Title: A METHOD OF SEPARATING THE LIPID FRACTION FROM PRIMARY SEWAGE SLUDGES

Abstract: The invention concerns a method for separating and recovering the lipid fraction from a primary sewage sludge, for example from the treatment of urban wastewater. The method provides for the treatment of the primary sludge with an oxidizing agent and the subsequent heating and centrifugation, all without the use of organic solvents. The lipid fraction rich in free fatty acids thus obtained is free of organic solvents and other contaminants and, advantageously, lends itself to use as a starting material in the production of biodiesel.
A method of separating the lipid fraction from primary sewage sludges

The present invention concerns a method for separating and recovering the lipid fraction from primary sewage sludges, for example from the treatment of urban wastewater.

In a typical municipal wastewater treatment plant (WWTP) two types of sludges are produced, primary sludges and secondary sludges, which differ significantly in composition.

Primary sludges are generally produced in raw wastewater sedimentation processes and collect the suspended solid phase of urban wastewater. They consist of fats as present as Free Fatty Acids (FFAs), sterols, fatty soaps, fatty alcohols, waxes, glycerides and estolides which account for up to 30% of total solids (TS); cellulose, which generally accounts for 15-20% of total solids (TS); hemicelluloses (10% of TS), proteins (20-25% of TS) and inorganic salts (15-20% of TS). The waters from the primary sedimentation tanks are then sent to biological oxidation tanks. Secondary sludges, on the other hand, are produced following a biological oxidation treatment and are characterized by a more complex structure than primary sludges, due to an increased presence of bacterial mass.

Primary sludges generally account for 60% of total sludges produced in WWTPs.

In the most virtuous of cases, the primary sludges are mixed with the secondary sludges and the mixture is used to feed an anaerobic digester. The biogas obtained is burned to obtain electrical energy, while the cogenerated thermal energy is used to maintain the overall mass in the digester at the operating temperature.

Conventional sludge management as described above is based on slow, non-lucrative processes, from an energy perspective, since the biogas produced at the end of anaerobic digestion is barely sufficient to support the energy needs of the entire process. As far as processing times are concerned, it generally takes almost 20 days for the digestion to be completed.
In other cases, the same sludge is treated as waste to be oxidized and reclaimed. For this purpose, even more expensive oxidative processes, both economically and energetically, are used.

The conventional treatment of sewage sludges described above actually results in a management cost of 50% of the total wastewater treatment.

On the other hand, recent studies have shown that the specific energy capacity of wastewaters entering a treatment plant is about ten times the energy value required for the treatment of the same urban wastewaters. In addition, more than half of this energy content is concentrated in recoverable suspended solids in the primary sludges. These data have guided the search for new technological solutions that better exploit these potential energy sources.

The most studied approach - but as of yet not applied - consists in an effective enhancement of the chemical nature of the sludges, with particular reference to the lipid component thereof. In particular, the part of the slurry separated by oil separators during the pre-treatment step in the form of fats and/or oils and the primary settling sludges represent the best process substrates on which to operate.

The most recent solutions proposed consist in extracting the lipids from these waste materials using organic solvents, such as hexane, toluene and xylene on sludges, including wet sludges, methylene chloride and methanol, or chloroform/methanol from previously dried sludges.

It has also been proposed to recover the oil fraction present in sewage sludges by using waste oil matrices as an extractor, and then producing biodiesel from the final mixture (CN 1962820 A).

WO 20040991 15 A1 describes the solvent extraction and subsequent transformation into biodiesel of the separated lipid fraction during the pre-treatment steps in wastewater treatment plants.
WO 20071 14919 A2 describes the recovery of the fat fraction from feces using strong acids in combination with solvents on previously dried material.

WO 201 1085461 A1 describes solvent-free demulsification processes using strong inorganic acids. However, at the end of the operations to recover the fat fractions, no mention is made of the fate of the residues obtained from this pre-treatment. In effect, together with the recovered fat stream, a spent residue is always generated, which has a strong acid anion content, making it a waste that is difficult to classify and dispose of and difficult to reuse in other processes.

If, from an energetic point of view, the preliminary removal of water from the sludges appears very expensive, the direct extraction of the lipid fraction from wet sludges by the use of solvents involves the contamination of the residual sludges with the solvent, generating a waste that is difficult to treat: in effect, even small traces of solvent inhibit the subsequent biological oxidation treatment and/or anaerobic digestion.

The use of oxidizing agents has been reported in the prior art as a method for dissolving complex solid substrates. US201 00044306 describes the use of H₂O₂ for the sole purpose of dissolving the solid organic substance initially present in urban solid organic wastes. WO201 1036550A1 describes the use of oxidizing agents on a wastewater sewage sludge, but also in this case the only purpose is to increase the soluble organic load. In both cases, the possible recovery of fat/lipid fractions from pre-treated sludge is not considered.

In WO 2005/035693 A2 the use of an oxidant is considered optional and useful only to change the degree of saturation of the recovered lipidic phase; a recovery that is, however, carried out by means of an organic solvent.

In US 2011/0197497A1 the use of an oxidizing agent is considered useful in the deodorization processes of a brown grease, and nevertheless does not apply to primary sludge.
The use of primary sewage sludges as a raw material to obtain fats, which are then converted into valuable compounds such as biofuels and biolubricants, has therefore been strongly inhibited by the problems resulting from the use of organic solvents and mineral acids during the extraction processes. In effect, even when using completely immiscible solvents, a fraction thereof is always adsorbed on the solid surface of the residual sludges, generating a new environmental contamination problem, as well as an obvious economic problem related to the recovery and reuse of the solvents. Recent studies have shown that organic solvents such as hexane and toluene have an inhibitory effect on subsequent aerobic and anaerobic treatments. Considering then that the amount of solvent trapped in the sludge is comparable to the amount of lipids removed during extraction, the recovery of the solvent by evaporation is absolutely necessary, but extremely expensive.

All this makes the solvent extraction processes described in the prior art complex, unprofitable and thus not suitable.

A recent study on the composition of sewage sludges has shown that a significant part of the lipid fraction contained in primary sludges is composed of calcium soaps. These compounds are normally solid, have a very high melting temperature and produce very stable aqueous micelles wherein free fatty acids and glycerides are also trapped together with water and fibers of various kinds.

These micelles may be broken using the already mentioned organic solvents but may also be induced by simply modifying the acidity of the sludge. For this reason, the use of strong acids during solvent extraction strongly influences the efficiency and yield of the extraction process. On the other hand, in the prior art, the use of only mineral acids in the absence of organic solvents has also been studied. However, the problem of how to treat spent residues produced from the acid treatment has not been addressed in the prior art.

There is therefore a need to provide a new method for recovering the lipid fraction from sewage sludges, in particular primary sludges preferably from the treatment of urban wastewaters, which does not have the disadvantages of the methods of the prior art, both in economic and environmental terms.
This need has now been met by the separation method as defined in the accompanying claim 1.

Further features and advantages of the separation method of the invention are defined in the dependent claims. The claims form an integral part of the description.

In the scope of the present invention, the term “primary sewage sludges” or “primary sewage sludge” is used to describe a sediment from wastewater treatment, preferably urban wastewater, characterized in that it contains a lipid fraction consisting mainly of calcium soaps. Preferably, the calcium soaps represent at least 50%, at least 60%, at least 70%, at least 80% or at least 90% by weight of the total lipids present in the primary sewage sludge.

The separation method of the invention has the advantage of not envisaging the use of any added acid or any organic solvent and to allow the recovery of a lipid fraction rich in free fatty acids in the form of an oil phase easily separable and without generating processing residues that are hazardous or difficult to dispose of.

Through the separation method of the invention, it is thus now possible to recover and exploit a waste material never used before, namely primary sewage sludge, to obtain spent fats in a simple, convenient and effective way, and, as indicated, without producing hazardous processing residues and/or wastes that are difficult to dispose of. Recovered lipid substances are easily used in the production of biofuels (such as biodiesel) and/or biolubricants.

The separation method of the invention thus makes it possible to effectively manage primary sewage sludges, on the one hand, reducing the residual volumes to be treated and, on the other, recovering new resources.

The separation method of the invention comprises the following steps:

a) providing a primary sewage sludge;
b) treating said primary sewage sludge with an oxidizing agent;
c) heating the primary sewage sludge treated in step b) to a temperature of at least 300 K; and
d) centrifuging the material obtained in step c), thus obtaining the separation of (i) an oil phase comprising a lipid fraction rich in free fatty acids, (ii) an aqueous phase, and (iii) a wet solid residue,
all the aforesaid steps a), b), c) and d) being carried out in the absence of any organic solvent.

In addition to free fatty acids obtained in the oil phase by the separation method of the invention, there may also be mono-, di-, tri-glycerides, waxes, hydroxy acids, estolides, sterols and other fats, as well as part of the soaps originally present in the primary sewage sludge.

The separation method of the present invention advantageously allows one to separate more than 85% of the lipidic substances initially present in the primary sewage sludge.

An extremely advantageous feature of the separation method of the invention is that it is completely free of organic solvents in all the phases thereof.

In a preferred embodiment, the oxidizing agent used in the method of the invention is selected from the group consisting of H₂O₂, O₃, UV radiation, O₂, sodium and/or potassium hypochlorite, C₁₀, peracetic acid, and combinations thereof.

In another preferred embodiment of the method of the invention, step c) of heating is conducted at a temperature between 300 and 373 K, most preferably at a temperature of 333 K. One skilled in the art may select the optimal heating temperature based on the composition of the resulting fatty acids and the melting points thereof.

In some embodiments, for example when the primary starting sludge has a low content of total solids (TS less than 4%), step b) is preceded by a centrifugation step to eliminate part of the water present in the starting material.
However, it should be noted that the primary sewage sludge used as a starting material in the separation method of the present invention may have any percentage of total solids (TS), for example, a TS between 1% and 30% by weight, preferably between 5% and 30% by weight.

All the aforementioned embodiments may be combined with any other.

In contrast to brown greases, sewer greases or trap greases (US 9868918, US 2011/0197497), it is not possible to separate the related lipid phase from the primary sewage sludges by heating alone, or even by means of hot centrifugation alone. The sequence of steps that characterizes the method of the present invention is absolutely necessary in order to recover the lipid fraction from primary sludges: in effect, even the combination of oxidation/heating does not produce any separation and thus no recovery of lipids unless accompanied by centrifugation.

The separation method of the invention takes a relatively short time, usually a few hours. As indicated above, at the end of the method, the separation of three different phases or streams are obtained:

i) An oil phase comprising a lipid fraction rich in free fatty acids and possibly other fatty-substances. This oil phase, being rich in free fatty acids, is advantageously suitable for use as a starting material for the production of biofuels and/or biolubricants, for example, through the two-step process (direct esterification of free fatty acids with a C1-C5 alcohol in the presence of an esterification catalyst and subsequent trans-esterification with C1-C5 alcohol in the presence of a basic catalyst) described in the Italian patent application n°102017000038638 of 07/04/2017, incorporated herein as a citation.

ii) An aqueous phase containing dissolved biodegradable organic substances. This phase may also be enhanced, for example by PHA production, fermentation and/or anaerobic digestion.

iii) A fraction of wet solid residues, with a significantly reduced volume, which may potentially be upgraded both thermochemically and by anaerobic co-digestion with secondary sewage sludges in order to obtain biogas.
The following experimental examples illustrate the various ways in which the separation method of the invention has been carried out. They are provided for exclusively illustrative purposes and do not limit the scope of the invention as defined in the accompanying claims.

EXAMPLES

Example 1 (reference)

**Determination of the lipid fraction of primary sludges**

Fresh sedimented primary sludges (total solids content 4%) were centrifuged beforehand at 3000 rpm for 5 minutes, bringing the solids content up to 10-12%. 2 ml of HCl concentrate and 50 ml of hexane were added to 50 g of centrifuged sludges. After careful stirring, the organic phase was separated and washed with two more volumes of 20 ml each of hexane, collecting the organic fractions in a single flask. The solvent was then evaporated. 1.3 ±0.1 g of an oil fraction was obtained and then converted into biodiesel using acid methanolysis.

Example 2

**Lipid fraction recovery from centrifuged primary sludges by addition of H2O2**

5 ml of H2O2 (50%) was added to 50 g of centrifuged primary sludges (total solids content 17%, fat content 20% of total solids). The mixture thus obtained was brought to 80°C for 2 hours. Then the same was directly hot-centrifuged (3000 rpm, 3 minutes). In this way it was possible to easily separate 1.30 g of the lipid phase (>75%). The residual solid obtained from the same centrifugation was 11 g wet (total solids content >25%) and was separated from an aqueous phase at pH 5.09.

Example 3

**Lipid fraction recovery from centrifuged primary sludges sedimented by addition of O3**
300 g of primary sedimented sludges (total solids content 8%, fat content 20% of total solids) was placed in a cylindrical glass reactor with a capacity of 500 ml equipped with a mechanical stirrer and in which was bubbled O₃ at a flow of 50 ml/minute. The output content in O₃ of the gases was 40-60 ppm. The administration of O₃ lasted for 8 hours at room temperature. The mixture obtained was then heated to 80°C for 2 hours, and was directly hot-centrifuged (3000 rpm, 3 minutes). In this way, it was possible to easily separate 4 g of the lipid phase (>67%). It should be noted that the residual solid obtained from the same centrifugation was 11 g wet (total solids content >25%), while the pH of the recovered aqueous phase was 5.36.

**Example 4 (reference)**

**Lipid fraction recovery from primary sludges by hot-centrifugation only**

50 g of centrifuged primary sludges (total solids content 17%, fat content 20% of total solids) was heated to 80°C for 2 hours. Then a centrifugation operation was carried out at 3000 rpm for 3 minutes, not resulting in any lipid separation, but only an additional thickening of the solid phase (total solids content 25%, with an unchanged fat content of 20% of total solids).

**Example 5**

**Transformation of fat fractions into biodiesel**

The fat fractions obtained in examples 2 and 3 were transformed into the respective fatty acid methyl esters (FAMEs) using the method described in the Italian patent application η°102017000038638 of 07/04/2017, incorporated herein by citation.

As an example, 10 g of fat was made to react with 10 g of methanol and 0.2 g of AlCb 6H₂O at 70°C for 2 hours. At the end of the reaction a biphasic system was obtained: a predominantly alcoholic supernatant, in which most of the catalyst was still dissolved, and an underlying predominantly oil phase containing the methyl esters of the fatty acids.

The titer of FAMEs was >95%, with a free residual acidity of 0.2%.
The following is the profile of the main fatty acids detected:

C14:0 = 5.8%, C16:0 = 53.5%, C16:1 = 1.6%, C18:0 = 1.3, C18:1 = 16.3%, C18:2 = 5.8%.
**CLAIMS**

1. A method of separating a lipid fraction rich in free fatty acids from a primary sewage sludge, the method comprising the following steps:
   a) providing a primary sewage sludge;
   b) treating the primary sewage sludge with an oxidizing agent;
   c) heating the primary sewage sludge treated in step b) to a temperature of at least 300 K;
   d) centrifuging the primary sewage sludge treated in step c), thereby obtaining the separation of: (i) an oil phase comprising a lipid fraction rich in free fatty acids, (ii) an aqueous phase, and (iii) a solid residue,
   all the aforesaid steps a), b), c) and d) being carried out in the absence of any organic solvent.

2. The method according to claim 1, wherein the percentage of total solids (TS) in the primary sewage sludge is between 1% and 30% by weight, preferably between 5% and 30% by weight.

3. The method according to claim 1 or 2, wherein the primary sewage sludge provided in step a) comprises a lipid fraction comprising at least 50% by weight of calcium soaps in relation to the weight of the total lipids.

4. The method according to any one of claims 1 to 3, wherein the oxidizing agent is selected from the group consisting of H2O2, O3, UV radiation, O2, sodium and/or potassium hypochlorite, C12O3C, peracetic acid and combinations thereof.

5. The method according to any one of claims 1 to 4, wherein the heating step c) is carried out at a temperature between 300 and 373 K.

6. The method according to claim 5, wherein the heating step c) is carried out at a temperature of approximately 333 K.

7. The method according to any one of claims 1 to 6, wherein step b) is preceded by a
centrifugation step to eliminate part of the water present in the primary sewage sludge.

8. The method according to any one of claims 1 to 7, wherein the heating step c) is followed by a further centrifugation step.

9. The method according to any one of claims 1 to 8, wherein the obtained oil phase comprising a lipid fraction rich in free fatty acids, is used as starting material in a biodiesel production process which comprises a first step of direct esterification of the free fatty acids with a C1-C5 alcohol in the presence of an esterification catalyst, and a second step of basic trans-esterification by reaction with a C1-C5 alcohol in the presence of a basic catalyst.
# INTERNATIONAL SEARCH REPORT

**International application No**
PCT/IB2019/052041

## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC.

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

| C11B | C02F | C11C | C16L |

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, BIOSIS, EMBASE, FSTA, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
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| X        | US 9 868 918 B2 (SCOTT MICHAEL [GB])  
16 January 2018 (2018-01-16)  
column 8, line 40 - column 10, line 47  
column 11, lines 25-29  
column 12, lines 59-63  
----- | 1-9 |
| X        | US 2011/197497 A1 (JIANG RONG [US])  
18 August 2011 (2011-08-18)  
paragraphs [0013], [0015], [0017]  
paragraphs [0026], [0027]  
paragraphs [0043], [0044], [0048], [0049]  
paragraphs [0055], [0056], [0065]  
paragraphs [0070]  
paragraphs [0083] - [0085], [0088], [0096], [0097]  
claims 5, 6, 11  
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Further documents are listed in the continuation of Box C.

See patent family annex.

- **X** Special categories of cited documents:
  - **A** document defining the general state of the art which is not considered to be of particular relevance
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**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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**S** document member of the same patent family

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Name and mailing address of the ISA:
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Authorized officer: Vermeulen, Stéphane
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