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(54) Title: CHLORINE FREE TECHNOLOGY OF POOL WATER TREATMENT

(57) Abstract: The invention relates to the treatment of pool water in a circulation circuit ensuring hygienic safety of pool water without the necessity of using chlorination. The technology is based upon the combination of advanced oxidation process utilising OH radicals in at least one technological stage and ozonization, said advanced oxidation process allowing to remove microorganisms and polluting compounds from the treated water to the maximum possible extent so as to ensure the sanitation of water in the pool with only a low concentration of ozone dissolved in water, with minimum 0.001 mg/l O_3 in the whole volume of the pool, while the concentration of ozone released from water above the water level does not exceed 200 $\mu g/m^3$.

Chlorine free technology of pool water treatment

Field of the invention

The invention relates to pool water treatment, especially treatment ensuring hygienic safety of pool water without the necessity of chlorination.

Prior art

Under the concept of pool in the description of the present invention any private pool, rehabilitation facility or public pool are understood, and at the same time also any swim spa, spa, whirlpool, whirling or massaging bath-tub and further similar apparatuses are understood. In the prevailing majority of pools of the present day chlorine based compounds are used as the sole disinfectant and oxidant. The minimum concentration of free chlorine in pool water varies around 0.3 mg/l, higher concentrations being used for higher water temperature and increased load of the pool. Numerous adverse impacts upon human health are related to the chlorination of pool water. Various pollutants, such as proteins, urea, cosmetic preparation substances etc. that are dragged into the water by the pool users, are the source of chlorination by-products. The chlorination by-products are the cause of water odour, of drying the skin, of sore eyes and irritated mucous membranes. They are toxic and some of them are suspected carcinogens. In addition to the adverse effects for the human health (e.g. a considerable share in developing asthma), these substances cause the corrosion of metallic materials in the hall of the pool facility, including some stainless steels.

Major proportions of the chlorination by-products consist of chloramines whose concentration in the pool water is monitored as the so-called content of combined chlorine. With the purpose of cutting down the concentration of the chlorination by-products, along with higher disinfecting efficiency, the existing chlorine technologies are improved by integrating UV reactors or ozonization stages. To decrease the content of combined chlorine and, also, for disinfection, the radiation of medium pressure UV discharge lamps [1-4] that can decompose monochloramine, dichloramine, and trichloramine at a sufficient dose is used ever more frequently. The ozonization of pool water can result into cutting down not only the chloramine contents, but also the concentration of their precursors, while enhancing the extent of

disinfection. The oxidizing and disinfecting effects of ozone are markedly better than those of chlorine. The German standard DIN 19 643 [2] indicates the option of using an ozonization stage including a reaction and degassing vessel for the treatment of pool water, but this requires the decomposition of the remaining dissolved ozone on an active carbon filter prior to the inflow of treated water into the pool. A similar technology has been used also in a patent [1] where the treated water feeding the pool does not contain ozone as well. In both mentioned cases chlorination has been used for the pool water sanitation. According to patents [3,4], ozone is applied in a simple way (without reaction tanks) and without any de-ozonization stage. In such cases, however, ozonization serves only for supporting the chlorination of pool water. The concentrations of dissolved ozone are negligible, and that is why no monitoring of their value is needed. All the above solutions, accordingly, only reduce the negative phenomena associated with chlorination, without handling their cause.

Since 2000 the company LIFETECH has installed ozonization technology working without chlorination in a number of public pools, using ozone as the sole disinfectant. With regard to valid legislation and to the fact that some of these pools are used for medical treatment of asthmatic and allergic children, these pools are subject to strict hygienic inspection. However, no problems related to water quality have been established down to the present day. The technology used in those pools is presented in Fig. 1 as the existing art. Water that outflows from the pool (1) proceeds to the balancing tank (2) wherefrom it is pumped (4) onto a filter with combined media of active carbon/sand (5). After the filtration ozone is dosed (6) into water. The ozonized water passes through the reaction and degassing tank (7) wherein oxidation reactions and disinfection take place and at the same time undissolved gases are taken away from the water (8,9). The following steps are the pH adjustment of the water (10) and, shortly before the inflow of treated water to the pool (12), the measurement of dissolved ozone concentration. The control system regulates the ozone dosage, maintaining the concentration of dissolved ozone at the chosen value. Although the passing time of the whole pool volume through the re-circulation system lies considerably under two hours, the concentration of dissolved ozone in the water leaving the pool is roughly half of that at the inflow. This is due to the consumption of ozone for the oxidation of impurities and for the disinfection, and also the consequence of spontaneous decomposition of ozone. The volume of the pool allowing practical utilisation of this technology, however, does not exceed approximately 200 m^3.

The patent [5] of 2005 describes an apparatus using, in addition to metal compounds and disinfectant solutions, also a controlled concentration of ozone in the re-circulated water for cleaning and disinfecting purposes. Other documents [6] show the utilization of UV rays in combination with previous application of ozone or hydrogen peroxide, the sanitation of the pool environment being ensured by the dosage of organic compounds of silver or by the dosage of silver and copper ions. Document [7] suggests, for achieving high quality of water, a method applying both ozone and UV radiation, as has been generally known over a long time from industrial and swimming pool applications as an advanced oxidation process. This document also anticipates chlorination of treated pool water prior to its inlet in the pool.

The optimum solution of the task is the replacement of the chlorination by chlorine-free technology of pool water treatment. For this purpose the strong disinfecting capacity of ozone can be used. When drafting the ozonization technology, however, both the instability of ozone and the requirement to maintain the regulation relating to maximum permissible concentration of ozone in ambient air and in water shall be taken into consideration. The solution of this condition resides in removing any impurities to the maximum possible degree and in carrying out highly efficient disinfection prior to the inlet of re-circulated water into the pool, followed by the application of a relatively low amount of ozone for the purpose of sanitation of water in the bathing facility.

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Summary of the invention

The above drawbacks related to chlorination in treating water for basin facilities are solved by the method of pool water treatment in the circulation circuit according to the present invention, ensuring hygienic safety while excluding chlorine based preparations, where water treatment is achieved by a combination of advanced oxidation process using OH radicals in at least one technological stage with ozonization, the purpose of the advanced oxidation process residing in maximum possible removal of micro-organisms and polluting compounds from the water to be treated, so as to achieve the follow-up sanitation of pool water by only low concentrations of ozone dissolved in water, i.e. at least 0.001 mg/l O_3 in the whole volume of the pool, while the concentration of ozone released from water above its level may not exceed 200 $\mu g/m^3$ for this method.

During the operation the water in the basin facility gets continuously contaminated by polluting compounds and microorganisms that can be oxidized, or disposed of by ozone. If only ozonization is used, the concentration of ozone in the whole volume of the pool should not drop under a few hundred $\mu g/m^3$ for the purpose of ensuring perfect disinfection of water. This value depends upon the water temperature, pH value, the content of salts in water, the bather load etc. The substance of the invention consists in a suitable method described below for treating the inlet water so as to minimize the content of contaminants that would otherwise react with ozone needed for the pool sanitation, thus reducing its concentration. Consequently, ozone is used as an oxidizing and disinfecting agent for the pool.

Regarding the quality of water after its preceding treatment the concentration of ozone dissolved in the pool water of the pool can be maintained at the least possible value, a minimum of 0.001 mg/l O_3, in the optimum case 0.05 to 0.1 mg/l O_3.

This fact relates also to the quality of the air above the water level, and possibly in the pool hall. In comparison with current technologies applying chlorine, chlorine in combination with ozone or ozone only, the use of the invention allows to achieve not only improved quality of water, but also that of ambient air, as the concentration of ozone released from water above its level in the pool will not exceed 200 $\mu g/m^3$. This will be positively reflected in the health of the visitors as well as of the personnel of the facility, including the possibility of trouble-free

utilisation of the facility by asthmatics and allergists, and also in cutting down the corrosion of materials used around the pool and in the hall of the pool facility.

Currently the most efficient method allowing to minimize water contamination and to carry out its highly efficient disinfection at the same time, resides in the use of oxidation ability of OH radicals, i.e. in applying the so-called Advanced Oxidation Process (AOP). If, for the purpose of relative comparison of oxidation abilities, the redox potential of chlorine is considered to be equal 1.00, then hypochlorous acid will have 1.10, chlorine dioxide 1.15, hydrogen peroxide 1.31, and ozone 1.52, but in the case of OH radicals the value will be 2.06, i.e. substantially higher than in any other oxidant that can be utilised for the pool technology. The lifetime of OH radicals amounts to microseconds, their oxidation reactions being very fast. The advanced oxidation process, accordingly, has small requirements for the retention of water in the area of the reactor, and at the same time the OH radicals cannot leave the space of the reactor.

An increased generation of OH radicals is achievable and can be utilised for the advanced oxidation process: 1) reaction of ozone with hydrogen peroxide, 2) interaction between ozone and UV radiation under the presence of water, 3) interaction between hydrogen peroxide and UV radiation under the presence of water, 4) interaction of UV radiation with water under the presence of TiO_2 based photocatalysts, 5) direct photolysis of water by short wave UV radiation (Vacuum UV). Under the concept of UV radiation for the purpose of describing the present invention also any UV radiation will be understood that is usually defined by the wavelengths from 10 to 390 nm, irrespective of its source, such as low pressure or medium pressure discharge lamps or excimer sources. Regarding the advanced oxidation process (AOP), for the purpose of description of this invention, one of the above methods of generating OH radicals in the treated water or their combination is meant. The subject of this text is no detailed description of the implementation of various types of the advanced oxidation process, these procedures being sufficiently known and their possible modifications having no impact upon the substance of the invention. As far as AOP uses ozone, then some dissolved ozone can be present in the water leaving this technological stage and its concentration can be regulated by way of a sensor monitoring the concentration at the inlet of water to the pool.

During the treatment of water further aspects can be made use of:

a. If the water serving to fill or to re-fill the pool or to dilute the pool water contains oxidizable compounds, it is recommendable to treat the water in advance. Among the currently occurring oxidizable ingredients e.g. iron and manganese cations can be named that can be

removed by inserting a filter for iron and manganese removal in the inlet pipeline or by installing an ozone oxidation stage.

b. Water flowing out of the pool into the balancing tank contains a certain amount of dissolved ozone, which means that the oxidation and disinfection processes continue also in the balancing tank. This effect can be enhanced by supplying an additional amount of ozone into the tank. It is also possible to create an oxidation stage using AOP in this part of the re-circulation technology, such as by dosing hydrogen peroxide into the balancing tank or by providing the tank with UV radiation sources.

c. Water leaving the balancing tank is pumped to the filtration. During the filtration the micro-flocculation effect of ozone is used, improving the efficiency of filtration and allowing cutting down the consumption of chemical flocculants. Unless the pump or the filter is made in an ozone resistant modification, dissolved ozone can be removed from the water pumped from the balancing tank. For this purpose filtration over active carbon, or an even more preferable alternative, namely a UV reactor can be used.

d. The higher the consumption of the ozone in the pool, be it due to its reaction with the contaminants, or due to its spontaneous decomposition, the shorter retention time of water in the pool should be ensured, in other words the velocity of water streaming through the pool should increase. If, in such case, the costs for the treatment technology related to the overall through-flow of water should be to high, a compromise solution can be found residing in that only a part of the overall flow can be treated by the method according to the present invention, whereas the remaining part of the stream will pass through filtration only and join the perfectly purified water afterwards (see Fig. 6).

e. One of the options for cutting down the necessary concentration in the water is dosing chlorine-free inorganic preparations BlueSpark® or BlueSpark Synergy® that have been developed by LIFETECH corporation. In addition to their algicide effects these preparations have also bacteriostatic effects, i.e. they prevent the proliferation of bacteria.

The way of preparing ozone is not essential for the substance of this invention. That is why different variants are not discussed, such as those based upon the generation of ozone by UV radiation, in a corona discharge, or by the electrolysis of water. Due to the same consideration further options of utilising ozone off-gas, such as for treating water in the balancing tank, are not discussed as being notoriously known.

The above options of embodiments according to the invention are further described by way of a number of examples.

Brief description of figures in the embodiments

Fig. 1 Technology reflecting the present art

Figs. 2 – 7 Alternative options of pool water re-circulation using the technology according to the invention

Description of elements in the figures

1	- Pool
2	- Balancing tank
3	- Inlet for filling, re-filling and diluting water
4	- Circulation pump with pre-filter
5, 5′	- Filtration (sand, active carbon etc.)
6	- Dosing of ozone into the water, possibly including a reaction/degassing tank and off-gas ozone destructor
6′	- Dosage of ozone into water, possibly including the reaction/degassing tank and off-gas ozone destructor, or introducing the residual gaseous ozone into the balancing tank in order to be used for oxidation and disinfection
7	- Reaction and degassing tank
8	- Vent valve
9, 15	- Destructor of residual ozone in the off-gas
10	- Correction of pH value
11	- Measurement of the ozone concentration in water at the outlet from the pool
12	- Measurement of the ozone concentration in water at the inlet to the pool
13	- Removal of iron and manganese
14	- Technology using the advanced oxidation process (AOP)
16	- Reactor with UV radiation source

Examples of embodiments of the invention

Example 1

Fig. 2 shows one arrangement alternative of the technology according to the present invention. The concentration of ozone dissolved in water (11) is measured in the water flowing

off from pool (1) to the balancing tank (2). The balancing tank (2) is closed by a cover and the residual ozone off-gas proceeds through the destructor (15) where it is safely decomposed to oxygen. Water from the balancing tank (2) is drawn by circulation pump (4) to the filtration (5), where it is freed from not dissolved impurities. The water further proceeds over the oxidation stage utilising AOP (14), here the oxidation and the decomposition of oxidizable material take place. The dosage of ozone into water (6′) follows, the added amounts being regulated by the control system, as based upon measured concentrations of dissolved ozone at the inlet to the pool (12) and at its outlet (11). Improved safety of the re-circulating technology is achieved by measuring the concentration of dissolved ozone always by two independent sensors, their data being compared. If the difference of the measured values exceeds the permitted tolerance, the situation is evaluated as a failure and the ozonization is switched off. another safety element shown in this picture is checking the concentration of ozone in the air above the water level in the pool. In case of exceeding the selected limit the system declares a disturbance and switches off the ozonization. Prior to water inflow to the pool its pH value (10) is corrected. If the filling water (3) contains oxidizable material, such as iron and manganese, it is appropriate to remove such substances prior to the inflow to the balancing tank (2), i.e. in such case in an iron and manganese removal stage (13).

Example 2

Fig. 3 shows a modification of the embodiment described in example 1. The water is pumped from the balancing tank (2) by circulation pump (4) to filtration (5), where it is freed from not dissolved impurities. The water proceeds further over an oxidation stage utilising AOP (14), where oxidation and decomposition of oxidizable substances take place. Then the water passes through another filter (5′) followed by ozone dosage in the water (6′). The amount of added ozone is regulated by the control system, as based upon the concentration of dissolved ozone determined at the inlet (12) and the outlet (11) from the pool.

Example 3

Another modification of the embodiment according to example 1 is shown in Fig. 4. The water from the balancing tank (2) passes through filter (5) first and then it is pumped by circulation pump (4) to the oxidation stage using AOP (14), where the oxidation and decomposition of oxidizable substances take place. After this stage the dosage of ozone in the water (6′) follows. The amount of added ozone is regulated by the control system as based upon the concentration of dissolved ozone determined at the inlet (12) and outlet (11) from the pool.

Example 4

Fig. 5 shows another possible embodiment according to the invention. The concentration of dissolved ozone (11) is measured in the water flowing from the pool (1) to the balancing tank (2) and then a further amount of ozone (6′) is added. The balancing tank (2) is closed by a cover, the residual ozone off-gas proceeds through the destructor (15), where it is safely decomposed to oxygen. The balancing tank (2) serves at the same time as an oxidation stage utilising AOP (14). The water from the balancing tank (2) is pumped by circulation pump (4) to filtration (5), where it is freed from not dissolved impurities. The dosage of ozone to water (6) takes place after the filtration. The ozone dosage is regulated by the control system as based upon the concentration of dissolved ozone determined at the inlet (12) and the outlet (11) from the pool. Prior to the water inflow to the pool the pH value (10) gets corrected.

Example 5

Fig. 6 shows an embodiment of the present invention for the case that does not allow the installation of a full through-flow system wherein all re-circulated water passes through an efficient filtration (5) and an oxidation stage utilising AOP (14). This arrangement differs from the embodiment in Fig. 2 in that a part of the water from the balancing tank (2) is pumped by pump (4′) over filtration (5′) with lower efficiency than that in filtration (5) and then returns to the main stream having passed through stages (5), (14) and (6′). This arrangement ensures the necessary speed of changing the water in the pool. The speed of decrease of the ozone concentration in the pool water will be higher, but due to the shorter retention time of water in the pool the difference of concentrations of ozone measured at the inlet (12) and at the outlet (11) will be acceptable.

Example 6

Fig. 7 shows a specific embodiment according to the invention. The concentration of the dissolved ozone (11) is measured in the water at the outflow from the pool (1) to the balancing tank (2). The balancing tank (2) is closed with a cover, the residual ozone off-gas proceeds through the destructor (15) wherein it is safely decomposed to oxygen. The water from the balancing tank (2) is pumped by circulation pump (4) to filter (5), where it is freed from not dissolved impurities. After the filtration the dosage of ozone (6′) into the water follows. The dose of ozone is regulated by the control system on the basis of measured values of dissolved ozone at the inlet (12) and the outlet (11) in the pool. Water containing ozone enters the UV

reactor (16) where a part of the ozone is transformed to OH radicals. The advanced oxidation process is controlled so as to ensure that the water leaving the UV reactor (16) contains dissolved ozone. In such embodiment the elements (6′) and (16) create jointly an oxidation stage utilising AOP (14). Prior to the water inflow to the pool its pH value (10) is corrected.

The above examples serve for illustration without exhausting all options of embodying the technology according to this invention, as will be obvious for a person skilled in the art on the basis of the above information.

CLAIMS

1. Method of pool water treatment in a circulation circuit ensuring hygienic safety and eliminating chlorine based preparations **characterized in that** the treatment of water is carried out by a combination of advanced oxidation process utilising OH radicals in at least one technological stage and ozonization, the aim of the advanced oxidation process residing in maximum possible removal of micro organisms and polluting compounds from the treated water allowing to ensure the follow-up sanitation of water in the pool by a low concentration of ozone dissolved in water, with minimum 0.001 mg/l O_3 in the whole volume of the pool, while the concentration of ozone released from the water above the water level does not exceed 200 $\mu g/m^3$ in this method.

2. Method of pool water treatment according to claim 1 **characterized in that** the optimum concentration of ozone dissolved in water is 0.05 to 0,1 mg/l O_3 and the concentration of ozone released from the water above its level does not exceed 100 $\mu g/m^3$.

3. Method of pool water treatment according to claim 1 **characterized in that** the OH radicals utilised in the advanced oxidation process are generated in reaction of ozone with hydrogen peroxide, without depending upon the order of dosage of ozone and hydrogen peroxide into the water.

4. Method of pool water treatment according to claim 1 **characterized in that** the OH radicals utilised in the advanced oxidation process are generated by the effect of UV radiation upon ozone.

5. Method of pool water treatment according to claim 1 **characterized in that** the OH radicals utilised in the advanced oxidation process are generated by the effect of UV radiation upon hydrogen peroxide.

6. Method of pool water treatment according to claim 1 **characterized in that** the OH radicals utilised in the advanced oxidation process are generated by the effect of UV radiation upon catalysts containing TiO_2.

7. Method of pool water treatment according to claim 1 **characterized in that** the OH radicals utilised in the advanced oxidation process are generated by photolysis of water due to UV radiation.

8. Method of pool water treatment according to claim 1 **characterized in that** the OH radicals are generated in a process that is any combination of advanced oxidation processes according to claims 3 to 7.

9. Method of pool water treatment according to claim 1 **characterized in that** at least a part of water passing through the circulation circuit is treated in at least one technological stage utilising the advanced oxidation process.

10. Method of pool water treatment according to claim 1 **characterized in that** the water at the outlet of pool (1) passes into the balancing tank (2) wherefrom it is pumped by pump (4) to filter (5) where it is freed from not dissolved impurities, whereupon ozone (6) is dosed into the water and the ozonized water enters the UV reactor (16) where it is treated by advanced oxidation process whereupon, after the correction of pH, it flows back to the pool, the amount of ozone dissolved in water being controlled so as to ensure at least 0.001 mg/l O_3 ozone concentration in the water returning to the pool.

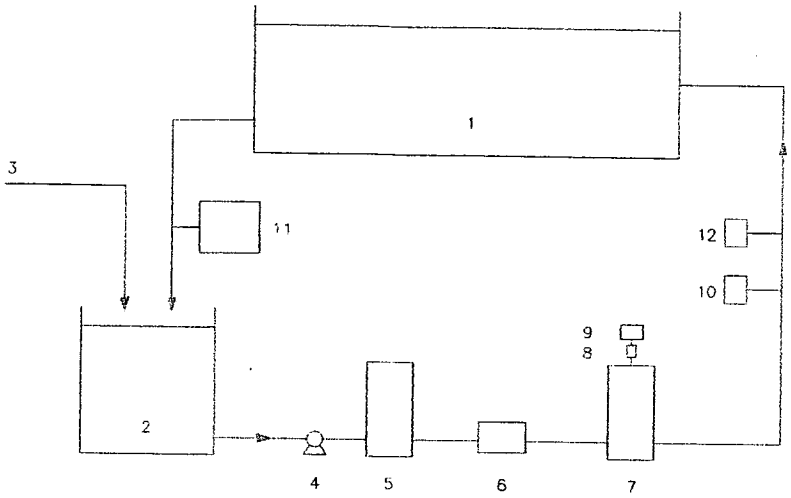


Fig.1

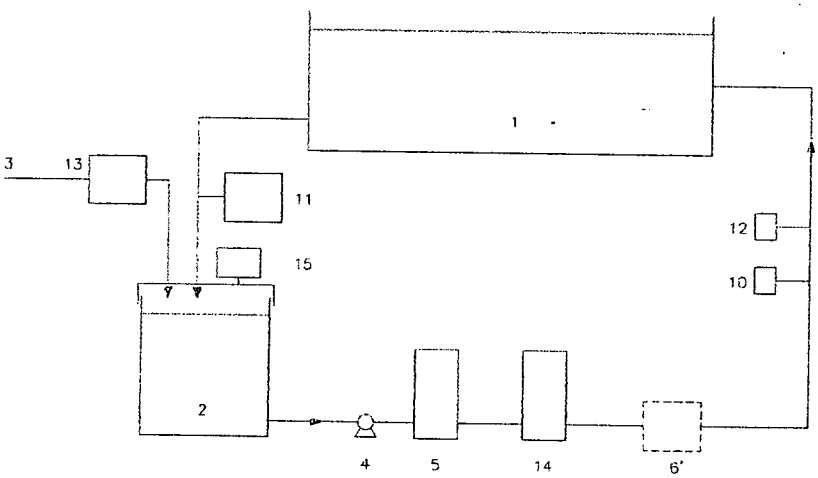


Fig.2

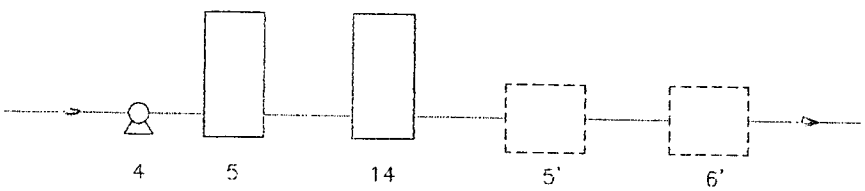


Fig.3

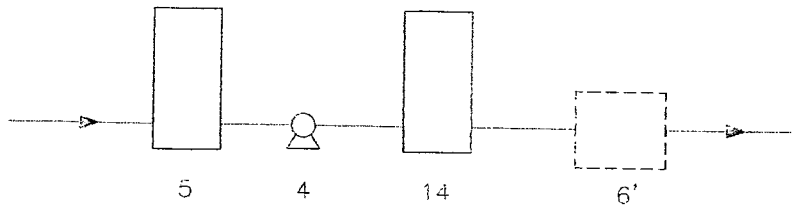


Fig.4

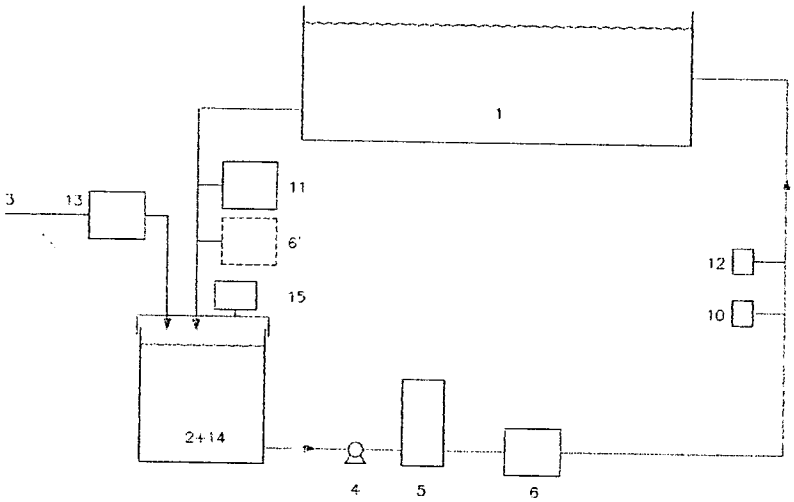


Fig.5

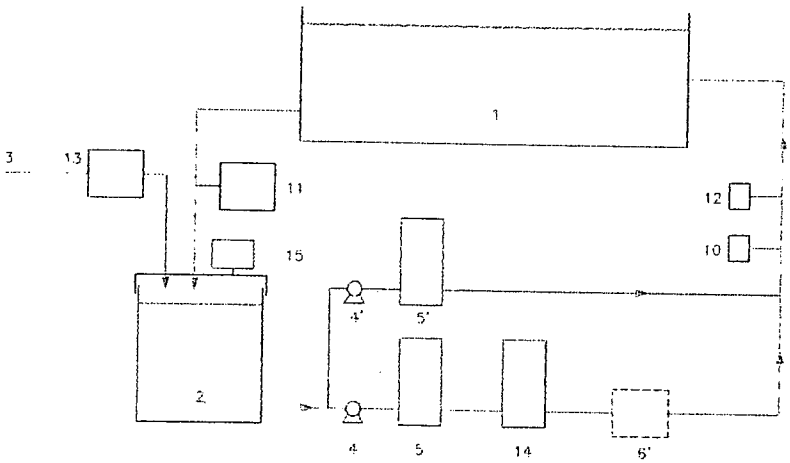


Fig.6

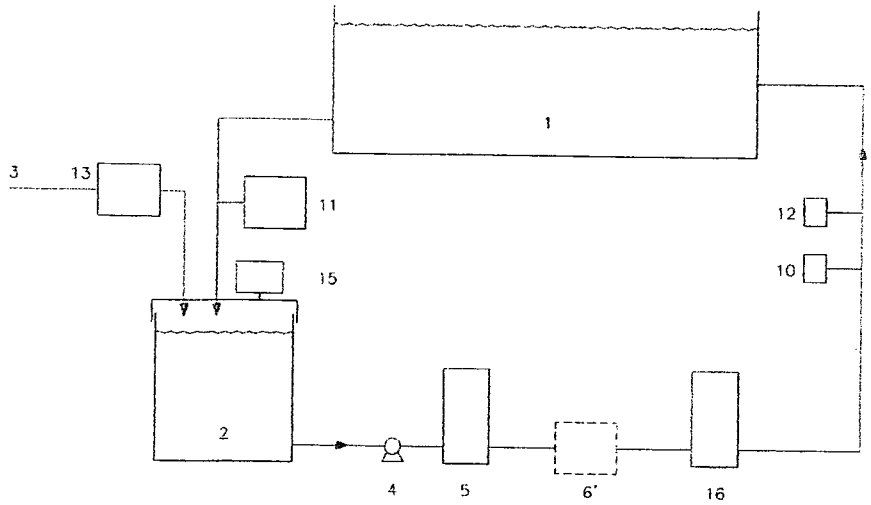


Fig.7