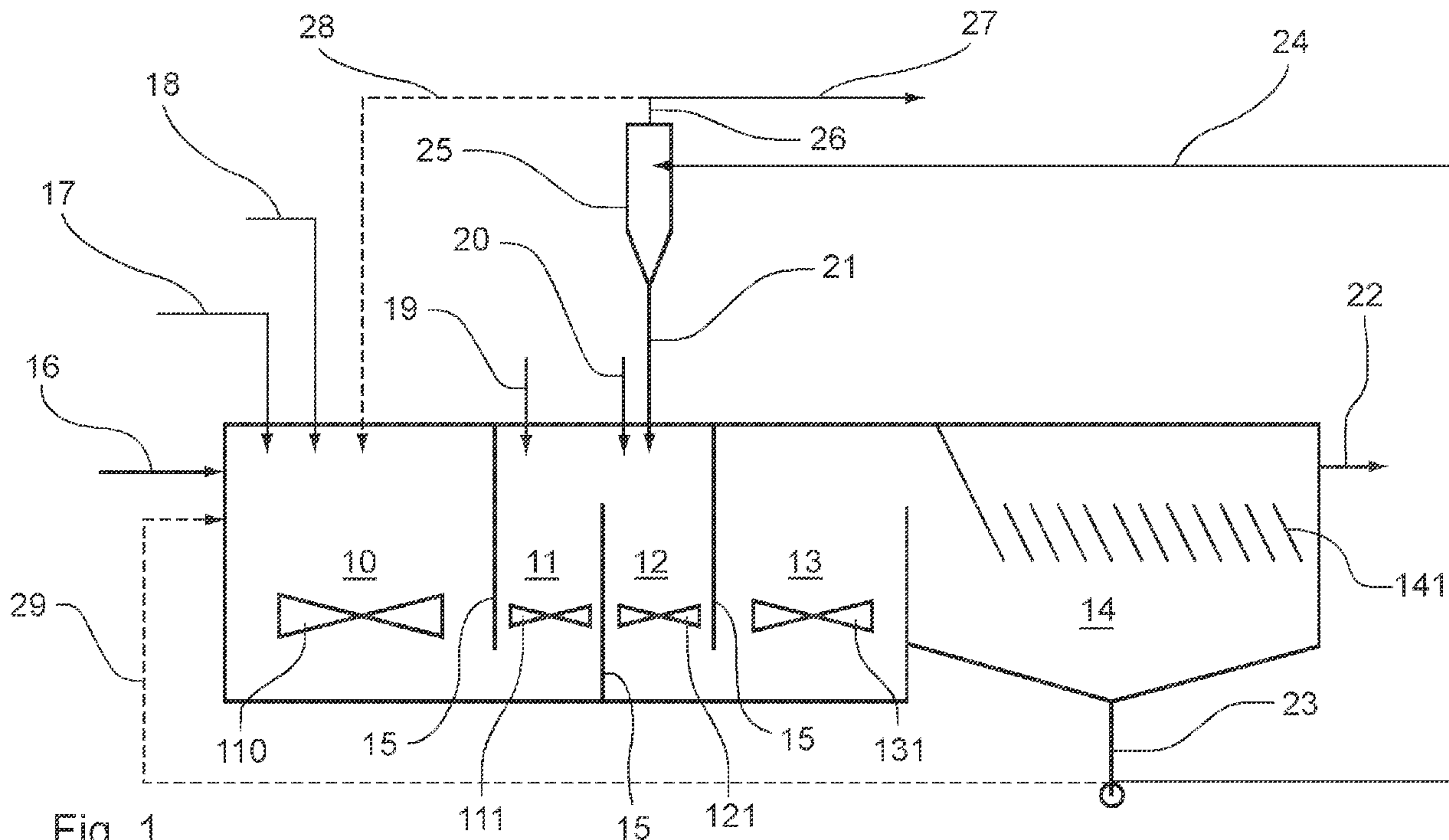




(86) Date de dépôt PCT/PCT Filing Date: 2008/11/27  
 (87) Date publication PCT/PCT Publication Date: 2009/07/09  
 (85) Entrée phase nationale/National Entry: 2010/06/09  
 (86) N° demande PCT/PCT Application No.: EP 2008/066286  
 (87) N° publication PCT/PCT Publication No.: 2009/083346  
 (30) Priorité/Priority: 2007/12/20 (FR0760141)

(51) Cl.Int./Int.Cl. *C02F 9/02* (2006.01),  
*C02F 1/72* (2006.01), *C02F 1/52* (2006.01)  
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(54) Titre : PROCEDE DE TRAITEMENT D'EAU PAR OXYDATION AVANCEE ET FLOCCULATION LESTEE, ET  
INSTALLATION DE TRAITEMENT CORRESPONDANTE  
 (54) Title: METHOD FOR TREATING WATER BY ADVANCED OXIDATION AND BALLASTED FLOCCULATION, AND  
CORRESPONDING TREATMENT PLANT



**Fig. 1**

(57) **Abrégé/Abstract:**

The invention relates to a method for treating water charged with colloidal impurities, either dissolved or suspended, in a treatment plant, wherein said method comprises: the step of contacting said water, in an advanced oxidation area (10), with hydrogen

(57) **Abrégé(suite)/Abstract(continued):**

peroxide in the presence of at least one transition-metal salt; a flocculation step that comprises contacting said water, in a flocculation area (12), with at least one flocculation additive and with at least one ballast comprising at least one non-soluble granular material denser than water and used as a biomass carrier; the step of feeding the water and floc mixture thus obtained into a settling area (14); the step of separating the treated water at the upper portion of said settling area (14) from a mixture of sludge and ballast resulting from the settling of said flocs; the step of extracting the sludge and ballast mixture at the lower portion (23) of said settling area (24); and the step of recycling at least a portion of the sludge into said advanced oxidation area (10).

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION  
EN MATIÈRE DE BREVETS (PCT)(19) Organisation Mondiale de la Propriété  
Intellectuelle  
Bureau international(43) Date de la publication internationale  
9 juillet 2009 (09.07.2009)

PCT

(10) Numéro de publication internationale  
**WO 2009/083346 A1**(51) Classification internationale des brevets :  
C02F 9/02 (2006.01) C02F 1/52 (2006.01)  
C02F 1/72 (2006.01)

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(21) Numéro de la demande internationale :  
PCT/EP2008/066286

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(22) Date de dépôt international :  
27 novembre 2008 (27.11.2008)

(81) États désignés (sauf indication contraire, pour tout titre de protection nationale disponible) : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Langue de dépôt : français

(26) Langue de publication : français

(30) Données relatives à la priorité :  
0760141 20 décembre 2007 (20.12.2007) FR

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[Suite sur la page suivante]

(54) Title: METHOD FOR TREATING WATER BY ADVANCED OXIDATION AND BALLASTED FLOCCULATION, AND CORRESPONDING TREATMENT PLANT

(54) Titre : PROCÉDÉ DE TRAITEMENT D'EAU PAR OXYDATION AVANCÉE ET FLOCCULATION LESTÉE, ET INSTALLATION DE TRAITEMENT CORRESPONDANTE

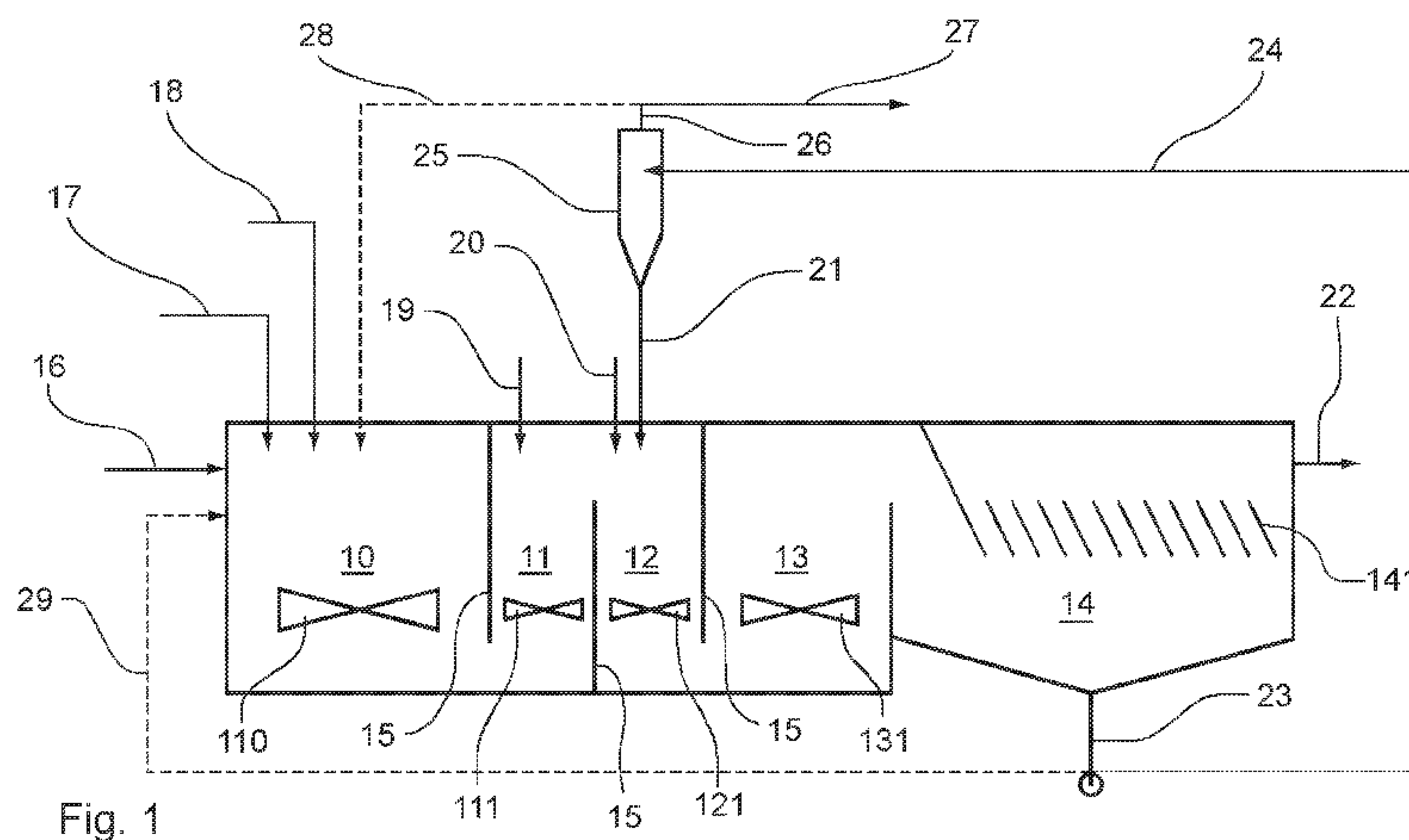


Fig. 1

(57) Abstract: The invention relates to a method for treating water charged with colloidal impurities, either dissolved or suspended, in a treatment plant, wherein said method comprises: the step of contacting said water, in an advanced oxidation area (10), with hydrogen peroxide in the presence of at least one transition-metal salt; a flocculation step that comprises contacting said water, in a flocculation area (12), with at least one flocculation additive and with at least one ballast comprising at least one non-soluble granular material denser than water and used as a biomass carrier; the step of feeding the water and floc mixture thus obtained into a settling area (14); the step of separating the treated water at the upper portion of said settling area (14) from a mixture of sludge and ballast resulting from the settling of said flocs; the step of extracting the sludge and ballast mixture at the lower portion (23) of said settling area (24); and the step of recycling at least a portion of the sludge into said advanced oxidation area (10).

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**WO 2009/083346 A1**

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), européen (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Publiée :**

— avec rapport de recherche internationale

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**(57) Abrégé :** L'invention concerne un procédé de traitement d'une eau chargée d'impuretés colloïdales, dissoutes ou en suspension, dans une installation de traitement, ledit procédé comprenant selon l'invention : - une étape de mise en contact, dans une zone d'oxydation avancée (10), de ladite eau avec du peroxyde d'hydrogène en présence d'au moins un sel de métal de transition; - une étape de floculation consistant à mettre en contact, dans une zone de floculation (12), ladite eau avec au moins un adjuvant de floculation, et avec au moins un ballast constitué d'au moins un matériau granulaire insoluble plus dense que l'eau et servant de support à une biomasse; - une étape d'introduction du mélange d'eau et de floccs ainsi formé dans une zone de décantation (14); - une étape de séparation de l'eau traitée en partie haute de ladite zone de décantation (14) d'un mélange de boue et de ballast résultant de la décantation desdits floccs; - une étape d'extraction du mélange de boue et de ballast en partie basse (23) de ladite zone de décantation (24); - une étape de recyclage d'au moins une partie des boues dans ladite zone d'oxydation avancée (10).



METHOD FOR TREATING WATER BY ADVANCED OXIDATION AND  
BALLASTED FLOCCULATION, AND CORRESPONDING TREATMENT  
PLANT

Field of the invention

The field of the invention is that of water treatment.

More precisely, the invention relates to the treatment of wastewater which simultaneously comprises  
5 specific organic and/or colloidal pollution and dissolved pollution.

In particular, this invention relates to the treatment of liquid industrial effluents and municipal water treatment.

10 This wastewater frequently comprises a specific pollution, colloidal pollution and dissolved pollution. The dissolved pollution includes easily biodegradable dissolved pollution expressed by the BOD (Biological Oxygen Demand) content soluble in water, which is  
15 treated via a biological treatment, and the non-biodegradable to poorly biodegradable dissolved pollution, expressed by the hard or refractory COD

(Chemical Oxygen Demand) content, which is treated by means of chemical products.

Prior art

5           The specific and/or colloidal pollution suspended in the water is normally and relatively easily treated by physico-chemical means, substantially by direct decantation or by decantation preceded by coagulation and/or flocculation.

10           The soluble and easily biodegradable pollution is normally treated by biological means, i.e., by placing the water being treated in contact with one or more biomasses containing bacteria capable of degrading same.

15 Disadvantages of the prior art

          Treatment of the organic pollution of wastewater, particularly that of industrial origin (chemical, pharmaceutical, textile industries), or of municipal origin, which may comprise a strong pollution component  
20 of industrial origin, involves relatively long treatment times. The length of these treatment times is related, in particular, to the nature of certain poorly biodegradable molecules, and to the inherent slowness of the biological processes normally implemented.

25           Furthermore, biologically treated industrial water generally contains a relatively high proportion of residual COD requiring subsequent chemical treatment.

          Certain advanced oxidation techniques have been implemented for the purpose of reducing the difficult-  
30 to-dissolve and non-biodegradable pollution of an effluent.

Ranked amongst these advanced oxidation techniques are those implementing Fenton's reagent, which enables free OH\* radicals to be generated from hydrogen peroxide in the presence of a transition metal such as iron, via the following reactions:



10

The OH\* hydroxyl radicals thus generated react with a broad range of organic pollutants in order to oxidise same.

These advanced oxidation techniques have thus far been used in combination with coagulation, flocculation and decantation techniques so as to simultaneously reduce the specific, colloidal and soluble pollution of the effluents.

The international patent application bearing the number WO 99/21801 thus describes a water treatment method using a combination of advanced oxidation and coagulation, flocculation and decantation.

This method enables specific pollution and the dissolved organic pollution to be treated simultaneously. However, the use of such a method involves relative long water treatment times of a minimum of 1 hour and 40 minutes and possibly reaching more than 5 hours.

The United States patent application bearing the number US-A1-2002/153329 likewise describes such a

30

method, which further requires the use of a heterogeneous catalyst.

Such a method likewise involves treatment times of a minimum of 4 hours and possibly reaching 24 hours, and likewise has the disadvantage of requiring the use of a heterogeneous catalyst involving a significant cost item.

Such treatment methods also have the disadvantage of requiring structures of a considerable size, and of being relatively costly. The use of same is thus uncommon.

#### Objectives of the invention

One objective of the invention in particular is to mitigate these disadvantages of the prior art.

More precisely, one objective of the invention is to provide a wastewater treatment technique which, in at least one embodiment, enables the specific pollution, the colloidal pollution and the dissolved pollution to be treated simultaneously.

In at least one embodiment, the invention likewise has the objective of reducing the residual COD concentration of water collected, for example, after biological treatment.

Another objective of the invention is to implement such a technique which, in at least one embodiment, enables the time for wastewater treatment to be reduced considerably.

In at least one embodiment, the invention likewise has the objective of providing such a technique which results in accelerating the wastewater treatment.



In at least one embodiment, the invention also has the objective of providing such a technique which is reliable, and the implementation of which is simple and inexpensive.

5

#### Disclosure of the invention

These objectives, as well as others which will become apparent later, are achieved by means of a method of treating water charged with colloidal  
10 impurities, either dissolved or in suspension, in a treatment plant.

According to the invention, said method includes:

- a step of placing said water, in an advanced oxidation area, in contact with hydrogen peroxide in  
15 the presence of at least one transition-metal salt;
- a flocculation step consisting in placing said water, in a flocculation area, in contact with at least one ballast consisting of at least one flocculant and with at least one insoluble granular material denser  
20 than water;
- a step of introducing the water and floc mixture thus formed into a settling area;
- a step of separating the treated water at the upper portion of said settling area with a mixture of  
25 sludge and ballast resulting from the settling of said floc;
- a step of extracting the mixture of sludge and ballast at the lower portion of said settling area;
- a step of recycling at least a portion of the  
30 sludge into said advanced oxidation area 10.

The invention is thus based on an innovative approach to the treatment of wastewater, which consists in combining an advanced oxidation treatment with an adsorbent treatment and a coagulation, flocculation and  
5 ballasted settling treatment.

Such an approach makes it possible to treat specific pollutions, colloidal pollutions and a high proportion of the non- or poorly biodegradable dissolved pollutions simultaneously and in very short  
10 time periods, or at the very least in time periods shorter than the treatment times required when implementing the techniques according to the prior art.

Furthermore, the fact of recycling at least a portion of the sludge derived from the settling process  
15 in the advanced oxidation area enables recycling of the metals which are deposited on the ballast and/or which are precipitated as fine particles of high-density metallic oxides over the course of the method. These metals and/or oxidised metals comprise "active metals"  
20 the presence of which contributes to improving the kinetics of the advanced oxidation reaction and to reducing the time required to treat the effluent.

As a matter of fact, the dissolved metals contribute to accelerating the treatment via Fenton's  
25 reaction. Metals in the form of oxides and/or oxyhydroxides accelerate the oxidation reaction and the oxyhydroxides provide an adsorbent effect.

Furthermore, recycling of the sludge and ballast promotes the increase of adsorbent mineral species of  
30 the iron oxyhydroxide type ( $\text{FeOOH}$ ) created *in situ*, which contribute to the elimination of the organic

matter via adsorption, as well as the elimination of the soluble metals present in the effluent. This likewise contributes to improving the reduction in dissolved pollution.

5       The implementation of a step of introducing an adsorbent agent into the water being treated can advantageously be anticipated.

10       The method according to the invention thus consists of a method enabling water treatment to be accelerated.

      According to one advantageous characteristic of the invention, the time period separating the placement of said water in contact with the hydrogen peroxide and the separation of the treated water is less than 1 hour.

15       Implementation of the invention thus enables a high proportion of the residual COD to be reduced in a short time period, at the very least in comparison with the techniques of the prior art.

20       The treatment method according to the invention preferably includes a sludge/ballast hydrocyclone separation step.

25       It can likewise be provided for the sludge/ballast separation to be obtained by another physical or gravity-type means such as a magnet, a filter or a settling tank.

      In this case, it advantageously includes a step of recycling the underflow of said hydrocyclone separation step into said flocculation area.

30       It may also include, according to a preferable characteristic, a recycling step of the separation

underflow of said separation by hydrocyclone step in said advanced oxidation area.

The hydrocyclone separation underflow consists of a mixture composed of a high proportion of ballast and metals which are precipitated as fine particles of high-density metallic oxides over the course of the method (and of sludge residues).

Recycling of the ballast thus enables these metallic oxide particles to be recycled. The kinetics of the advanced oxidation reaction is then improved, owing thereto, and the time required to treat the effluent is reduced.

The treatment method according to the invention preferably includes a step of recycling a portion of the sludge derived from the overflow of said hydrocyclone separation step into said advanced oxidation area.

Recycling of the sludge which contains active metals leads to an acceleration of the advanced oxidation and therefore the treatment.

Furthermore, recycling of the sludge and the ballast contributes to improving the reduction of dissolved pollution. As a matter of fact, as already explained, it promotes the increase in adsorbent mineral species of the iron oxyhydroxide type ( $\text{FeOOH}$ ), created *in situ*, which promote the elimination of the organic matter by adsorption, as well as the elimination of the soluble metals present in the effluent.

According to one advantageous characteristic of the invention, the treatment method according to the



invention includes a step of placing said water in contact with at least one coagulating salt in a coagulation area.

In this case, said coagulating salt is preferably  
5 ferric chloride.

The use of ferric chloride contributes in part to providing the sludge and ballast mixture with active metals, which, during recycling of the sludge and/or ballast, are involved in accelerating the treatment.

10 Said transition-metal salt is advantageously chosen from the group consisting of the following metals: iron and copper.

The use of this type of transition metal enables good oxidation to be obtained.

15 According to a preferred characteristic, said flocculation step includes a ripening step in a ripening area positioned upstream from said settling area.

20 The ripening step makes it possible to ensure that the oxidation reactions, coagulation and flocculation are completed prior to starting the settling step, thereby enabling the result thereof to be improved.

Said water is preferably placed in contact with said flocculant at least one minute after placing said  
25 water in contact with each of said salts.

This enables the flocculation to be initiated after oxidation and coagulation of the dissolved pollution and to thus promote the formation of floc.

30 The residence time of said contact with the hydrogen peroxide in said advanced oxidation area is

between 2.5 and 45 minutes, and preferably between 7 and 20 minutes.

Such time periods enable obtainment of an appropriate level of oxidation of said dissolved  
5 pollution.

According to a preferred characteristic, the residence time of said contact with said flocculant and said ballast in said flocculation and/or ripening area is greater than 3 minutes, and preferably between 5 and  
10 15 minutes.

Such time periods enable obtainment of an effective degree of flocculation and the formation of solid floc. This contributes to facilitating the subsequent settling of the floc and to increasing the  
15 mirror settling speed.

The flow rate of said water via the horizontal surface of said settling area is greater than 15 m/h, and is preferably between 30 and 120 m/h.

Such settling speeds enable the overall water  
20 treatment time to be reduced.

The invention likewise relates to a water treatment plant for implementing the water treatment method according to the invention. Such a plant includes:

25 - an advanced oxidation area provided with means of injecting hydrogen peroxide, means of injecting said transition-metal salt, and at least one stirrer;

- a pipeline for feeding said water into said advanced oxidation area;

30 - a flocculation area provided with means of injecting said flocculant and at least one stirrer;

- means of injecting said ballast, which are connected to said flocculation area or to said advanced oxidation area;

- a settling area provided with an outlet for said treated water at the upper portion, and with an outlet for said mixture of sludge and ballast at the lower portion;

- means of recycling at least a portion of the sludge into said advanced oxidation area.

10 A plant according to the invention preferably includes a coagulation area, which is upstream from said flocculation area and which is provided with at least one stirrer and means of injecting said coagulating salt.

15 It is thus possible to proceed with a coagulation step so as to facilitate the formation of the floc.

According to one advantageous characteristic, a plant according to the invention includes a ripening area, which positioned upstream from said settling area and which is provided with at least one stirrer.

20 The implementation of such a ripening area enables an appropriate degree of flocculation to be ensured so as to improve the subsequent settling of the floc.

Said flocculation area and said ripening area are advantageously merged.

This enables the plant to be simplified without thereby degrading the quality of the results obtained by implementing the method according to the invention.

30 According to a preferred characteristic, at least one of said stirrers is surrounded by a substantially cylindrical and vertical flow guide.

This enables a good mixture to be obtained, while at the same time limiting the shear rates, and therefore aids in preventing the floc formed from being broken up.

5

#### List of the figures

Other characteristics and advantageous of the invention will become more apparent upon reading the following description of preferred embodiments, which are given for illustrative and non-limiting purposes only, and from the appended drawings, in which:

10

- figure 1 shows a schematic representation of a first embodiment of a water treatment plant according to the invention;

15

- figure 2 shows a schematic representation of a second embodiment of a water treatment plant according to the invention, wherein the flocculation and ripening areas are joined together in a single area;

20

- figure 3 shows a schematic representation of a third embodiment of a water treatment plant according to the invention, wherein the underflow and a portion of the overflows are recycled into the advanced oxidation area;

25

- figure 4 shows a schematic representation of an alternative capable of being implemented in the embodiments described and according to which the stirrers are housed inside flow guides.

#### Description of an embodiment of the invention

30

##### 1. Recall of the principle of the invention



The general principle of the invention is based on the combined implementation of an advanced oxidation area associated with ballasted flocculation/settling and recycling of at least a portion of the sludge formed into the advanced oxidation area, so as to treat the specific pollutions, colloidal pollutions and easily or poorly biodegradable soluble pollutions simultaneously and in relatively short periods of time.

Such an approach enables wastewater to be treated rapidly and to significantly reduce the residual COD thereof.

## 2. Example of a first embodiment of a plant according to the invention

An embodiment of a water treatment plant according to the invention is shown in connection with figure 1.

As shown in figure 1, such a plant includes an advanced oxidation area 10, a coagulation area 11, a flocculation area 12, and a ripening area 13, arranged one after the other and each accommodating a stirrer 110, 111, 121, 131.

A settling area 14 is arranged downstream from the ripening area 13. At the upper portion, it accommodates a plurality of inclined plates 141. In other embodiments, the plates 141 may extend in a substantially vertical direction or else not be present.

These areas 10, 11, 12, 13 and 14 are separated from one another by means of walls 15 designed such that these areas are interconnected.

An inlet pipeline 16 for an effluent being treated opens out into an advanced oxidation area 10.

Furthermore, the advanced oxidation area 10 is provided with injection means 17, e.g., an injector, for hydrogen peroxide, and means of injecting 18 a transition-metal salt.

5 As seen in figure 1, the coagulation area 11 is provided with means of injecting a coagulating salt.

The flocculation area 12 is provided with means of injecting 20 a flocculant, and means of injecting a ballast 21.

10 The settling area 14 is provided at the upper portion thereof with an outlet 22 for a treated effluent, and at the lower portion thereof for a mixture of sludge and ballast.

The lower outlet 23 of the settling area 14 is  
15 connected via a recycling pipeline 24 to a hydrocyclone 25 (or any other means, e.g., such as a settling tank, a magnet filter...) the underflow 21 of which is connected to the flocculation area 12 and the overflow 26 of which is connected to an excess sludge extraction  
20 pipeline 27.

As seen in this figure 1, a portion of the overflow 26 is connected to a pipeline 28 for recycling a portion of the sludge into the advanced oxidation area 10.

25 As also seen in this figure 1, in an alternative to this embodiment, provisions can be made for the lower outlet 23 of the settling area to be connected to the advanced oxidation area 10 via a pipeline 29.

30 3. Example of a second embodiment of a plant according to the invention

Figure 2 shows a second embodiment of a water treatment plant according to the invention.

Such a plant implements numerous elements equivalent to those implemented in the plant according to the first embodiment described above, and which bear the same numerical references.

In this second embodiment, provisions are made for the flocculation area 12 and the ripening area 13 to be joined together in a single tank 200, which is provided with means of injecting a flocculant 20 and means of injecting a ballast 21.

#### 4. Example of a third embodiment of a plant according to the invention

A third embodiment of the treatment plant according to the invention is shown in connection with figure 3.

As shown, such an installation implements means equivalent to those implemented in the second embodiment described above. However, this plant according to the third embodiment differs from the plant according to the second embodiment by the fact that the ballast-injecting means 21 are connected to the advanced oxidation area 10.

25

#### 5. Alternatives

Figure 4 shows an alternative capable of being implemented equally in each of the embodiments described above.

This alternative consists in providing for the stirrers, or at the very least some of them, to be

30

housed inside flow guides 40 having the shape of tubes of circular cross-section.

Another alternative can consist in providing for the implementation of means measuring (not shown) information representative of a pH value in the advanced oxidation area 10 and/or upstream or downstream from the settling area 14, and means of injecting at least one pH adjustment reagent into the advanced oxidation area 10 and/or upstream or downstream from the settling area 14.

One alternative may likewise consist in implementing a system for scraping the mixture of sludge and ballast at the bottom of the settling area 14.

#### 6. Water treatment method according to the invention

An exemplary water treatment method according to the invention will now be described.

Such a treatment method can, for example, be implemented in one of the water treatment plants according to the invention, as described above.

The method consists in introducing an effluent to be treated into the advanced oxidation area 10 by means of the inlet pipeline 16. The effluent introduced into the advanced oxidation area 10 is placed in contact, under agitation, with hydrogen peroxide in the presence of a transition-metal salt, by activating the injection means 17 and 18.

The transition-metal salt is preferably an iron salt, and advantageous a ferrous salt such as ferrous



sulphate. In another embodiment, it can be provided for the transition metal implemented to be copper.

It is noted that the contact time between the effluent and the hydrogen peroxide is advantageously  
5 between 2.5 and 45 minutes, and preferably between 7 and 20 minutes.

The effluent is next directed into the coagulation area 11 in which it is placed in contact with a coagulating salt, preferably an iron salt such as  
10 ferric chloride, by activating the injection means 19.

In an alternative, the ferrous salt and the iron salt may be introduced into the advanced oxidation area 10. To accomplish this, the injection means 19 will be provided in the advanced oxidation area 10.

15 The effluent is next placed in contact, under agitation, with a flocculant in the flocculation area 12. The flocculant is preferably a flocculating polymer, e.g., such as polyacrylamide. The effluent is placed in contact with the flocculant advantageously at least one  
20 minute after each of the salts has been introduced.

The effluent is likewise placed in contact in this flocculation area 12 with at least one granular material (or ballast) which is denser than the effluent, by activating the injection means 21. The granular  
25 material preferably consists of fine sand the effective diameter can advantageously be between 50 and 200 micrometres. However, the granular material can also be magnetite, other mineral oxides containing iron or copper, synthetic or natural mineral polyoxides,  
30 magnesium oxides (e.g., hydrotalcite), aluminium (e.g., activated alumina). The grain-size distribution used is

similar to that of the sand, with a larger developed surface area enabling better adsorption.

The granular material can be introduced into the flocculant. In alternatives, it can be injected  
5 upstream from the flocculant-injecting means, advantageously into the oxidation area 10. In other alternatives, it may be introduced equally at any point.

The effluent is kept in contact with the granular material and the flocculant for at least 3 minutes, and  
10 preferably for a time period of between 5 and 15 minutes. When the ripening area 13 is implemented, the effluent can advantageously be kept in contact therein with the granular material and the flocculant.

The mixture of effluent and floc formed in the  
15 flocculation area 12 is directed towards the settling area 14, advantageously at a mirror speed greater than 15 m/h, and preferably between 30 and 120 m/h.

It is noted that the "mirror speed" is defined as being equal to the ratio of the flow rate of water  
20 being treated, expressed in  $\text{m}^3/\text{h}$  and the horizontal surface area of the settling area, expressed in  $\text{m}^2$ .

The treated water is next separated from a mixture of sludge and granular material resulting from the settling of the floc, and then discharged via outlet 22.

25 As for the mixture of sludge and ballast, it is extracted at the lower portion of the settling area 14 via outlet 23.

The mixture of sludge and ballast is next conveyed in the direction of a hydrocyclone 25 by means of a  
30 pipeline 24, for the purpose of separating them from one another, at the very least partially.

The underflow 21 of the hydrocyclone, consisting of a mixture containing a high proportion of ballast, and metals which are precipitated as fine particles of high-density metallic oxides over the course of the method (and sludge residues), is recycled into the flocculation area 12. In another embodiment, the underflow 21 can be recycled directly into the advanced oxidation area 10.

Recycling of the ballast makes it possible to recycle the metals deposited on the ballast and/or precipitated as fine particles of metallic oxides, as indicated above. More precisely, a portion of the metals is deposited on the ballast and the other portion precipitates. The heaviest forms of the portion which precipitates follow the ballast, whereas the less dense forms follow the sludge. This contributes to improving the catalysis of the advanced oxidation reaction and to reducing the time required to treat the effluent.

The overflow 26, consisting of a mixture containing a high proportion of sludge (and possibly a ballast residue), is discharged by means of an outlet pipeline 27 for the excess sludge.

A portion of the overflows 26 of the hydrocyclone is recycled, by means of pipeline 28, into the advanced oxidation area 10. It can likewise be provided for same to be recycled into the coagulation area 11. Because the recycled sludge contains active metals, this enables the advanced oxidation to be accelerated. In this regard, it bears noting that the separation of the sludge and ballast by means of the hydrocyclone

tends to increase the concentration of metallic precipitates contained in the overflow 26.

Furthermore, recycling of the sludge and ballast promotes the increase of adsorbent mineral species of the iron oxyhydroxide type (FeOOH) created *in situ*, which contribute to the elimination of the organic matter via adsorption, as well as the elimination of the soluble metals present in the effluent. This likewise contributes to improving the reduction in dissolved pollution.

In another alternative, a portion of the sludge and ballast mixture extracted at the lower portion of the settling area is directly recycled into the forced oxidation area. This can enable advantage to be taken from the additional catalysis which the precipitated metallic compounds in the sludge may provide. This may appear to be useful in particular in the case where the effluent is highly charged with soluble pollution, e.g., above 300 mg/l of soluble COD, and lightly charged with SS. It is noted that the percentage of recycled sludge may be increased by increasing the diameter of the hydrocyclone underflow, thereby enabling the heaviest, most active metal-laden sludge to be selected.

In an alternative of the method according to the invention, said method can include a step consisting in measuring the pH value in the advanced oxidation area 10 and/or upstream or downstream from the settling area 14, and a step of injecting at least one pH adjustment reagent into the oxidation area 10 and/or upstream or downstream from the settling area 14, so as to maintain



the pH value therein at between 3 and 6 and 6 and 8, respectively.

Implementing a method according to the invention makes it possible to reduce the water treatment time and, in particular, to limit the time that elapses between the time when the water is placed in contact with the hydrogen peroxide and the extraction of the treated water to one hour at most, while at the same time making it possible to reduce the residual COD contained in the treated water collected after treatment.

A reduction such as this in the water treatment time can be explained by the implementation of a ballasted floc-settling operation, which makes it possible to reduce the settling time, but to likewise result in an excellent reduction in the fine particles formed during the advanced oxidation reaction, which appear to be quickly trapped in the rapidly settling ballasted floc.

However, recycling of the ballast and sludge plays an important role in reducing the water treatment time according to the invention, in that it makes it possible to reduce the required pre-settling contact time:

- the solidity of the floc enables significant velocity gradients in flocculation, thereby bringing about an improvement in the reaction exchanges and a decrease in the required contact time for the reaction;
- recycling of the ballast makes it possible to recycle the metals which have been deposited on the grains of sand or precipitated as high-density metallic

particles, thereby improving the catalysis of the advanced oxidation reaction;

- recycling of a portion of the sludge, which contains active metals, can enable the advanced oxidation reaction to be accelerated, while increasing the concentration of the metals in the active form thereof;

- recycling of the sludge and ballast promotes the increase in the concentration of adsorbent mineral species promoting the elimination of the organic matter by adsorption, as well as the elimination of soluble metals present in the effluent.

#### 7. Tests

The following tests were conducted at an industrial pilot plant measuring 50 m<sup>3</sup>/h, such as the one shown in figure 1, treating fine chemical effluents, effluents from the dye and artificial textile industries, and having the following characteristics:

- introduction of ferrous sulphate at rates of between 50 and 200 mg/l;

- introduction of hydrogen peroxide at rates of between 6 and 11 mg/l on-line, upstream from the coagulation area;

- contact times of 2.5 minutes at a non-adjusted pH(usually between 7 and 7.5) prior to entering the coagulation area;

- agitated coagulation for 5 minutes prior to injecting ferric chloride at rates of between 300 and 600 mg/l;

- agitated flocculation with accommodation of the sandy ballast (effective diameter of 125 micrometres), with 1.9 mg/l of a polymer for a residence time of 5 minutes;

- 5       - flocculation-ripening for 10 minutes;  
      - extraction of the mixture of sand and sludge at a rate of 11 m<sup>3</sup>/h including 2.5 m<sup>3</sup>/h of recycled sand in the flocculation area.

The tests were conducted with effluents coming  
10 from a biological treatment and further comprising 225 to 324 mg/l of total COD, 194 to 240 mg/l of filtered COD (on 0.45-micrometre paper), almost of the refractory type since derived from a biological treatment, and 19 to 46 mg/l of SS.

15       The tests demonstrated a notable increase in the reduction efficiency:

      - of the filtered COD (representative of the soluble COD), which shifted from a value of 21% without any use of hydrogen peroxide to a value of 37% with  
20 hydrogen peroxide;

      - of the total COD, which shifted from an average of 29% to an average of 43%;

      - of the apparent colour index (ACI) which shifted from an average of 27% to an average of 47%;

25       - the overall residence times in the plants, over the course of these tests, was of the order of 25 minutes.

CLAIMS

1. Method of treating water charged with colloidal, dissolved or suspended impurities, in a treatment plant, said method including :

- 5           - a step of placing said water, in an advance oxidation area (10), in contact with hydrogen peroxide in the present of at least one transition-metal salt;
- a flocculation step consisting in placing said water, in a flocculation area (12), in contact with at  
10 least one ballast consisting of at least one flocculant and with at least one insoluble granular material denser than water;
- a step of introducing the water and floc mixture thus formed into a settling area (14);
- 15           - as step of separating the treated water at the upper portion of said settling area (14) with a mixture of sludge and ballast resulting from the settling of said floc;
- a step of extracting the mixture of sludge and  
20 ballast at the lower portion (23) of said settling area (14);



- a step of recycling at least a portion of the sludge into said advanced oxidation area (10).

2. Treatment method according to claim 1, characterised in that the time period separating the placement of said water in contact with the hydrogen peroxide and the separation of the treated water is less than 1 hour.

3. Treatment method according to any of claims 1 to 2, characterised in that it includes a sludge/ballast hydrocyclone separation step.

4. Treatment method according to claim 3, characterised in that it includes a step of recycling the underflow (21) of said hydrocyclone separation step into said flocculation area (12).

5. Treatment method according to claim 3, characterised in that it includes a step of recycling the underflow (21) of said hydrocyclone separation step into said advanced oxidation step (10).

6. Treatment method according to any of claims 3 to 5, characterised in that it includes a step of recycling a portion of the sludge derived from the overflow (26) of said hydrocyclone separation step into said advanced oxidation step (10).

7. Treatment method according to any of claims 1 to 6, characterised in that it includes a step of placing said water in contact with at least one coagulating salt in a coagulating area (11).

8. Treatment method according to claim 7, characterised in that said coagulating salt is ferric chloride.

9. Treatment method according to any of claims 1 to 8, characterised in that said transition-metal salt is chosen from the group consisting of the following metals: iron and copper.

5 10. Treatment method according to any of claims 1 to 9, characterised in that said flocculation step includes a ripening step in a ripening area (13) positioned upstream from said settling area (14).

10 11. Treatment method according to any of claims 1 to 10, characterised in that said water is placed in contact with said flocculant at least one minute after placing said water in contact with each of said salts.

15 12. Treatment method according to any of claims 1 to 11, characterised in that the residence time of said water placed in contact with the hydrogen peroxide in said advanced oxidation area (10) is between 2.5 and 45 minutes.

20 13. Treatment method according to any of claims 1 to 12, characterised in that the residence time of said water placed in contact with the hydrogen peroxide in said advanced oxidation area (10) is between 7 and 20 minutes.

25 14. Treatment method according to any of claims 1 to 13, characterised in that the residence time of said water placed in contact with said flocculant and said ballast in said flocculation and/or ripening area (12) is greater than 3 minutes.

30 15. Treatment method according to any of claims 1 to 14, characterised in that the residence time of said water in contact with said flocculant and said ballast,

in said flocculation and/said ripening area (12) is between 5 and 15 minutes.

16. Treatment method according to any of claims 1 to 15, characterised in that the flow rate of said water via the horizontal surface of said settling area (14) is greater than 15 m/h.

17. Treatment method according to any of claims 1 to 16, characterised in that the flow rate of said water via the horizontal surface of said settling area (14) is between 30 and 120 m/h.

18. Water treatment plant for implementing the water treatment method according to any of claims 1 to 17, characterised in that it includes:

- an advanced oxidation area (10) provided with means of injecting hydrogen peroxide (17), means of injecting said transition-metal salt (18), and at least one stirrer (110);

- a pipeline (16) for feeding said water into said advanced oxidation area (10);

- a flocculation area (12) provided with means of injecting said flocculant (20) and at least one stirrer (121);

- means of injecting said ballast (21), which are connected to said flocculation area (12) or to said advanced oxidation area (10);

- a settling area (14) provided with an outlet (22) for said treated water at the upper portion, and with an outlet (23) for said mixture of sludge and ballast at the lower portion;

- means of recycling at least a portion of the sludge into said advanced oxidation area (10).

19. Water treatment plant according to claim 18, characterised in that it includes a coagulation area (11) upstream from said flocculation area (12) and provided with at least one stirrer (111) and means of injecting said coagulating salt (19).

20. Water treatment plant according to any of claims 18 and 19, characterised in that it includes a ripening area (13) positioned upstream from said settling area (14) and provided with at least one stirrer (131).

21. Water treatment plant according to any of claims 18 to 20, characterised in that said flocculation area (12) and said ripening area (13) are merged.

22. Water treatment plant according to any of claims 18 to 21, characterised in that at least one of said stirrers is surrounded by a substantially cylindrical and vertical flow guide (40).

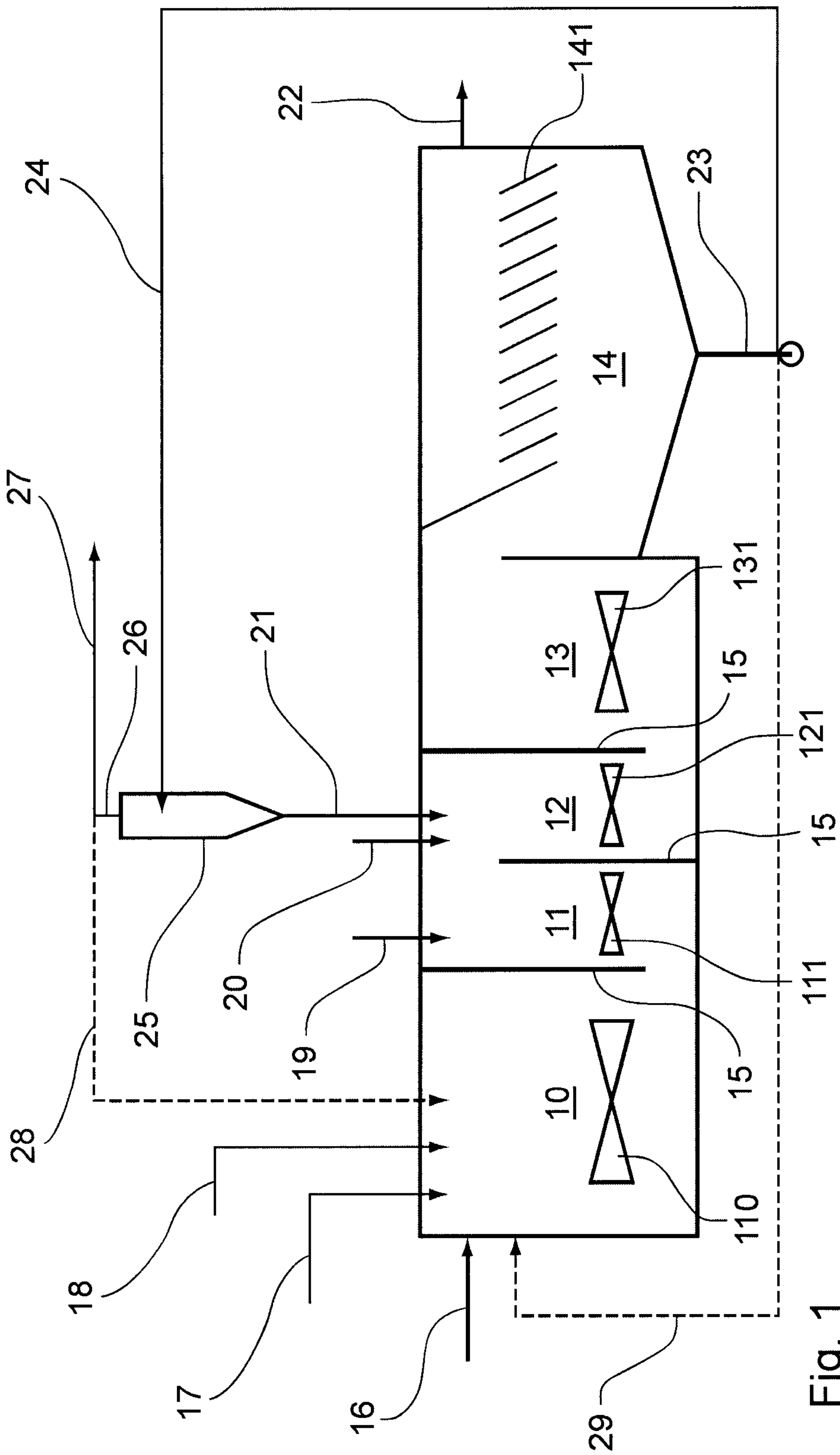


Fig. 1



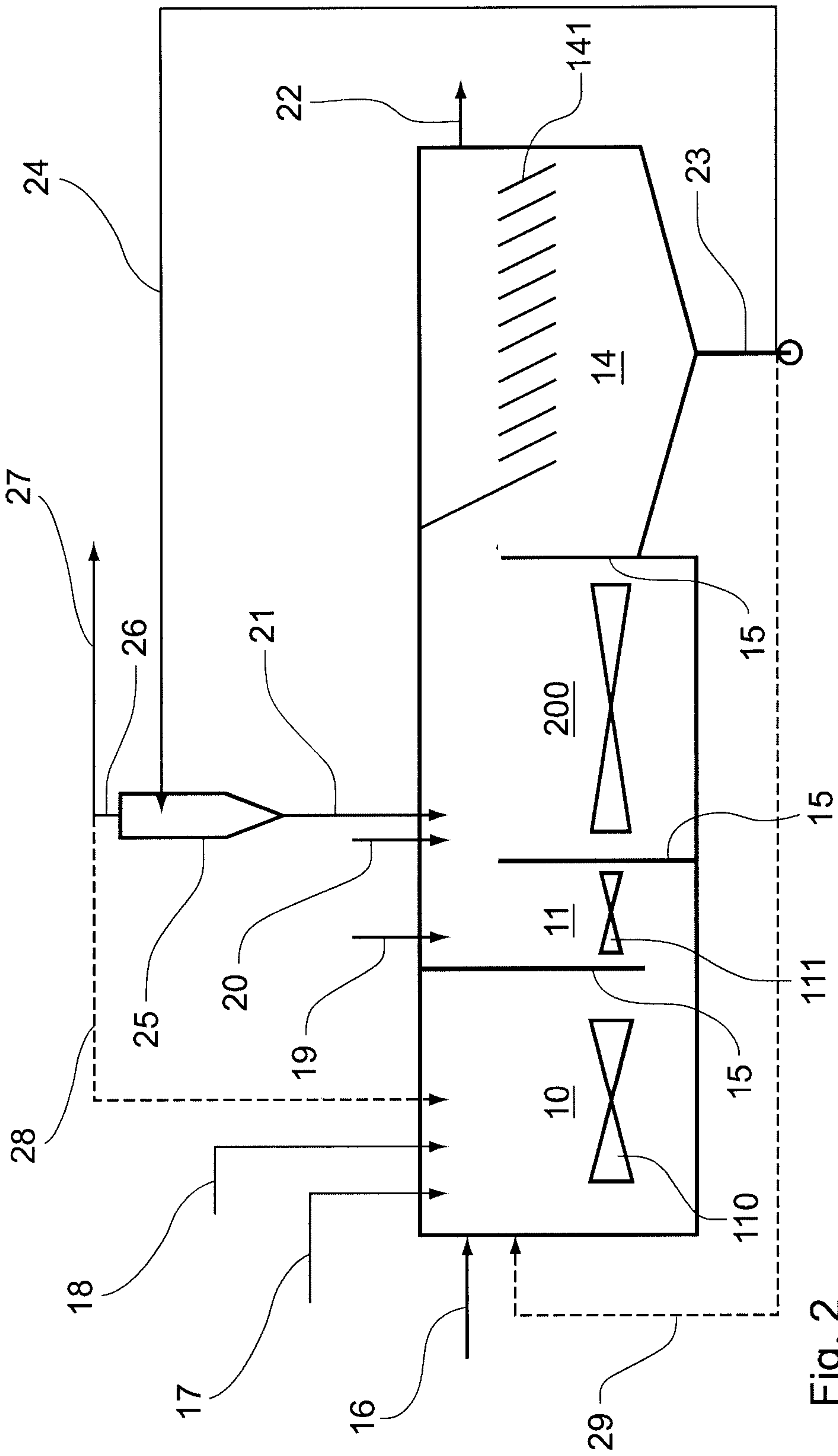


Fig. 2

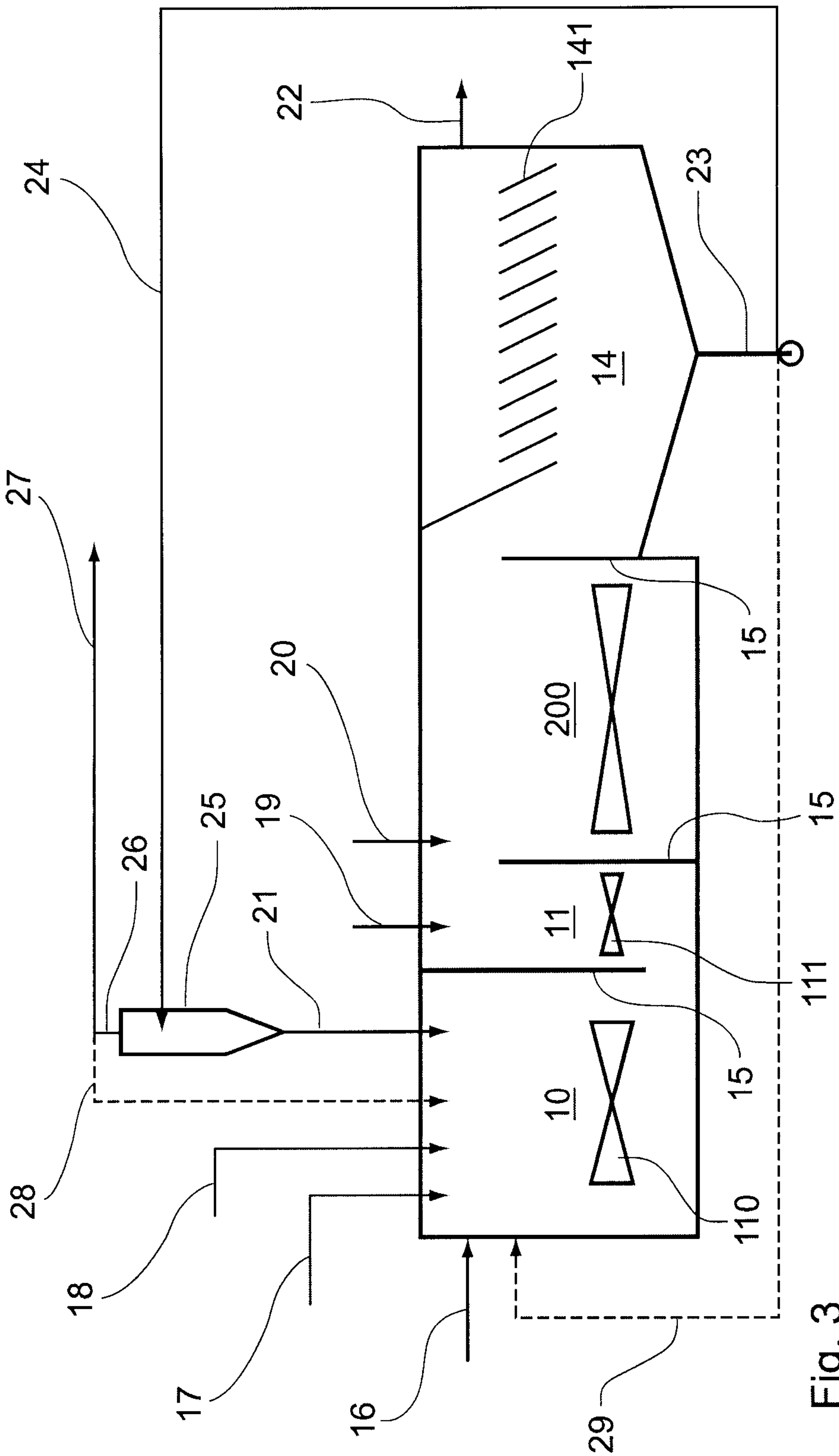


Fig. 3

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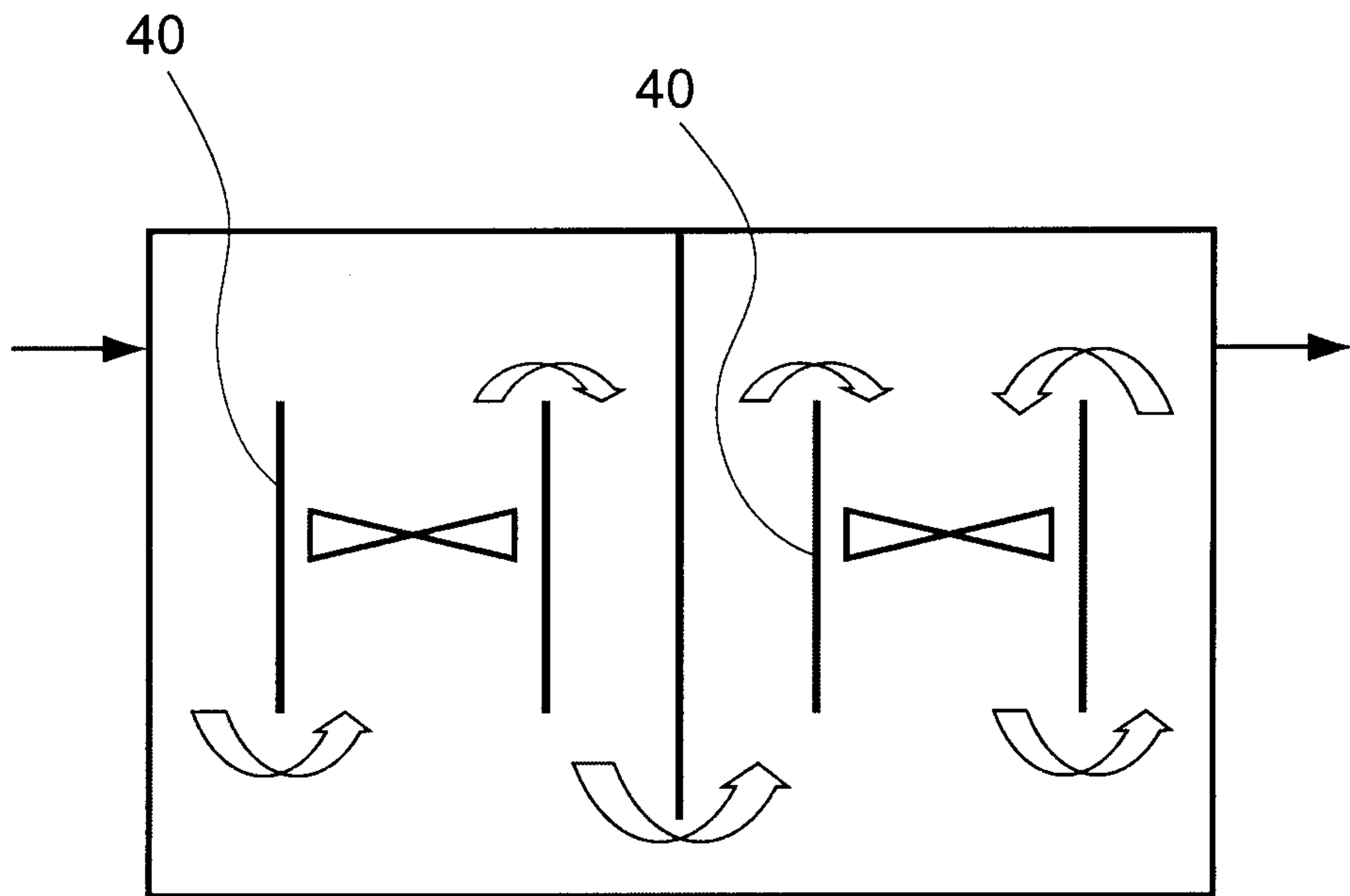


Fig. 4

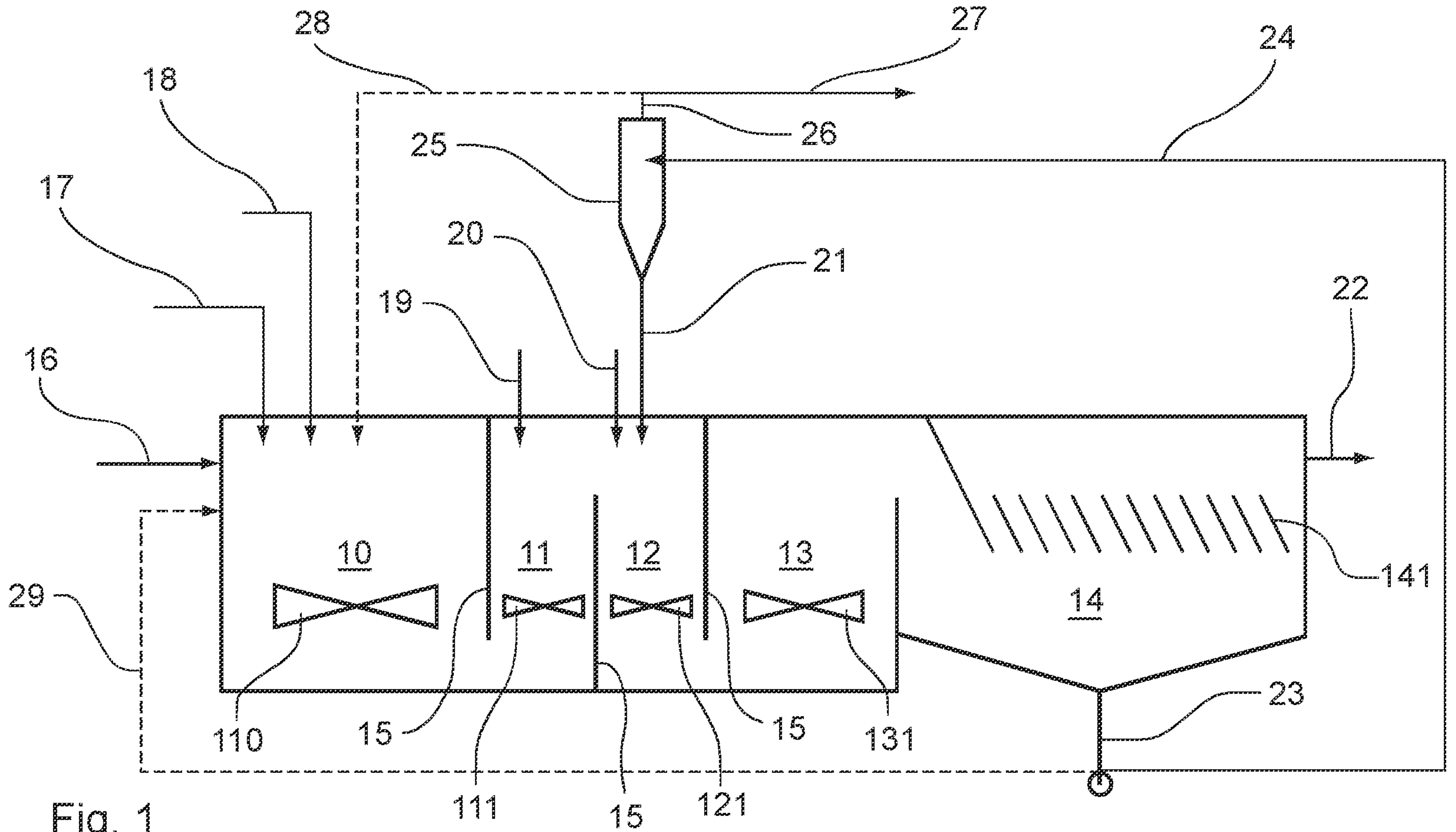


Fig. 1