(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 November 2014 (20.11.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/186167 A1

(51) International Patent Classification:
C02F 1/78 (2006.01)

(21) International Application Number:
PCT/US2014/036827

(22) International Filing Date:
5 May 2014 (05.05.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201310183623.2 17 May 2013 (17.05.2013) CN

(71) Applicant: **ECOLAB USA INC.** [US/US]; 370 N. Wabasha Street, St. Paul, Minnesota 55102 (US).

(72) Inventors: **LI, Shu**; 1-3F of Building C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai 201206 (CN). **CHENG, Liang**; No. 28, 280 Yangchen Road, Shanghai 200043 (CN). **ZHANG, Lujun**; Rm. 1702, No. 8, Ln. 989, Xikang Rd., Shanghai 200060 (CN). **DANG, Xiaojun**; 619 Yaohong Road, Building #2, Apt. 1102, Shanghai 200336 (CN).

(74) Agent: **SORENSEN, Andrew D.**; Ecolab USA Inc., 655 Lone Oak Drive, Eagan, Minnesota 55121 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, 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, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

[Continued on next page]

(54) Title: AUTOMATIC CONTROL SYSTEM FOR OZONE DOSING IN THE COMBINATION OF OZONE AND BIOTREATMENT PROCESS

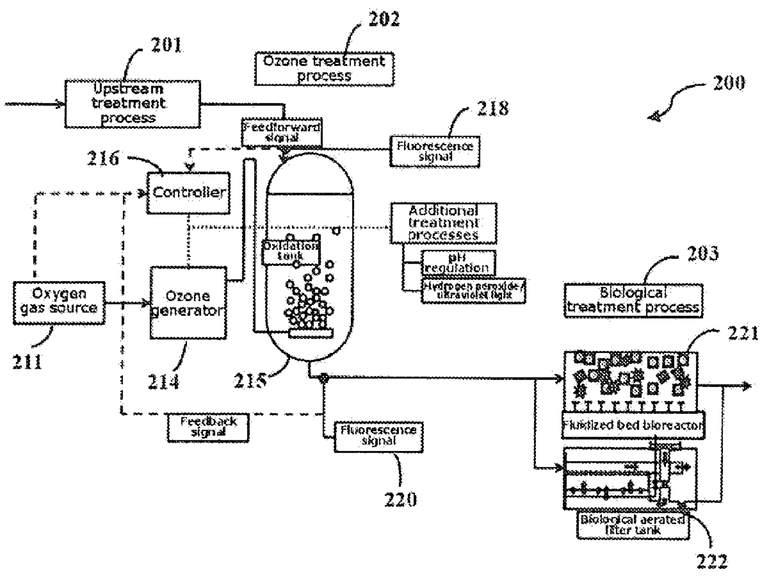


Fig. 2

(57) Abstract: The present invention relates to a water treatment system, which comprises an ozone treatment subsystem and a biological treatment subsystem, wherein the ozone treatment subsystem comprises an ozone generator, which generates ozone to be dosed into the water flow to be treated; an ozone processor, which utilizes ozone to treat water and outputs the ozone-treated water to the biological treatment subsystem; at least one water quality parameter indicators, which is used for acquiring at least one indication signal with correlation to the water quality parameters of the water to be measured, and is arranged in at least one of the following positions: at the upstream of the ozone processor, between the ozone processor and the biological treatment subsystem, and at the downstream of the biological treatment subsystem; and a controller, which is configured to receive the at least one indication signal from the at least one water quality parameter indicator, and determines in real time the optimal dosage of ozone according to the at least one indication signal, wherein the ozone generator doses ozone to the ozone processor based on the optimal dosage determined by the controller.

WO 2014/186167 A1

Published:

— *with international search report (Art. 21(3))*

AUTOMATIC CONTROL SYSTEM FOR OZONE DOSING IN THE COMBINATION OF OZONE AND BIOTREATMENT PROCESS

TECHNICAL FIELD

The present invention relates to a water treatment system, specifically relates to the automatic control of dosing ozone for water treatment, and particularly relates to an automatic control system for dosing ozone in a combined ozone-biological treatment process in industrial wastewater treatment.

BACKGROUND ART

Along with the more and more strict requirements of the government for energy saving and emission reduction in industrial production, the tertiary treatment of industrial wastewater is in need of the support from new technologies in two aspects, namely meeting emission standards and reuse of reclaimed water. Ozone is a highly efficient oxidant widely used in the disinfection and sterilization of drinking water, and owing to its special oxidation performance, ozone has nowadays become one of the best choices for removing refractory organic substances in industrial wastewater. However, the preparation of ozone is not cheap, and requires consumption of electric energy and feed gas (air or oxygen). Thus, with regard to the refractory organic substances in industrial wastewater, a key direction in research and development of the tertiary treatment of industrial wastewater is how to economically and effectively utilize ozone to remove organic substances, allowing it to meet emission standards and become recyclable.

During the oxidation of organic substances, ozone usually firstly oxidizes the organic substances into aldehyde, ketone and alcohol substances in a stepwise manner, and then performs further mineralization. Due to the production of small organic molecules, the oxidation efficiency of ozone is gradually reduced along with the oxidation process. In engineering practices, for the combined process of ozone and biological treatment, just the strong oxidization property of ozone is utilized to oxidize the refractory organic substances to obtain readily biodegradable organic intermediates, and then further remove the produced organic intermediates by the degradation function of the biological treatment. Such combined ozone-biological treatment process utilizes the respective advantages of ozone and the biological treatment, such that economic and effective removal of refractory organic substances is made possible.

However, in the combined ozone-biological treatment process, the dosage of ozone is a very critical parameter. Since in the industrial application of the combined ozone-biological treatment process, the water quality of each system is different and design parameters are different, it is very critical to find the optimization value of the dosage of ozone. If the dosage is too small or large, the effect of the post-stage biological treatment can be affected, thereby affecting the treatment effect of the overall combined process and increasing the operating costs etc. Therefore, in the engineering practices, the control of the optimal ozone dosage is an important factor in determining whether the combined ozone-biological treatment process can be successfully spread and applied in the market of tertiary treatment of industrial wastewater.

At present, in the application of ozone in industrial wastewater treatment, technical solutions implementing on-line control of the ozone dosage are very few. Since the industrial wastewater quality fluctuation is relatively high, if ozone dosing is controlled according to the specific conditions of the wastewater quality, and the oxidation level is correspondingly adjusted to ensure the effectiveness if the subsequent biochemical stage, then great saving of the operating cost can be achieved and the optimized control of the overall treatment system is achieved. The on-line dosing of ozone can be controlled by adopting different parameters, including ozone residual concentration in tail gas or water and characterizing pollutant concentration in water. In the combined ozone-biological treatment process, the concentration of the organic substance and the biodegradability are indicators of most interest, so direct monitoring of the concentration of the organic substance in wastewater is one of the optimal methods for directly controlling the ozone dosage.

Optical detection methods for measuring organic substance content in water have special technical advantages of their own: using a simple system, and no need of dosing chemical reagents; rapid measurement, and high reading reliability; relatively-low operation and device investments, etc. Most of the optical detections for organic substances adopt the ultraviolet absorption method, and there are many related commercially available products. Compared with ultraviolet absorption methods, fluorescence analysis is more sensitive, and has lower device costs.

Although an automatic control system can bring many additional values for the combination of the ozone-biological system, practical application of on-line control of the ozone-dosing system by water quality information is still rare in industrial wastewater treatment at present. The reasons lie in the following two aspects: one is the limitation to the application of the ozone-biological system in the wastewater tertiary treatment field in the prior art due to factors such as costs and control precision, and the other one is the lack of suitable and reliable on-line sensors.

There are some patents and commercial products related to automatic control devices for dosing ozone based on the monitoring of the concentration of water pollutants, most of which are based on ultraviolet absorption as the principle. The monitored indicator is the absorption constant of a sample at the wavelength of 254 nm. UV 254 is a commonly used principle of optical sensors for monitoring the organic substances in water, with the advantages of high correlation, simple operation and easy implementing of continuous operations, but the ultraviolet absorption needs relatively-precise light sources, as a result, these sensors generally have high costs, and insufficient sensitivity as compared with fluorometers used in the fluorescence analysis.

For example, Japanese patent application publication JP H3-56196 discloses a control device for the injection amount of ozone in a water treatment device, wherein ozone is used for removing odor substances in water, and an ultraviolet absorption photometer is used to monitor the concentration of organic substances in water.

In another example, Japanese patent application publication JP H8-318285 discloses an ozone treatment method and device for high-level water purification treatment, wherein the ultraviolet absorption photometer is also used to monitor the concentration of organic substances in water.

In more another example, Japanese patent application publication JP H6-269786 discloses a control method for the injection amount of ozone in a water treatment process, wherein ozone was used for removing odor substances in water, and a TOC (total organic carbon) analyzer is used for determining the total organic carbon (TOC) concentration in water.

Some related patents utilizing fluorescence as the indicator for controlling the automatic ozone dosing are as follows:

for example, Japanese patent application publication JP H10-43776 discloses a control system for an ozone injection device, wherein a fluorescence analyzer is used to detect the organic substance concentration in water, but the objective of the dosing of ozone is to reduce the production of trichloromethane.

In another example, US patent application US2004/0045880 A1 discloses a water treatment control system using a fluorescence analyzer, wherein a fluorescence analyzer is used to detect the concentration of the organic substances in water, but the objective of the dosing of ozone is also to reduce the production of trichloromethane.

Specifically, trichloromethane is a by-product in sterilization, which is harmful to human health and produced by reaction of different organic components with chlorine during the treatment process of drinking water. It can be seen that, the above Japanese patent application publication JP H10-43776 and US patent application US2004/0045880 A1 discloses technical solutions for controlling the dosage of ozone in the drinking water to reduce trichloromethane, but neither consider nor solve the problem of the on-line optimization of the dosage of ozone under the condition of the fluctuation in industrial wastewater quality.

In addition, the above technical solutions use the fluorescence monitoring technique to automatically control the dosage of ozone. The specific dosage of ozone is only directly corresponding to the fluorescence reading. In the systems of these patents, there is only a single ozone oxidation step, and the combined ozone-biological treatment process is not used. If the single ozone oxidation step is used for treating wastewater, for meeting the wastewater emission standards, a very large amount of ozone is consumed, so it is not a feasible method for wastewater tertiary treatment.

Therefore, there is a need for a water treatment system in the prior art, which can optimize the dosage of ozone in the combined ozone-biological treatment process, thereby improving overall treatment efficiency and reducing operating costs.

SUMMARY OF THE INVENTION

An objective of the invention is to provide a water treatment system, to solve the above problems in the prior art particularly in industrial wastewater treatment, thereby to optimize the dosage of ozone in the combined ozone-biological treatment process, improve overall treatment efficiency of water treatment and reduce operating costs.

In one aspect of the present invention, a water treatment system is provided, which comprises an ozone treatment subsystem which utilizes ozone to treat water, and a biological treatment subsystem, which is arranged at the downstream of the ozone treatment subsystem and treats water by a biological treatment process, wherein the ozone treatment subsystem comprises an ozone generator, which generates ozone to be dosed into the water flow to be treated; an ozone processor, which treats water with ozone and outputs the ozone-treated water to the biological treatment subsystem; at least one water quality parameter indicator, for acquiring at least one indication signal with correlation to the water quality parameters of the water to be measured, and arranged in at least one of the following positions: at the upstream of the ozone processor, between the ozone processor and the biological treatment subsystem, and at the downstream of the biological treatment subsystem; and a controller, which is configured to receive said at least one indication signal from said at least one water quality parameter indicator, and determines in real time the optimal dosage of ozone according to the at least one indication signal, wherein the ozone generator doses ozone to the ozone processor based on the optimal dosage determined by the controller.

The combined ozone-biological treatment process as a tertiary treatment method in industrial wastewater treatment, has very high technical feasibility, particularly for refractory organic substances, wherein the combined ozone-biological treatment process changes the biodegradability thereof by ozone oxidation, and further reduces the organic substance content by economic and effective biological treatments, such that emission indicators such as chemical oxygen demand (COD) and total organic carbon (TOC) meet the requirements. In the combination, the dosage of ozone determines the daily operating costs, and the production of ozone requires consuming oxygen gas and electric energy; if the dosage of ozone can be minimized, the application prospect of the combined process can be greatly improved. With the present invention, the dosage of ozone can be saved, and the operating cost is reduced, such that the combined ozone-biological treatment process can be widely used in industrial wastewater treatment.

As to the treatment mode of the combined ozone-biological treatment process per se and the characteristics of industrial wastewater, the minimization of the dosage of ozone can be considered from the following two aspects: the first one is to correspondingly regulate the dosage of ozone according to the fluctuation in the water quality of inlet water. Due to the fluctuation of industrial production, the concentration of organic substances in wastewater fluctuates. The dosage of ozone is regulated according to the concentrations of the organic substances, which can maximally reduce the operating costs. The second one is to regulate the dosage of ozone according to the biodegradability of the ozonized wastewater, thus ensuring refractory organic substances are converted into biodegradable chemical compositions during the ozone oxidation stage. If the dosage of ozone is insufficient, the biodegradability of the outlet water will be insufficient, as a result the biological treatment in the post-stage may not meet the predetermined target, and the overall system treatment efficiency is low; If the dosage of ozone is excessive, then although the concentration of the organic substances is reduced, biodegradable BOD is undesirably reduced when the dosage of ozone is excessive, such that the treatment effect of the biological stage is not good; even if the organic substances during the overall treatment meet the determined target, the operating costs are relatively high due to the excessive dosing of ozone.

Although the fluctuation of the industrial wastewater quality as described above hinders the application of techniques of the on-line control of the dosage of ozone in the ozone-biological system in the field of industrial wastewater treatment, but it is believed that, in certain industries, such as papermaking, pulping, coking and petrochemical industries, if a reliable automatic control platform can be realized and the dosage of ozone is regulated according to the water quality and the post-stage biodegradation conditions, thereby achieving the minimization of the operating costs, then the application prospects of the combined process of the ozone-biological treatment for waste water treatment can be greatly enhanced.

Therefore, the technical solution of the present invention can monitor in real time the water quality indicators in the middle stage of the combined process, to ensure the normal operation of the biological treatment stage, and the outlet water meeting the requirements for water quality indicators.

Alternatively, each of said at least water quality parameter indicator is a fluorometer or an ultraviolet absorption photometer, and correspondingly each of said at least one indication signal is a fluorescence signal or an ultraviolet absorption luminosity signal. Said water quality parameters can be one or more of chemical oxygen demand (COD), biological oxygen demand (BOD), the ratio of biological oxygen demand (BOD)/chemical oxygen demand (COD), or total organic carbon (TOC). However, the fluorescence signals for organic substances have good correlation with the biodegradability of the organic substances. Therefore, for certain industrial wastewater, by using an appropriate excitation wavelength, a fluorescence signal of good correlation with the concentration of the organic substance can be obtained. The use of the fluorescence signal to control the dosage of an oxidant in the ozone stage in the combined ozone-biological treatment process, can improve the efficiency of the organic substance removal during the overall combined process, thereby reducing the operating costs. At the same time, with regard to the characteristic of a relatively high fluctuation in water quality of the industrial wastewater, using the on-line technique to monitor the treatment effect also improves the engineering stability, ensuring the predetermined treatment effect is achieved. In addition, the fluorometer has low manufacture costs, is convenient to use, and preferably is suitable as a wastewater quality monitoring sensor. Particularly, the excitation wavelength of the fluorescence signal used in the water treatment system of the present invention is 360-380 nm, preferably 365 nm and, thus the same fluorometer can be used in industrial wastewater from different industries, thereby reducing the production and application costs of the system according to the present invention.

Said water treatment system establishes a correlation equation representing the correlation between the water quality parameters and the indication signals for the wastewater to be treated, such that said controller determines the corresponding water quality parameters with said at least one indication signal according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters. In one preferred embodiment, a first water quality parameter indicator is arranged at the upstream of the ozone processor, and said controller determines corresponding water quality parameters with a first indication signal acquired by the first water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters. In another preferred embodiment, a second water quality parameter indicator is arranged between the ozone processor and the biological treatment subsystem, and said controller determines corresponding water quality parameters with a second indication signal acquired by the second water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters. In yet another preferred embodiment, the first water quality parameter indicator is arranged at the upstream of the ozone processor, the second water quality parameter indicator is arranged between the ozone processor and the biological treatment subsystem, and said controller determines corresponding water quality parameters with the first indication signal acquired by the first water quality parameter indicator and the second indication signal acquired by the second water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters. In further another embodiment, the first water quality parameter indicator is arranged at the upstream of the ozone processor, the second water quality parameter indicator is arranged between the ozone processor and the biological treatment subsystem, a third water quality parameter indicator is arranged at the downstream of the biological treatment subsystem, and said controller determines corresponding water quality parameters with the first indication signal acquired by the first water quality parameter indicator, the second indication signal acquired by the second water quality parameter indicator and a third indication signal acquired by the third water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters.

In the present invention, the correlation of the water quality parameters and the indication signals can be determined by laboratory measurement data or data obtained by on-line measurement and can be represented by a correlation equation. Moreover, in the present invention, the treatment effect of the ozone stage and the biological stage in various control schemes can be synthetically considered to obtain the optimal dosage of ozone, thereby to realize the globally optimized control of the system performance and costs, rather than only the locally optimized control of the ozone stage.

Preferably, the water treatment system of the invention is an industrial wastewater tertiary treatment system, and said ozone processor treats water with ozone for the ozonization of refractory organic substances. Said water treatment system is applied for treating industrial wastewater of papermaking, pulping, coking and/or petrochemical industries. Particularly, the system of the invention can effectively reduce the cost and improve the control precision in the combined ozone-biological treatment process of the industrial wastewater tertiary treatment.

In one preferred embodiment of the invention, said controller self-adaptively updates said correlation according to the change of the at least one indication signal received from said at least one water quality parameter indicator, such that said controller can determine the optimal dosage corresponding to the change of water quality in response to the change of water quality. Thus, the on-line control of the ozone dosage can adapt to the change of the quality of the water to be treated, thereby ensuring stable outlet water quality and reducing the cost of manual calibration. Said system also can comprise a memory for storing the empirical data of the correlation between the type of the water to be treated and the concentration of the organic substance; and said controller automatically determines and self-adaptively updates said correlation based on the type of the water to be treated selected by a user of said system. By using the empirical data corresponding to different industries, the water treatment system of the invention can select the empirical data of the water type close to the water to be treated as the initial data for optimizing the dosage of ozone, thereby shortening the time required by the optimization, and reducing the costs for deploying the water treatment system of the present invention.

A pre-stage treatment subsystem is provided at the upstream of said ozone oxidation subsystem, and a post-stage treatment subsystem is provided at the downstream of said biological treatment subsystem. Said ozone treatment subsystem further comprises one or more additional treatment units, and said additional treatment unit is arranged at the downstream of the ozone treatment unit and the upstream of the biological treatment subsystem, and said additional treatment unit comprises one or more of a pH value regulation unit, a hydrogen peroxide treatment unit and an ultraviolet light treatment unit, wherein: said at least one water quality parameter indicator is further arranged at the upstream or downstream of said one or more additional treatment units.

At the same time, said water treatment system can acquire necessary operation information of the wastewater treatment process, and can perform data transmission with the centralized control center of a wastewater treatment plant, facilitating to the realization of the global control of the wastewater treatment plant for the treatment of various industrial wastewater.

Said controller further additionally takes into account the technical parameters of the ozone generator to determine in real time the optimal dosage of ozone, so as to balance the yield of the ozone generator and the ozone dosing demand in the optimized control. For example, said technical parameters can be the amount of the ozone generated by the ozone generator, the supply amount of air or oxygen gas, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a water treatment system including an ozone oxidation stage and a biological treatment stage and using a combined ozone-biological treatment process;

Figure 2 is a system block diagram of a water treatment system using a combined ozone-biological treatment process according to one embodiment of the present invention;

Figure 3 is a simplified schematic diagram showing the control of the dosage of ozone according to one embodiment of the present invention;

Figure 4 is a simplified schematic diagram showing the control of the dosage of ozone according to another embodiment of the present invention;

Figure 5 is a curve chart showing the changes of chemical oxygen demand (COD) and biological oxygen demand (BOD) as functions of the dosage of ozone in a combined ozone-biological treatment process;

Figure 6 is a chart showing the relationship between a COD signal and an F fluorescence signal in one embodiment of the present invention; and

Figure 7(A)-7(C) are synchronous fluorescence spectra of industrial wastewater, showing the responses of industrial wastewater to different types to fluorescence signals of different excitation wavelengths.

DETAILED DESCRIPTION

In the following, the particular embodiments of the invention will be described in detail with reference to the drawings. It should be understood that, the description of the particular embodiments are intended to illustratively explain the principle of the present invention and features, such as exemplary structures and methods. Those skilled in the art should understand that, the embodiments of the present invention are not limited to the particular embodiments described herein, but comprise all embodiments falling into the scope of the claims in the present application.

Figure 1 is a schematic diagram of a water treatment system 100 including an ozone oxidation stage and a biological treatment stage and using a combined ozone-biological treatment process. As illustratively shown in the figure 1, a combined ozone-biological treatment process generally comprises but not limited to the following treatments:

a pre-stage treatment 101 generally includes a primary treatment and a secondary (biochemical) treatment of wastewater. In the primary treatment, solid pollutants in a suspension state is removed from wastewater mostly by physical treatment methods, and in the secondary treatment, organic pollutants usually is substantially removed from wastewater by biochemical methods. Preferably, the ozone oxidation stage and the biological treatment stage can be part of the tertiary wastewater treatment. The task of the tertiary treatment generally is to further remove pollutants which are not removed in the secondary treatment, particularly refractory organic substances in industrial wastewater.

An ozone oxidation stage 102 usually executes a high-level oxidation process on the basis of ozone, and can comprise appropriate pH value regulation, and a high-level oxidation process formed with other oxidants (such as hydrogen peroxide) or units (such as UV), etc.

A biological treatment stage 103 usually performs biological aerobic treatment to low-concentration organic substances, such as a biological aeration tank, etc.

The post-stage treatment 104 can be filtration on the basis of membrane materials, such as reverse osmosis membranes.

Figure 2 is a system block diagram of a water treatment system 200 using a combined ozone-biological treatment process according to one embodiment of the present invention. In the embodiment shown in figure 2, as an example, the upstream treatment process 201 can comprise the primary treatment and the secondary treatment of wastewater. The water treatment system 200 further comprises: an ozone treatment subsystem 202, which treats water with ozone, and a biological treatment subsystem 203, which is arranged at the downstream of the ozone treatment subsystem, and treats water with a biological treatment process. As a non-limiting example, the biological treatment subsystem may further comprise a fluidized bed bioreactor 221 and/or a biological aerated filter tank 222. The ozone treatment subsystem comprises: an ozone generator 214, which generates ozone to be dosed into the water flow to be treated with oxygen gas supplied by an oxygen gas source 211 as raw material; it should be understood that the oxygen gas source can supply air or pure oxygen gas according to requirements; an ozone processor 215, which treats water with ozone, and outputs the ozone-treated water to the biological treatment subsystem 203, and as a non-limiting example, the ozone processor in the example is embodied as an oxidation tank; a first fluorometer and a second fluorometer as the water quality parameter indicators arranged respectively at the upstream and the downstream of the ozone processor 215, for acquiring at least one indication signal 218, 220 with correlation to the water quality parameters of the water to be measured, and a controller 216, which is configured to receive fluorescence signals from the first and/or the second fluorometers, and determines in real time the optimal dosage of ozone according the at least one indication signal 218, 220, wherein: the ozone generator 214 doses ozone to the ozone processor 215 based on the optimal dosage determined by the controller 216. Those skilled in the art should understand that, the water quality parameters may include but not limited to one or more of chemical oxygen demand (COD), biological oxygen demand (COD), the ratio of biological oxygen demand (COD)/chemical oxygen demand (COD), or total organic carbon (TOC).

Figure 3 is a simplified schematic diagram showing the control of the dosage of ozone on the basis of water quality parameters in a water treatment system 300 according to one embodiment of the present invention. As an example rather than limitation, in a control method of the dosage of ozone according to the present invention, a correlation equation f1(COD-1) using COD-1 of the inlet water in the ozone oxidation stage 302 as a variable can be used as the control signal of the dosage of ozone. Alternatively, the correlation equation f1(B/C-2) using the ratio of biological oxygen demand (BOD)/chemical oxygen demand (COD) B/C-2 of the outlet water in the ozone oxidation stage 302/the inlet water in the biological treatment stage 303 as a variable can be used as the control signal of the dosage of ozone. In addition, the correlation equation f2(COD-1, B/C-2) using COD-1 and B/C-2 as common variables can also be used as the control signal of the dosage of ozone.

Figure 4 further illustrates the simplified schematic diagram of the control of the dosage of ozone based on water quality parameter indication signals on the basis of the figure 3. Figure 4 shows an embodiment in which said water quality parameter indicators are arranged at the upstream of the ozone processor, between the ozone processor and the biological treatment subsystem, and the downstream of the biological treatment subsystem. Those skilled in the art can understand that the water quality parameter indicators can also be arranged in one or two of the three positions as described above.

When the water quality parameter indicators are arranged at the upstream of the ozone processor and between the ozone processor and the biological treatment subsystem, the structure as shown in figure 2 can be used.

In the embodiment as shown in figure 4, the correlation equation can be obtained from the two parameters COD-1 and B/C-2 as the control variables by fluorescence signals F-1, F-2 and F-3 at three different detection points. In an embodiment, the correlation equations are as follows:

COD -1 = f1(F-1);

COD-2 = f1(F-2);

In addition, COD-3 can be used as an alarm signal, and COD -3 = f2(F-3).

Moreover, the correlation equation between the ratio of biological oxygen demand (BOD)/chemical oxygen demand (COD) and the fluorescence signal can also be established, for example B/C-2 = f3(F-1, F-2, F-3).

It should be noted that the form of expression of the specific correlation equation may be different due to system, water quality, and the type of pollutants, etc. For example, as shown in figure 4, the correlation equation COD-1 = f1(F-1) between the fluorescence signal F1 and the COD signal COD -1 is the same as the correlation equation COD-2 = f1(F-2) between the fluorescence signal F2 and the COD signal COD -2, but is different from the correlation equation COD-3 = f2(F-3) between the fluorescence signal F3 and the COD signal COD-3. Those skilled in the art should understand that, in different embodiments of the present invention, correlation equations between other water quality parameters such as BOD, B/C or TOC and the fluorescence signal can be established, and correlation equations between multiple water quality parameters and the fluorescence signal can be established without departing from the scope of the present invention. In addition, on-line control of the dosage of ozone can also be specifically implemented, according to the technical parameters of an ozone generator, etc. Usually, for each wastewater system, there is a need to establish a particular control method, i.e. a correlation equation, and the correlation between the water quality parameters (e.g. COD) and the fluorescence signal can be achieved by performing experiments on the water sample of wastewater to be treated.

In the combined ozone-biological treatment process, a fluorescence analysis probe is used to automatically control the dosage of ozone, according to the intensity of the fluorescence signal in water and correlation of the fluorescence signal with the concentration and biodegradability of organic substances in water. In the example as described above, the fluorescence signal can be detected in the inlet water of the ozone process stage, and the correlation equation is obtained according to the fluorescence signal and the concentration of the organic substance (COD) in water. In actual engineering practices, the treatment effect of the post-stage biological stage can also be used as one of the parameters, and a control function y = f(x) can be synthetically obtained. This control function comprises two variables: variable y being the dosage of ozone, and it is capable of communicating with the controller of the ozone generation system, thereby to realize the on-line control of the dosage of ozone. The other variable x i.e. is the fluorescence signal in the water (can be one or more fluorescence signals). Usually, the function f(x) used in each wastewater treatment system is required to be tuned in the actual systems, and is synthetically obtained by combining the concentration of the organic substance in water and the post-stage biological treatment effect. If the ozone oxidation system also comprises other treatment modules, such as additional treatment processes of pH regulation, hydrogen peroxide and ultraviolet light, and these additional treatment processes can also be controlled simultaneously by using the fluorescence signals.

The experiment carried out by the present inventors based on a wastewater shows that, in the ozonization process, there is a very good correlation between the fluorescence signal of the wastewater sample with the concentration of the organic substance (represented by chemical oxygen demand (COD)). The results are shown as in figure 7 below, and the fluorescence signal is obtained by actual on-line measurement of a NALCO 3DT fluorometer.

Figure 5 is a curve chart showing the change of chemical oxygen demand (COD) and biological oxygen demand (BOD) as functions of the dosage of ozone in a combined ozone-biological treatment process. In figure 5, the chemical oxygen demand of wastewater is represented by curve 501, and the biodegradability of wastewater is represented by curve 502. As shown in figure 5, along with the increase of the dosage of ozone, the biodegradability presents a trend of first increasing and then decreasing. Therefore, the dosage of ozone corresponding to the maximum value of BOD is the optimal dosage. At the dosage, the optimal balance between the treatment effect and the cost of the ozone treatment subsystem and the biological treatment subsystem at the downstream can be achieved.

Figure 6 is a chart showing the relationship between a COD signal and an F fluorescence signal in another embodiment of the present invention. In a combined ozone-biological treatment process, the water treatment system of the present invention automatically controls the ozone dosage of the ozone oxidation stage based on the on-line fluorescence signal of wastewater. Thus, it is important to determine and update the correlation between COD and the fluorometer reading i.e. the fluorescence signal with respect to different water types and the change of water quality. According to the embodiments of the invention, the correlation can be determined by the laboratory measurement data or the data obtained by on-line measurement, and can be expressed by a correlation equation, and the control of the dosing of ozone can be realized based on the determined correlation equation. In figure 6, the ordinate represents the COD signal using part per million (ppm) as the unit, and the abscissa represents the fluorescence signal expressed by the fluorescence count. As shown in figure 6, on the basis of the laboratory measurement data and the data obtained by on-line measurement, the correlation equation between the fluorescence signal and COD can be obtained, and in this example, a polynomial expression Poly.(COD-1=f(F-1)) of the correlation equation COD-1=f1(F-1) is obtained by fitting between COD-1 and F-1 data obtained from laboratory measurement and on-line measurement, and specifically the correlation equation is:

$$COD = -0.0001(F)^2+0.2687(F)+57.253$$

wherein discriminant coefficient $R^2=0.7005$ indicates that there is very good correlation between the COD signal and the fluorescence signal. Those skilled in the art should understand that, the correlation equation varies depending on the specific system, water quality, pollutant type, etc., and the correlation equations of different forms can be used without departing from the scope of the present invention. In the wastewater treatment system of the embodiment, the control of the dosing of ozone is realized based on the determined correlation equation.

Those skilled in the art can understand that, the responses of different industrial wastewater to the fluorescence signals of different excitation wavelengths are different. Figure 7(A) to figure 7(C) are the synchronous fluorescence spectra of industrial wastewater showing responses of industrial wastewater of different types to the fluorescence signals of different excitation wavelengths, specifically they are the synchronous fluorescence spectra of industrial wastewater with the wastewater fluorescence signals detected by using the UV band as the excitation wavelengths. As shown in the above figures, when the excitation wavelength is about 360-380 nm, the fluorescence signals of the highest intensity can be obtained for wastewater of different types. In this example, the tested wastewater includes wastewater from paper plants as shown in figure 7(A), coking wastewater-1 as shown in figure 7(B) and coking wastewater-2 as shown in figure 7(C). Thus, the fluorescence signal using the excitation wavelength in such a specific range has higher sensitivity. Preferably, the fluorescence signal using the excitation wavelength of 365 nm can achieve high sensitivity in industrial wastewater of different types and facilitate reducing costs for configuring and maintaining fluorometers with different excitation wavelengths.

It should be understood that, the description of the above systems, modules, units, functions and method steps are only used for illustratively describing the principle of the present invention and should not be considered to limit the scope of protection of the present application. The present invention can be implemented by using different combination forms of the above systems, modules, units, functions and method steps. The scope of protection of the present invention is defined by the claims. It also should be understood that, alteration and modification can be made by those skilled in the art to the above systems, modules, units, functions and method steps without departing from the scope of protection of the present invention.

CLAIMS

1. A water treatment system, comprising:

an ozone treatment subsystem, which utilizes ozone to treat water, and

a biological treatment subsystem, which is arranged at the downstream of the ozone treatment subsystem and treats water by a biological treatment process, wherein

the ozone treatment subsystem comprises:

an ozone generator, which generates ozone to be dosed into the water flow to be treated;

an ozone processor, which treats water with ozone and outputs the ozone-treated water to the biological treatment subsystem;

at least one water quality parameter indicator, which is used for acquiring at least one indication signal with correlation to the water quality parameters of the water to be measured, and which is arranged at least one of the positions selected from the group consisting of: upstream of the ozone processor, between the ozone processor and the biological treatment subsystem, and downstream of the biological treatment subsystem; and

a controller, which is configured to receive said at least one indication signal from said at least one water quality parameter indicator, and determines in real time the optimal dosage of ozone according to the at least one indication signal, wherein:

the ozone generator doses ozone to the ozone processor based on the optimal dosage determined by the controller.

2. The water treatment system according to claim 1, wherein each of said at least one water quality parameter indicator is a fluorometer or an ultraviolet absorption photometer, and accordingly each of said at least one indication signal is a fluorescence signal or an ultraviolet absorption luminosity signal.

3. The water treatment system according to claim 1 or 2, wherein said water quality parameter is one or more of chemical oxygen demand (COD), biological oxygen demand (BOD), the ratio of biological oxygen demand (BOD)/chemical oxygen demand (COD), or total organic carbon (TOC).

4. The water treatment system according to claim 1, wherein said water treatment system establishes a correlation equation representing the correlation between the water quality parameters and the indication signals for the wastewater to be treated, such that said controller determines the corresponding water quality parameters with said at least one indication signal according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters.

5. The water treatment system according to claim 4, wherein a first water quality parameter indicator is arranged at the upstream of the ozone processor, and said controller determines the corresponding water quality parameters with the first indication signal acquired by the first water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters.

6. The water treatment system according to claim 4, wherein a second water quality parameter indicator is arranged between the ozone processor and the biological treatment subsystem, and said controller determines the corresponding water quality parameters with a second indication signal acquired by the second water quality parameter indicator

according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters.

7. The water treatment system according to claim 4, wherein the first water quality parameter indicator is arranged at the upstream of the ozone processor, the second water quality parameter indicator is arranged between the ozone processor and the biological treatment subsystem, and said controller determines the corresponding water quality parameters with the first indication signal acquired by the first water quality parameter indicator and the second indication signal acquired by the second water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters.

8. The water treatment system according to claim 4, wherein the first water quality parameter indicator is arranged at the upstream of the ozone processor, the second water quality parameter indicator is arranged between the ozone processor and the biological treatment subsystem, a third water quality parameter indicator is arranged at the downstream of the biological treatment subsystem, and said controller determines the corresponding water quality parameters with the first indication signal acquired by the first water quality parameter indicator, the second indication signal acquired by the second water quality parameter indicator and a third indication signal acquired by the third water quality parameter indicator according to said correlation equation, and thereby further determines the optimal dosage of ozone according to the determined water quality parameters.

9. The water treatment system according to claim 3, wherein

said water treatment system is an industrial wastewater tertiary treatment system, and said ozone processor treats water with ozone for the ozonization of refractory organic substances.

10. The water treatment system according to claim 1, wherein said water treatment system is applied in treating industrial wastewater from papermaking, pulping, coking and/or petrochemical industries.

11. The water treatment system according to claim 1 or 2, wherein said controller self-adaptively updates said correlation according to the change of the at least one indication signal received from said at least one water quality parameter indicator, such that said controller can determine the optimal dosage corresponding to the change of water quality in response to the change of water quality.

12. The water treatment system according to claim 1 or 2, wherein said system further comprises a memory for storing the empirical data of the correlation between the type of the water to be treated and the concentration of the organic substances, and said controller automatically determines and self-adaptively updates said correlation based on the type of the water to be treated selected by a user of said system.

13. The water treatment system according to claim 1, wherein a pre-stage treatment subsystem is provided at the upstream of the ozone oxidation subsystem, and a post-stage treatment subsystem is provided at the downstream of said biological treatment subsystem.

14. The water treatment system according to claim 1, wherein said ozone treatment subsystem further comprises one or more additional

treatment units, said additional treatment units are arranged at the downstream of the ozone treatment subsystem and the upstream of the biological treatment subsystem and comprise one or more of a pH value regulation unit, a hydrogen peroxide treatment unit and an ultraviolet light treatment unit, wherein:

said at least one water quality parameter indicator is further arranged at the upstream or downstream of said one or more additional treatment units.

15. The water treatment system according to claim 1, wherein said water treatment system can acquire information about the operation of the wastewater treatment process, and can perform data transmission with the centralized control center of a wastewater treatment plant.

16. The water treatment system according to claim 1, wherein said controller further additionally takes into account the technical parameters of said ozone generator to determine in real time the optimal dosage of ozone.

17. The water treatment system according to claim 2, wherein the excitation wavelength of said fluorescence signal is 360-380 nm.

18. The water treatment system according to claim 17, wherein the excitation wavelength of said fluorescence signal is 365 nm.

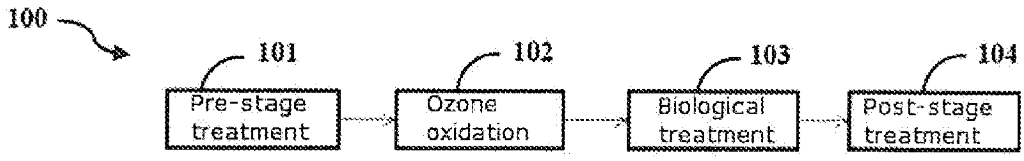

100
101
Pre-stage treatment
102
Ozone oxidation
103
Biological treatment
104
Post-stage treatment

Fig. 1

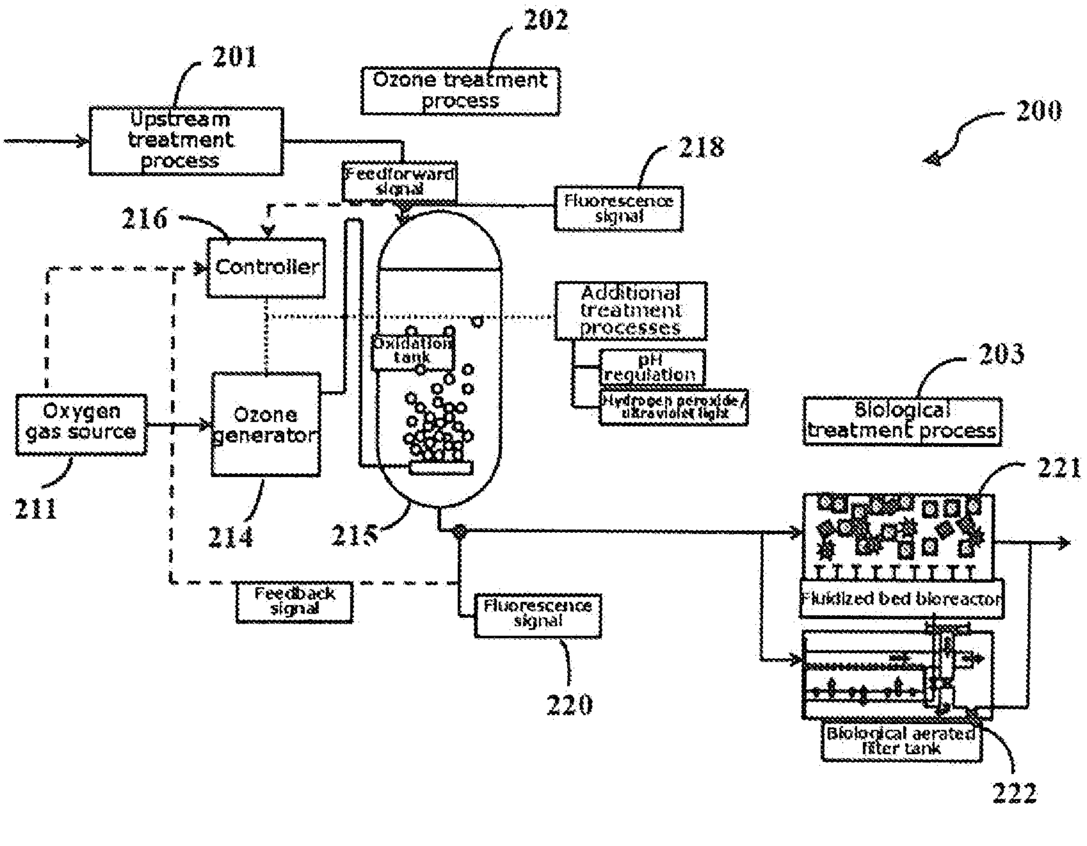

202
Ozone treatment process
201
Upstream treatment process
200
Feedforward signal
218
Fluorescence signal
216
Controller
Additional treatment processes
Oxidation tank
pH regulation
Hydrogen peroxide/ ultraviolet light
203
Oxygen gas source
Ozone generator
Biological treatment process
211
214
215
221
Fluidized bed bioreactor
Feedback signal
Fluorescence signal
220
Biological aerated filter tank
222

Fig. 2

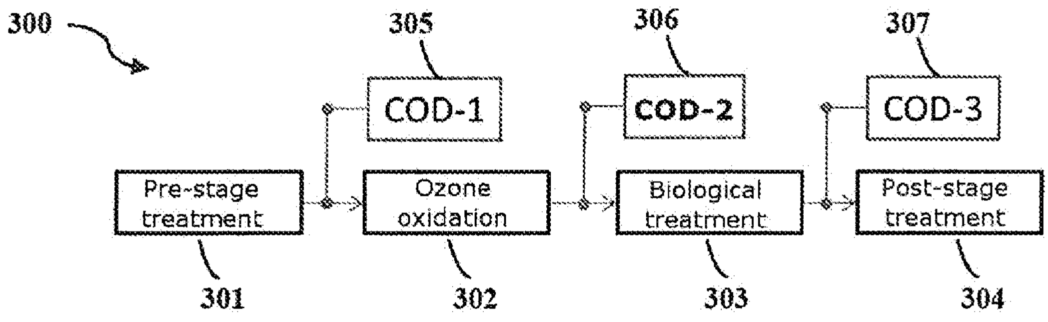

300
305
306
307
COD-1
COD-2
COD-3
Pre-stage treatment
Ozone oxidation
Biological treatment
Post-stage treatment
301
302
303
304

Fig. 3

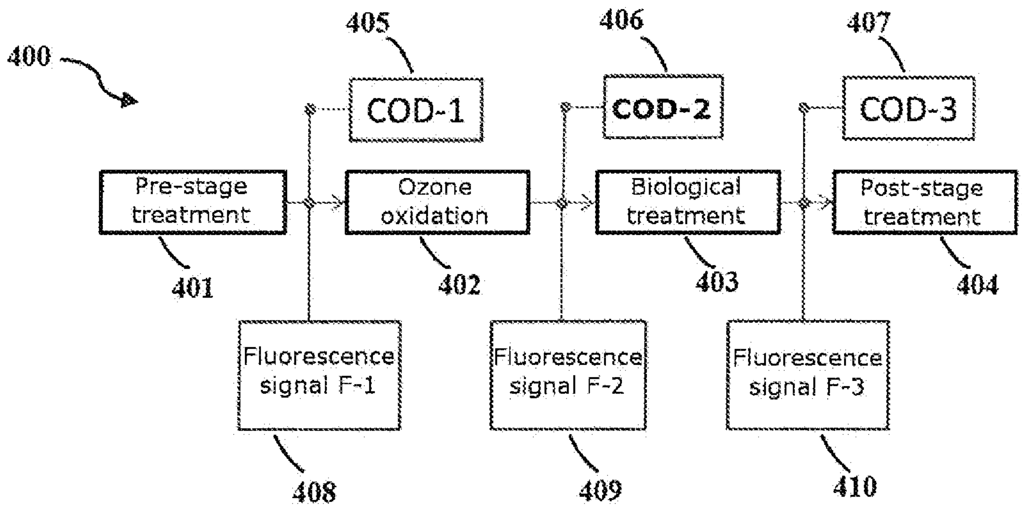

400
405
406
407
COD-1
COD-2
COD-3
Pre-stage treatment
Ozone oxidation
Biological treatment
Post-stage treatment
401
402
403
404
Fluorescence signal F-1
Fluorescence signal F-2
Fluorescence signal F-3
408
409
410

Fig. 4

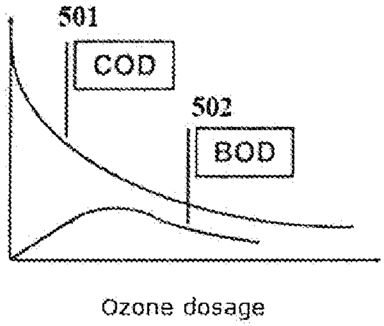

501
COD
502
BOD
Ozone dosage

Fig. 5

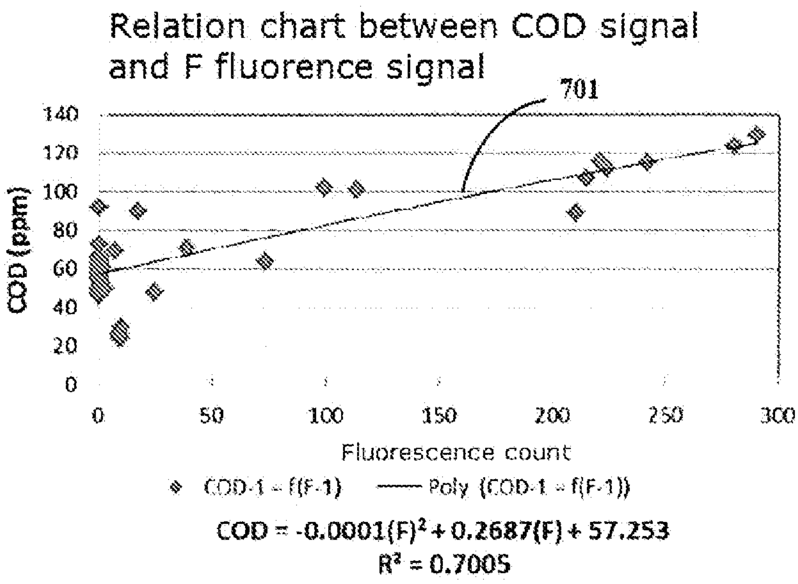
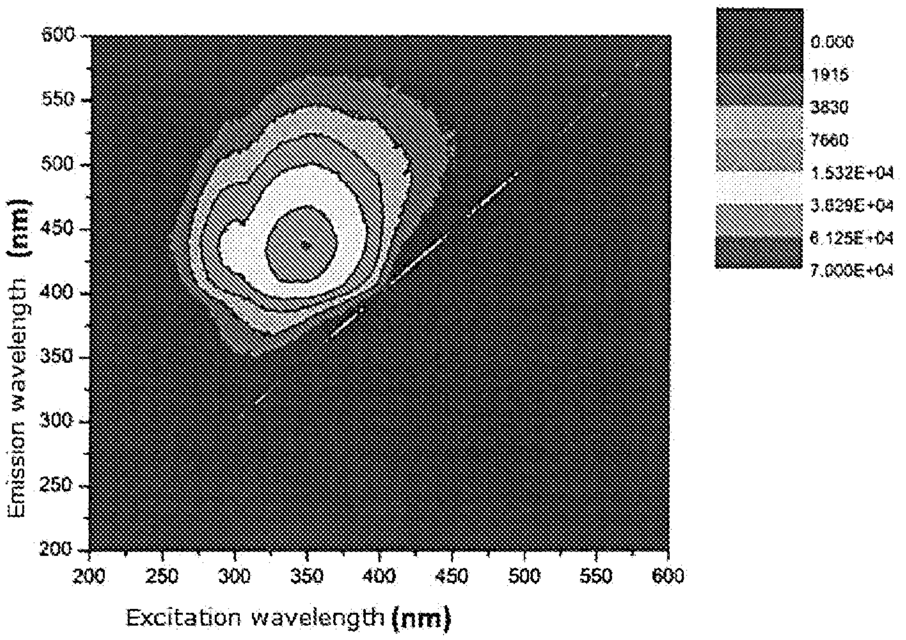
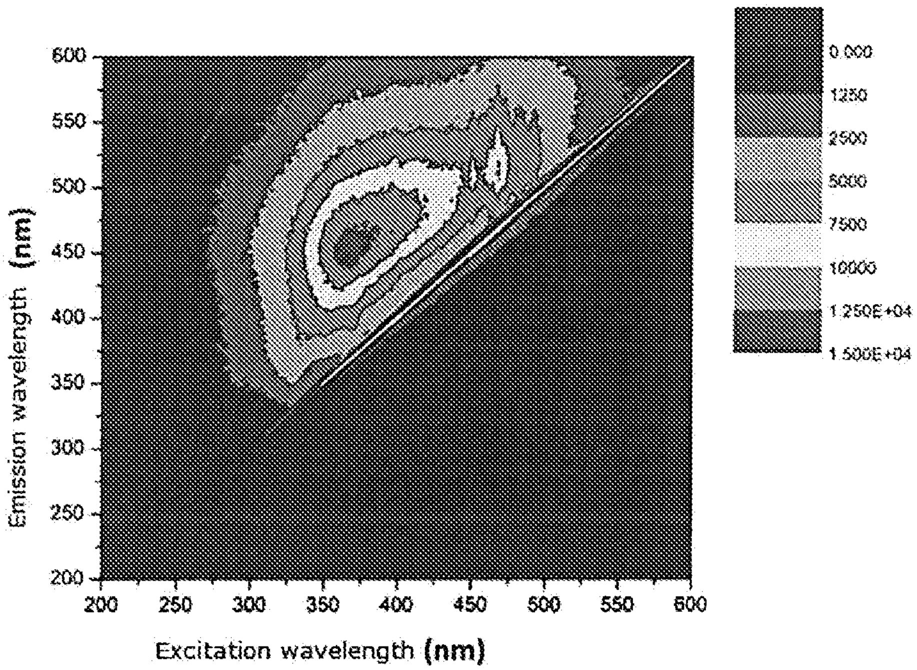

Relation chart between COD signal and F fluorence signal
701
140
120
100
80
60
40
20
0
COD (ppm)
0
50
100
150
200
250
300
Fluorescence count
COD-1 = f(F-1)
Poly (COD-1 = f(F-1))
COD = -0.0001(F)² + 0.2687(F) + 57.253
R² = 0.7005

Fig. 6



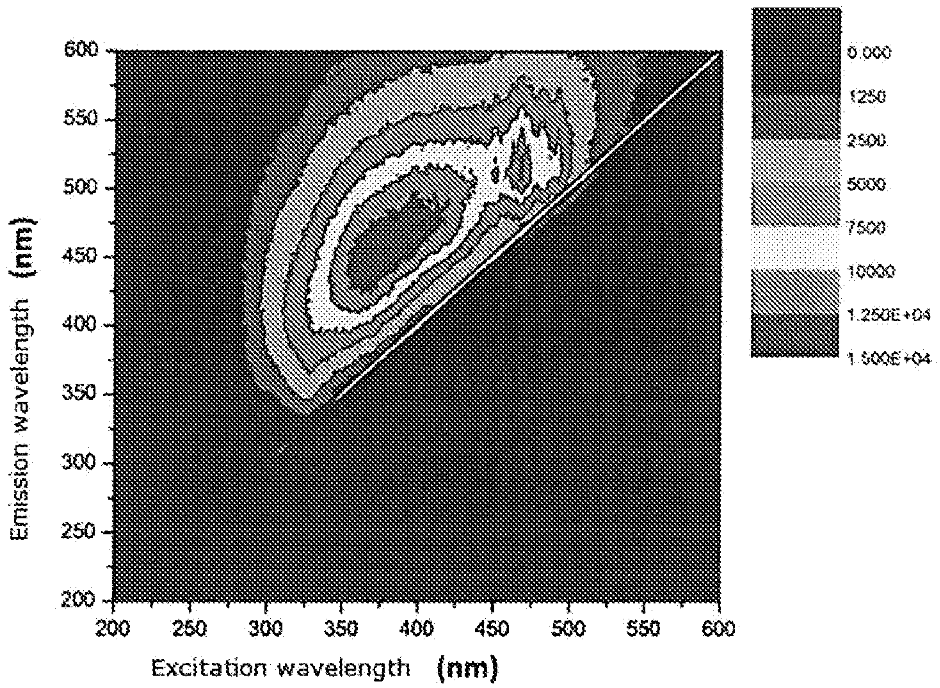
Paper plant wastewater

Fig. 7(A)



Coking wastewater-1

Fig. 7(B)



Coking wastewater-2

Fig. 7(C)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/036827

A. CLASSIFICATION OF SUBJECT MATTER

C02F 1/78(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F 1/78; C02F 1/50; C02F 3/04; C02F 1/72

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:water treatment, ozone-biological treatment, optimal ozone dosage, indicator, automatic controller

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2006-272080 A (TAKUMA CO., LTD.) 12 October 2006 See abstract; claims 5, 6; paragraphs [0012], [0020]-[0028], [0108]; and figure 1.	1-3,9,10,13-18
Y		4-8,11,12
Y	JP 06-063570 A (FUJI ELECTRIC CO., LTD.) 08 March 1994 See abstract; claims 1-4; and paragraphs [0007], [0016].	4-8,12
Y	JP 2003-001265 A (MITSUBISHI ELECTRIC CO.) 07 January 2003 See abstract; claims 1-3; and paragraph [0007].	11
A	JP 2008-207122 A (KURITA WATER IND. LTD.) 11 September 2008 See abstract; claims 1, 3; and paragraphs [0008], [0019], [0020].	1-18
A	JP 2001-239280 A (ATAKA CONSTRUCTION & ENGINEERING CO., LTD.) 04 September 2001 See abstract; and claims 1, 2.	1-18

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 2014 (26.08.2014)	**26 August 2014 (26.08.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
KIM, Eun Hee
Telephone No. +82-42-481-5543

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2014/036827

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2006-272080 A	12/10/2006	JP 5126926 B2	23/01/2013
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JP 2003-001265 A	07/01/2003	None	
JP 2008-207122 A	11/09/2008	None	
JP 2001-239280 A	04/09/2001	None	