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(54) **DEVICE AND METHOD FOR REDUCING THE HYDROGEN PEROXIDE AND PERACETIC ACID CONTENT IN A WATER FLOW**

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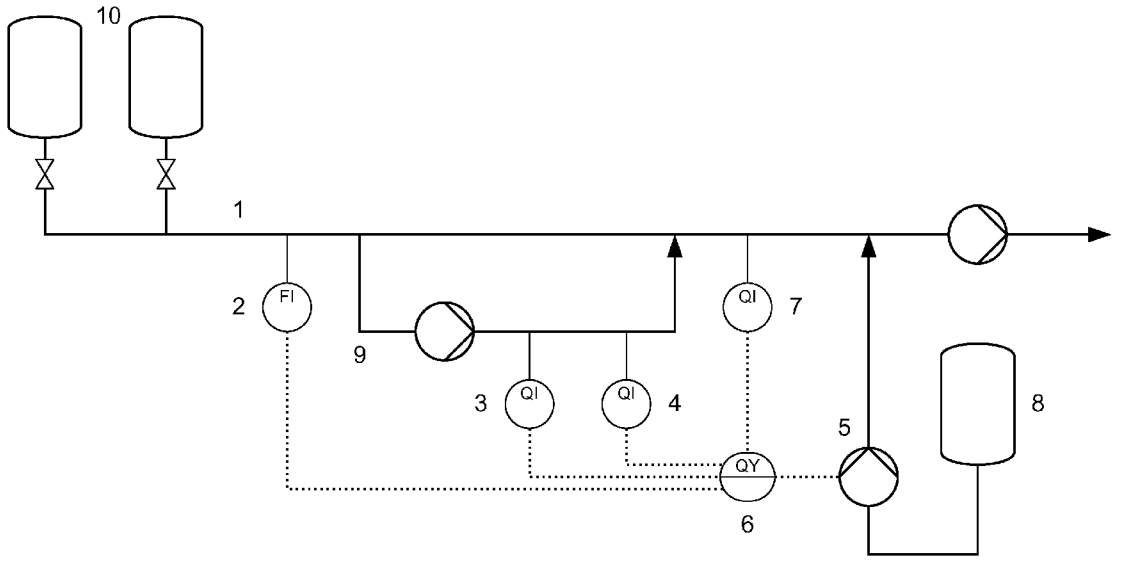
(57) **ABSTRACT**

A device comprising a measuring device for determining the flow rate of a water stream, a measuring device for determining the concentration of hydrogen peroxide in the water stream, a measuring device for determining the concentration of peracetic acid in the water stream, a metering device for metering a reducing agent into the water stream downstream of the measuring devices for the concentrations, and a control device which, from the flow rate of the water stream, the concentration of hydrogen peroxide in the water stream and the concentration of peracetic acid in the water stream, calculates an amount of reducing agent for reducing the content of hydrogen peroxide and peracetic acid to a desired value and actuates the metering device for metering the reducing agent, makes possible reliable reduction of the content of hydrogen peroxide and peracetic acid in a water stream. The device is suitable for reducing the content of hydrogen peroxide and peracetic acid in a water stream which is withdrawn from ballast water tanks of a ship.



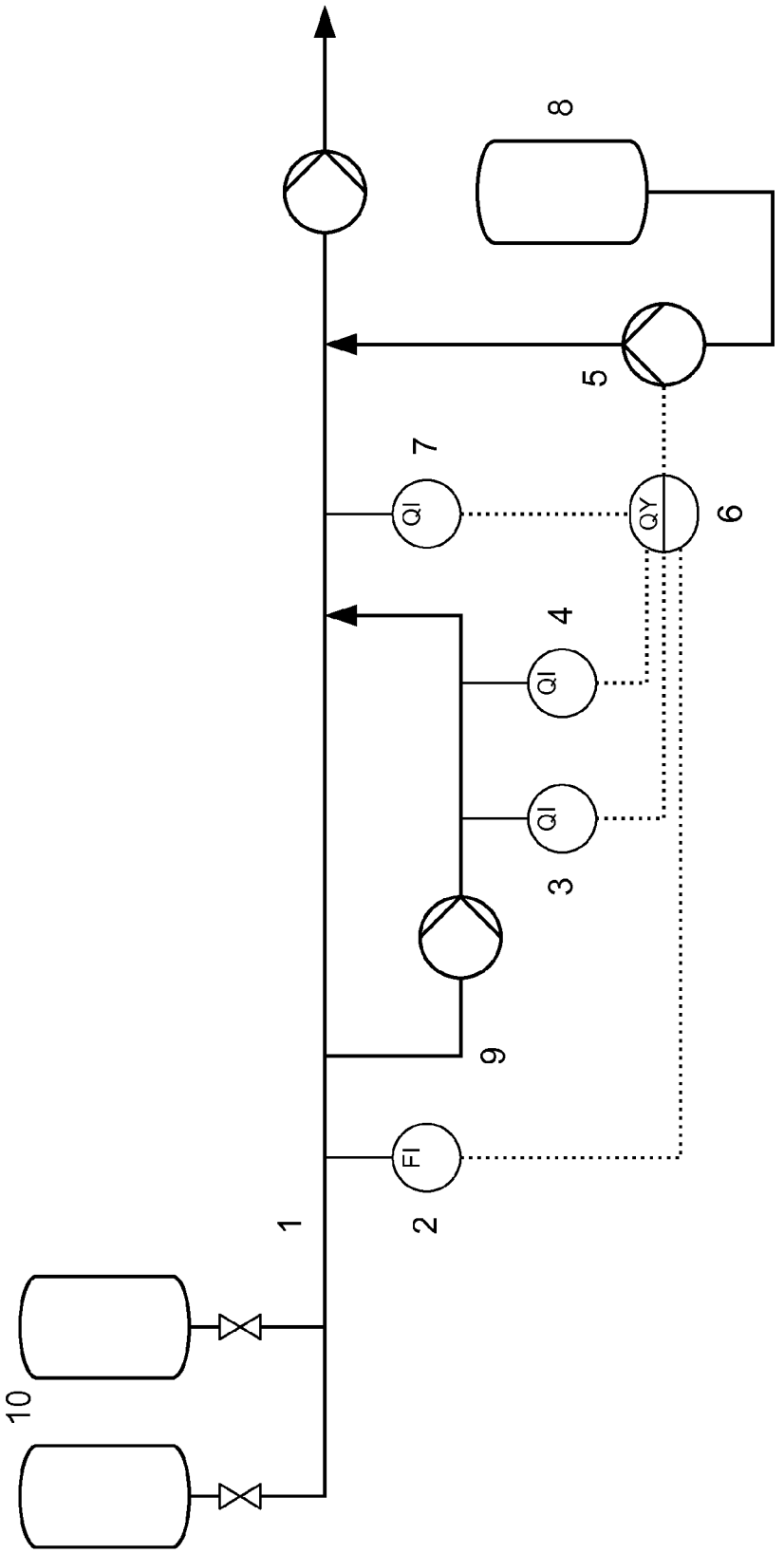


Fig. 1

DEVICE AND METHOD FOR REDUCING THE HYDROGEN PEROXIDE AND PERACETIC ACID CONTENT IN A WATER FLOW

[0001] The invention relates to a device and a method for reducing the content of hydrogen peroxide and peracetic acid in a water stream, in particular in a water stream which is withdrawn from ballast water tanks of a ship.

[0002] Peracetic acid is a biocide which has a number of advantages compared with other biocides. Peracetic acid, even at low concentrations of less than 5 ppm, exhibits a broad biocidal activity against bacteria, phytoplankton and zooplankton, without resistances occurring. In contrast to most other biocides, peracetic acid in dilute aqueous solutions is rapidly degraded by hydrolysis and decomposition to substances which are no longer biocidally active. In contrast to ozone or chlorine dioxide, peracetic acid can safely be transported and stored in the form of equilibrium peracetic acid. A treatment of water streams with peracetic acid, in contrast to chlorine or hypochlorite, does not lead, or leads only to a small extent, to the formation of halogenated organic compounds and therefore does not lead to an increase in the AOX content. Peracetic acid is therefore suitable for the biocidal treatment of water streams which are released into the surroundings in a large amount after the treatment, such as, for example, cooling water streams or sewage treatment plant discharges and, in particular, ballast water of ships. The treatment of ballast water with peracetic acid in the SEDNA® method is approved by the International Maritime Organization (IMO) for the removal of phytoplankton and zooplankton.

[0003] Although peracetic acid and the hydrogen peroxide that is present in equilibrium peracetic acid due to the production process rapidly degrade in the treated water, it can be necessary in some applications, in particular in the treatment of ballast water, to remove any residual amounts of peracetic acid and hydrogen peroxide still present after the treatment before the treated water is released to the surroundings.

[0004] For removing chloramines or bromamines from treated ballast water, WO 02/072478 proposed to add a reducing agent such as sodium thiosulphate or sodium sulphite in a molar excess to the treated ballast water. In this method, however, after reducing the chloramine or bromamine, oxygen must further be introduced into the treated water before it can be released to the surroundings.

[0005] WO 2004/054932 proposes to add a solution of sodium thiosulphate to the ballast water and control this metering via the redox potential of the chlorine-containing ballast water ror removing electrolytically generated chlorine from treated ballast water.

[0006] WO 2006/058261 and WO 2008/153808 propose to add a solution of sodium sulphite to the ballast water and control this metering via a sulphite analyser, which releases SO_2 by acid addition and determines this with a sensor, in such a manner that the treated ballast water contains excess sodium sulphite for removing electrolytically generated hypochlorite from treated ballast water.

[0007] US 2010/072144 proposes to add a solution of sodium sulphite to the ballast water and control this metering via measurement of the redox potential in the ballast water after addition of the sodium sulphite solution in such a manner that the redox potential is in the range from 200 to 500 mV for removing hypochlorite from treated ballast water.

[0008] U.S. Pat. No. 7,776,224 proposes to measure the concentration of hydrogen peroxide in the ballast water and add a reducing agent on the basis of the measured value for removing hydrogen peroxide from treated ballast water. It is further proposed to check after addition of the reducing agent with a hydrogen peroxide densitometer or measurement of the redox potential whether unreacted hydrogen peroxide is present.

[0009] EP 1 671 932 proposes to add one of the substances iron(II) sulphate, iodide or catalase with the oxidizing agent for a treatment of ballast water with hydrogen peroxide or equilibrium peracetic acid, in order to achieve decomposition of hydrogen peroxide during the ballast water treatment.

[0010] However, there is still a need for a device and a method that allows to reduce the content of hydrogen peroxide and peracetic acid in a water stream as required and with which the water stream, after removal of hydrogen peroxide and peracetic acid, contains no substances hazardous to water.

[0011] The inventors of the present invention have established that the method known from US 2010/072144 for removing hypochlorite is not suitable for removal of hydrogen peroxide from a water stream, since, by measuring the redox potential in the water after addition of a reducing agent, it cannot be reliably established that the water does not contain either unreacted hydrogen peroxide or excess reducing agent. Also, the method known from WO 2004/054932 for removing chlorine is not suitable for removing peracetic acid and hydrogen peroxide from a water stream, since the amount of reducing agent which would be required for removing peracetic acid and hydrogen peroxide cannot be calculated in advance from the redox potential of a water stream containing peracetic acid and hydrogen peroxide.

[0012] The inventors of the present invention have therefore developed a device and a method by means of which the contents of hydrogen peroxide and peracetic acid can be reliably reduced in a water stream.

[0013] The invention relates to a device for reducing the content of hydrogen peroxide and peracetic acid in a water stream (**1**), comprising a first measuring device (**2**) for determining the flow rate of the water stream, a second measuring device (**3**) for determining the concentration of hydrogen peroxide in the water stream, a third measuring device (**4**) for determining the concentration of peracetic acid in the water stream, a metering device (**5**) for metering a reducing agent into the water stream downstream of the second and third measuring devices and a control device (**6**) which, from the flow rate of the water stream, the concentration of hydrogen peroxide in the water stream, and the concentration of peracetic acid in the water stream, calculates an amount of reducing agent for reducing the content of hydrogen peroxide and peracetic acid to a desired value and actuates the metering device for metering the reducing agent.

[0014] The invention additionally relates to a method for reducing the content of hydrogen peroxide and peracetic acid in a water stream, comprising metering a liquid reducing agent into the water stream using a device according to the invention. The water stream is preferably withdrawn from ballast water tanks (**10**) of a ship.

[0015] FIG. **1** shows a device according to the invention in an embodiment having an additional measuring device (**7**) for determining the salinity and an arrangement of the second and the third measuring device in a side stream (**9**).

[0016] The device according to the invention comprises a first measuring device (**2**) for determining the flow rate of the water stream (**1**). For this purpose, measuring devices which which determine a mass flow rate as well as measuring devices which determine a volumetric flow rate are both suitable. For the device according to the invention, all measuring devices known from the prior art for determining the flow rate of a water stream may be used such as, for example, mass flow meters, differential pressure measurements at orifice plates and inductive flow meters. Preferably, a mass flow meter is used for determining the flow rate of the water stream in order to determine the flow rate of the water stream reliably even for water streams having different salt contents.

[0017] The device according to the invention additionally comprises a second measuring device (**3**) for determining the concentration of hydrogen peroxide in the water stream (**1**). Suitable measuring devices are all those known from the prior art with which the concentration of hydrogen peroxide may be determined in water and which do not exhibit, or exhibit only to a slight extent, a cross-sensitivity to peracetic acid. Suitable measuring devices are, for example, those which determine the concentration of hydrogen peroxide colorimetrically and use a colour reaction specific for hydrogen peroxide such as, for example, the reaction of hydrogen peroxide with titanyl sulphate, forming a soluble titanium(IV) peroxo complex. Preferably, an amperometric sensor is used for determining the concentration of hydrogen peroxide, particularly preferably an amperometric sensor at which an oxidation of hydrogen peroxide proceeds according to the reaction equation

$$H_2O_2 \rightarrow O_2 + 2\,H^+ + 2\,e^-.$$

[0018] Suitable amperometric sensors for hydrogen peroxide that do not exhibit cross-sensitivity to peracetic acid are commercially available, for example from ProMinent® under the name DULCOTEST® PEROX. The response time of these sensors can be adapted by the manufacturer by exchanging the membrane which covers the sensor to the rate of change of the hydrogen peroxide concentration in the water stream that is to be treated.

[0019] The device according to the invention further comprises a third measuring device (**4**) for determining the concentration of peracetic acid in the water stream (**1**). Suitable measuring devices are all those known from the prior art with which the concentration of peracetic acid may be determined in water and which do not show, or show only to a minor extent, a cross-sensitivity to hydrogen peroxide. Suitable measuring devices are, for example, those which determine the concentration of peracetic acid colorimetrically and use a colour reaction specific to peracetic acid, such as, for example, the reaction of peracetic acid with 2,2-azinobis(3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS), forming a soluble dye. Preferably, an amperometric sensor is used for determining the concentration of peracetic acid, particularly preferably an amperometric sensor at which a reduction of peracetic acid proceeds according to the reaction equation

$$CH_3COOOH + 2\,H^+ + 2\,e^- \rightarrow CH_3COOH + H_2O.$$

[0020] Suitable amperometric sensors for peracetic acid which show a sufficiently low cross-sensitivity to hydrogen peroxide are commercially available, for example from ProMinent® under the name DULCOTEST® PAA. The response time of these sensors can be adapted by the manufacturer, by exchanging the membrane which covers the sensor, to the rate of change of peracetic acid concentration in the water stream that is to be treated. Amperometric sensors that are likewise suitable are commercially available amperometric sensors for determining the total chlorine content, for example the sensors marketed by ProMinent® under the name DULCOTEST® CTE-1. Since, due to the rapid reaction of chlorine and hypochlorite with hydrogen peroxide, a water stream containing hydrogen peroxide can contain only small amounts of chlorine and hypochlorite, and the amperometric sensors for determining the total chlorine content also determine peracetic acid with low cross-sensitivity to hydrogen peroxide, the content of peracetic acid can also be reliably determined in the water stream using such sensors.

[0021] The use of amperometric sensors for determining the concentrations of hydrogen peroxide and peracetic acid makes possible a substantially automated operation of the device according to the invention by staff such as, for example, a ship's crew, that has no training in operating analytical equipment.

[0022] Instead of two separate measuring devices for determining the concentrations of hydrogen peroxide and peracetic acid, it is also possible to use one measuring device, which determines both the concentration of hydrogen peroxide and the concentration of peracetic acid, in the device according to the invention. One example of such a measuring device is an automated titration with sequential cerimetric determination of the hydrogen peroxide concentration and iodometric determination of the peracetic acid concentration.

[0023] The measuring devices for determining the concentrations of hydrogen peroxide and peracetic acid are preferably arranged in a side stream (**9**) of the water stream in order to avoid damage to the measuring devices by solids carried by the water stream. For the same purpose, preferably a filter is arranged in the side stream upstream of the measuring devices.

[0024] The device according to the invention additionally comprises a metering device (**5**) for metering a reducing agent into the water stream (**1**) downstream of the second and third measuring devices. Suitable metering devices are those for continuous or intermittent metering of a reducing agent, which reducing agent is preferably gaseous or liquid, and particularly preferably liquid. Preferably, the metering device comprises a storage vessel (**8**) and a controllable metering pump (**5**) for liquid reducing agent, such that a continuous metering of the liquid reducing agent is possible with a variable volumetric flow rate. Particularly preferably, the metering device comprises a positive-displacement metering pump such as, for example, a diaphragm pump, gear pump or piston pump which makes possible setting a calculated volumetric flow rate for metering liquid reducing agent.

[0025] The device according to the invention further comprises a control device (**6**) which calculates an amount of reducing agent for reducing the content of hydrogen peroxide and peracetic acid to a desired value from the flow rate of the water stream (**1**), the concentration of hydrogen peroxide in the water stream and the concentration of peracetic acid in the water stream, and actuates the metering device (**5**) for metering the reducing agent. The control device can be designed as a hard-wired controller or as a calculation and control program on a process control computer. The calculation of the amount of reducing agent from the flow rate of the water stream, the concentration of hydrogen peroxide in the water stream and the concentration of peracetic acid in the water stream can proceed using empirical conversion factors deter-

mined by experiments or, preferably, using conversion factors calculated from the stoichiometry of the reduction reaction. For salt-free water streams and a reduction using an aqueous solution of sodium sulphite, the conversion factors can be calculated on the basis of the reaction equations (I) and (II).

$$H_2O_2+Na_2SO_3 \rightarrow H_2O+Na_2SO_4 \quad (I)$$

$$CH_3COOOH+Na_2SO_3 \rightarrow CH_3COOH+Na_2SO_4 \quad (II)$$

[0026] For liquid reducing agents which are metered via a positive-displacement metering pump, the volumetric flow rate to be set at the metering pump can be calculated directly from the calculated amount of reducing agent and the metering pump actuated accordingly.

[0027] In a preferred embodiment, the device according to the invention comprises an additional measuring device (**7**) for determining the salinity in the water stream (**1**). The expression salinity here designates the dimensionless salinity S on the Practical Salinity Scale 1978. The salinity can be determined on the basis of density measurements, and preferably on the basis of the electrical conductivity using a conductivity sensor. In this embodiment, the amount of reducing agent is calculated by the control device with the salinity. Preferably, here, the amount of reducing agent calculated for a salt-free water stream is corrected by a correction factor for the salinity determined by experiments. For salt-containing water streams and a reduction with an aqueous solution of sodium sulphite, preferably the amount of reducing agent calculated for a salt-free water stream is increased by a fraction proportional to the salinity. Taking into account the salinity in metering the reducing agent makes possible reliable reduction of the content of hydrogen peroxide and peracetic acid to below predetermined limits even for a variable salt content of the water stream, without overdosing of reducing agent occurring.

[0028] In the method according to the invention for reducing the content of hydrogen peroxide and peracetic acid in a water stream, a liquid reducing agent is metered into the water stream (**1**) by a device according to the invention. The water stream is preferably a water stream treated by adding equilibrium peracetic acid as biocide, in particular a cooling water stream, or a sewage treatment plant discharge, and most preferably, a water stream which is withdrawn from ballast water tanks (**10**) of a ship.

[0029] In the method according to the invention, preferably, an aqueous solution of sodium sulphite is used as liquid reducing agent.

[0030] The method according to the invention makes possible a reliable reduction of the content of hydrogen peroxide and peracetic acid in a water stream below predetermined limiting values, wherein, by using sodium sulphite as reducing agent, the water stream after the treatment no longer has properties impairing the water quality. This makes it possible to discharge a ballast water treated with equilibrium peracetic acid for destroying phytoplankton and zooplankton into bodies of water such as, for example, constricted port basins in which the ballast water is diluted only poorly, without impairing the water quality of the body of water.

EXAMPLES

[0031] For the working exemples embodiments, water which had been taken from a drinking water supply network was treated with 80 ppm equilibrium peracetic acid that contained 14.4% by weight peracetic acid and 13.5% by weight hydrogen peroxide. After the treatment with equilibrium peracetic acid, the water contained 11.9 ppm peracetic acid and 13.3 ppm hydrogen peroxide on a weight basis.

[0032] To a stream of the water that had been treated with equilibrium peracetic acid, an aqueous solution of sodium sulphite was metered continuously in a device according to the invention as per FIG. 1. The concentrations of hydrogen peroxide and peracetic acid were determined here using amperometric sensors from ProMinent®. In Example 1, 1.03 times the stoichiometric amount of sodium sulphite, calculated according to reaction equations (I) and (II) from the concentrations of hydrogen peroxide and peracetic acid and the flow rate of water, was metered. In Example 2, 1.21 times the calculated stoichiometric amount of sodium sulphite was metered.

[0033] In Example 1, the water contained 0.1 ppm peracetic acid and 1.0 ppm hydrogen peroxide, on a weight basis, after metering sodium sulphite. In Example 2, the water contained 0.2 ppm peracetic acid and 0.1 ppm hydrogen peroxide, on a weight basis, after the metering of sodium sulphite.

[0034] For the water treated with equilibrium peracetic acid and the water streams obtained in Examples 1 and 2, the inhibition of algal growth and the acute immobilization of daphnia were determined in accordance with OECD guidelines 201 and 202 for the testing of chemicals.

[0035] The water treated with equilibrium peracetic acid caused, undiluted, complete inhibition of the algal growth of *Desmodesmus subspicatus* with an EC_{50} value of 46% for the inhibition of the growth rate and 25% for the inhibition of the yield. In contrast, the water stream obtained in

[0036] Example 1 caused, undiluted, only a statistically insignificant inhibition of the growth rate of 5%. The water stream obtained in Example 2 caused, undiluted, an inhibition of the growth rate of 13%.

[0037] The water treated with equilibrium peracetic acid caused, undiluted, complete immobilization of *Daphnia magna* with an EC_{50} value of 12%. In contrast, the water streams obtained in Examples 1 and 2 caused, even undiluted, no immobilization and displayed no recognizable effect on daphnia.

[0038] The examples show that, with the device according to the invention and the method according to the invention, the contents of hydrogen peroxide and peracetic acid may be reliably reduced in a water stream containing hydrogen peroxide and peracetic acid in such a manner that upon introduction into bodies of water the water stream has no harmful effects on water organisms.

LIST OF REFERENCE NUMERALS

[0039] (**1**) water stream
[0040] (**2**) measuring device for determining the flow rate
[0041] (**3**) measuring device for determining the concentration of hydrogen peroxide
[0042] (**4**) measuring device for determining the concentration of peracetic acid
[0043] (**5**) metering device for metering a reducing agent
[0044] (**6**) control device
[0045] (**7**) measuring device for determining salinity
[0046] (**8**) storage vessel for liquid reducing agent
[0047] (**9**) side stream
[0048] (**10**) ballast water tanks

1-10. (canceled)

11. A device for reducing the content of hydrogen peroxide and peracetic acid in a water stream, comprising:

a) a first measuring device for determining the flow rate of said water stream;

b) a second measuring device for determining the concentration of hydrogen peroxide in said water stream;

c) a third measuring device for determining the concentration of peracetic acid in said water stream;

d) an additional measuring device for determining the salinity in said water stream;

e) a metering device for metering a reducing agent into said water stream downstream of the second and third measuring devices; and

f) a control device which, from the flow rate of said water stream, the concentration of hydrogen peroxide in said water stream, the concentration of peracetic acid in said water stream and the salinity, calculates an amount of reducing agent for reducing the content of hydrogen peroxide and peracetic acid to a desired value and actuates the metering device for metering the reducing agent.

12. The device of claim **11**, wherein the measuring device for determining the concentration of hydrogen peroxide in said water stream comprises an amperometric sensor.

13. The device of claim **11**, wherein the measuring device for determining the concentration of peracetic acid in said water stream comprises an amperometric sensor.

14. The device of claim **11**, wherein the measuring device for determining the salinity comprises a conductivity sensor.

15. The device of claim **11**, wherein the metering device for metering a reducing agent comprises a storage vessel and a controllable metering pump for liquid reducing agent.

16. The device of claim **11**, wherein the second and third measuring devices are arranged in a side stream of said water stream.

17. A method for reducing the content of hydrogen peroxide and peracetic acid in a water stream, comprising metering a liquid reducing agent into the water stream using the device of claim **11**.

18. The method of claim **17**, wherein said water stream is withdrawn from ballast water tanks of a ship.

19. The method of claim **17**, wherein the liquid reducing agent is an aqueous solution of sodium sulphite.

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