

DESCRIPTION

WATER TREATMENT METHOD AND WATER TREATMENT SYSTEM

TECHNICAL FIELD

[0001]

5 The present invention relates to a water treatment method and a water treatment system, and more particularly, to a water treatment method and a water treatment system for reducing COD (chemical oxygen demand) .

BACKGROUND ART

10 [0002]

COD, which is generally used as an index of water quality, indicates the amount of oxygen that is required to oxidize an amount of a substance to be oxidized in the water. COD is also used as a standard value for the discharge water from factories, for example.

15 From the perspective of protecting the environment, regulations on the total amount of COD are becoming stricter every year.

[0003]

An example of a typical conventional method for reducing COD is a flocculation and separation method, in which a flocculant such

20 as aluminum sulfate, PAC, ferric chloride, ferric sulfate, and polyferric sulfate is added, and then a filtration apparatus or a sedimentation apparatus is used for separation. However, in a flocculation and separation method, the COD reduction rate is low, which makes it difficult to meet the recent regulations on total

25 COD amount.

[0004]

Another method for reducing COD is biochemical removal in a bioreactor. However, this method suffers from the problem that it has a low reduction rate, especially for soluble persistent organic
5 matter.

[0005]

A further example for reducing COD is adsorption and removal using active carbon. However, some kinds of organic matter (for example, highly polar matter, matter having a large molecular
10 structure etc.) are not easily adsorbed on active carbon, so that the reduction rate cannot be said to be sufficient.

[0006]

Conventionally, investigations have been carried out into a method for reducing COD using a manganese filter medium, instead
15 of the above-described reduction methods (for example, see Patent Literature 2). Further, investigations have also been carried out into a manganese filter medium that removes organic matter (for example, see Patent Literatures 3 to 5). However, the manganese filter media for reducing COD or removing organic matter that have
20 been conventionally investigated have been very impractical in terms of durability and production cost. Therefore, while they were briefly looked at, such manganese filter media are currently still not ready for practical use. Consequently, most COD reduction equipment now being employed use one or a combination of flocculation

and separation, biochemical removal, sand filtration, and active carbon adsorption and removal.

[0007]

Further, recently there is a lot of attention being paid to
5 the problem of endocrine disrupters and the like, and there is a high level of interest in whether organic matter that may change into endocrine disrupters (for example, phenol) is being removed. Therefore, it is no longer enough for current water treatment techniques to just be capable of reducing COD, these techniques
10 also need to be capable of removing specific organic matter. Such organic matter includes persistent organic matter (for example, phenol etc.)

[0008]

Thus, the COD reduction rate with the conventional methods
15 is insufficient, and it is becoming more difficult to meet the recent regulations on COD discharge.

PRIOR ART LITERATURE

PATENT DOCUMENTS

[0009]

20 [Patent Literature 1] Japanese Patent Application Laid-Open No. 2003-053350

[Patent Literature 2] Japanese Patent Application Laid-Open No. Sho. 56-84688

[Patent Literature 3] Japanese Patent Application Laid-Open No.
25 Sho. 59-173192

[Patent Literature 4] Japanese Patent Application Laid-Open No.
Hei. 1-99689

[Patent Literature 5] Japanese Patent Application Laid-Open No.
Sho. 49-64248

5 SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0010]

Examples of the problems that the present invention is directed
to resolving include the above-described problems. Accordingly,
10 it is an object of the present invention to resolve the problems
in the conventional art, to realize a manganese filter medium that
can be practically used as a filter medium for water treatment,
and to provide a water treatment method and a water treatment system
that can reduce COD at a high reduction rate.

15 [0011]

It is another object of the present invention to provide a
water treatment method and a water treatment system that can also
remove specific organic matter that may change into an endocrine
disrupter and is a persistent substance (for example, phenol) etc.),
20 even if such organic matter is included in the target treatment
water.

MEANS FOR SOLVING THE PROBLEMS

[0012]

The water treatment method of the present invention is a water
25 treatment method adding a chlorine oxidizing agent to target

treatment water that contains organic matter, passing the target treatment water through a manganese filter medium, and decomposing the organic matter by catalytic oxidation to reduce COD (chemical oxygen demand), and is characterized in that the manganese filter medium is in which a crystal powder of natural manganese dioxide (MnO_2) that includes β - MnO_2 is supported with a binder on a surface of a particulate carrier, without performing sintering, calcining, or a heat treatment at a temperature at which the β - MnO_2 undergoes crystal transformation.

10 [0013]

The target treatment water that is treated by the present invention can include phenol, which may change into an endocrine disrupter and is persistent. Because the manganese filter medium can also remove phenol by catalytic oxidative decomposition therewith. At that point, the manganese filter medium includes both natural β - MnO_2 and γ - MnO_2 . Further, it is preferred that the β - MnO_2 content be higher than the γ - MnO_2 content.

[0014]

In addition, it is preferred that the carrier be formed from ceramic particles, and that the manganese filter medium have the following properties.

[Table 1]

MAIN COMPONENT	SiO ₂	Al ₂ O ₃	MnO ₂	K ₂ O	Na ₂ O	BALANCE
CONTENT(%)	30.0 ~ 75.0	1.0 ~ 20.0	3.0 ~ 50.0	0.0 ~ 3.0	0.0 ~ 3.0	0.0 ~ 5.0

PARTICLE SIZE	DENSITY(g/cm ³)	BULK DENSITY(g/cm ³)	ATTRITION PERCENTAGE
ES:0.35~1.0mm UC:1.5 OR LESS	ABOUT 2.5	ABOUT 1.2	2.8% OR LESS

[0015]

Since the manganese filter medium of the present invention has a high durability, the COD reduction performance can be maintained over a long distance even if the manganese filter medium is cleaned by periodically subjecting a filtration apparatus filled with the manganese filter medium to back washing. For example, if the COD regulated value is low (i.e., if the regulations are strict), the above water treatment method can further include a step of adsorbing and removing organic matter by passing target treatment water which has already undergone catalytic oxidative decomposition through active carbon. Further, for example, if the SS concentration is high, the above water treatment method can further include a step of separating and removing suspended components by adding a flocculant to the target treatment water before passing the target treatment water through the manganese filter medium.

[0016]

The water treatment system of the present invention is a water treatment system for reducing COD (chemical oxygen demand), and includes means for adding a chlorine oxidizing agent to target treatment water containing organic matter, and a filtration

apparatus that includes a manganese filter medium through which the target treatment water to which the chlorine oxidizing agent has been added passes, and is characterized in that the manganese filter medium is a filter medium in which a crystal powder of natural manganese dioxide (MnO_2) that includes $\beta\text{-MnO}_2$ is supported with a binder on a surface of a particulate carrier, without performing sintering, calcining, or a heat treatment at a temperature at which the $\beta\text{-MnO}_2$ undergoes crystal transformation.

[0017]

For example, if the COD regulated value is low (i.e., if the regulations are strict), the above water treatment system can further include an adsorption apparatus that includes active carbon, through which target treatment water which has passed through the manganese filter medium passes. Further, for example, if the SS concentration is high, the above water treatment system can further include means for adding a flocculant to the target treatment water before the target treatment water passes through the manganese filter medium, and another filtration apparatus through which the target treatment water to which the flocculant has been added passes.

ADVANTAGES OF THE INVENTION

[0018]

According to the present invention, COD is reduced by adding a chlorine oxidizing agent to target treatment water that contains organic matter, passing the target treatment water through a manganese filter medium, and decomposing the organic matter by

catalytic oxidation. In this case, the manganese filter medium is used in which a crystal powder of natural manganese dioxide (MnO_2) that includes $\beta\text{-MnO}_2$ is supported with a binder on a surface of a particulate carrier, without performing sintering, calcining, or
5 a heat treatment at a temperature at which the $\beta\text{-MnO}_2$ undergoes crystal transformation. Therefore, the crystal structure is more stable than that in a manganese filter medium artificially produced by electrolysis or the like. In addition, this stable crystal structure can be maintained, because the crystal power is not subjected to
10 sintering, calcining, or a heat treatment at a temperature at which the $\beta\text{-MnO}_2$ undergoes crystal transformation. Therefore, due to this stable crystal structure, the filter medium has a high durability. Further, because electrolysis or a high-temperature heat treatment is not carried out, so production costs can be reduced by the amount
15 that it would cost for such a treatment. Consequently, the COD reduction performance can be maintained over a long distance even if the filtration apparatus is a type that can be subjected to back washing. In addition, as is clear from the below test data, the filter medium has a function for reducing COD and for removing phenol
20 at a high decomposition rate. Consequently, this filter medium can be practically used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Fig. 1 is a diagram illustrating the main configuration of a water treatment system according to a preferred embodiment of the present invention.

Fig.2 illustrates X-ray diffraction charts of the manganese filter medium used in the above water treatment system.

BEST MODE FOR CARRYING OUT THE INVENTION

[0020]

The water treatment method and water treatment system according to a preferred embodiment of the present invention will now be described with reference to the attached drawings. However, the technical scope of the present invention should not be interpreted as being limited to the embodiment described below.

[0021]

Fig. 1 illustrates an example of a water treatment system according to a preferred embodiment of the present invention. As illustrated in Fig. 1, the water treatment system 1 according to the present embodiment includes a raw water tank 2 which stores organic matter-containing water (raw water) that is the target treatment water, means 3 for adding a flocculant to the target treatment water, a first filtration apparatus 4 for separating suspended matter from the target treatment water, means 5 for feeding a chlorine oxidizing agent to the target treatment water, a second filtration apparatus 6 that has a manganese filter medium for decomposing organic matter contained in the target treatment water by catalytic oxidation, and an adsorption apparatus 7 that has active

carbon for adsorbing organic matter contained in the target treatment water. Reference numerals 21, 22, and 23 in the figure represent pumps for pumping the target treatment water between the respective apparatuses.

5 [0022]

In addition, the water treatment system 1 according to the present embodiment includes a tank 8 for storing target treatment water that has been treated by the second filtration apparatus 6. A portion of the target treatment water stored in the tank 8 is
10 fed to the first and second filtration apparatuses 4 and 6, through which the flow of water has been temporarily stopped, as a cleaning solution for washing (i.e., back washing) the first and second filtration apparatuses 4 and 6. The cleaned discharge water is sent back to the upstream equipment as feed raw water. The back washing
15 is carried out by feeding the cleaning solution into the filtration apparatus, separating from the filter medium the impurities such as SS trapped in the filter medium based on a shearing action of the water flow in the apparatus, and discharging the separated impurities with the cleaning solution from the apparatus. The
20 destination where the cleaned discharge water is sent may also be the raw water tank 2.

[0023]

The first filtration apparatus 4 mainly has the role of separating by filtration the suspended matter in the target treatment
25 water to which a flocculant has been added by the flocculant addition

means 3. As a preferred example, the first filtration apparatus 4 has a filtration layer formed so that water passes through, in order, anthracite 41, sand (filter medium) 42, and filtration gravel 43. The water may be made to pass through by a gravity system, or 5 by a pressure system that uses a pump, for example. The anthracite 41 has, for example, an effective size of 1.2 mm, and a uniformity coefficient of 1.4 or less. The sand (filter medium) 42 has, for example, an effective size of 0.6 mm, and a uniformity coefficient of 1.4 or less. However, the average particle size and the uniformity 10 coefficient are not limited to the values described above. The filtration gravel 43 acts as a support layer for the anthracite 41 and sand (filter medium) 42. Further, the filtration gravel 43 also has the role of making the water pass through evenly, and the back washing be carried out uniformly. However, the filtration 15 gravel 43 can be replaced with a support member that has a plurality of water-passing holes or slits.

[0024]

The second filtration apparatus 6 mainly has the role of decomposing by catalytic oxidation the organic matter in the target 20 treatment water to which a chlorine oxidizing agent is added by the oxidizing agent addition means 5. As a preferred example, the second filtration apparatus 6 has a filtration layer formed so that water passes through, in order, anthracite 61, a manganese filter medium 62, and filtration gravel 63. The water may be made to pass 25 through by a gravity system, or by a pressure system that uses a

pump, for example. The anthracite 61 has, for example, an effective diameter of 0.8 mm, and a uniformity coefficient of 1.4 or less. Further, the anthracite 61 is also provided to prevent suspended matter that could not be removed by the first filtration apparatus 5 4 from adhering to the manganese filter medium 62 and hindering the catalytic oxidation. In addition, the filtration gravel 63 has the same role as that of the above-described filtration gravel 43. [0025]

More specifically, the decomposition of organic matter by 10 catalytic oxidation, which is the main role of the second filtration apparatus 6, is based on the action of the manganese filter medium 62. However, the manganese filter medium 62 of the present embodiment should be a filter medium that can be put to practical use, especially as regards durability and production costs. Therefore, a filter 15 medium in which a crystal powder of natural manganese dioxide (MnO_2) that includes β - MnO_2 is supported with a binder on the surface of a particulate carrier is used. The crystal powder of natural manganese dioxide may be obtained by, for example, mining an ore that includes manganese dioxide, crushing the mined ore into a powdery 20 (for example, average particle size of 20 to 40 μm) material using a crusher or an attritor for example, and then purifying the powdery material to a purity of 90% or more by separating out impurities using a magnetic separator or the like. Specifically, this is different from manganese dioxides which are artificially produced 25 by electrolysis or by heating. Still the mining method and the method

for forming the powdery material are not limited to the methods described above.

[0026]

Although the natural manganese dioxide ore contains both β -MnO₂ and γ -MnO₂, the β -MnO₂ content is higher than the γ -MnO₂ content. Therefore, the manganese filter medium 62 of the present embodiment contains more β -MnO₂ than γ -MnO₂. Fig. 2 illustrates examples of X-ray diffraction, from which it can be confirmed that the manganese filter medium 62 in this lot contained β -MnO₂ and γ -MnO₂ in a ratio of 6:4.

[0027]

A particulate ceramic is used for the carrier supporting the crystal powder. The ceramic is mainly formed from SiO₂ and Al₂O₃. When a ceramic is used for the carrier, it is preferred that the ceramic be a filter medium that has the properties shown in the below table. Amongst those, it is preferred that SiO₂ is 72.0%, Al₂O₃ is 16.0%, MnO₂ is 3.0%, K₂O is 3.0%, Na₂O is 2.0%, and the balance (for example, impurities etc.) is 4.0%.

[Table 2]

MAIN COMPONENT	SiO ₂	Al ₂ O ₃	MnO ₂	K ₂ O	Na ₂ O	BALANCE
CONTENT (%)	30.0 ~ 75.0	1.0 ~ 20.0	3.0 ~ 50.0	0.0 ~ 3.0	0.0 ~ 3.0	0.0 ~ 5.0

PARTICLE SIZE	DENSITY(g/cm ³)	BULK DENSITY(g/cm ³)	ATTRITION PERCENTAGE
ES:0.35~1.0mm UC:1.5 OR LESS	ABOUT 2.5	ABOUT 1.2	2.8% OR LESS

20

[0028]

Another feature of the manganese filter medium 62 used in the present embodiment is that the crystal powder of natural manganese dioxide is supported with a binder on the carrier surface, without performing sintering, calcining, or a heat treatment at a temperature
5 at which the β -MnO₂ undergoes crystal transformation. An example of the support method is to support the crystal powder on the carrier surface via a binder by coating the binder on the surface of the carrier, and then adding the crystal powder and granulating. However, the support method is not limited to this. Further, the components
10 of the binder are not especially limited. A known binder may be used, including inorganic or organic binders. However, a binder that requires sintering or calcining in order to harden, such as an alumina cement, is not used. An example of a usable binder is a binder formed from a mixture of an aluminum compound and an alkaline
15 earth metal compound. In the present embodiment, in which a crystal powder of manganese dioxide is supported on the carrier surface, if the average particle size of the manganese dioxide crystal powder is more than 40 μ m, it is difficult to uniformly support the crystal powder over the whole carrier surface. Conversely, if the average
20 particle size is less than 20 μ m, the powder flies around during granulation, so that the granulation efficiency deteriorates.

[0029]

The adsorption apparatus 7 mainly has the role of adsorbing the organic matter contained in the target treatment water. The
25 adsorption apparatus 7 has, for example, an active carbon layer

71 formed from particulate active carbon. An example of the active carbon that can be used is active carbon (trade name: ACW8-32#) manufactured by Serachem Co., Ltd. However, the type and shape of the active carbon are not limited to this. Any known active carbon
5 may be used.

[0030]

The flocculant addition means 3 and the oxidizing agent addition means 5 are configured so that channels (for example, pipes and the like) 31 and 51, which are respectively in communication
10 with (not illustrated) supply sources, are connected to a target treatment water channel so that the flocculant and the chlorine oxidizing agent can be added to the target treatment water. The added amount can be regulated by, for example, flow regulation means 32 and 52, which may be a valve or the like. To improve the miscibility
15 with the target treatment water, a stirring apparatus, such as a line mixer or a stirred tank, may be provided. It is noted that the supply location illustrated in Fig. 1 is an example. The supply location is not limited to this position. The flocculant should be added upstream from the first filtration apparatus 4. The
20 oxidizing agent should be added upstream from the second filtration apparatus 6. Further, the flocculant may be added at more than one location. For effective removal of residual suspended matter with the anthracite 61 of the second filtration apparatus 6, flocculant addition means for adding the flocculant may be additionally provided

between the first filtration apparatus 4 and the second filtration apparatus 6.

[0031]

Examples of flocculants that can be used include inorganic
5 flocculants such as PAC (chemical name: polyaluminum chloride),
polyiron (chemical name: polyferric sulfate), and alum earth
(chemical name: aluminum sulfate), and polyacrylamide organic
flocculants. Among these, PAC is preferred. The main purpose of
adding the flocculant is to flocculate the suspended matter in the
10 target treatment water. And the flocculated suspended matter is
separated by filtration, whereby the TOC (total organic carbon)
in the target treatment water is reduced and hindering of the catalytic
oxidation due to suspended matter adhering to the manganese filter
medium 62 is prevented.

15 [0032]

Examples of chlorine oxidizing agents that can be used include
chlorine dioxide (ClO_2), hypochlorites such as sodium hypochlorite
(NaClO), and potassium permanganate (KMnO_4). The main purpose of
adding the chlorine oxidizing agent is to decompose the organic
20 matter by oxidation with the manganese filter medium 62 acting as
a catalyst. An especially preferred example of the oxidizing agent
employed for the oxidative decomposition of the organic matter using
the manganese filter medium 62 is chlorine dioxide (ClO_2). Further,
when emphasizing phenol decomposition efficiency, sodium
25 hypochlorite (NaClO) is preferred.

[0033]

Next, the method for reducing the COD using the water treatment system 1 illustrated in Fig. 1 will be described. The type and pollution of the target treatment water (raw water) that is treated
5 by the present system are not especially limited. The target treatment water may be various types of organic matter-containing water, such as general discharge water, industrial discharge water, sewage, river water, groundwater, and lake water. The raw water that is treated in the below examples has a color degree of 14.1,
10 a turbidity of 14.11, and a pH of 7.65. However, the target treatment water is not limited to this. Further, if the raw water is acidic or alkaline, appropriate pH adjustment can be carried out in advance as a pre-treatment.

[0034]

15 The target treatment water (raw water) treated by the present system is temporarily stored in the raw water tank 2, then pumped by the pump 21 towards the first filtration apparatus 4. During this pumping, the flocculant is added by the flocculant addition means 3. The added amount of the flocculant is set to 5 to 30 mg/l,
20 for example. The target treatment water to which the flocculant has been added is fed to the first filtration apparatus 4, where suspended matter is removed by separation when passing through the filter medium.

[0035]

To the target treatment water (separated solution) from which the suspended matter has been separated by the first filtration apparatus 4, the chlorine oxidizing agent is added by the oxidizing agent addition means 5. The added amount of the oxidizing agent is set, for example, to 1.25 mg/l for chlorine dioxide (ClO_2), and to 5 mg/l for sodium hypochlorite (NaClO). The target treatment water to which the oxidizing agent has been added is fed to the second filtration apparatus 6. When the target treatment water passes through the manganese filter medium 62, organic matter is decomposed by oxidation by the chlorine dioxide with the manganese filter medium 62 acting as a catalyst.

[0036]

The target treatment water, in which organic matter has been decomposed by oxidation by the second filtration apparatus 6, is temporarily stored in the tank 8, then pumped by the pump 23 towards the adsorption apparatus 7. When the target treatment water passes through the active carbon layer 71 in the adsorption apparatus 7, the organic matter is adsorbed on the active carbon layer 71. The thus-obtained COD-reduced target treatment water has an acceptable COD for release, as is clear from the results of the below examples.

[0037]

Thus, according to the present embodiment, by adding a chlorine oxidizing agent to target treatment water that contains organic matter, and passing this target treatment water through a manganese filter medium 62, the organic matter is decomposed by catalytic

oxidation, so that the COD can be reduced. Moreover, the manganese filter medium 62 of the present embodiment is configured such that a crystal powder of natural manganese dioxide (MnO_2) that includes $\beta\text{-MnO}_2$ is supported with a binder on the surface of a particulate carrier. Therefore, compared with a manganese filter medium artificially produced by electrolysis and like, for example, the crystal structure is more stable. In addition, this stable crystal structure can be maintained, because the crystal powder is not subjected to sintering, calcining, or a heat treatment at a temperature at which the $\beta\text{-MnO}_2$ undergoes crystal transformation. Therefore, due to this stable crystal structure, the filter medium 62 of the present embodiment has a high durability. Further, because electrolysis or a high-temperature heat treatment is not carried out, production costs can be reduced by the amount that it would cost for such a treatment. In addition, as is clear from the below test data, the above filter medium not only merely reduces the COD, but it is also capable of removing persistent phenol at a high decomposition rate. Consequently, this manganese filter medium can be practically used.

[0038]

The above-mentioned Patent Literature 2 discloses a manganese filter medium for reducing COD. However, it is not clear whether the manganese dioxide in Patent Literature 2 is a natural product or an artificial product. Further, the manganese filter medium is sintered and molded during the production process. Therefore, it

is highly likely that the manganese dioxide crystal structure is deformed and unstable. If that is the case, the manganese filter medium will break up during back washing. Patent Literature 5, in which calcining at 400 to 1000°C is carried out, is also the same.

5 [0039]

Further, Patent Literature 3 discloses a filter medium that has a mixed layer of β -MnO₂ and γ -MnO₂. However, the β -MnO₂ is formed in layers on the carrier surface due to the manganese salt solution being heat treated. Further, the β -MnO₂ acts as a binder supporting
10 the γ -MnO₂ particles on the surface of the carrier, which means that the decomposition performance depends on the γ -MnO₂. Therefore, as is clear from the blending ratio disclosed in the examples, the ratio of γ -MnO₂ is far greater than the ratio of β -MnO₂. Moreover, γ -MnO₂ has a brittle crystal structure, and often breaks up during
15 back washing. Consequently, the decomposition performance deteriorates with use.

[0040]

In addition, Patent Literature 4 discloses a filter medium in which β -MnO₂ particles produced by electrolysis or particles that
20 have undergone crystal transformation to β -MnO₂ by heat treating γ -MnO₂ is supported. In this case also, the above-described problems tend to occur.

[0041]

Employing the manganese filter medium 62 the present embodiment
25 allows the second filtration apparatus 6 to be used as a back w

ashing type apparatus, which can periodically perform back washing. Consequently, this allows the COD reduction performance to be maintained. On the other hand, since conventional manganese filter media are either artificially produced using a chemical reaction or include artificially produced components, a high-temperature heat treatment is required during the production process. In such a case, the ratio of γ - MnO_2 unavoidably increases. γ - MnO_2 has a brittle crystal structure, and has undergone crystal transformation, so that durability is substantially reduced. Although back washing of a filter medium is known per se, for a manganese dioxide filter medium, if the filtration apparatus is simply a type that can perform back washing, the filter medium breaks apart during the back washing, which means that the filtration performance cannot be exhibited over a long period of time (i.e., the filter medium life is short).

[0042]

According to the present embodiment, COD can be reliably reduced by, after the above-described catalytic oxidative decomposition, passing the target treatment water through active carbon so that the organic components that were decomposed by catalytic oxidation are adsorbed. As stated above, although it is difficult to adsorb some kinds of organic matter (for example, highly polar matter, matter having a large molecular structure etc.), the catalytic oxidative decomposition decomposes the organic matter into molecules that can easily be adsorbed on the active carbon.

Consequently, the COD reduction rate due to the active carbon can be improved.

[0043]

In addition, according to the present embodiment, COD can be
5 reliably reduced by, before passing the target treatment water
through the manganese filter medium 62, removing suspended matter
by a flocculation and separation method to prevent the catalytic
oxidative power of the manganese filter medium 62 from deteriorating.

[0044]

10 In the above, the present invention was described in detail
based on a specific embodiment. However, a person having ordinary
knowledge in the art pertaining to the subject technical field would
clearly understand that various substitutions, modifications,
changes and the like relating to the form and details of the invention
15 could be made that fall within the spirit and scope of the invention
as prescribed in the claims. Therefore, the scope of the present
invention is not limited to the above embodiment and attached drawings,
and should be construed based on the claims and equivalent subject
matter thereto.

20 [Examples]

[0045]

Examples carried out to confirm the advantageous effects of
the present invention will now be described. However, the technical
scope of the present invention should not be interpreted as being
25 limited to the examples described below.

[0046]

(Example 1)

In Example 1, raw water was treated based on the flow illustrated in Fig. 1. The main test conditions are listed below. Samples taken
5 from the raw water and the target treatment water after a first filtration treatment, after catalytic oxidative decomposition, and after an adsorption treatment by active carbon, respectively, were measured for color degree, turbidity, and COD. The measurement results are shown in Table 3. A sulfuric acid-acidic potassium
10 permanganate method was employed for the back washing, turbidity, and COD measurement method.

- First filtration

Anthracite (1.2 - 1.4) 300 mmH

15 Sand (0.6 - 1.4) 300 mmH

Filtration rate (LV) = 10 m/hr

- Flocculant

Addition of 30 mg/l PAC

- Catalytic oxidation

20 Anthracite (1.0 - 1.4) 200 mmH

Manganese filter medium (shown in Table 3) 600 mmH

Flow rate SV = 10/hr

However, 10 mg/l of polyiron was added as a flocculant before the catalytic oxidation.

25 - Active carbon

Active carbon 800 mmH

Flow rate SV = 10/h

[0047]

[Table 3]

EXAMPLE 1

	COLOR DEGREE (DEGREES)	TURBIDITY (DEGREES)	COD (mg/l)
RAW WATER	14.1	14.11	16.5
AFTER FIRST FILTRATION TREATMENT (ADDITION OF 30 mg/l OF PAC)	9.5	4.59	15.3
AFTER CONTACT OXIDATION (ADDITION OF 1.25 mg/l OF ClO ₂ AND 10 mg/l OF POLYIRON)	9.9	4.05	7.8
AFTER ADSORPTION TREATMENT	4.6	3.65	2.4

5

[0048]

(Example 2)

In Example 2, hypochlorous acid was added as the oxidizing agent instead of the chlorine dioxide used in Example 1. Other than
10 changing the oxidizing agent, the conditions and the like were the same as in Example 1. The measurement results of the color degree, turbidity, and COD of each sample are shown in Table 4.

[0049]

[Table 4]

EXAMPLE 2

	COLOR DEGREE (DEGREES)	TURBIDITY (DEGREES)	COD (mg/l)
RAW WATER	14.1	14.11	16.5
AFTER FIRST FILTRATION TREATMENT (ADDITION OF 30 mg/l OF PAC)	9.5	4.59	15.3
AFTER CONTACT OXIDATION (ADDITION OF 5 mg/l OF NaClO AND 10 mg/l OF POLYIRON)	7.3	3.17	8.8
AFTER ADSORPTION TREATMENT	3.2	3.11	6.3

15

[0050]

(Comparative Example 1)

Comparative Example 1 was carried out in the same manner as Example 1, except that catalytic oxidation was not carried out.

5 Specifically, in terms of the flow illustrated in Fig. 1, the second filtration apparatus was omitted, so that the target treatment water that had been subjected to the first filtration treatment was passed through the active carbon. The measurement results of the color degree, turbidity, and COD of each sample are shown in Table 5.

10 [0051]

[Table 5]

COMPARATIVE EXAMPLE 1

	COLOR DEGREE (DEGREES)	TURBIDITY (DEGREES)	COD (mg/l)
RAW WATER	14.1	14.11	16.5
AFTER FIRST FILTRATION TREATMENT (ADDITION OF 30 mg/l OF PAC)	9.5	4.59	15.3
AFTER ADSORPTION TREATMENT	7.8	4.46	12.4

[0052]

The results in Tables 3 to 5 clearly confirm that COD can be
15 reduced by passing target treatment water to which a chlorine oxidizing agent had been added through a manganese filter medium. It was also confirmed that COD can be reliably reduced by passing target treatment water that has been subjected to catalytic oxidation through active carbon. As the oxidizing agent, although NaClO is
20 more effective when focusing on chromaticity and turbidity, regarding COD reduction, it was confirmed that ClO₂ is more effective.

When using ClO_2 , the COD after passing through active carbon is reduced to 2.4 mg/l. More specifically, it was confirmed that ClO_2 can decompose organic matter in a manner that enables it to be more easily adsorbed on the active carbon.

5 [0053]

(Test Example 1)

In Test Example 1, it was confirmed whether the manganese filter medium used in the above examples has a phenol decomposition function. The test was carried out by filling a sample of the filter medium to a height of 600 mm in a 1000 mm column with a diameter of 50 mm, then adding chlorine dioxide and sodium hypochlorite to raw water and performing a water-passing test at a filtration rate $\text{SV} = 5/\text{hr}$. The added amounts of the chlorine dioxide and sodium hypochlorite were set so that the respective concentrations were the same as in Examples 1 and 2. Thirty minutes after passing the water, a sample was taken from the treated water and its phenol concentration was measured. The results are shown in Table 6. It is clear from the results in Table 6 that in the samples to which sodium hypochlorite had been added, phenol was decomposed to 1.2 mg/l, and that in the samples to which chlorine dioxide had been added, phenol was decomposed to 6.4 mg/l. Thus, from these test results, it was confirmed that the manganese filter medium of the present invention has a function for removing phenol, which may change into an endocrine disrupter, and is a persistent substance.

25 [Table 6]

PHENOL DECOMPOSITION TEST

RAW WATER	FILTER MEDIUM + SODIUM HYPOCHLORITE	FILTER MEDIUM + CHLORINE DIOXIDE
10mg/l	1. 2mg/l	6. 4mg/l

DESCRIPTION OF REFERENCE NUMERALS

[0054]

- 1 water treatment system
- 5 3 means for adding a flocculant
- 4 first filtration apparatus
- 5 means 5 for adding an oxidizing agent
- 6 second filtration apparatus
- 62 manganese filter medium
- 10 7 adsorption apparatus
- 71 active carbon layer

CLAIMS

1. A water treatment method, comprising: adding a chlorine oxidizing agent to target treatment water that contains organic matter; passing the target treatment water through a manganese filter medium; and decomposing the organic matter by catalytic oxidation to reduce COD (chemical oxygen demand),

the method characterized in that the manganese filter medium is a filter medium in which a crystal powder of natural manganese dioxide (MnO_2) that includes β - MnO_2 is supported with a binder on a surface of a particulate carrier, without performing sintering, calcining, or a heat treatment at a temperature at which the β - MnO_2 undergoes crystal transformation.

2. The water treatment method according to claim 1, characterized in that the target treatment water includes phenol, which is a persistent substance, and that phenol is removed by catalytic oxidative decomposition with the manganese filter medium supporting the crystal powder of natural manganese dioxide (MnO_2).

3. The water treatment method according to claim 1 or 2, characterized in that the crystal powder of natural manganese dioxide includes both natural β - MnO_2 and γ - MnO_2 , and that a β - MnO_2 content is higher than a γ - MnO_2 content.

4. The water treatment method according to any one of claims 1 to 3, characterized in that the carrier is formed from ceramic particles, and that the manganese filter medium has the following properties,

5 [Table 1]

MAIN COMPONENT	SiO ₂	Al ₂ O ₃	MnO ₂	K ₂ O	Na ₂ O	BALANCE
CONTENT (%)	30.0 ~ 75.0	1.0 ~ 20.0	3.0 ~ 50.0	0.0 ~ 3.0	0.0 ~ 3.0	0.0 ~ 5.0

5. The water treatment method according to any one of claims 1 to 4, characterized by periodically subjecting a filtration apparatus filled with the manganese filter medium to back washing
10 to clean the manganese filter medium.

6. The water treatment method according to any one of claims 1 to 5, characterized by further comprising a step of passing target treatment water which has already undergone catalytic oxidative
15 decomposition through active carbon to adsorb and removing organic matter.

7. The water treatment method according to any one of claims 1 to 6, characterized by further comprising a step of adding a flocculant to the target treatment water before passing the target treatment water through the manganese filter medium to separate and remove a suspended component.

8. A water treatment system for reducing COD (chemical oxygen demand), characterized by comprising:

means for adding a chlorine oxidizing agent to target treatment water containing organic matter; and

a filtration apparatus that includes a manganese filter medium through which the target treatment water to which the chlorine oxidizing agent has been added passes,

wherein the manganese filter medium is a filter medium in which a crystal powder of natural manganese dioxide (MnO_2) that includes β - MnO_2 is supported with a binder on a surface of a particulate carrier, without performing sintering, calcining, or a heat treatment at a temperature at which the β - MnO_2 undergoes crystal transformation.

9. The water treatment system according to claim 8, characterized in that the target treatment water includes phenol, which is a persistent substance, and that phenol is removed by catalytic oxidative decomposition with the manganese filter medium supporting the crystal powder of natural manganese dioxide (MnO_2).

10. The water treatment system according to claim 8 or 9, characterized in that the crystal powder of natural manganese dioxide includes both natural β -MnO₂ and γ -MnO₂, and that a β -MnO₂ content is higher than a γ -MnO₂ content.

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11. The water treatment system according to any one of claims 8 to 10, characterized by further comprising an adsorption apparatus that includes active carbon, through which target treatment water which has passed through the manganese filter medium passes.

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12. The water treatment system according to any one of claims 8 to 11, characterized by further comprising means for adding a flocculant to the target treatment water before the target treatment water passes through the manganese filter medium, and another
15 filtration apparatus through which the target treatment water to which the flocculant has been added passes.