PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number:
C02F 3/00, 3/34	A1	WO 93/15023
		(43) International Publication Date: 5 August 1993 (05.08.93)

(21) International Application Number: PCT/NO93/00016

(22) International Filing Date: 20 January 1993 (20.01.93)

(30) Priority data:
920290 22 January 1992 (22.01.92) NO

(71) Applicant *(for all designated States except US):* NORSKE MEIERIER [NO/NO]; Breigt. 10, N-0187 Oslo (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only) :* EIDE, Ola [NO/NO]; Hjemliveien 6, N-0667 Oslo (NO). STORRØ, Ivar [NO/NO]; Ullinsveien 16A, N-7033 Trondheim (NO). OTERHOLM, Bjarne [NO/NO]; Langbakken 60, N-1430 Ås (NO).

(74) Agent: MOSTUE, Roger; Bryns Patentkontor A/S, P.O. Box 9566, Egertorget, N-0128 Oslo (NO).

(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).

Published
With international search report.
In English translation (filed in Norwegian).

(54) Title: BIOLOGICAL AND CHEMICAL SINGLE STEP PURIFICATION OF DISCHARGED WATER

(57) Abstract

A method for biological and chemical single-step purification of discharged water. A flocculant and dispersed water are used and biocatalyst particles with immobilized microorganisms or enzymes are added for the conversion of residual products in the discharged water.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**FR**	France	**MR**	Mauritania
AU	Australia	**GA**	Gabon	**MW**	Malawi
BB	Barbados	**GB**	United Kingdom	**NL**	Netherlands
BE	Belgium	**GN**	Guinea	**NO**	Norway
BF	Burkina Faso	**GR**	Greece	**NZ**	New Zealand
BG	Bulgaria	**HU**	Hungary	**PL**	Poland
BJ	Benin	**IE**	Ireland	**PT**	Portugal
BR	Brazil	**IT**	Italy	**RO**	Romania
CA	Canada	**JP**	Japan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SK**	Slovak Republic
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SN**	Senegal
CM	Cameroon	**LI**	Liechtenstein	**SU**	Soviet Union
CS	Czechoslovakia	**LK**	Sri Lanka	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**MC**	Monaco	**UA**	Ukraine
DK	Denmark	**MG**	Madagascar	**US**	United States of America
ES	Spain	**ML**	Mali	**VN**	Viet Nam
FI	Finland	**MN**	Mongolia		

BIOLOGICAL AND CHEMICAL SINGLE STEP PURIFICATION OF DISCHARGED WATER

The invention relates to a method for the purification of discharged water from industrial plants, and more specifically a combination of a specific biological and a general chemical purification process. The Authorities and the community are demanding increasingly stricter standards for the discharge of waste water into the environment. In the following the invention will be explained with reference to discharged water from the dairy industry, but it may be used with every relevant purification process, where substances are to be converted to environmently friendly compounds.

There are today two main processes for the purification of discharged water based on biological and chemical techniques. The principle applied in biological purification is that living micro-organisms are used to metabolize pollutants into harmless compounds and gases.

One of the principles with chemical purification of discharged water from the food industry is that by lowering the pH almost to the isoelectric point of proteins, these are precipitated. With the addition of a flocculant and dispersed air the precipitated proteins will float together with fat which due to the density will float to the surface in a water solution. Sugar and other soluble components are not cleansed through this chemical method.

Chemical purification of discharged water from the food industry is in use or has been in use at several enterprises. Most plants use mineral acid together with a flocculant such as ferric chloride or CMC (carboxyl-methyl cellulose) to adjust pH and as a precipitant for protein which is removed together with fat through flotation or through the addition of dispersed air. If one should want to recover the protein in the chemical sludge for use in animal

feed, other types of precipitants should preferably be used. There exists a batch-type plant where CMC is used as flocculant together with mineral acid, e.g. sulphuric acid and where the sludge is separated through flotation. Figure 1 is an example of such a plant.

The discharged water contains proteins, sugar and fat. It is desirable to obtain a better purification result by also purifying the soluble sugar from the water phase.

The procedure for purification of discharged water in process tanks where a flocculant and dispersed water are used is characterized in that biocatalyst particles with immobilizing micro-organisms or enzymes for conversion of waste products are added to the discharged water. The procedure is further characterized in that sugar, proteins or fat are converted to acid which precipitate the remaining proteins isoelectrically in a combined biological and chemical purification phase. The procedure is also characterized in that proteins and fat are recovered by means of flotation through the addition of a flocculant and dispersed water.

In the process described in the invention this addition of mineral acid is avoided in that in its place bacteria are added, for instance lactic acid bacteria which are immobilized in approximately monodispersed and gasfree biocatalyst particles. In this context biocatalyst means a biological system which comprises micro-organisms or cells, as well as parts of these, for instance enzymes. With biocatalyst particles is meant biocatalysts which are fixed (immobilized) by means of a microscopic carrier, for instance a hydro-colloid cell so that the system may carry out metabolic processes.

With the procedure according to the invention an automatic acid production takes place when these micro-organisms, for

instance lactic acid bacteria, are converting sugar for instance into lactic acid in the discharged water. pH falls to the isoelectric point for proteins, and these precipitate. After an addition of a flocculant and dispersed air the desired purification of organic material is obtained through this combined use of biologic and chemical purification in one step. Thus proteins, fat and sugar are removed. A further advantage with this process may be that the flocculated mass may contain biocatalyst particles with for instance lactic acid bacteria which are a favourable component of animal feed.

In the following the process is explained with reference to Figure 1 which shows a simplified diagram of a batchwise flotation plant for the purification of discharged water from the food industry.

The flotation plant in Figure 1 is a downscaled industrial plant and is a batchwise plants with two process tanks (1) which are filled up alternately. In the experiments each process tank had a diameter of 1.4 m and they were able to treat up to 2.5 m^3 discharged water per batch which was supplied via a pipe (2). On average the consumption of tap water (9) was 10-15% of the quantity of discharged water supplied (2).

The flotation plant was PLC controlled (10) (Programmable Logic Control). It was operated in such a way that pH in the process tank was adjusted to 4.2 when acid was added. Alternatively, pH may be adjusted by converting lactic sugar to organic acid, for instance lactic acid by using biocatalyst particles. Flocculant (approx. 8 mg/1 CMC) was added and flotation began. Otherwise the plant was equipped with a battery of pump valves (3), an acid tank (4), a tank for the flocculant (5), compressor (6), dispersion water tank (7) as well as sampling points (8).

The temperature and pH of the discharged water were continuously measured and recorded. During the production periods the temperature of the discharged water varied mostly between 10 and 50° C, with extreme values ranging from 5 to 55°. Normally the pH value in the discharged water was between pH 5 and pH 10. However, extreme values from pH 3.5 to Ph 12 were measured. Most of the time the pH value was on the alkaline side.

A characterization of the crude water, based on water-chemical analyses of a mixture of weekly samples and a mixture of samples during a 24 hour period is shown in Table 1.

TABLE 1

	WEEKLY MIX				24 HOUR MIX			
	MEAN	MAX	MIN	NUMBER OF SAMPLES	MEAN	MAX	MIN.	NUMBER OF SAMPLES
Total COD, g/m^3	3190	4730	1420	22	3310	8200	1070	44
Filtered COD, g/m^3	1050	2290	650	3	1410	3546	433	36
Total BOD_7 g/m^3	1950	2200	1670	3				
Filtered BOD_7 g/m^3	970	1100	640	3				
Total BOD_7 COD	0.59	0.65	0.52	3				
Filtered BOD_7/,	0.74	0.75	0.56	3				
Total P, g/m^3	6.7	12.1	4.4	28	8.5	26.4	1.0	31
Total N, g/m^3	43	46	33	3				
Suspended substances (SS) g/m^3					820	3000	220	28
Fat, g/m^3					690	1900	270	16

Table 1. Characterization of non-purified dairy discharge water in the period week 13 to week 37 1990, based on mixed 24 hour samples and mixed weekly samples, with proportionate water quantity. The dairy is a plant based on special milk products for consumption.
COD=chemical oxygen consumption, BOC=biological oxygen consumption, P=phosphorous, N=Nitrogen

The mean value for total COD (Chemical Oxygen Demand) shows a concentration of 3200-3300 g/m^3. However, there were relatively large variations from week to week, and especially from one day to another. 24-hour emissions with concentrations up to 2.5 times higher than the mean values for organic compounds were registered. It is important to take these variations into account when dimensioning a purification plant.

When testing various purification processes a batchwise flotation plant in laboratory scale was used. With the laboratory plant it is possible to test a larger number of precipitants in a relatively short time. In order to obtain optimal purification effect of the given flocculants, it is customary to adjust pH by adding a mineral acid, for instance sulphuric acid. There was a desire to use the laboratory plant to test the adjusting of pH with lactic acid as an alternative to sulphuric acid.

A survey was performed in the plant of combinations of various precipitants and flocculants. Table 2 provides an overview of alternative combinations.

Table 2

Alt.	pH adjustment	Flocculant
1	H_2SO_4	Ferric chloride
2	H_2SO_4	Ultrazine
3	H_2SO_4	CMC
4	Lactic acid	CMC
5	Biocatalyst particles	CMC

Table 2. Alternative combinations in the laboratory flotation plant.

The tests with the laboratory flotation plant showed that

use of Ultrazine gave the poorest result. This process variant therefore was considered the least interesting alternative. The bar diagram in Figure 2 sums up which purifying effects may be achieved under optimal conditions with four other combinations. Ferric chloride (JCL) removed 2-3% more of total COD than H_2SO_4+CMC, which in turn removed 1-2% more of total COD than lactic acid + CMC. It is possible with biocatalyst particles to remove over 30% more of total COD than with the other methods, since sugar is also removed through this method. Protein was removed somewhat more efficiently with ferric chloride than with the other combinations. However, this is not a very advantageous method when the process concentrate (the sludge) is to be used as animal feed.

On the basis of the test results, table 3 gives a proposal for the precipitation, coagulation and flotation conditions for chemical purification of discharged water from dairies, and for combined biological and single-step chemical purification of discharged water from a dairy.

Table 3

Flocculant type	Flocculant dosage	pH adjusting component	Desired pH	Dispersion water qty.
FCL	0.3 ml/l	H_2SO_4 or NaOH	4.5-5.5	20%
CMC	6-10 mg/l	H_2SO_4	4.1-4.3	10%
CMC	6-10 mg/l	Lactic acid	4.1-4.3	10%
CMC	6-10 mg/l	Biocatalyst particles	4.1-4.3	10%

The use of lactic acid direct as an alternative to sulphuric acid for pH adjustment is most interesting. Particularly because lactic acid is an advantage if the sludge is to be used for animal feed. The laboratory tests showed that the use of lactic acid resulted in a purification factor which was only insignificantly lower than with the use of

sulphuric acid.

By adding spherical biocatalyst particles together with e.g. immobilized anaerobic micro-organisms, e.g. lactic acid bacteria, the same precipitation of protein is achieved as by adding lactic acid when the bacteria converted the sugar in the discharged water to organic acids, for instance lactic acid. By adding bacteria to these particles it is thus possible to achieve good purification results since none of the other methods removes sugar. The addition of acid is avoided since the bacteria convert the sugar to lactic acid, and the sludge will after dehydration to process concentrate be well suited for use in animal food mixtures. By using gasifying micro-organisms, e.g. hetero-fermentable lactic acid bacteria, alternatively facultative anaerobic micro-organisms, the resulting gas production will help reduce the need for dispersed air used for the flotation of the protein material.

The biocatalyst particles to be used may be produced by any appropriate method, and one method is e.g. described in a parallel patent application, cp. No. C29881.

The invention is mainly described with reference to the use of lactic acid bacteria, but the process is not limited to using these bacteria. The type of bacteria may vary according to the substances and compounds one wishes to convert into harmless, eco-friendly products. In the place of bacteria, enzymes may also be used in the biocatalyst particles in order to metabolise special compounds.

Patent claims

1.

A method for the purification of discharged water in process tanks where a flocculant and dispersed air in water are used, characterized in that biocatalyst particles with immobilized micro-organisms or enzymes are added, for the conversion of residual products in discharged water, so that sugar, proteins or fat is converted into acid which precipitates the remaining proteins isoelectrically in a combined biological and chemical purification phase.

2.

A method according to claim 1, characterized in that proteins and fat are recovered by means of flotation through the addition of a flocculant and dispersed air in water.

3.

A method according to claims 1-2, characterized in that the consumption of dispersed air in water may be reduced through the addition of gasifying micro-organisms immobilized in the particles.

4.

A method according to claims 1-3, characterized in that flotation results in a process concentrate which e.g. may be used as animal feed.

5. A method according to claims 1-4, characterized in that biocatalyst particles become part of the process concentrate.

6.

A method according to claims 1-5, characterized in that the temperature in the process water is kept between 10 and 50^{o}C.

FIG.1

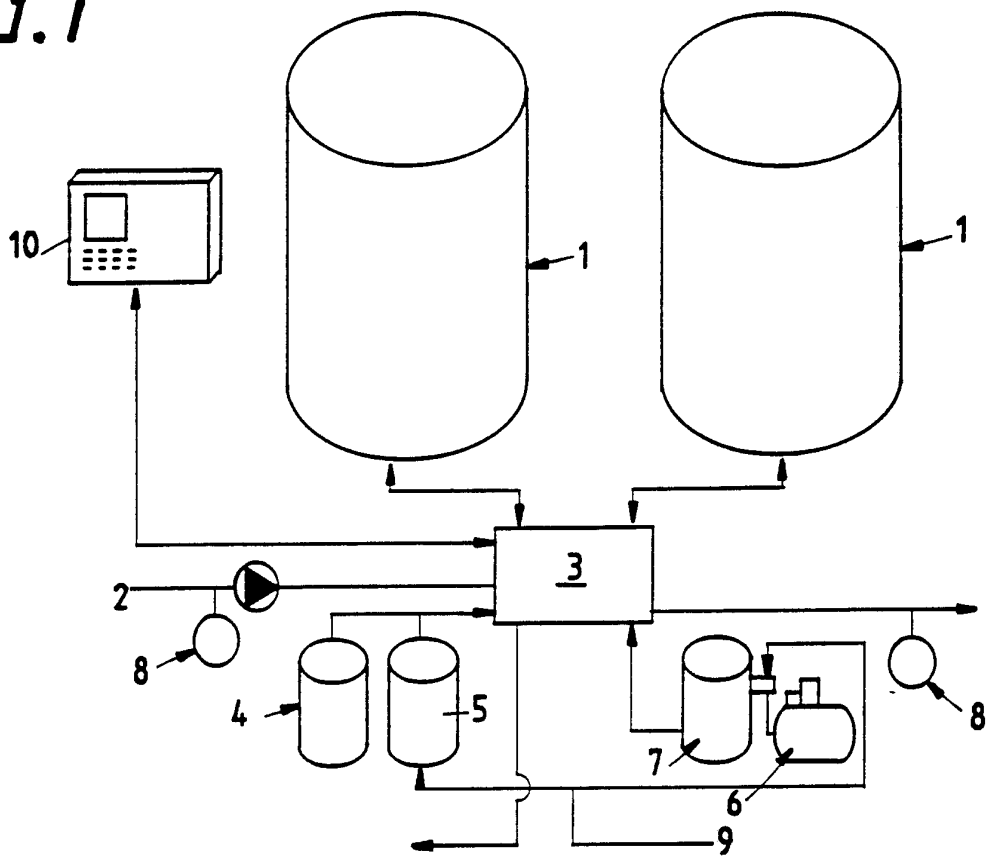
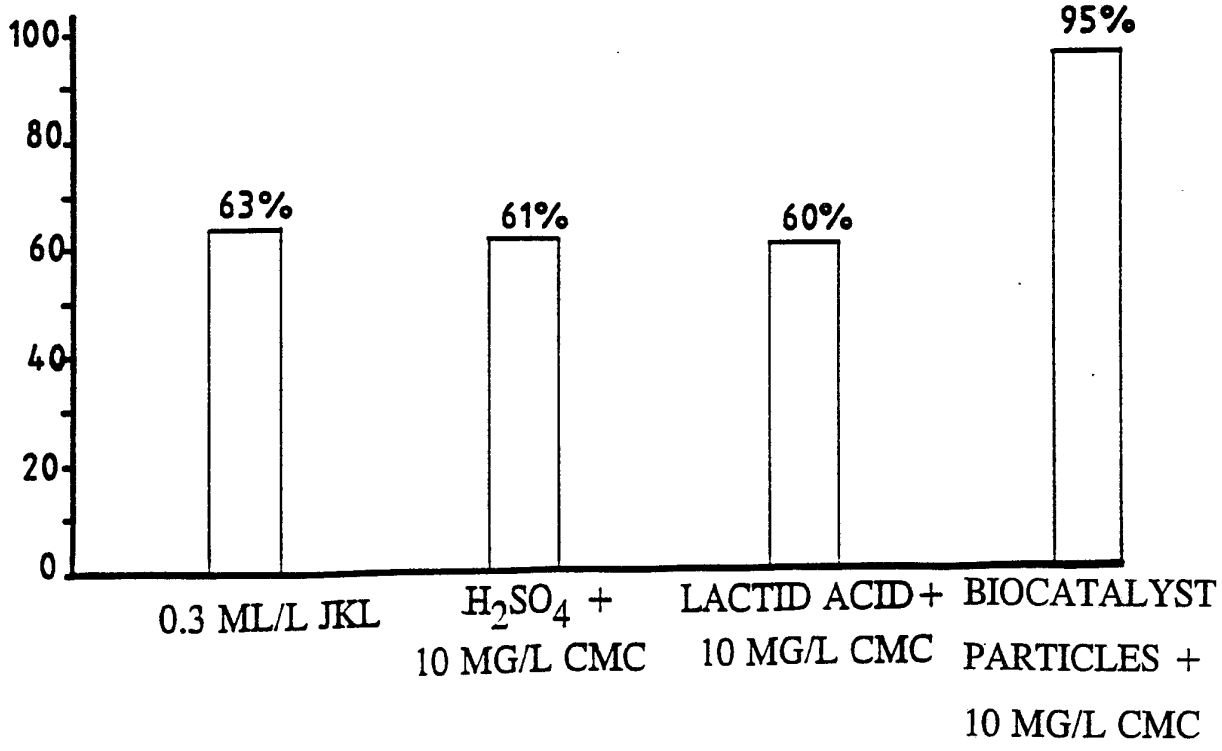

10
1
1
3
2
8
4
5
7
6
8
9

FIG.2


100
80
60
40
20
0
63%
61%
60%
95%
0.3 ML/L JKL
H_2SO_4 + 10 MG/L CMC
LACTID ACID + 10 MG/L CMC
BIOCATALYST PARTICLES + 10 MG/L CMC

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 93/00016

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C02F 3/00, C02F 3/34
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)

IPC5: C02F

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

SE,DK,FI,NO classes as above

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

WPI, CLAIMS, FILE 399

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4436624 (EBERHARD KREUZBURG ET AL), 13 March 1984 (13.03.84), column 4, line 28 - line 65, claim 1 --	1
A	GB, A, 2167399 (VEB PROJEKTIERUNG WASSERWIRTSCHAFT), 29 May 1986 (29.05.86), page 3, line 106 - page 4, line 8, claims 1,2 --	1
A	FR, A, 2142159 (WEGMANN RAYMOND ET AL), 26 January 1973 (26.01.73), page 1, line 11 - line 19, claim 1 --	1

[X] Further documents are listed in the continuation of Box C. [X] 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" erlier document 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	Date of mailing of the international search report
10 May 1993	12 -05- 1993
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Bo Bergström Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 93/00016

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Patent Abstracts of Japan, Vol 9,No 130, C-284, abstract of JP, A, 60-14996 (kokuzeicho), 25 January 1985 (25.01.85) -- --------	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

31/03/93

International application No.
PCT/NO 93/00016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4436624	13/03/84	DE-A- 3011844	01/10/81
		FR-A,B- 2479020	02/10/81
		GB-A- 2072650	07/10/81
		JP-A- 56158057	05/12/81
		SE-A- 8101878	28/09/81
GB-A- 2167399	29/05/86	AT-B- 391856	10/12/90
		DE-A- 3441690	15/05/86
		FR-A,B- 2573748	30/05/86
FR-A- 2142159	26/01/73	NONE	