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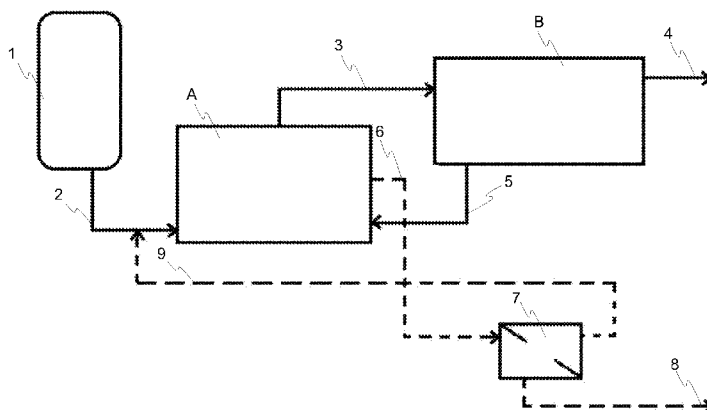
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(54) Title: METHOD FOR WATER RECOVERY IN HIGH VOLUME AND GOOD QUALITY FROM INDUSTRIAL
WASTEWATERS

FIGURE 1



(57) Abstract: The invention, is related to purifying industrial wastewaters, using hybrid and integrated different combinations of the technological configurations of novel, innovative oxidation process/membrane processes (AOP/MP); in order to (i) recover good quality industrial reuse water at high volumes by reducing the volumes and/or loads of membrane concentrate pollutants and to (ii) provide a more economical industrial water recovery method in comparison to MP applications which do not comprise concentrate management with final concentrate disposal costs that are decreased in connection with reduced concentrate volumes.

DESCRIPTION

METHOD FOR WATER RECOVERY IN HIGH VOLUME AND GOOD QUALITY FROM INDUSTRIAL WASTEWATERS

5

Technical Field

The present invention is related to a water recovery method which enables high
10 volume and good quality water to be recovered from industrial wastewaters.

The invention, is particularly related to purifying industrial wastewaters, using
hybrid and integrated different combinations of the technological configurations
of novel, innovative oxidation process/membrane processes (AOP/MP); in order
15 to (i) recover good quality industrial reuse water at high volumes by reducing the
volumes and/or loads of membrane concentrate pollutants and to (ii) provide a
more economical industrial water recovery method in comparison to MP
applications which do not comprise concentrate management with final
concentrate disposal costs that are decreased in connection with reduced
20 concentrate volumes.

Prior Art

Concentrate streams which are difficult to be disposed of are frequently
25 encountered during treatments (purification) in field scale focusing on recovering
by-products and water from various industrial wastewaters using membrane
processes (MP). Together with membrane contamination, the difficulties faced
during the management processes of concentrate waste, are factors which
basically technologically and economically limits the widespread usage of
30 integrated membrane applications. In fact, wastewaters of high water-consuming
industries such as textile can be treated by using membrane processes that result
in high volume of membrane concentrate streams and generally, these

concentrates that fall under the category of hazardous waste can be incinerated according to zero liquid discharge approach but high disposal costs are encountered up to 30-150 \$/m³ of concentrate if incineration is selected as an option. On the other hand, applications selected for water recovery in large amounts have high operating costs due to increased energy expenditure and simultaneously, the pollutant removal efficiency performance of the membrane (rejection) can significantly decrease. These considerations bring about the treatment of relevant industrial wastewaters and the water recycling and reuse from these waters that need to develop innovative applications of membrane treatment system having different combinations of processes and cost effective in field which include environmentally sustainable management methods and/or applications for membrane concentrates.

The disposal methods of industrial membrane concentrate streams change according to wastewater characteristics. Some methods are following: (i) Landfill application, (ii) Incineration, or (iii) Discharge to a centralized wastewater treatment plant, and these methods are widely accepted as main practices for disposal options in our country. However, such disposal methods in industry are generally used for the removal of the membrane concentrates having low/very low volumetric loads. At the industries having intensive water consumption, not only for our country but also around the world, the innovative concentrate management methods for more effective environmental protection and its practical usage needs to be developed. Particularly, the textile industry is one of the intense water-consuming industries and a method named as zero liquid discharge approach was firstly proposed in 2004 together with its methodology and technology. In this approach, the incineration process can be used for ultimate stream of concentrates but the inert solid waste after the incineration is obtained whereby the presence of liquid wastes to be discharged to a receiving environment can be prevented and excessive energy consumption in the process and hence a very high operating cost for the treatment facility has not still permit to use the zero liquid-discharged disposal methods for membrane concentrates in practice.

Nowadays, the increase in field applications of membrane processes requires the development of effective and suitable disposal methods for membrane concentrate streams. Indeed, depending on the specificity of treatment practices with various
5 membrane processes the development of appropriate disposal method at the technical, economic and environmental integrity is to be very difficult. Therefore, the operating cost for a specified membrane treatment system increases depending on the costs of concentrate disposal methods, and this leads to decreasing of its practical applications.

10

For the final disposal of membrane concentrates, although there is a large number of method in practice but an absolute environmental protection at concentrated management is literally impossible. As concentrated flows of the membranes contain several pollutants at high concentrations, these types of wastewaters have
15 a high impact on discharge points and its close vicinity. Therefore the qualities of high pollutant concentrations and especially the volumetric loads of the concentrates highly restrict disposal options of these wastes in financial point of view. In this context, problems are faced drying the reduction stage of the final concentrate volume after water is recovered for reuse from high water-consuming
20 industries, using pressure driven membranes. At this point, advanced oxidation process (AOP) and especially pressure driven membrane processes (MP) which are leading technologies draw attention in treatment of industrial wastewaters that contain complex organic matters and/or matters that are resistant to biological treatment.

25

In the Chinese patent document numbered CN203754570 of the known state of the art, a method which is used for recovering water from wastewater in the textile sector is described. In said method, a tank in which the oxidation process is carried out and a filtering tank in which the membrane process is carried out is
30 present.

- In the Chinese patent document numbered CN103496807 of the known state of the art, a wastewater recycling process is described which comprises an oxidation and a membrane process.
- 5 In the German patent document numbered DE19806768 of the known state of the art, a system which comprises a reactor for the oxidation process and in which the wastewater obtained from the membrane process is delivered to the reactor is described.
- 10 However the methods mentioned in these patent documents are not sufficient to solve the problems mentioned in detail, above.

The Objects and Brief Description of the Invention

- 15 The aim of this invention is to carry out an integrated treatment method without any reduction in the chemical oxidation reaction performances of the AOP process and by reducing the operation costs of a treatment plant including the disposal of concentrates with higher synergic performance in AOP and MP.
- 20 Another aim of the invention is to provide a treatment method by means of an integrated AOP/MP industrial wastewater treatment system, wherein said system comprises achieving lower final disposal costs for concentrates by reducing volume and loads in membrane concentrate streams, providing the operation of a treatment plant with lower costs, and enabling a more economical production of
- 25 re-use water having good quality and high volume, in comparison to MP applications which do not utilize concentrate management , by means of treating industrial wastewaters that are by-products of various industries.

- Proposed AOP/MP treatment system will be applied to target industrial
- 30 wastewaters in two sequenced steps under an integrated structure. The hybrid AOP/MP ("advanced oxidation+submerged membrane" within the same reactor)

application is present in the I. stage treatment step. Following this step, during the II. stage, MP treatment applications (external MP applications integrated to the hybrid AOP/MP application) having different configurations are carried out. With this innovative treatment system, (i) Organic substrate treatment is achieved
5 by chemical oxidation reactions (oxidation, catalytic oxidation, photo-oxidation or photo-catalytic oxidation) that occur in the hybrid AOP reactor during the I. stage treatment step which reduces the loads of organic pollutants on external membrane processes during the II. stage treatment step; as a result the submerged membrane process will be operated with lower pollution and higher water flux
10 due to simultaneous chemical reaction present in surface fouling layer on submerged membrane. (ii) Due to carrying out of submerged membrane application in hybrid AOP reactor during the I. stage treatment step, the separation of sludge generated by chemical oxidation reactions in the reactor is performed with an additional sedimentation with highly diminishing treatment time, and
15 therefore this decreases the investment and installation area and simplifies operation by combining two processes in a hybrid reactor without an additional clarification/sedimentation process. (iii) By means of the integrated AOP/MP industrial wastewater treatment system, concentrated flows of external membrane processes at the II. stage treatment are rerouted to AOP reactor at I. stage
20 treatment step and cyclic treatment is achieved; as a result the decrease in the pollutant load and volume of the membrane concentrates generated in the II. stage treatment step is obtained in the overall treatment system. Low volume of the final concentrated wastes at lower concentration of resistant organics are produced relative to the application of configuration of integrated MP/AOP (external MP at
25 treatment I Stage + AOP at treatment II. stage) treatment of membrane process concentrates at the final step with AOP.

Detailed Description of the Invention

The combined membrane systems that have been provided to achieve the method used in order to reach the aims of the invention have been illustrated in the
5 attached figures.

According to the Figures;

Figure 1, is the schematic view of the industrial wastewater treatment method
10 with advanced oxidation/membrane processes (AOP/MP), reduction of the load of membrane concentrates and recovering good quality water with high volume.

Figure 2, Is the schematic view of the different membrane processes which belong to the two or three step external MP applications of the AOP/MP technological
15 configuration.

The parts in the figures have each been numbered and their references have been listed below.

- 20 (A) Hybrid AOP/submerged MP treatment step of AOP/MP integrated industrial wastewater treatment facility (I. Stage purification step)
- (B) Treatment step of one, two- or three-step integrated MP application of AOP/MP integrated industrial wastewater treatment facility (II. Stage purification step)
- 25 (C) Technological configuration of AOP/MP containing hybrid AOP/submerged MR reactor following by one step external MP application (single phase external MP application of the II. Stage purification step)
- (D) Technological configuration of AOP/MP containing hybrid AOP/submerged MR reactor following by two step external MP application (double phase external
30 MP application of the II. Stage purification step)

(E) Technological configuration of AOP/MP containing hybrid AOP/submerged MR reactor following by three step external MP application (triple phase external MP application of the II. Stage purification step)

- 5 1) Raw wastewater feed tank
- 2) Wastewater feed line to hybrid reactor
- 3) Submerged membrane process permeate flow
- 4) Treated reuse water discharge line
- 5) Return line of membrane concentrates to hybrid reactor
- 10 6) External membrane process (MF and/or UF) feed line for further decreasing the volume of volume-reduced concentrate
- 7) External membrane process (MF and/or UF) used to further decrease the volume of volume-reduced concentrate
- 8) Final volume-reduced concentrate discharge line
- 15 9) Back feed line of sludge free (filtered from the solids it contains) external membrane process permeate flow to hybrid reactor,
- 10) Hybrid AOP/Submerged MP reactor (Hybrid AOP reactor)
- 11) First step external membrane process permeate flow (reuse water discharge line of configuration (C))
- 20 12) Second step external membrane process permeate flow (reuse waste discharge line of configuration (D))
- 13) Third step external membrane process permeate flow (reuse waste discharge line of configuration (E))
- 14) First step external membrane process concentrate flow
- 25 15) Second step external membrane process concentrate flow
- 16) Optional second step external membrane process concentrate flow
- 17) Third step external membrane process concentrate flow
- 18) Optional third step external membrane process concentrate flow I
- 19) Optional third step external membrane process concentrate flow II
- 30 20) Submerged MF and/or UF membrane process
- 21) Diffusers

- 22) First step external membrane process (MD, NF_{loose}, NF_{tight} or RO)
 - 23) Second step external membrane process (MD, NF_{tight} or RO)
 - 24) Third step external membrane process (MD or RO)
 - 25) Second and third step membrane process concentrates return line optional
- 5 to first step external membrane process

Integrated AOP/MP industrial wastewater treatment system where general operational lines is given in Figure 1, treats wastewater from industries being used water in high volumes and addition to that it produce reuse water from wastewater

10 for industrial recovery so decrease the volumetric or waste loads of the membrane concentrates. With this system, industrial wastewater treatment and water recovery process will be achieved at lower operational expenses due to lower concentrate elimination cost in respect to common MP/AOP industrial wastewater treatment system. In system operation firstly, wastewater stored in raw industrial

15 wastewater storage tank (1) is fed to hybrid reactor (hybrid AOP/submerged membran) via the raw wastewater feed line (2) where the AOP/MP integrated industrial waste water treatment plant AOP/submerged MP treatment step (A) is carried out. Sumerged MF and/or UF membrane process (20) and air and/or gas blowing diffusers (21) that have been projectively installed into the hybrid

20 AOP/submerged MP reactor are provided in order to draw the wastewater that has been treated with oxidation out of the reactor. The wastewater that has been treated in the hybrid reactor using intermittent, semi continuous and continuous operations, is drawn out of the reactor by means of a submerged MP permeate line (3) and is directed to integrated external MP step (treatment step (B) of single or

25 successive two or three stepped integrated MP applications of the AOP/MP integrated industrial wastewater treatment plant). Following the treatment of the hybrid reactor output water using intermittent, semi-continuous or continuous treatments within the integrated MP applications treatment step of single or successive two or three stepped integrated MP applications of the AOP/MP

30 integrated industrial wastewater treatment plant; the treated re-use water is received from the treated re-use water discharge line (4) and the clean water is

used as re-use water during the process or in the industry. The membrane concentrates created by external MP treatments are rerouted to hybrid reactor via return line (5) and treated again. Independent from the intermittent, semi continuous and continuous operations carried out in treatment steps (A) and (B),
5 by means of the continuous cycle what can be achieved in a circular time period where minimum discharge criteria is met, cleaner water production at higher volumes (in other words decreased volumetric and/or waste load of concentrates) can be achieved. An additional volume reduction procedure can be achieved voluntarily or as an obligation in the membrane concentration, by means of an
10 external membrane process (7) which is used to additionally decrease the volume of concentrate. When the time scale specified for application choices of AOP chemical reactions and MP combinations having waste water characteristics that may impair the quality of the discharge water for reuse during the discharging of the treatment step (B) is completed; excess concentrate flow in hybrid reactor,
15 which has not been treated or cannot be further treated, is directed to external membrane process (MF,UF or MD) (7) that is used to further reduce the concentrate volume, via the feed line (6) in order to further reduce the concentrate volume of the reduced volume concentrate in order to separate the flow from its solid contents (sludge). During the membrane process used that is independent
20 from the system, in order to additionally reduce the volume of the concentrate, the membrane concentrate whose final volume has been reduced by to 1/10th to its original volume is directed to the final disposal area via the concentrate discharge line (8) which is used to discharge concentrates whose final volume have been reduced. Permeate stream of external membrane process without any sludge
25 content, where the sludge is removed (from which the solids it contains have been removed) which may contain soluble organics besides high concentration of soluble inorganic matter is fed to the hybrid reactor via the feedback line (9). Feeding process is performed by diluting the permeate with raw wastewater to decrease the discharge water quality of the treated water to the level of input flow
30 value wherein the next cyclic time scale can be continued safely. The membrane concentrate which is continuously treated in the hybrid reactor for definite time

cycle can be discharged out of the system as the final membrane concentrate, without being treated by external MP if additional process of concentrations are not needed, and the concentrate can be consequently eliminated by using one of the appropriate ultimate waste disposal methods.

5

In the integrated AOP/MP industrial wastewater treatment system of the invention, the treatment step (A) is the hybrid membrane process where AOP is used together with submerged microfiltration and/or ultrafiltration (UF). The target wastewater is removed from its suspended solids by passing from grid filter
10 prior to the hybrid AOP reactor process. Therefore a more effective oxidation performance of AOP and operation of submerged membrane under lower suspended solid loads can be achieved. AOP contains not only UV radiation as a high energy source but also strong oxidizing agents (H_2O_2 , O_3 , Fe^{6+} etc.) and micro and/or nano particle catalysers ((Fe, Mn, Cu, TiO_2 etc.). The operation of
15 the process can be carried out by using one of the desired efficient wastewater methods from selected oxidation processes (homogenous (UV, H_2O_2 , O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, etc.), and catalyser assisted heterogenic (Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), Fenton like, photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$), etc.)). The main operation principle of AOP is to create a free hydroxyl radical in
20 water to oxidize resistant organics, thereby transforming organic pollutants to final stable products (such as CO_2 , N_2). The membrane concentrate of treatment step (B) which cycled back to reactor, is mixed with the raw wastewater that has been fed to the reactor and is diluted inside the reactor under reduced organic pollutant loads. By this means, the reactor is operated for longer period of times
25 at lower organic pollutant levels. In this context, lower volumes of concentrates are achieved in unit operation time as opposed to integrated MP/AOP configuration applications where raw wastewater is treated first in MP and then membrane concentrates, separately or together treated by AOP. At this point, it should be noted that concentrate disposal costs are higher than the expenses of
30 industrial wastewater treatment; therefore hybrid and integrated AOP/MP systems provide a lower concentrate disposal cost and relatively lower unit wastewater

- treatment expenses in respect to the known applications of MP/AOP. The invention subject to the patent contributes to the reduction of the direct or indirect adverse environmental effects of the relevant sectoral activities through the reduction of the consumption of natural resources (water, purification chemicals, energy, etc.) by increasing water recycling and by the industrial membrane diversion loads which are quite harmful to the environment, in addition to the economic benefits to the target sectors, which focus on water and wastewater management.
- 10 For purpose of high volume and good quality industrial water reclamation using hybrid and integrated AOP/MP industrial wastewater treatment facility, applications of external MP (treatment step (B)) which are integrated to the hybrid reactor AOP/MP (treatment step (A)) with different process combinations at one, two- or three-steps can be seen in Figure 2 schematically. Membrane technologies
- 15 under the scope of external MP applications during treatment step (A) targeting industrial water recovery from wastewater are membrane distillation (MD), nanofiltration (NF) and reverse osmosis (RO) applications and the NF process is named as NF_{loose} and NF_{tight} according to molecular weight cut-off of the membrane (for instance, pore size of 1000 Da and 400 Da respectively). General
- 20 operation principles and external MP application combinations with one step or sequential two or three steps in the context of treatment step (B) of the advanced industrial wastewater treatment system which is subject of the patent is presented in detail below.
- 25 MD process is a membrane process which provides recovery of treated water with good quality and high filtration performance (>99% for soluble organics and inorganics except for volatile organics) by using a heat-driven micro pore membrane (mainly hydrophobic). Solely by temperature difference without pressure application the membrane allows passage of water vapour through the
- 30 pores while preventing the passage of water flow there-through. The water vapour that passes through the membrane is condensed at the cold flow side and as a

result treated water is produced. As a result the MD process provides permeate/distillate having high purity by preventing mixing of non-volatile substances to water vapor. The process can be applied having 4 different contents including direct contact, air gap, sweeping gas and vacuum depending on its technological structure. Efficiency of the process is well-known in the treatment of industrial wastewaters, but its field-scale applications with different technological contents are already among remarkable subjects of MD researchers.

NF process is the foremost one of the pressure-driven processes. The process has operational pressure of 5-30 bars and it is located between the UF and RO processes in respect to contaminant separation size and it is used effectively in treatment of water and wastewater (90% or above) for two or more charged soluble inorganics and organics having large molecular sizes (1000 Da or above). NF is commonly preferred for wastewater management applications at the scope of recovery from organic-inorganic mixed waters and it is known that the process is used to recover water in process quality from pulp and paper industrial wastewater with the combination of NF_{loose} followed by NF_{tight}.

RO process is the last step in pressure-driven membrane processes and it possesses the least molecular separation size. The process uses high pressure (10-130 bar, commonly 20-60 bar), and high performance filtration (99% or above) which can be achieved even in very low molecular-sized soluble organics (100 Da) as well as monovalent soluble inorganic matter. It is widely used in order to recover clean water in good enough quality from primarily sea water and industrial wastewaters.

The (B) treatment step of the hybrid and integrated AOP/MP advanced industrial wastewater system comprises an operation which provides a second step external membrane process permeate flow ((D) reuse water discharge line whose configuration has been treated) (12) and third step external membrane process permeate flow ((E) reuse water discharge line (4) whose configuration has been

treated) (13) from the treated reuse water discharge line (reuse water discharge line whose configuration has been treated by first step external membrane process permeate flow (C) for (C), (D) and (E) respectively) (11), by treating the submerged membrane process permeate flow (3) of the (A) treatment step

5 discharge waters using one of the different process combinations that belong to external MP applications having one (C), two (D), or three (E) steps; (first step external membrane process (22) (MD, NF_{loose}, NF_{tight} or RO) for (C), (D) and (E) respectively, (first step external membrane process (22) (MD, NF_{loose}, NF_{tight} or RO) and second step external membrane process (23) (MD, NF_{tight} or RO), or by

10 first step external membrane process (22) (MD, NF_{loose}, NF_{tight} or RO) , second step external membrane process (23) (MD, NF_{tight} or RO) and third step external membrane process (MD or RO) (24). Different external MP combinations during the treatment step (B) are present to meet the criteria of the different characteristics of industrial wastewaters belonging to high water-consuming

15 industries and the desired qualities of industrial recovery water. In other words, for the purpose of water recovery from target wastewaters, one of the best system design combinations of AOP/MP advanced industrial wastewater treatment (that enables the lowest operational expense, industrial water recovery at the highest water quality and water recovery ratio providing minimal concentrate load)

20 subject to the invention is preferably implemented in practice.

In sequence with the treatment step (A) (hybrid AOP/submerged MP reactor), all combinations of the treatment step (B) which are used to recover water in high volume and good quality from target industrial wastewaters and that are used to

25 obtain lower membrane concentrate loads are given down below:

- ✓ External MP application (C) treatment system combinations in one step, comprises 3 different applications; where the first step external membrane process concentrate stream (14) is delivered to the hybrid AOP/submerged
- 30 MP reactor (10) via the membrane concentrate direct return line (5) of the hybrid reactor;

- $\square$ (C)-(I) : (A) + MD
- $\square$ (C)-(II) : (A) + NF_{tight}
- $\square$ (C)-(III) : (A) + RO

5

- ✓ Treatment system combinations with external MP applications (D) in two steps, comprises 8 different applications where the first step external membrane process concentrate stream (14) and second step external membrane process concentrate stream (15) is delivered to the AOP/submerged MP reactor (10) via the membrane concentrate return line (5) of the hybrid reactor, along with the returning of optional second step external membrane process concentrate stream (16) to the first step external membrane process (22), and to the optional first step external membrane process, via optionally the second and third step membrane process concentrates return line (25).

15

- $\square$ (D)-(I) : (A) + MD + NF_{tight}
- $\square$ (D)-(II) : (A) + MD + RO
- $\square$ (D)-(III) : (A) + NF_{loose} + NF_{tight}
- $\square$ (D)-(IV) : (A) + NF_{loose} + RO
- $\square$ (D)-(V) : (A) + NF_{loose} + MD
- $\square$ (D)-(VI) : (A) + NF_{tight} + RO
- $\square$ (D)-(VII) : (A) + NF_{tight} + MD
- $\square$ (D)-(VIII) : (A) + RO + MD

20

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- ✓ Treatment system combinations with external MP applications (E) in three steps, comprises 7 different applications, where the optional second step external membrane process concentrate stream (16) is delivered to the first step external membrane process (22), and optional third external membrane process concentrate stream I (18) and optional third step external

30

membrane process concentrate stream (II) (19) are delivered to the second external membrane process (23) and the first external membrane process (22) respectively by means of the optional third step external membrane process concentrate stream I (18) and the first step external membrane process, optional second and third membrane process concentrates return line (25); wherein the membrane concentrate streams (first step external membrane process concentrate stream (14), second step external membrane process concentrate stream (15) and third step external membrane process concentrate stream (17)) are returned (5) via the membrane concentrates return line (5) of the hybrid reactor, to the AOP/submerged MP reactor (10).

- ✓ □ (E)-(I) : (A) + MD + NF_{tight} + RO
- ✓ □ (E)-(II) : (A) + NF_{loose} + NF_{tight} + MD
- ✓ □ (E)-(III) : (A) + NF_{loose} + NF_{tight} + RO
- ✓ □ (E)-(IV) : (A) + NF_{loose} + RO + MD
- ✓ □ (E)-(V) : (A) + NF_{loose} + MD + RO
- ✓ □ (E)-(VI) : (A) + NF_{tight} + RO + MD
- ✓ □ (E)-(VII) : (A) + NF_{tight} + MD + RO

The aim of this invention is to provide a treatment method by means of an integrated AOP/MP industrial wastewater treatment system, wherein said system comprises achieving lower final disposal costs for concentrates by reducing volume and loads in membrane concentrate streams, providing the operation of a treatment plant with lower costs, and enabling a more economical production of re-use water having good quality and high volume, in comparison to MP applications which do not utilize concentrate management, by means of treating industrial wastewaters that are by-products of various industries.

CLAIMS

- 1) The invention is an integrated advanced industrial wastewater treatment method, having different combinations of the AOP/MP technological configuration which enable to reduce the volume/loads of membrane concentrate streams and to provide industrial water recovery and treatment of industrial wastewaters, characterized in that; it comprises step (A) and following this, step (B) ("A)+(B)"), and in that it the system also externally comprises the MF, UF and/or MD process which enables to reduce additional membrane concentrate loads.
- 2) A method according to claim 1 characterized in that; within the scope of the first step treatment (A), the treatment of the membrane concentrate stream of the raw wastewater that has been returned via the membrane concentrate return line (5) of the hybrid reactor, during the (B) treatment step is carried out together, simultaneously/successively with the advanced oxidation and submerged membrane process application over the raw waste water feed line (2) of the hybrid reactor, inside the hybrid AOP/submerged MP reactor (10).
- 3) A method according to claim 1 and 2, characterized in that; the submerged membrane process permeate stream (3) obtained from the (A) treatment process, is treated with one of the different process combinations (Respectively 22;22 and 23; 22,23 and 24 for (C), (D) (E)) of external MP applications having one (C), two (D) or three (E) stages in the (B) treatment step, which is the second treatment step, and as result good quality, and high amounts of process/industrial water recovery is obtained via the treated re-use water discharge line (4).
- 4) A method according to claims 1, 2 and 3, characterized in that in the (B) treatment step, the membrane concentrates that are obtained, are returned to the Hybrid AOP/submerged MP reactor (10) in the (A) treatment step, via the membrane concentrates return line (5) of the hybrid reactor, and the concentrates

are treated together with the raw wastewater in a cyclic process, and as a result lower volumes of final membrane concentrates are obtained in comparison to integrated treatment applications within the scope of known MP/AOP configurations.

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5) A method according to claims 3 and 4, characterized in that, said method aims to increase the rate of the recovered water by reducing the volume of membrane concentrates and to decrease the water recovery costs by means of the increased rates of water recovery and reduced final concentrate disposal costs.

10

FIGURE 1

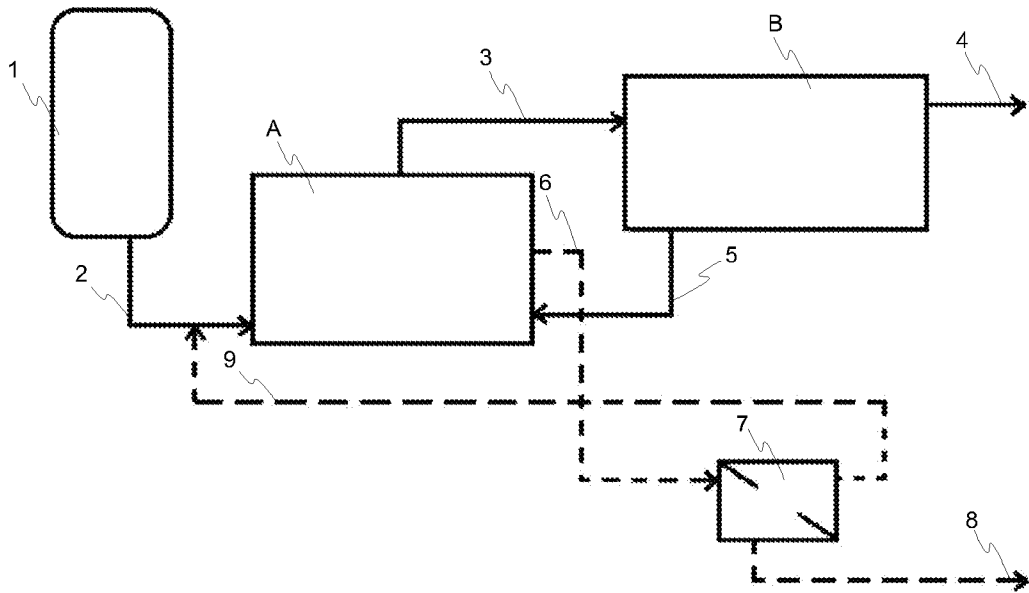
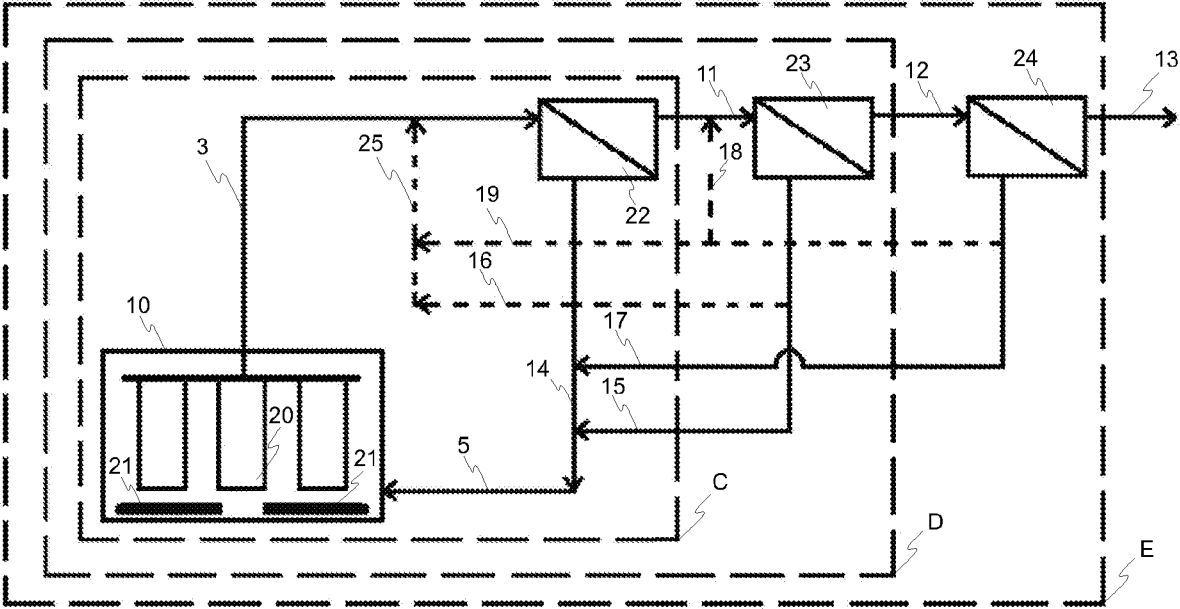


FIGURE 2



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/32 C02F1/44 C02F1/72
ADD.

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)

EP0-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.
X	US 2011/192795 A1 (GAIS ABDELKADER [FR]) 11 August 2011 (2011-08-11) paragraphs [0029] - [0036] paragraphs [0067] - [0070] -----	1-5
X	US 2007/119779 A1 (MURAMOTO TAKAHISA [JP] ET AL) 31 May 2007 (2007-05-31) paragraphs [0029] - [0031], [0066], [0067], [0096], [0106] paragraphs [0110] - [0130] paragraphs [0181] - [0192]; figure 3 -----	1-5
X	US 2015/321935 A1 (LESAGE NICOLAS [FR] ET AL) 12 November 2015 (2015-11-12) paragraphs [0002], [0023] - [0027], [0038], [0070] ----- -/--	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of the actual completion of the international search

17 March 2017

Date of mailing of the international search report

24/03/2017

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No
PCT/TR2016/050568

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 2007/023363 A1 (DAINES CATHERINE [FR] ET AL) 1 February 2007 (2007-02-01) paragraphs [0002], [0006], [0019], [0030] - [0033], [0036] - [0044], [0059], [0060], [0061]; figure 1 paragraphs [0089] - [0117] -----</p>	1-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/TR2016/050568

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011192795 A1	11-08-2011	AU 2009290885 A1 EP 2334603 A1 FR 2935697 A1 US 2011192795 A1 WO 2010029155 A1	18-03-2010 22-06-2011 12-03-2010 11-08-2011 18-03-2010
US 2007119779 A1	31-05-2007	AU 2005206407 A1 CA 2552768 A1 EP 1707538 A1 RU 2375312 C2 TW 200526529 A US 2007119779 A1 WO 2005070833 A1	04-08-2005 04-08-2005 04-10-2006 10-12-2009 16-08-2005 31-05-2007 04-08-2005
US 2015321935 A1	12-11-2015	AR 093915 A1 AU 2013357120 A1 EP 2931668 A1 FR 2999170 A1 US 2015321935 A1 WO 2014091141 A1	24-06-2015 02-07-2015 21-10-2015 13-06-2014 12-11-2015 19-06-2014
US 2007023363 A1	01-02-2007	AT 490945 T AU 2004289490 A1 BR PI0415926 A CN 1886345 A DK 1711435 T3 EP 1711435 A1 ES 2358647 T3 FR 2861718 A1 JP 2007509740 A KR 20060114333 A RU 2359919 C2 US 2007023363 A1 WO 2005047191 A1 ZA 200603434 B	15-12-2010 26-05-2005 26-12-2006 27-12-2006 21-03-2011 18-10-2006 12-05-2011 06-05-2005 19-04-2007 06-11-2006 27-06-2009 01-02-2007 26-05-2005 27-06-2007