



(43) International Publication Date
29 August 2013 (29.08.2013)

(10) International Publication Number
WO 2013/124237 A1

(51) International Patent Classification:

C02F 1/66 (2006.01) *C02F 1/52* (2006.01)
C02F 11/14 (2006.01) *C02F 1/56* (2006.01)
C02F 1/20 (2006.01) *C02F 11/18* (2006.01)

(21) International Application Number:

PCT/EP2013/053171

(22) International Filing Date:

18 February 2013 (18.02.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12156214.4 20 February 2012 (20.02.2012) EP

(71) Applicant: **KEMIRA OYJ** [FI/FI]; Porkkalankatu 3, FIN-00180 Helsinki (FI).

(72) Inventor: **GRÖNFORS, Outi**; Luoteisrinne 2, FIN-02270 Espoo (FI).

(74) Agent: **WENNBERG, Malin**; Awapatent Ab, P.O. Box 51117, S-200 71 Malmö (SE).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD OF TREATMENT OF A SLURRY COMPRISING ANAEROBICALLY DIGESTED ORGANIC MATERIAL

(57) Abstract: The present invention relates to a method of treating a slurry comprising anaerobically digested organic material, which comprises the steps of: a) obtaining an acidic slurry at a pH of below 7 by addition of an acidic material to the slurry comprising anaerobically digested organic material, if the slurry comprising anaerobically digested organic material is not already at a pH below 7, so that an acidic slurry at a pH below 7 is obtained, b) adding an oxidizing agent to the acidic slurry and allowing to react, c) adding an alkaline compound to the slurry obtained in b) to obtain a pH > 8, d) adding a flocculating polymer to the slurry obtained in c), e) separating the slurry obtained in d) into a liquid and solid phase.



WO 2013/124237 A1

METHOD OF TREATMENT OF A SLURRY COMPRISING ANAEROBICALLY DIGESTED ORGANIC MATERIAL

Field of the art

The present invention relates to treatment of digested organic matter.

Background

5 Dewatering of digested material at biogas plants may be difficult. Often the amount of suspended solids remain high in the reject water after mechanical dewatering. These solids may cause problems in a subsequent ammonia stripping process that typically is run at a pH above 10 for nitrogen removal purposes or if reject is recycled back to the process. Also, biological
10 processes used for nitrogen removal from reject water may be influenced by the high load of suspended solids in the reject water. At the moment municipal waste water treatment plants are facing problems treating the reject waters from biogas plants. In many of the biogas plants used today the reject water contains 4 to 10 times as much suspended solids in the reject water at
15 alkaline pH as the subsequent ammonia stripper is adapted for in its design.

WO2004/094320 discloses a method of treating digested sludge with improved dewatering and hygienization. The method discloses the use of acid, iron salt, and oxidizing agent followed by dewatering under acidic conditions.

20 US2005/0077245 discloses a method for stabilizing and conditioning wastewater sludge. The method discloses the use of acid, oxidizing agents and flocculant followed by dewatering under acidic conditions.

WO2010/108558 discloses a method for producing biogas by anaerobic digestion of organic matter. In the document it is disclosed that
25 hydrogen peroxide may be used to hygenisate the digested sludge produced and also reduce the amount of water in the hygenisated sludge after dewatering.

There is a need for alternative and improved separation of solid and liquid compounds of treated digested organic material.

Summary of the present invention

A reduction of the content of suspended solids in the reject water is important for a biogas plant since it may affect the subsequent processes and the waste treatment costs at the municipal wastewater treatment plant.

5 The present invention relates to a method that precipitates the solids at alkaline process conditions and in an efficient way removes the existing suspended solids. This is achieved by an adjustment of an acidic slurry mixture treated with an oxidizing agent to an alkaline pH before an addition of a flocculating polymer to the process. The suspended solids are then
10 precipitating at a pH of 8 and above. As the polymer is added to the slurry mixture after the adjustment of pH to ≥ 8 , the polymer flocculates the suspended solids and the formed precipitated solids are then removed by fractioning of solids from liquid. After dewatering, this method results in a liquid fraction in which the suspended solids remain on low level even when
15 pH is further increased before or during subsequent processes, like e.g. ammonia stripping process. The reject water from the present method exhibit a low content of suspended solids, which water may be subjected to further increases of the pH without causing problematic subsequent precipitation.

The present method is especially suited for applications where low
20 amounts of suspended solids are required for the reject water, due to requirements in subsequent processes, e.g. for ammonia removal by stripping from reject water, or for reducing the amount of suspended solids for following biological or membrane processes or for recycling the reject back to the process.

25 The present method also provides an improved reduction in COD and a total amount of phosphorous.

The present method relates to treatment of a slurry comprising anaerobically digested organic material, which comprises the steps of:

- 30 a) obtaining an acidic slurry at a pH of below 7 by addition of an acidic material to the slurry comprising anaerobically digested organic material, if the slurry comprising anaerobically digested organic material is not already at a pH below 7, so that an acidic slurry at a pH below 7 is obtained,
 b) adding an oxidizing agent to the acidic slurry and allowing to react,

c) adding an alkaline compound to the slurry obtained in b) to obtain a pH ≥ 8 ,

d) adding a flocculating polymer to the slurry obtained in c),

e) separating the slurry obtained in d) into a liquid and solid phase..

5 Detailed description of the exemplary embodiments

The present method decreases the amount of suspended solids in the filtrate at alkaline conditions and prevents unwanted precipitation in further processing at an increased pH.

10 The wording “anaerobically digested organic material” as used herein is to be interpreted as any type of organic material that has been digested, by anaerobic digestion. The organic material may be chosen from untreated or treated organic materials, e.g. biomass, sludge, effluent waste stream or water, and organic waste. Organic waste may be biomass waste. If untreated
15 organic material is used or other types of non-digested organic material is used, the material is digested before the process according to the present method. In one embodiment the digested organic material is the digestate from a biogas plant.

When organic material has been subjected to an anaerobic digestion, the organic material is at least partly degraded. Degradation of organic
20 material results in a mixture of a solid fraction comprising not degraded material and a fluid fraction comprising degraded material. The fluid fraction may comprise a liquid and/or a gaseous portion. As explained above, degradation of organic material may result in a solid, a liquid and a gaseous phase. The solid and liquid phases form a slurry and the formed gaseous
25 phase may be captured for further use.

The wording “slurry” as used herein is to be interpreted as an aqueous mass, i.e. a mixture of solids with an aqueous liquid. A slurry is a suspension of insoluble particles in a liquid. Slurries may in some ways behave like thick fluids, flowing under gravity and being capable of being
30 pumped, if not too thick. Thick slurries may behave more like a semisolid material.

The dry solids content of the slurry comprising anaerobically digested organic material to be treated may be about 2 to about 12 % by weight, or

about 3-7 % by weight. The dry solids content of the slurry is measured by drying a sample of the slurry to constant mass at $(105 \pm 5)^{\circ}\text{C}$. The difference in mass before and after drying is used to calculate the dry solids content.

In the present method the slurry is adjusted to a pH below 7, if it not
5 already is at such a pH. The pH of the slurry may be adjusted to be in a range of 1-6.5, or 2-6.5, or 4-6. The adjustment of the pH may be done with at least one acidic material, which may be selected from inorganic or organic acids or acidic metal salts thereof, or a combination thereof. Examples of inorganic
10 acids are sulphuric acid, hydrochloric acid and nitric acid, which also may be used as metal salts or in any combination. Examples of organic acids are formic acid and oxalic acid which also may be used as metal salts or in combination. Examples of acidic metal salts are iron salts.

The addition of the acidic material is made to lower the pH of the slurry. The slurry may be kept in this state before further processing. The acidic
15 slurry may stay acidic for a time period of minutes to several days before any further processing of the slurry. As examples the acidic slurry may be kept for 24h or 48h before the slurry is processed further or the slurry may be kept for a time period of between 1 minute and 2h.

The acidic slurry is brought in contact with an oxidizing agent. The
20 oxidizing agent may be hydrogen peroxide, sodium percarbonate, peracid or potassium permanganate, or a combination thereof. Examples of peracids are peracetic acid and performic acid, which may be used by themselves or in combination. The amount of the oxidizing agent is typically 3–50 kg/ton dry solids. In one embodiment the amount of hydrogen peroxide is 5–30 kg/ton
25 dry solids. The temperature of the slurry during the reaction with the oxidizing agent is in the range of $10\text{--}80^{\circ}\text{C}$, or $20\text{--}75^{\circ}\text{C}$. When the oxidizing agent has been added to the slurry it is allowed to react. A reaction may proceed for a time period of minutes to several days, e.g. 24-72h, 1-24h or 1 minute to 1 hour.

30 Thereafter, the pH of the slurry reacted with oxidizing agent is increased by the addition of an alkaline compound. Suitable alkaline compounds are for example sodium hydroxide, potassium hydroxide and

calcium oxide/hydroxide. The pH is in this step raised to a value above or equal to 8, e.g. 8-13, 8.5-12, 8.5-11, or 9-10.

After the slurry has been adjusted to be within an alkaline range, the slurry is brought in contact with a flocculating polymer. Suitable flocculating polymers may be cationic, nonionic or anionic polymers. Cationic polymers are preferred. Examples of flocculation polymers are starch derivatives, polysaccharides, polyethyleneimines and polyacrylamides. In one embodiment the flocculating polymer is cationic polyacrylamide. The molecular weight of the cationic polyacrylamide is preferably from at least about 500,000, with a range of preferably about 2,000,000 to 15,000,000. The degree of cationic substitution for the cationic polyacrylamide is preferably at least about 1 mol%, with a range of preferably about 5 to 50 mol%. The flocculating polymer assists in a subsequent separation step. Inorganic coagulants like polyaluminum chloride or ferric sulfate may be used with combination of polymeric flocculants. Also, the use of flocculation aids like bentonite is possible.

After the flocculating polymer has been added to and mixed with the alkaline mixture, a separation step is performed, which separates material into a liquid and a solid phase. Such a separation may be performed by any suitable means like by decantation, centrifugation, or filtration.

The filtrate obtained after the separation step may then proceed with further process steps under alkaline conditions, at even a higher pH, without further precipitation or only low amounts of suspended solids appearing due to the increased pH. For example reject waters from a biogas plant may be processed according to the present method and then before a subsequent ammonia stripper the waters would not trigger precipitation of a large amount of suspended solids resulting from the pH increase performed before entry into the ammonia stripper.

Example

An digestate sample (dry solids content 3.87% by weight) of 2.0 kg was taken from a biogas process after a thermal hygienization. The pH of the sample was reduced from the original pH of 7.7 to pH 5 by using H₂SO₄ (95-97% by weight). Defoamer Fennodefo 330 (Kemira Oyj) was used to control

the foam during the addition of the acid. The obtained slurry was mixed for 10 min, after which 3.33 ml of H₂O₂ (50% by weight) was added. The pH then dropped to 4.9. Then the sample was further treated as follows:

Comparative treatment process:

- 5 A sample of 250 ml from the above mentioned treated digestate sample was taken and put into a jar. Then 37.5 ml of a 0.1 weight% solution of cationic high molecular weight polymer (Superfloc C494HMW, Kemira Oyj) was added to and mixed with the slurry. The obtained flocculated slurry was filtered through a 52/32 mesh screen for water separation. The turbidity of the
- 10 obtained filtrate was measured and it was 33 FTU. The pH of the filtrate was then increased to pH 10.82 by using a 50 weight% NaOH solution. Precipitation started to form at pH 7.84. The measured turbidity at pH 10.82 was >1000 FTU.

Treatment process 1:

- 15 A sample of 250 ml from the above mentioned treated digestate sample was taken and put into a jar. The pH was adjusted to 8.07 by using a 50 weight% NaOH solution before addition of a polymer. Then 38.5 ml of a 0.1 weight% solution of cationic high molecular weight polymer (Superfloc C494HMW, Kemira Oyj) was added and mixed with the slurry. The obtained
- 20 flocculated slurry was filtered through a 52/32 mesh screen for water separation. The turbidity of the obtained filtrate was measured and it was 64 FTU. The pH of the filtrate was then increased to pH 10.5 by using 50 weight% NaOH solution. No precipitation was observed and the measured turbidity was 71 FTU.

25 Treatment process 2:

- A sample of 250 ml from the above mentioned treated digestate sample was taken and put into a jar. The pH was adjusted to 9.5 by using a 50 weight% NaOH solution before addition of a polymer. Then 38.5 ml of a 0.1 weight% solution of cationic high molecular weight polymer (Superfloc
- 30 C494HMW, Kemira Oyj) was added and mixed with the slurry. The obtained flocculated slurry was filtered through a 52/32 mesh screen for water separation. The turbidity of the obtained filtrate was measured and it was 42

FTU. The pH of the filtrate was then increased to pH 10.5 by using 50 weight% NaOH solution. No precipitation was observed.

From the above example it is apparent that treatment process 1 and 2 according to the present method clearly limits an unwanted precipitation after a further increase of the pH to 10.5 in comparison with the comparative treatment process. An increased pH before addition of a polymer results in a lower final turbidity value as can be seen from the comparative example of >1000 FTU and the treatment process 1 of 71 FTU. The further increase of the pH in the filtrate are done to imitate the conditions in e.g. an ammonia stripper. The use of an increased pH before the polymer addition results in no precipitation after an increase of the pH of the filtrate obtained after the filtration step. The turbidity values for treatment process 1 only increased from 64 to 71 FTU after the further addition of NaOH, while for the comparative treatment process the values went from 33 to >1000 FTU.

CLAIMS

1. A method of treating a slurry comprising anaerobically digested organic material, which comprises the steps of:

- 5 a) obtaining an acidic slurry at a pH of below 7 by addition of an acidic material to the slurry comprising anaerobically digested organic material, if the slurry comprising anaerobically digested organic material is not already at a pH below 7, so that an acidic slurry at a pH below 7 is obtained,
- 10 b) adding an oxidizing agent to the acidic slurry and allowing to react,
- c) adding an alkaline compound to the slurry obtained in b) to obtain a pH ≥ 8 ,
- d) adding a flocculating polymer to the slurry obtained in c),
- e) separating the slurry obtained in d) into a liquid and solid phase.

15 2. The method according to claim 1, wherein the acidic slurry is obtained by addition of an acid selected from an inorganic acid, preferably sulphuric acid, hydrochloric acid or nitric acid, or a metal salt thereof, or a combination thereof.

20 3. The method according to claim 1, wherein the acidic slurry is obtained by addition of an acid selected from an organic acid, preferably formic acid or oxalic acid, or a metal salt thereof, or a combination thereof.

25 4. The method according to anyone of claims 1-3, wherein the pH of the acidic slurry in step a) is 1-6.5, preferably 2-6.5, preferably 4-6.

 5. The method according to anyone of claims 1-4, wherein the oxidizing agent is hydrogen peroxide, sodium percarbonate, peracid or potassium permanganate.

30

 6. The method according to claim 5, wherein the peracid is peracetic acid or performic acid, or a combination thereof.

9

7. The method according to anyone of claims 1-6, wherein the acidic slurry is treated with the oxidizing agent at a temperature of 10-80°C, preferably 20-75 °C.

5

8. The method according to anyone of claims 1-7, wherein the obtained pH of step c) is 8-13, preferably 8.5-12, preferably 8.5-11, preferably 9-10.

10

9. The method according to anyone of claims 1-8, wherein step e) is performed by decantation, centrifugation, filtration; preferably centrifugation or filtration.

15

10. The method according to anyone of claims 1-9, wherein the digested organic material is the digestate from a biogas plant.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/053171

A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/66 C02F11/14
ADD. C02F1/20 C02F1/52 C02F1/56 C02F11/18

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)
C02F

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 724 084 A (PAHMEIER MAX C [US] ET AL) 9 February 1988 (1988-02-09) column 1, line 49 - column 2, line 45 column 3, line 38 - line 41 column 4, line 27 - line 31 -----	1-10
X	WO 2004/094320 A1 (KEMIRA KEMI AB [SE]; KARLSSON GOERAN [SE]; KARLSSON INGEMAR [SE]; RECK) 4 November 2004 (2004-11-04) cited in the application page 7, line 31 - page 13, line 26 page 2, line 12 - line 15 -----	1-10
A	US 2005/077245 A1 (BLAIS JEAN-FRANCOIS [CA] ET AL) 14 April 2005 (2005-04-14) cited in the application paragraph [0039] ----- -/-	1-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 April 2013

Date of mailing of the international search report

09/04/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Châtellier, Xavier

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/053171

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 221 661 A (SHIMIZU TOHRU ET AL) 9 September 1980 (1980-09-09) example 5 column 4, line 24 - line 31 -----	1-10
X	US 6 368 511 B1 (WEISSENBERG HEINZ-GUENTHER [DE] ET AL) 9 April 2002 (2002-04-09) column 6, line 9 - column 7, line 25 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/053171

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4724084	A	09-02-1988	DE 3650097 D1 17-11-1994
		DE 3650097 T2 16-02-1995	
		DE 3689119 D1 04-11-1993	
		DE 3689119 T2 27-01-1994	
		EP 0238731 A2 30-09-1987	
		EP 0404276 A1 27-12-1990	
		US 4724084 A 09-02-1988	
WO 2004094320	A1	04-11-2004	AT 440806 T 15-09-2009
		BR PI0409786 A 30-05-2006	
		CA 2523225 A1 04-11-2004	
		CN 1787974 A 14-06-2006	
		DK 1615854 T3 21-12-2009	
		EP 1615854 A1 18-01-2006	
		ES 2333123 T3 17-02-2010	
		HK 1092449 A1 04-01-2008	
		HR P20090591 T1 31-12-2009	
		JP 2006524128 A 26-10-2006	
		KR 20060009268 A 31-01-2006	
		NO 331442 B1 02-01-2012	
		PT 1615854 E 26-11-2009	
		RU 2338699 C2 20-11-2008	
		SE 525083 C2 23-11-2004	
		SE 0301171 A 24-10-2004	
		SI 1615854 T1 29-01-2010	
		US 2005000908 A1 06-01-2005	
		WO 2004094320 A1 04-11-2004	
US 2005077245	A1	14-04-2005	AT 488473 T 15-12-2010
		AU 2002221407 A1 10-06-2003	
		AU 2002349219 A1 10-06-2003	
		CA 2468714 A1 05-06-2003	
		EP 1461292 A1 29-09-2004	
		JP 2005510354 A 21-04-2005	
		US 2005077245 A1 14-04-2005	
		WO 03045851 A1 05-06-2003	
		WO 03045852 A1 05-06-2003	
US 4221661	A	09-09-1980	DE 2838386 A1 03-01-1980
		JP S551851 A 09-01-1980	
		US 4221661 A 09-09-1980	
US 6368511	B1	09-04-2002	AU 2278999 A 09-08-1999
		CA 2318092 A1 29-07-1999	
		DE 19802238 A1 29-07-1999	
		EP 1049652 A1 08-11-2000	
		JP 2002500953 A 15-01-2002	
		US 6368511 B1 09-04-2002	
		WO 9937585 A1 29-07-1999	