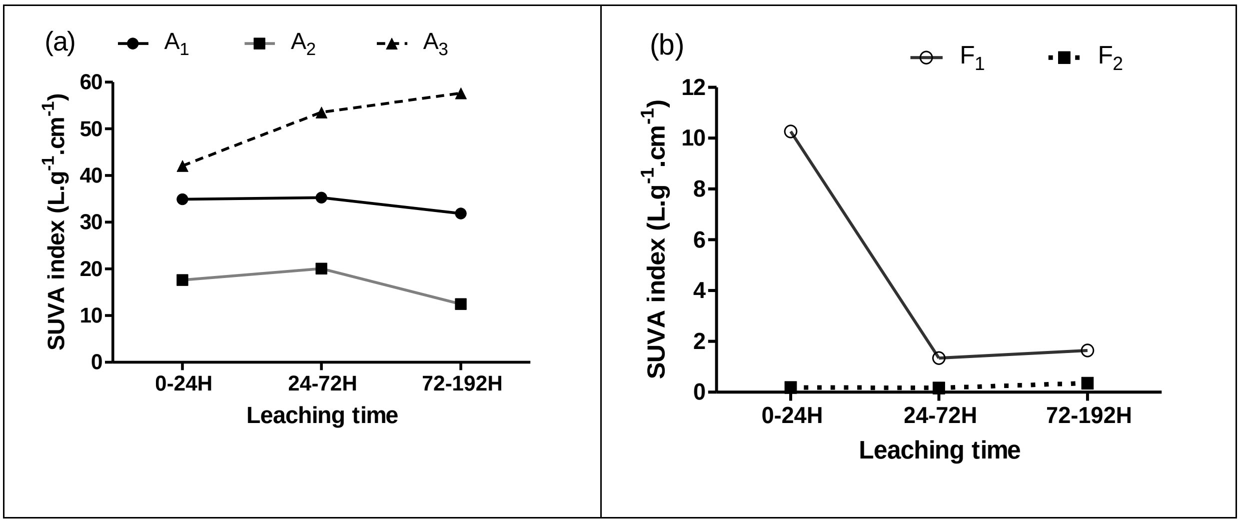

Figure 8: Evolution of SUVA index with animal wastes (a) and pineapple fruits wastes (b) during leaching test with solution renewal

3.7. Mass balance of carbon and nitrogen compounds

Carbon and nitrogen balance masses were made after 192 h in order to quantify the hydrosoluble fraction in the liquid phase from the non-hydrosoluble fraction remained in the solid phase. The organic carbon in the solid phase was similar (345 ± 14 $g_C.kg^{-1}{}_{DM}$) in opposite to the content of nitrogen which was more higher in animal wastes (A_1, A_2, A_3) than fruits wastes (F_1, F_2) (Figure 9).

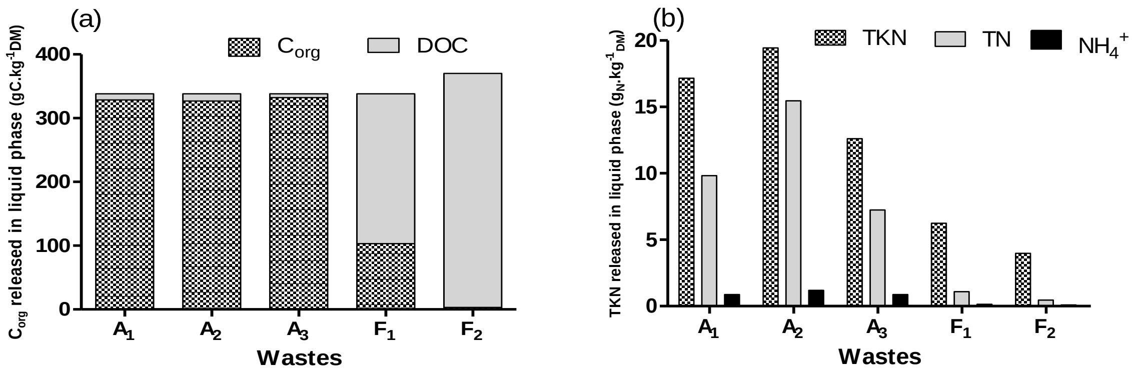

Figure 9: Mass balance of carbon (a) and nitrogen (b)

The organic carbon (C_{org}) released in the liquid phase (DOC: dissolved organic carbon) varied from 1.8 to 3.4 % for animal wastes and 70 to 99% for fruits wastes. The high solubilization noticed in the case of fruits wastes could be due to the easy releases of sugars contained in fruits wastes.

In the case of nitrogen balance, the ammonium generated in the liquid phase represented 6.1 ± 0.9 % of TKN of the solid in the case of animal wastes and 2.3 ± 0.2 % for fruits wastes. The total nitrogen (TN) released varied from 57 to 79.5 % and 11.6 to 17.6 % for animal and fruits wastes respectively. The percentages of TN mobilized in the liquid phase of fruits wastes are similar to that of household wastes situated between 11 and 13 % [6]. The low rate of nitrogen mobilization and ammonium generation in the case of fruits wastes could be due to itsthe low content in nitrogen and the low load of bacteria because of the acidic pH. In opposite, the high mobilization in the case of animal wastes were certainly helped by the neutral pH which helps the grow-up of diversity and high load of bacteria. The low mobilization of organic carbon and TKN in the liquid phase in the case of A_3 compared to A_1 and A_2 could be explained by it storage.

3.8. Pineapple and farm wastes biogas production

The average volumic production of biogas after 60 days of anaerobic digestion was less and more than 0.5 $m^3_{biogas}.kg^{-1}_{VS}$ for animal and fruits wastes respectively (Figure 10).

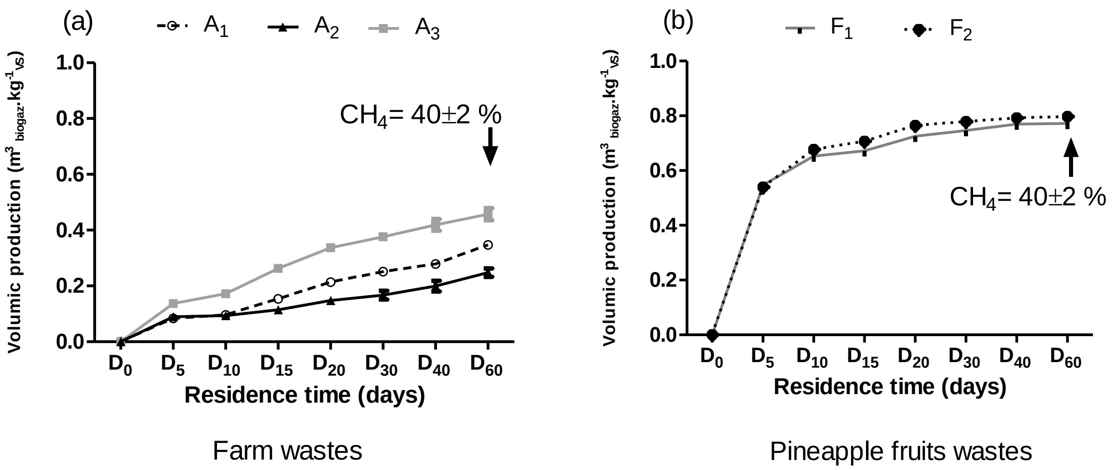

Figure 10: Quantitative and qualitative of animal and pineapple fruits wastes biogas

For animal wastes, the volumic production was significantly different from one another. The high and the low production were registered for the stored slaughterhouses wastes A_3 (0.46 ± 0.04 $m^3_{biogas}.kg^{-1}_{VS}$ or 0.18 $m^3_{methane}.kg^{-1}_{VS}$) and unstored one A_2 (0.25 ± 0.02 $m^3_{biogas}.kg^{-1}_{VS}$ or 0.1 $m^3_{methane}.kg^{-1}_{VS}$). So, wastes storage improved biogas production. The production was in line with that reported by [23] which were 0.22 $m^3_{methane}.kg^{-1}_{VS}$ or 0.15 $m^3_{methane}.kg^{-1}_{VS}$for cattle manure and slaughterhouses wastes respectively. The production of biogas by pineapple fruits wastes were at least two times higher and estimated to 0,78 ± 0,02 $m^3_{biogas}.kg^{-1}_{VS}$. The content in methane during BMP test was 40 ± 2 % similar to that of [24] situated between 31 and 50 %.

4. Conclusion

The study shows that, the leaching test with solution renewal could be used to evaluate quickly the trend of compounds mobilization. The qualitative and quantitative releasing of molecules with animal wastes is far different to fruits wastes. The nitrogen released by wastes is higher than that of carbon. The organic carbon fractions released during the first step of leaching test differ over the time. The organic carbon fractions released by animal wastes are more aromatic than that released by fruits wastes.

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