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ARTICLE

Rapid characterisation of agro-industrial effluents for environmental fate by UV–visible and infrared spectroscopy from fractions obtained by centrifugation

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ABSTRACT

Agro-industrial systems (e.g. dairy farms, feed lot, pig breeding and food processing plants) provide large quantity of organic wastes that could be recycled within the productive systems. However, the basic chemical characterisation is not enough to predict the effect that they may generate on the environment. In this study, a centrifugation process was applied at various speeds between 3000 and 15,000 rpm and carried out separately on two different livestock effluents (dairy farm and pig anaerobic digestate), in order to obtain supernatants and precipitates, which were studied separately. The more water soluble fractions, with lighter components and/or simpler structures, remained as liquid supernatants, while the more complex fractions, with higher molecular weight and/or water insoluble fractions, constituted the solid precipitates. An increase in the centrifugation rate did not produce the differential precipitation of dissimilar functional groups. Hence, 5000 rpm was the most adequate velocity since it generated clear supernatants without denaturation of the organic matter. A basic cost-effective chemical analysis, complemented with ultraviolet–visible and Fourier transform infrared spectroscopy, enables a set of properties to be established qualitatively and quickly for the multiple components of the organic matter for its later use as fertilisers or amendments. This rapid and economical technique allows for a characterisation prior to the reuse of the effluents, which is necessary to optimise their application and avoid environmental problems.

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1. Introduction

Agricultural production generates a marked impoverishment of the soil in fragile environments, which are characterised by semi-arid climates and unevolved soils with low organic matter and high susceptibility to degradation. In rainfed regions, it is essential to

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use sustainable management systems with very low intensification, while intensification in areas under irrigation makes it essential to incorporate organic matter to restore or improve the physical, chemical and biological properties of soils.

Argentina is the Latin American country with the highest arid, semi-arid and dry subhumid areas (75% of the national territory). These regions account for 50% of the value of agricultural production and 47% of livestock. Approximately, 30% of the national population lives in these areas. The most important activities are developed under irrigation zones (1.5 million ha), of which 40% present desertification problems due to water or wind erosion and salinisation [1]. Intensive agro-industrial systems (dairy farms, feed lot, pig breeding and food processing plants) coexist in these regions, providing large quantity of organic wastes that could be recycled within the productive system. Thus, before its application to the soil, its energy potential can be exploited through biomethanisation, which transforms organic matter into a mixture of methane and carbon dioxide as biogas, through a complex group of microorganisms under anaerobic conditions. This process leaves a waste material in the liquid phase, called digestate, composed of water, labile organic material (which is constituted of intermediates of the process), recalcitrant organic matter, available nutrients and microbial biomass. Biogas production is an excellent way to reduce organic waste and decrease greenhouse gas emissions [2], bad odour, pathogen content and weed seeds [3]; finally, it allows the nutrients to be recycled when applied to the soil [4], helping to maintain the carbon balance [5], promote microbial communities and regulate the nutrient cycle [3].

The recycling of nutrients depends on the biodegradability of the organic matter that constitutes them, being the carbohydrates and amino acids the compounds that degrade more rapidly (in time intervals that can vary from hours to days), whereas the macromolecules require longer decomposition periods [6]. However, no single variable can be used to estimate biodegradability, and it is necessary to complement with several determinations such as carbon and nitrogen contents, cellulose, hemicellulose and lignin, amino acids, proteins and phenolic acids. Therefore, in order to make extensive use of this type of materials as an immediate agro-ecological resource to improve soils, it is essential to develop techniques that combine speed and low costs [7]. Soil analysis methods with such characteristics incorporate ultraviolet–visible (UV–vis) and infrared (IR) spectroscopies, which make it easy to obtain information on the structural elucidation of many molecules, facilitating the interpretation of their properties [8].

In this regard, IR spectroscopy has served as a non-destructive qualitative tool to characterise the main types of chemical functional groups that comprise the organic matter of soils and effluents [9–11]. The presence of aromatic compounds and their hydroxylated, amino and/or nitrogen derivatives, mainly soluble in water at very low concentration, make UV–vis spectroscopy a complementary analytical technique very useful and necessary in this kind of research [12,13]. Although UV spectroscopy has a limited significance because it cannot be used to identify the functional groups present [], it provides important structural information. The obtained spectrum constitutes the average absorptions of the molecules that compose the sample [14] and can be used to estimate the aromaticity degree of the organic matter present.

In order to quickly and economically characterise agro-industrial effluents to improve their utilisation, the following hypotheses were considered: (1) centrifugation at different speeds allows for the differential precipitation of diverse functional groups, (2) the

centrifugation and separation of the sample (supernatant and precipitate) improve the effluent characterisation and (3) the complementation of the basic chemical determinations with spectroscopic methods (UV–vis and Fourier transform infrared spectroscopy [FTIR]) makes it possible to obtain a structural characterisation that replaces the expensive and complex determinations, when effluents may be used as an agro-ecological resource.

2. Experimental

2.1. *Effluents studied*

The used effluents were collected at different sites and are the end product of different agro-industrial processes. One effluent that comes from a dairy farm, denominated dairy effluent (DE) constituted of washing water from the holding yard and milking facilities, manure, urine and leftover milk. It was collected without any treatment, at the end of the milking from a dairy farm in Mayor Buratovich, which is located in the inferior Valley of the Colorado River, Buenos Aires province, Argentina. The other effluent is a digestate of pig slurry biomethanisation, denominated pig digestate (PD), consisting of manure, urine, food waste and washing water, which was collected at the exit of the bioreactor from a pig farm in Coronel Pringles, Buenos Aires province, Argentina.

Pig feeding is carried out by balanced feed with maize and sorghum, while cow feeding is by direct grazing alfalfa pastures. It is important to note that differences in the digestive systems (monogastric vs. ruminant), feed type and biomethanisation process generate marked differences in the structural characteristics of the effluents.

2.2. *Phase separation by centrifugation*

The effluents were centrifuged at 3000, 4000, 5000, 7500, 10,000 and 15,000 rpm in a Hanil Combi 514R centrifuge. The supernatants were stored refrigerated at 4°C during the determinations. The precipitates were oven dried at 40°C to circumvent modifications on their properties and then ground in a ceramic mortar and stored in a dry stove to avoid rehydration.

2.3. *Chemical analyses*

Total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (NH_4–N) and nitrate nitrogen (NO_3–N) were determined by semi-micro Kjeldahl on the samples of effluents (DE and PD) and supernatants without any processing. A 4-mL aliquot of each sample was then applied on the LECO inert material absorbent (combustion aid for liquids, 501–427), oven dried at 40°C, and total carbon (C) was determined by dry combustion (1500°C LECO C Analyser). The content of carbon (C), hydrogen (H) and nitrogen (N) was determined in the precipitates using a PerkinElmer CHNS/O 2400 Series II elemental analyser.

2.4. *UV–vis spectroscopy*

The effluents without centrifugation and the supernatants were subjected to a UV–vis spectroscopic scanning at 18 wavelengths between 180 and 665 nm (UV–vis

spectrophotometer PG instruments T60). The samples were diluted in distilled water with ratios from 1:10 to 1:200 according to the effluent or supernatant concentration to obtain a complete spectroscopic scan without signal saturation. Each record was performed in triplicate.

2.5. *Fourier transform infrared spectroscopy (FTIR)*

Spectra were obtained within the mean IR range (4000–400 cm^{-1}) with 64 scans, using a Nicolet iS50 FTIR Thermo Scientific spectrometer. Solid samples were prepared as 1% Merck Uvasol potassium bromide tablets (1.8 mg dry sample in 180 mg KBr). The liquid samples were also recorded as pellets, which were obtained by incorporating 0.30 mL into 180 mg KBr, in order to achieve a dry base concentration of 0.5–1.0%.

3. Results and discussion

3.1. *Chemical analyses*

The chemical characterisation of effluents (DE and PD) without centrifugation and supernatants (S) obtained at different centrifugation speeds is presented in Table 1. The chemical characterisation of the precipitates (P) obtained at different centrifugation rates is included in Table 2.

With respect to the effluent without centrifugation, the PD contains much more quantity of nitrogen (as NO_3–N, NH_4–N, TKN) and carbon than the DE, which is in accordance with the nature of the components of the pig slurry, richer in protein, carbohydrates and fatty acids.

The greater influence of the centrifugation speed increase is observed in the DE supernatant for which the content of NO_3–N diminishes considerably, whereas that of NH_4–N increases. This allows us to suppose that at a higher centrifugation rate, the supernatant is enriched in ammoniacal nitrogenous compounds, capable of being water solubilised, while the nitrates are transferred to the solid phase. In contrast, the increase in spin speed decreases the NH_4–N content but does not significantly modify the NO_3–N content in PD supernatant. It is possible to infer that for this effluent, the nitrogenous

Table 1. Chemical characterisation of effluents (DE and PD) and supernatants (S).

	ppm					
Reference	NH_4–N	NO_3–N	TKN	C	NH_4/TKN	C/N
DE	323.4	14.6	365.0	1070	0.89	2.93
SDE – 3000	30.0	57.3	194.0	430	0.15	2.22
SDE – 4000	33.1	18.6	247.9	320	0.13	1.29
SDE – 5000	46.0	2.2	269.5	340	0.17	1.26
SDE – 7500	44.2	2.3	226.4	360	0.20	1.59
SDE – 10,000	44.4	1.2	258.7	410	0.17	1.58
SDE – 15,000	110.1	5.4	291.1	380	0.38	1.31
PD	1980.4	40.8	2716.6	4450	0.73	1.64
SPD – 3000	936.3	23.1	2188.3	2630	0.43	1.20
SPD – 4000	959.4	24.6	2285.4	2240	0.42	0.98
SPD – 5000	943.3	23.9	3072.3	2130	0.31	0.69
SPD – 7500	870.9	20.0	2253.0	1980	0.39	0.88
SPD – 10,000	934.0	20.8	2285.4	1630	0.41	0.71
SPD – 15,000	814.7	23.1	2145.2	1590	0.38	0.74

Table 2. Chemical characterisation of the precipitates (P).

Reference	%C	%H	%N	C/N
PDE – 3000	38.9	6.3	3.8	10.2
PDE – 4000	37.2	5.9	3.7	10.1
PDE – 5000	39.6	6.1	3.9	10.2
PDE – 7500	41.7	6.4	4.2	9.9
PDE – 10,000	39.7	6.0	3.8	10.4
PDE – 15,000	39.9	6.1	3.9	10.2
PPD – 3000	21.7	3.3	2.5	8.7
PPD – 4000	23.4	3.4	2.7	8.7
PPD – 5000	23.8	3.3	2.8	8.5
PPD – 7500	26.1	3.6	3.0	8.7
PPD – 10,000	27.8	3.8	3.3	8.4
PPD – 15,000	29.1	4.1	3.6	8.1

components are less hydrophilic and/or have a more complex composition, and they do not remain solubilised in the aqueous liquid phase. In turn, the supernatant at 3000 rpm in the DE, and at 3000 and 4000 rpm in PD, shows higher values in the carbon content, which agrees with the observation of turbidity, probably due to solids in suspension.

With respect to the precipitates, those that came from DE showed fluctuation in C and N content, but with a tendency to a slight increase, whereas in those obtained from PD, they increased steadily. This result demonstrated a high stability in the elemental composition of the solid phase for both effluents, maintaining almost constant C/N proportions. Therefore, it is inferred that the precipitates are constituted by organic carbon nitrogenous structures, more complex than in the supernatant and resistant to the centrifugation processes.

Figure 1 shows the variations of C and TKN in the supernatants for each effluent (DE and PD), while Figure 2 illustrates the variations of C, H and N in the precipitates, depending on the different centrifugation rates. A very slight gradual increase of the contents (ppm) of TKN and C in the supernatants (Figure 1(a)) was observed for DE, while for the precipitates, no significant changes were registered in the percentages of C, H and N (slope less than 0.0006) (Figure 2(a)). On the contrary, for PD, there is a decrease in the contents of C and TKN (slope less than 0.07) in the supernatants

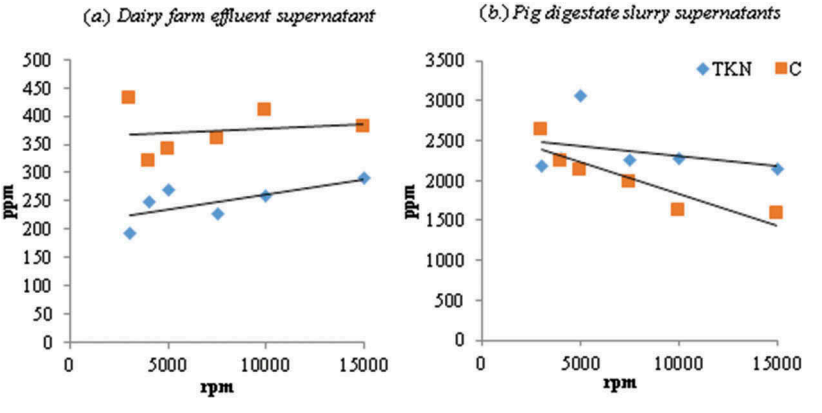

Figure 1. Supernatants: Carbon and nitrogen concentration (ppm) at different centrifugate rates (rpm). (a) Dairy from effluent supernatant. (b) Pig digestate slurry supernatants.

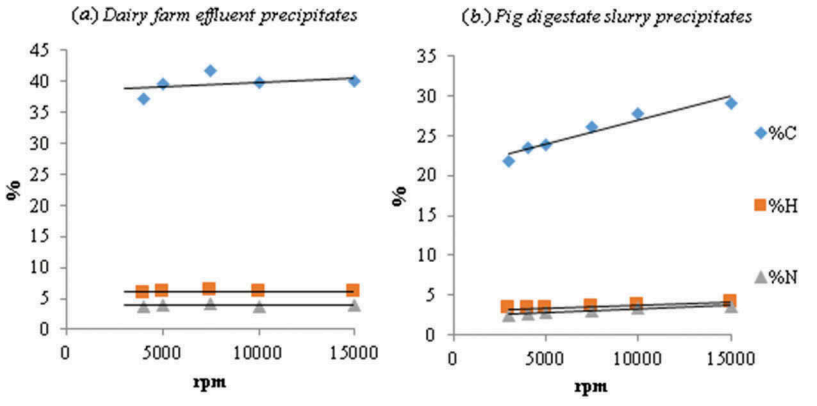

Figure 2. Precipitates: Carbon, hydrogen and nitrogen concentration (%) at different centrifugate rates (rpm).

(Figure 1(b)), and for the precipitates, only the percentage of C changes while H and N remain almost constant (Figure 2(b)).

3.2. *UV–vis spectroscopy*

The UV–vis spectra of the analysed effluents, regardless of their origin, were characterised by the absence of defined maxima so that the absorptions decrease continuously as the wavelength increases, coinciding with what was reported by Chen [15] and by Domeizel [16]. This behaviour can be explained by taking into account that between 220 and 400 nm frequency range, the most intense absorptions occur and the molecules undergo electronic transitions between different energy levels.

Table 3 shows, for both the uncentrifuged effluents and the corresponding supernatants obtained at different centrifugation speeds, the absorptions at six different wavelengths and the three ratios of absorbance commonly reported in the literature: E2/E3 (254/365) [17], E2/E4 (254/465) [18] and E4/E6 (465/665) [19,20]. For both effluents without centrifugation, a continuous decrease of the maximum absorption is observed while increasing the wavelength; this fact reflects a high concentration of functional groups able to absorb in the medium UV region.

PD differs from DE because its absorbance values are much higher, being the result of a more complex composition of the pig digestate slurry. This fact is in agreement with the information obtained by the chemical analysis.

The E2/E3 ratio is considered to be the measure of the aromaticity degree that characterises natural organic matter. If their values fall within a narrow range, between 3.0 and 4.5 (as in this case), it means that the samples have similar levels of conjugation, as well as similar molecular weights [21].

The E2/E4 ratio gives an idea of the interaction between the hydrocarbon structure of conjugated double bonds and the auxochromic groups. If it is within a broad range, between 2.1 and 14.5, it means that there is a high density of organic carbon with a high degree of conjugation, and a lower content of oxygen and nitrogen [15]. This result can be observed in the case of the two studied effluents and could be related to

Table 3. Absorbance values and absorbance ratios for effluents without centrifugation and supernatants at different rates (rpm).

References	250	254	280	365	465	665	E2/E3	E2/E4	E4/E6
DE – 0	6.78	6.62	6.10	4.07	3.30	2.20	1.66	2.01	1.50
SDE – 3000	3.91	3.70	3.10	1.25	0.72	0.32	3.13	5.14	2.25
SDE – 4000	3.79	3.60	2.99	1.16	0.66	0.29	3.27	5.45	2.28
SDE – 5000	3.55	3.49	2.80	1.05	0.58	0.25	3.38	6.02	2.32
SDE – 7500	2.33	2.19	1.84	0.62	0.26	0.09	3.76	8.42	2.89
SDE – 10,000	2.04	1.93	1.62	0.50	0.17	0.06	4.08	11.35	2.83
SDE – 15,000	1.84	1.73	1.45	0.41	0.12	0.04	4.49	14.42	3.00
PD – 0	66.45	63.50	55.8	30.45	19.95	11.25	2.18	3.18	1.77
SPD – 3000	42.77	40.43	32.46	12.31	6.25	2.29	3.47	6.47	2.73
SPD – 4000	33.75	31.8	25.05	8.85	4.40	1.50	3.81	7.23	2.93
SPD – 5000	31.07	29.33	22.8	7.6	3.67	1.13	4.09	7.99	3.25
SPD – 7500	27.07	25.52	19.85	6.05	2.65	0.83	4.47	9.63	3.19
SPD – 10,000	21.65	20.45	15.53	4.18	1.63	0.35	5.18	12.55	4.66
SPD – 15,000	18.50	17.53	13.18	3.33	1.23	0.28	5.56	14.25	4.39

supernatants containing less complex organic molecules, of low molecular weight or small structures, which render them soluble in water.

E4/E6 ratio is an indicator of the presence of highly conjugated structures which can still absorb in the visible region of the electromagnetic spectrum [22]. As shown in Table 3, the values increase slightly. This could be attributed to a decrease in the absorptions within the frequencies range of 500 and 800 nm. This decrease is due to the presence of molecules in which there is no highly extended conjugation or by the fact that more complex structures are able to absorb in the visible region, which have been destroyed by the centrifugation process.

Figure 3 shows the absorbance as a function of the wavelengths for the supernatants of DE and PD, at different centrifugation rates. There is a constant decrease in the intensity within the wavelengths between 180 and 665 nm. The absorbance decrease in the 180–320 nm range as the spin speed is increased. This indicates a reduction in aromatic, condensed aromatic, conjugated aromatic with electron attractor chromophores (C=C, C=O), substituted aromatic with auxochromes electron donors (HO–, –HN–) and highly conjugated olefinic species in the supernatants. This effect can be attributed to the fact that more voluminous or higher molecular weight compounds precipitate because the hydrogen bridges, which cause association and greater structural complexity by polymerisation, tend to break when centrifuging at higher speed. The more hydrophilic compounds, soluble in water due to their polarity or having a lower molecular weight, can remain water soluble.

3.3. *Fourier transform infrared spectroscopy (FTIR)*

The FTIR spectra of both effluents are illustrated in Figures 4(a) and 5(a). The main features of these spectra and their corresponding assignments are as follows:

(I) a band of strong intensity between 3600 and 3100 cm^{-1} attributed to the stretching vibration of OH bonds in phenols, alcohols and carboxylic acids and NH bonds in amines and primary and secondary amides; (II) three low-intensity bands between 2950 and 2850 cm^{-1} corresponding to the stretching vibration of C–H bond in aliphatic hydrocarbon structures and alkyl substituent groups; (III) a band between 1700 and

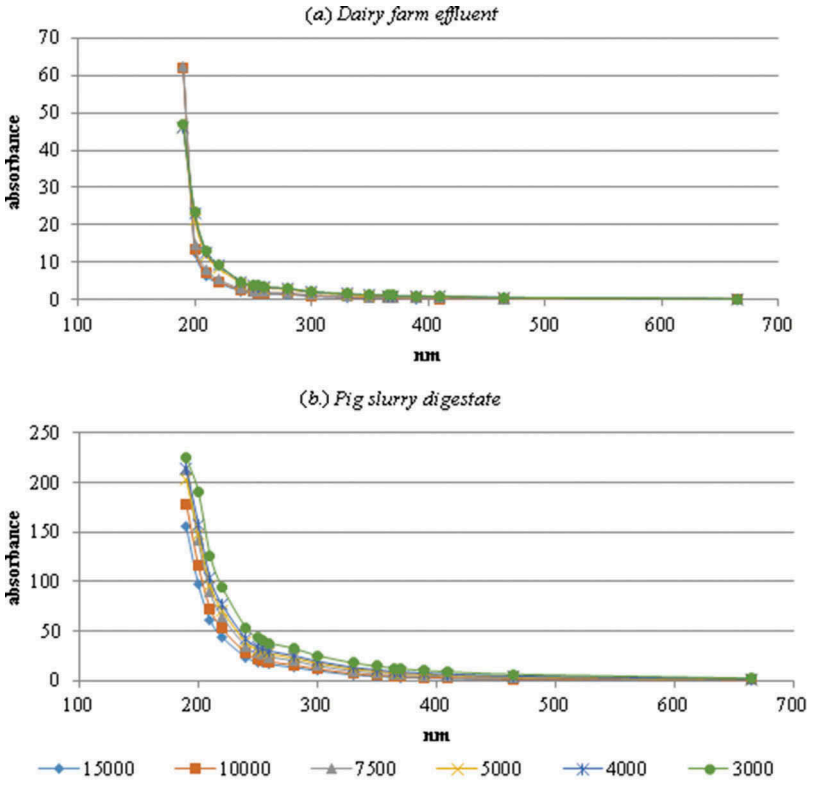

Figure 3. Absorbance variation as a function of the centrifugation rate for the supernatants from DE (a) and PD (b).

1600 cm^{-1} which may correspond to C=O stretching in amides, acids or ketones and OH deformation in alcohols and phenols; (IV) a band between 1580 and 1540 cm^{-1} due to N–H deformation in amines and amides and C=C stretching in aromatics; (V) a band at around 1460 cm^{-1} which may correspond both to C–O and N–O stretching in carbonates and nitrates, respectively, and C–H bending inaliphatic compounds; (VI) a wide band between 1200 and 1050 cm^{-1} which is characteristic of C–O and C–N stretching in esters, alcohols, phenols, amines and amides, and O–H bending of carboxyl, phenols and alcohols; and (VII) a band between 835 and 815 cm^{-1} possibly due to the out-of-plane deformation of the N–H bond [23–25].

The most significant differences between both effluents are observed in two regions of the spectra: (1) a band of great intensity at 1397 cm^{-1} corresponding to COO- antisymmetric stretching in carboxylates and C–H bending of methyl and methylene groups in the PD and absent in the DE; and (2) 2-weak intensity bands between 500 and 590 cm^{-1}, which could correspond to stretching vibrations of soluble compounds of inorganic nature, corresponding to DE.

The centrifugation of the organic effluents allows a good separation of phases. The choice of 5000 rpm speed is due to the need to achieve a clear liquid phase, avoiding turbidity by suspended solids (which occurs at 3000 rpm) and possible ruptures of the organic matrix (which occurs at 7500 rpm or greater).

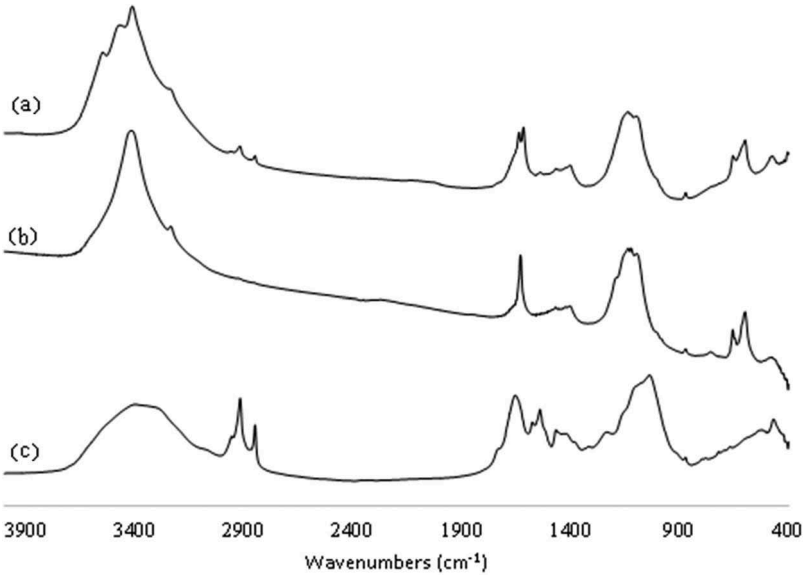

Figure 4. Dairy from effluent (DE) without centrifugation (a), supernatant (b) and precipitate (c) at 5000 rpm.

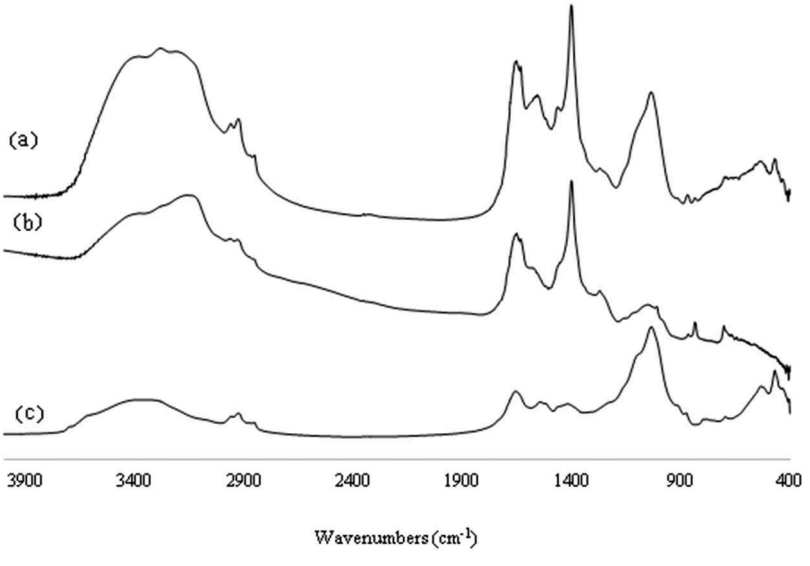

Figure 5. Pig slurry digestate (PD) without centrifugation (a), supernatant (b) and precipitate (c) at 5000 rpm.

Thus, the IR spectra of the supernatants of the dairy farm effluent (Figure 4(b)) show no appreciable differences relative to the original effluent. The same absorption zones are observed, with a slight narrowing of the band between 3600 and 3100 cm^{-1} (region I); the low intensity bands disappear between 2950 and 2850 cm^{-1} (region II); the bands are sharpened between 1700 and 1600 cm^{-1} (region III); and the bands between 1200

and 1050 cm^{-1} (region IV) and between 650 and 590 cm^{-1} (region V) remained practically unchanged, with a slight increase in intensity in all of them.

In contrast, in the IR spectra of the precipitates (Figure 4(c)), there are notable differences with respect to the effluent: a widening of the band in region I, a marked increase in band intensity in region II, an increase in the intensity and a better resolution in the band in region III, an increase in the intensity of the band in region IV, the disappearance or vanishing of the band in region V and a better resolution of the band below 500 cm^{-1}.

These results suggest that the organic components of the dairy effluent, with a greater degree of association and/or that contain a hydrocarbon skeleton in their structure, are of high molecular weight and insoluble, causing the precipitation of acids, aromatic compounds, amides, amines and long-chain aliphatic compounds. After the effect of centrifugation, there would remain the aqueous phase: oxygenated and/or nitrogenated components of a less complex structure, monofunctional or the ones resulting from a degradation of macromolecules.

In the case of the PD, there are evident differences between the spectra of each of the phases. The spectra comparison of the supernatant (Figure 5(b)) and the precipitate (Figure 5(c)) allows the following observations:

(1) In the supernatant, the band between 3400 and 3100 cm^{-1} is displaced towards lower wavenumber values with a decrease in intensity, supposing the presence of water-soluble compounds with possibilities of association by intermolecular hydrogen bridge formations. In the precipitate, on the other hand, a decrease in the intensity of this band is observed.
(2) The band between 2950 and 2850 cm^{-1} shows an intensity decrease in the supernatant and a slight increase in the precipitate so that precipitation of structures with long-chain aliphatic hydrocarbon support is inferred.
(3) In the precipitate, there is a widening and a decrease in the band intensity between 1650 and 1500 cm^{-1}, and it may be assumed that the amides, amines and low-molecular weight-unsaturated compounds remain in the supernatant.
(4) In the precipitate, a peak is defined and broadened in 1511 cm^{-1}, possibly due to the precipitation of higher weight and/or hydrophobic aromatic and olefinic compounds.
(5) The peak at 1397 cm^{-1} remains in the supernatant and disappears in the precipitate, suggesting that correspond to carboxylic acids (intermediates from the decomposition of complex organic carbons by anaerobic bacteria).
(6) There is a marked decrease in the supernatant and a marked increase in the precipitate in the band between 1150 and 900 cm^{-1} due to the precipitation of esters, alcohols, phenols and higher molecular weight polyhydroxyl compounds.
(7) There is a clear increase of the peak at 833 cm^{-1} in the supernatant while it disappears in the precipitate. This fact allows for the assumption that the amides and/or primary amines are maintained in the supernatant. Moreover, the permanence in the precipitate of absorptions between 600 and 400 cm^{-1} shows the presence of inorganic compounds, insoluble in water.

As in the DE, the centrifugation process generated supernatants and precipitates whose IR spectra can be easily differentiated from each other. However, the increase in velocity did not produce appreciable modifications in the spectra corresponding to each of the phases.

4. Conclusions

The carbon/nitrogen ratio decreases in the supernatants and increases in the precipitates, for the two types of effluent. This fact shows that the liquid phases are richer in nitrogen, whereas the solid phases are richer in carbon.

By means of UV–vis spectroscopy, it is inferred that there is an evident change between the spectra of the centrifuged samples and the effluents without centrifugation and, that at a higher centrifugation rate, there is a continuous decrease in the absorbance values while wavelengths increase. This fact indicates that in the supernatants, the most hydrophilic components remain, with lower molecular weight and with a less degree of conjugation.

From the IR spectra, it showed that in both effluents, the organic matter is composed mainly of hydrophilic substances and O–H, N–H, C=O and C–H functional groups of aliphatic and aromatic compounds. Moreover, it seems that when the centrifugation rate is increased, there are no observable differences in the absorptions corresponding to these functional groups.

These three methods show 5000 rpm as the best rate of centrifugation. This ensures a good separation of phases without denaturalisation of the organic matrix.

Rapidly and without complex physicochemical (previous) treatments, it is possible to easily make a qualitative evaluation of the effluent components through their functional groups and the interactions between solubility, molecular weight and structural complexity, by means of both spectroscopic methods. In addition, the basic chemical analyses give quantitative information on some of the nutrients. Using the proposed methodology, different organic effluents (liquid wastes) can be characterised quickly and easily for their correct use without damaging the environment.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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