Separation of cellulose from industrial paper mill wastewater dried sludge using a commercial and cheap ionic liquid

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ABSTRACT

Industrial wastewaters and their treatment are now placed at the heart of the environmental concerns that industries face. Some research work has been carried out in order to limit the impact of these wastes on the environment as well as their costs. In this study, wastewater dehydrated sludge (55% wt. water content) from paper industry was used to recover cellulose by using (hydroxymethyl) phosphonium chloride $[P(CH_2OH)_4]Cl$ ionic liquid as a solvent. The ionic liquid has shown remarkable results in terms of cellulose extraction in addition to its non-volatility and lower toxicity compared to organic volatile solvents. All cellulose, based on dry sludge, was recovered from the industrial dehydrated sludge with better operation conditions.

The influence of temperature and the quantity of ionic liquid was preliminary studied in order to optimize the extraction conditions.

Keywords: Cellulose; Separation; Industrial paper mill wastewater; Ionic liquid; Sludge valorisation

INTRODUCTION

The global production of paper was 400 million tons in 2015. Production is expected to increase to attain a world production of 550 million tons in 2050 (Faubert et al., 2016). The pulp and paper industry is a regular and intensive consumer of water. It is considered as the third water user for its processes, behind the metallurgical or chemical industry (Buruberri et al., 2015). For all this, the paper industry generates large amounts of wastewater in its processes, between 1.5 and 60.0 m^3 per day and ton of paper produced. The treatment of this wastewater also generates between 40 and 50 kg of dried sludge per ton of paper produced (Adhikari and Bhattacharyya, 2015). Of this amount, 70% comes from primary sludge and 30% from biological sludge (Jaria et al., 2017). The management of waste sludge is a serious problem for the paper industry and the solution adopted is usually the incineration of these, often with a high economic cost and the consequent emissions of greenhouse gases (Faubert et al., 2016). Other alternative possibilities widely used are: application in agriculture as fertilizer, building materials or production of bioethanol (Farghaly et al., 2017).

However, the European paper industries, associated with the Confederation of European Paper Industries (CEPI), fully support the European framework directive on waste (2008/98/EC) which establishes a series of recommendations for proper waste management. Among them are the prioritization of recycling over the incineration or deposition in agricultural fields and finally, over the production of energy. Moreover, the European Commission Roadmap to

Resource Efficient Europe (COM (2011) 571) foresees the sustainability of Europe's economy by 2050, where waste is managed as a resource and energy recovery can only be used with non-recyclable materials. This last milestone wants to be achieved in 2020 (Molina-Sánchez et al., 2018).

The application of these directives has led to the production of new materials with the sludge produced during the wastewater treatment of the paper industry. Some examples are the production of pesticides and fertilizers or thermal insulation materials (Jaria et al., 2017). Another possibility to enhance the residual sludge is to extract the cellulose, which can then be reused or converted into other materials with higher added value.

There are some conventional processes to recover the cellulose in the pulp and paper industries: Kraft process (Reeve, 2002); Organosolv process (Chundawat et al., 2010); Viscose process (Zhang et al., 2018); Lyocell (NMMO) process (Zhang et al., 2018). All the processes work well but they have some inconveniences, they are harmful to health by the toxicity of the solvents, have a nauseating smell and are pollutant. In addition, products or by-products cannot be easily used and valorised or some of the organic solvents are difficult to recover and reuse. For this reason, it is necessary to find alternatives or new friendlier processes.

Moreover, it is widely known that ionic liquids have great ability to dissolve cellulose and other lignocellulosic biopolymers (Wang et al., 2012). Ionic liquids were successfully used to precipitate cellulose from municipal sewage sludge (Olkiewicz et al., 2015a). Thus, the technical feasibility of using ionic liquids to recover cellulose from an industrial sludge was investigated in the present study.

METHODS

Materials

The dehydrated sludge (55% wt. water content) was provided by the paper international company Gomà-Camps, S.A., La Riba, Tarragona, Spain. The company, founded 250 years ago, has two paper fibre production lines, the first one with virgin cellulose pulp and the second with recycled paper. The sludge is a mixture of primary sludge coming from the physic-chemical treatment used to clean the recovered cellulose and the secondary sludge from a membrane biological reactor. Sludge is dried with air, stocked and is used to produce energy.

After reception, the dried sludge was stored at 4ºC in a fridge prior to use. Sludge was used as received. To realise the precipitation of cellulose, the sludge was suspended with deionised water until a final concentration of 5 $g_{\text{dried sludge}}$/L.

The ionic liquid used to recover cellulose from industrial dried sludge was Tetrakis (hydroxymethyl) phosphonium chloride ($[P(CH_2OH)_4]Cl$, hydrated ionic liquid, 80% in water, density 1.34 g/cm^3). It was supplied by Sigma-Aldrich.

Methanol, highest purity sulfuric acid, sodium bicarbonate, n-hexane, hydrochloric acid and magnesium sulfate monohydrate were provided by Sigma-Aldrich. Sodium tartrate, sodium chloride and diluted Folin reagent used for the sludge analyses were also provided by Sigma-Aldrich. The 80% phenol dissolution was prepared fresh. Deionized water was used in all laboratory procedures.

Experimental procedure

The process of the separation of cellulose from rehydrated dried sludge is summarized in Figure 1. The process was carried out using a similar method conducted for the extraction of lipids from primary sewage sludge (Olkiewicz et al., 2015a). The method is as follow: the necessary volume of rehydrated sludge to have 1 g of total solids was placed in a round bottomed flask. Then, it was added a certain amount of ionic liquid, 2, 5 or 10 mL, depending on the ratio sludge:IL investigated. The flask containing the reagents, wastewater and ionic liquid, was heated at a determined temperature in an oil bath (80ºC or 100ºC) for a fixed duration of time (24 h). The solution was mixed by a magnetic stirring of 500 rpm. The flask was connected with a condenser on the top to condensate the liquid in the process. A blank experiment was realised to see the effect of the ionic liquid on the recovery of carbohydrates. The conditions were: 24h of time, 80ºC of temperature and 1:10 ratio between sludge and water instead of ionic liquid. The rest of procedures were the same.

During the reaction, the sludge was dissolved by the ionic liquid. This dissolution caused the formation of a gel because of the higher viscosity of the solution. When the reaction was over, the mixture was cooled to room temperature. Then, 5 mL of methanol where added to provoke the separation of phases and the precipitation of the cellulose. At that point, 10 mL of hexane were added to the mixture to easily separate the lipids from the rest of phases. The mixture was stirred and placed in a laboratory centrifuge at 3500 rpm for 10 minutes. Two liquid phases were obtained. The yellow organic upper phase contained lipids and hexane. The aqueous liquid phase consisted of methanol, ionic liquid, and water. The precipitated phase containing cellulose was found in the bottom.

Firstly, lipids in hexane were separated using a pipette. Hexane was added again in order to complete lipid separation. The operation was repeated 3 or 4 times until the organic phase became uncoloured after 3 or 4 additions of hexane, which meant that all the lipids had been extracted.

Then, to recover the cellulose, the mixture of aqueous phase and precipitate was homogenized and placed in a laboratory centrifuge at 6000 rpm for 10 minutes. The aqueous phase was eliminated by a pipette. After this, methanol was added to the aqueous phase to eliminate the ionic liquid in the precipitated phase and centrifuged again. The process was repeated 3 or 4 times until the ionic liquid was totally eliminated in the aqueous phase which was signed by a white colour. The aqueous phase recovered from the extraction was also filtered to separate the traces of the precipitated phase. The precipitated solid obtained after filtration was put in an oven at 105ºC of temperature for 24 hours in order to measure the total solid.

The final solid obtained after elimination of the aqueous and the organic phase contained traces of methanol. The methanol in the solid phase was evaporated in a rotary evaporator. The solid obtained was kept in a desiccator to avoid absorption of water. The solid phase or precipitate was then weighed.

To see the influence of the sequence on the operative protocol, another experiment was realised, modifying the protocol of separation, centrifuging just after heating. The rest of the procedures were exactly the same, just adding methanol, then hexane, to both phases, solid phase and supernatant.

Total solids (TS), volatile solids (VS) and ash content were analysed to characterize the precipitate following the procedures described in the analytical characterization. A sample of precipitated solid was then examined by Fourier Transform Infrared (FTIR) spectroscopy. The yield of precipitate was calculated based on 100 g total solid equivalent as:

$$\text{Precipitate yield } \% = \frac{\text{Precipitate obtained [g]} \times \text{its fraction of dry weight}}{\text{wet sludge [g]} \times \text{its fraction of dry weight}} \times 100$$

Analytical characterization

Total solids (TS) and volatile solids (VS) were both determined by the standard method 2540B (Rice et al., 2012). Ash content was also defined as described by the standard method 2540E (Rice et al., 2012).

The total carbohydrate composition was determined using phenol-sulfuric acid according to Dubois method (Dubois et al., 1956), the absorbance was read at 480 nm.

Protein composition was determined by the Lowry method (Lowry et al., 1951), the absorbance was read at 750 nm.

Lipid composition from dried sludge was evaluated using a classical methodology with a Soxhlet apparatus and hexane as a solvent according to standard method 5520E (Rice et al, 2012). Around 20 ml of wet sludge was first acidified to pH=2, then 25 g of dry $MgSO_4,H_2O$ were added in order to eliminate the water and obtain an homogenous paste. The sludge was then left for 30 minutes. The solid obtained was crushed into fine powder. The powder was placed in a cellulose extraction thimble and coved with a glass wool. The extraction was then conducted using a Soxhlet and hexane solvent at 20 cycles/hour during 4 hours. Afterwards, the hexane was evaporated using a rotary evaporator. The lipids were stored in a desiccator to avoid water absorption and weighed on the next day. The lipid yield was expressed as gram of lipids per gram of dry sludge. The following equation shows how lipid yield was calculated:

$$\text{lipid yield } \% = \frac{\text{fats and oils [g]}}{\text{wet sludge [g]} \times \text{ fraction of dry solid}} \times 100$$

The precipitated solid was analysed by Fourier Transform Infrared (FTIR) spectroscopy to check the presence of carbohydrates. These samples, without any further preparation, were directly scanned using a Fourier Jasco FT/IR-600 Plus spectrometer with a diamond golden gate ATR (GS10542, Specac Ltd) reflectance cell.

RESULTS AND DISCUSSION

Table 1 presents the results obtained for the characterisation of the dried industrial sludge. As it can be seen in the table, sludge was not totally dried as it contains 56% of water. Total solids represent 44% of the sludge. The composition of the total solids is 54.6% (w/w_{TS}) of volatile solids and 45.4% (w/w_{TS}) of ashes. There is high value of ashes because the sludge contains inks and other metallic substances extracted during the washing of the recovered paper. The composition of volatile solids is essentially carbohydrates, 54.8% (w/w_{TS}), basically cellulose, proteins, 2.6% (w/w_{TS}) and lipids, 1.0% (w/w_{TS}). The values of proteins and lipids is essentially due to the presence of micro-organisms from the secondary membrane bioreactor used to treat wastewater. This composition is totally different of the composition of primary sludge (Olkiewicz et al., 2015a) where lipids accounted for 27.2% (w/w_{TS}), proteins for 24.2% (w/w_{TS}) and carbohydrates for 26.2% (w/w_{TS}). As expected, the composition of carbohydrates (cellulose) is higher in the industrial sludge but the high presence of ashes implies a better cleaning of the precipitate to allow the possibility to reuse cellulose.

In Table 2, the yields of cellulose and ash in precipitated material obtained after extraction of raw primary sludge with the ionic liquid are presented. The values are expressed as a percentage based on dry paper sludge. The results are obtained after reaction with 2 different temperatures using the same amount of ionic liquid (1:10 mL) and the same time of reaction (24h). In the first case (80ºC) it was obtained 52.6% (w/w_{TS}) of cellulose and 10.6% (w/w_{TS}) of ash whereas at 100ºC it was obtained 53% (w/w_{TS}) of cellulose and 11.1% (w/w_{TS}) of ash. As it can be seen in Table 2, there is no influence of temperature on the cellulose and ash yield in the precipitated material, in both cases similar results were obtained, however lower temperature conditions may have some effect and will be studied in the future.

The results of the blank experiment to see the effect of the ionic liquid on the recovery of carbohydrates are also presented in Table 2. The unique difference was the use of water instead of ionic liquid in the 1:10 ratio experiment. As it can be seen in the table, the recovery of carbohydrates is slightly lower but the quantity of ashes is more or less quadrupled. This demonstrates that the effect of ionic liquid is especially important on the separation of ashes from carbohydrates. The design of new ionic liquids must increase this separation until there is no presence of ashes in the carbohydrates.

The results of the experiment with a modified protocol are also presented in Table 2. The unique modification was to centrifuge the mixture just after heating. After centrifugation, methanol was added to both phases solid and liquid. In the liquid phase containing the ionic liquid nothing occurred. No additional solid precipitated, this signifying that all carbohydrates were in the solid phase. The ashes in this liquid phase, calculated by difference, where 38.4% dried sludge basis. This value is similar to the classical protocol. The addition of methanol in the solid phase, and after mixing, did not allow the separation of carbohydrates from the rest of ashes. The content of ashes in the solid phase was 7.2% dried sludge basis, a little less than the obtained in the other experiments with classical protocol. Moreover, the addition of hexane to liquid and solid phases to recover lipids, showed that all lipids were in the solid phase. The lipids where recovered as in the classical protocol, the obtained value was similar, 0.8% dried sludge basis. This demonstrates that the sequence of operation does not have a great influence in the results of the separation. Prior centrifugation does not really improve the complete separation of compounds. Again, right design of ionic liquid will be the responsible of a total separation.

In Table 3 we see the results obtained after reaction with 3 different ratios of sludge:IL (2, 5 and 10 mL) using the same temperature (100ºC) and the same time of reaction (24h). As it is shown in Table 3, the cellulose and ash content depends on the amount of ionic liquid used. The less volume of ionic liquid was used, the more cellulosic material was obtained. With 2 mL of ionic liquid it was obtained 56.9% (w/w_{TS}) of cellulose and with 10 mL, 53.0% (w/w_{TS}) of cellulose. However, lower amount of ionic liquid (1:2 sludge:IL ratio) gave higher amount of ashes, 18.3% (w/w_{TS}), in the precipitated material, resulting on a cellulose material more contaminated with ashes. According to the results, the optimum ratio of sludge to ionic liquid is 1:5 (g_{TS}:mL_{IL}) giving high amount of cellulose and low amount of ashes.

Table 4 shows the full characterisation of the entire process of recovery of cellulose by the ionic liquid. The experimental conditions were: 100ºC of temperature, 24 hours of reaction and 1 g_{TS}:5 mL_{IL} sludge:IL ratio. The first phase to be quantified were the lipids. After separation of organic upper phase, hexane was evaporated and lipids were weighted. The obtained value, 1.1% w/w_{TS}, is almost identic to the value of lipids obtained by soxhlet extraction and presented in Table 1, 1.0% w/w_{TS}. The separation of lipids obtained with ionic liquid was complete, signifying that ionic lipids are more or less able to separate all fractions from the sludge in a single operation.

The determination of protein in the liquid aqueous phase by Lowry method (Lowry et al., 1951) provided a value of 1.4% w/w_{TS}. This value is more than 50% of the protein initially contained in the sludge, proving that the ionic liquid used for the recovery of cellulose is not totally selective for the separation of cellulose. The content of protein in the solid phase was determined by mass balance.

As it can be seen in the table, the ionic liquid was also unable to eliminate all ashes in the precipitate. The amount of ashes found in the precipitate, 9.0% w/w_{TS} is more or less 20% of the total ashes contained in the sludge. The presence of these ashes are responsible for the final slightly dark colour of the precipitate.

The carbohydrates content in the precipitated solid after separation with ionic liquid was calculated from the difference between the value of volatile solids in the precipitate and the proteins in precipitate. The value of carbohydrates obtained by mass balance, 56.1% w/w_{TS} is close to the initial carbohydrate content measured by Dubois method (Dubois et al., 1956) and presented in Table 1, 54.8% w/w_{TS}. Considering the accuracy of these results, it is possible to say that almost all the cellulose is in the precipitate. This is very important because a commercial ionic liquid is able to separate all the cellulose from a wastewater sludge. Specific design of new ionic liquids must be able to decrease the quantities of ashes and protein in the precipitate.

In order to confirm the structure of the obtained solid, cellulose sample and precipitated solid were analysed by Fourier Transform Infrared (FTIR) spectroscopy. Figure 2 presents the spectra of the precipitated solid after extraction of cellulose with ionic liquid. The broad peak around 1035 cm^{-1} (assigned as the C-O stretching vibration of carbohydrates) is presented in both samples. Also, a peak at 1160 cm^{-1} in both spectra, which is assigned to C-O-C stretching vibration is particularly associated with cellulose. Based on FTIR data it could be said that precipitated solid after ionic liquid extraction contains cellulose.

Additionally, the possibility of recoverability and reusability of the ionic liquid in a new cycle of purification is very important because the energetic and economic balance of the process. In the current work, recoverability and reusability of the ionic liquid were not checked as this study is a fast technical feasibility one. This was investigated in an older work using the same ionic liquid to extract lipids from microalgae (Olkiewicz et al., 2015b). In this work, the stability of the ionic liquid was tested by ^{1}H NMR spectroscopy, comparing fresh and used ionic liquid. The same peaks were found signifying a high steadiness of the ionic liquid. No supplementary peaks appeared for the reused ionic liquid, suggesting its stability and allowing reusability. The recycling and reuse of the recovered ionic liquid was examined by carrying out four runs. All tests showed similar high performances of the recovered ionic liquid than fresh ionic liquid, allowing its suitability in repeated processes.

Concerning the feasibility and economy of the process, the cost of ionic liquid, temperature and time of reaction of process are parameters that make the practical application of the process questionable when compared to currently applied processes. It is true that the cost of the ionic liquid is not cheap. But this work is a proof of concept. It is a first evaluation of the possibility to recover cellulose from industrial paper wastewater or sludge. The process is not yet optimised and needs a lot of extra work. For example, more selective and green ionic liquids should be optimised and designed, temperature should be decreased, time of reaction should be shortened, ratios sludge:IL should be improved and surely other parameters. Furthermore, this work was performed with dried sludge. As it was demonstrated with municipal primary sludge in previous works, it is possible to work directly with wet sludge, avoiding high costs of drying operation (Olkiewicz et al., 2015a). The only thing that is currently questionable is the full recovery of ionic liquid. Separation and purification of ionic liquid after the recovery of the cellulose is a challenge. However, it has been demonstrated that ionic liquid can be reused as commented in the previous paragraph. Further studies with membrane separation processes might be able to recover the ionic liquid. Then, the problem of cost will also be solved. Finally, it is well known that the scale-up of the process to a semi-industrial continuous setup will improve the performances of the process. When all will be done, it will be then possible to compare the process with other currently applied processes.

CONCLUSIONS

The ionic liquid tetrakis hydroxymethyl phosphonium chloride $[P(CH_2OH)_4]Cl$ has shown potential for the recovery of the cellulose from the industrial paper sludge. The amount of carbohydrates measured by the conventional method in the paper sludge and the amount of cellulose recovered using ionic liquid method are comparable. The ionic liquid is able to dissolve ashes from paper sludge. The study shows dependence between quantity of ionic liquid used for reaction and amount of cellulose recovered. The less ionic liquid used, the more cellulose obtained. It is necessary to study milder reaction conditions to optimise the process in order to reduce energy and therefore the cost of the process. It is necessary to study a purification process to further clean the cellulose.

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FIGURE CAPTIONS

Figure 1. Scheme of the experimental procedure of extraction of cellulose from industrial paper sludge with ionic liquid.

Figure 2. FTIR analysis of precipitated solid after ionic liquid extraction and of pure cellulose.

Table 1. Characterisation of industrial paper wastewater dried sludge.

	Characterisation of dried sludge [a] (%)	Mass of the fractions of dried sludge (g) [e]
Moisture	56.0 [b]	56.0
Total solids (TS)	44.0 [b]	44.0
Ashes	45.4 ± 1.1 [c]	20.0
Volatile solids (VS)	54.6 [c]	24.0
Carbohydrates	54.8 ± 3.0 [c]	24.1
Protein	2.6 ± 0.2 [c]	1.1
Lipids	1.0 ± 0.2 [c]	0.4
Total	103.8 [c,d]	45.6 [d]

Values are mean, ±SD, n=3

[a] All analysis according to conventional methods; ashes-2540B (SMEWW), proteins – Lowry method, carbohydrates - Dubois method, lipids by extraction with Soxhlet apparatus.

[b] (%, w/w_{sample}).

[c] (%, w/w_{TS}).

[d] Sum of ashes, carbohydrates, protein and lipids (corresponding to total solids).

[e] Calculated on basis of 100 g of sludge as received.

Table 2. Influence of extraction temperature on the yield of cellulose from, 5% of total solids, industrial paper sludge using $[P(CH_2OH)_4]Cl$ ionic liquid (24 h, 1:10 ratio sludge:IL).

			Precipitated material (%, dried sludge)	
Temperature (ºC)	Time (h)	Ratio sludge:IL (g_{TS}:mL_{IL})	Cellulose	Ashes
80 B.E.	24	1:10 (water)	48.8	37.0
80	24	1:10	52.6	10.6
80 P.M.	24	1:10	44.3	7.2
100	24	1:10	53.0	11.1

B.E.: Blank experiment

P.M.: Protocol modified, centrifugation just after 24 h heating.

Table 3. Influence of ratio sludge:IL on the yield of cellulose from, 5% of total solids, industrial paper sludge using [P(CH_2OH)$_4$]Cl ionic liquid (100ºC, 24 h).

			Precipitated material (%, dried sludge)	
Temperature (ºC)	Time (h)	Ratio sludge:IL (g_{TS}:mL_{IL})	Cellulose	Ashes
100	24	1:2	56.9	18.3
100	24	1:5	56.1	9.0
100	24	1:10	53.0	11.1

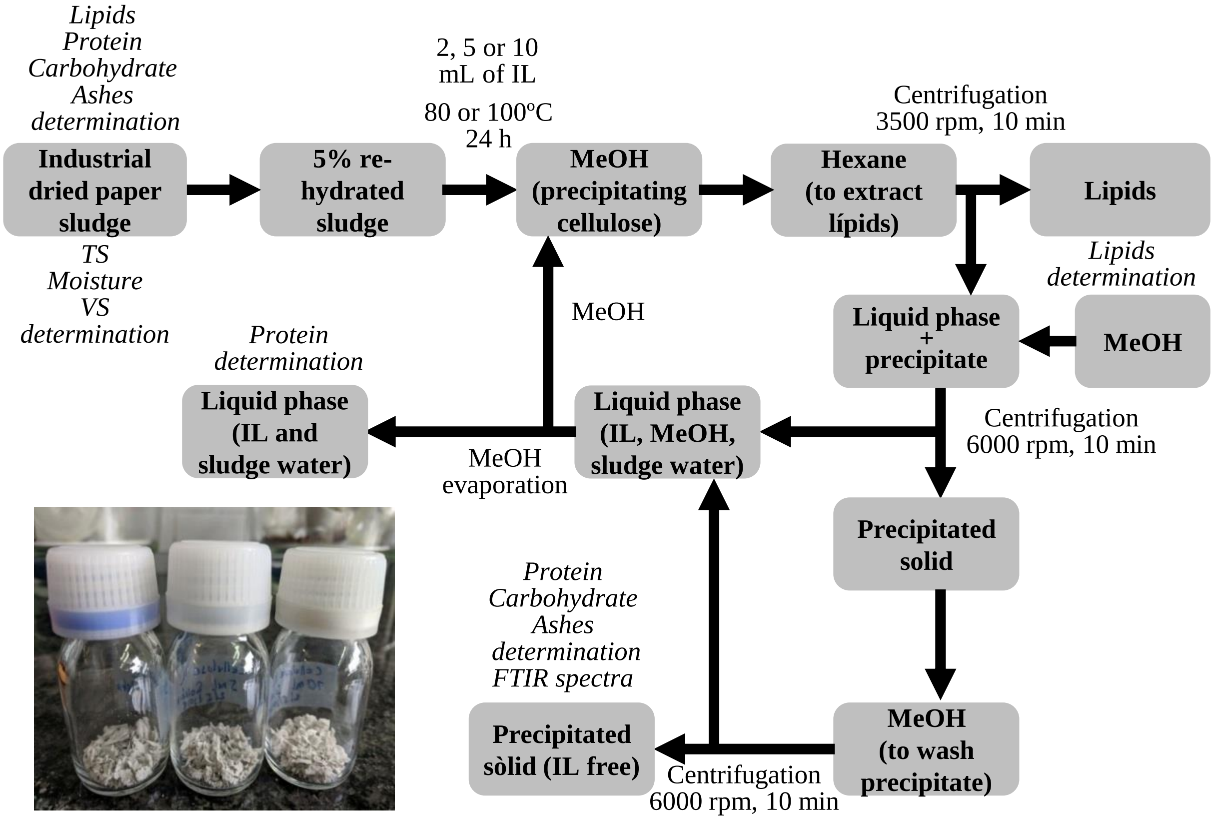
Table 4. Characterisation of the fractions after their separation by ionic liquids (100ºC, 24 h, 1:5 sludge:IL ratio).

	Organic phase	Liquid aqueous phase containing the ionic liquid	Solid phase: precipitate
Ashes (%, w/w_{TS})	-	36.4	9.0
Carbohydrates (%, w/w_{TS})	-	-	56.1 [a]
Proteins (%, w/w_{TS})	-	1.4	1.2 [b]
Lipids (%, w/w_{TS})	1.1	-	-
Total (%, w/w_{TS})	105.2		

[a] Calculated from the difference between the volatile solids in the precipitate and the proteins in the precipitate.

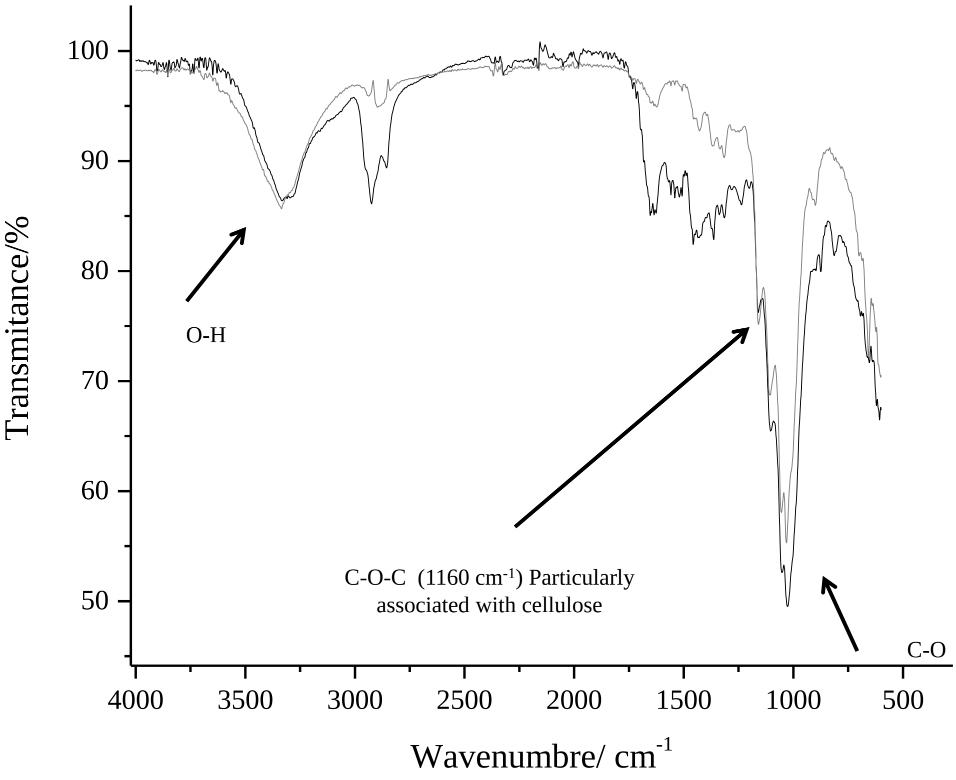
[b] Calculated from the difference between the total proteins obtained from the dried sludge and the protein analysed in the liquid aqueous phase.

Figure 1.



Lipids
Protein
Carbohydrate
Ashes
determination
Industrial dried paper sludge
TS
Moisture
VS
determination
5% re-hydrated sludge
2, 5 or 10 mL of IL
80 or 100ºC
24 h
MeOH (precipitating cellulose)
Hexane (to extract lípids)
Centrifugation
3500 rpm, 10 min
Lipids
Lipids determination
Liquid phase + precipitate
MeOH
Centrifugation
6000 rpm, 10 min
Liquid phase (IL, MeOH, sludge water)
MeOH
MeOH evaporation
Liquid phase (IL and sludge water)
Protein determination
Precipitated solid
MeOH (to wash precipitate)
Centrifugation
6000 rpm, 10 min
Precipitated sòlid (IL free)
Protein
Carbohydrate
Ashes
determination
FTIR spectra

378 Figure 2.



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