

D E S C R I P T I O N

METHOD OF PURIFYING SOIL AND/OR GROUNDWATER

5 **Technical Field**

[0001]

The present invention relates to a method of purifying soil and/or groundwater adopting a conventional approach in which hydrogen peroxide is used as an oxidizer, wherein it is possible
10 to accomplish purification of pollution without decreasing pH of a purification object and to shorten the purification period, and further it is possible to apply to the purification of highly concentrated pollution.

15 **Background Art**

[0002]

As a fact that pollution by organic matters in soil and/or groundwater significantly affects the environment becomes apparent, various regulations are enhanced. Under the
20 circumstances, the pollution that has been accumulated or neglected until now needs to be purified. The term "organic matters" used here refers mainly to persistent organic compounds which are difficult to be decomposed by living organisms and includes agrichemicals, preservatives, aromatic compounds
25 contained in petroleum and any fractions thereof, chlorinated organic compounds, and the like.

[0003]

Various physical, chemical, and biological methods of purification have been tried to apply to purify the pollution

by such organic matters. A physical method of purification can purify polluted sites, but has a disadvantage that secondary processing is required for the eliminated pollutants. A biological method of purification is a method less affecting the ambient environment but has a disadvantage of difficulty in accomplishing a satisfactory effect for highly concentrated pollution. On the other hand, a chemical method of purification is a method that decomposes target pollutants and, therefore, secondary processing is not required, and a satisfactory effect can be accomplished for highly concentrated pollution as well.

[0004]

There is known a Fenton process in which an oxidizer such as hydrogen peroxide and a compound (e.g.; ferrous sulfate heptahydrate) that can supply iron ions functioning as a catalyst are added to generate hydroxyl radicals, which are then reacted with organic matters so as to oxidatively decompose the organic matters. An attempt has been made in which this Fenton process is applied in the method of purifying soil polluted by persistent organic compounds (refer to Patent Document 1).

[0005]

It is said that the optimum pH range is 3 to 4 in a usual Fenton process. In the reaction in a pH range above neutrality, iron ions as a catalyst are converted to hydroxide so as to be precipitated, with the result that the reaction hardly proceeds. However, assuming that the purification of soil is carried out in the optimum pH range 3 to 4, secondary pollution may occur and spread due to elution of heavy-metal components in soil. In order to cover this disadvantage, an approach has been proposed in which a buffering agent is used to carry out purification at

a constant pH of near neutrality. Patent Documents 2 and 3 propose addition of an oxidizer and a buffering agent in order to prevent decrease of pH due to decomposition of pollutant organic matters. However, the above documents do not describe
5 a means for preventing precipitation of metallic ions such as iron as a catalyst in a high pH range. Without this means, blocking of a passage or piping is likely to occur due to precipitation of metal components contained in groundwater, such as iron, depending on the kind of oxidizers or environment of
10 a site to be purified, thereby posing a problem in a purification work.

[0006]

Further, addition of an oxidizer and a chelating agent is proposed in order to prevent precipitation of metallic ions
15 such as iron as a catalyst. In an invention disclosed in Patent Document 4, addition of the chelating agent is carried out in order to prevent precipitation of mainly iron. However, since the pH range used is in acidic side, a specified molar ratio of the chelating agent to be added is as small as 1/3 based upon
20 that of iron, so that there remains a danger that secondary pollution such as elution of heavy metal occurs in terms of the pH range of the liquid. Also in an invention disclosed in Patent Document 5, a combination of a chelating agent and an oxidizer is proposed. However, addition of the chelating agent is
25 conducted in order only to prevent precipitation of metallic ions such as iron and there is no description about a means for preventing decrease of pH caused by a buffering agent and the like, so that secondary pollution such as elution of heavy metal more likely to occur in terms of the pH range of the liquid.

[0007]

Further, addition of a chelating agent in a pH range near neutrality is proposed. Patent Document 6 proposes addition of a chelating agent such as EDTA. However, EDTA is persistent and therefore may significantly affect the ambient environment such as ecosystems when being used in actual purification of soil, especially, used in situ, which may cause a serious problem. Further, as described in Patent Document 5, shortage of the amount of the chelating agent to be added causes precipitation of metallic ions and excessive amount thereof reduces purification effect; thus, in either case, purification cannot be carried out effectively.

Patent Document 1:

15 Jpn. Pat. Appln. Laid-Open Publication No. 7-75772

Patent Document 2:

Jpn. Pat. Appln. Laid-Open Publication No. 2004-202357

Patent Document 3:

Jpn. Pat. Appln. Laid-Open Publication No. 2004-305959

20 Patent Document 4:

Jpn. Pat. Appln. Laid-Open Publication No. 2002-159959

Patent Document 5:

Jpn. Pat. Appln. Laid-Open Publication No. 2000-301172

Patent Document 6:

25 PCT Appln. Laid-open Publication No. 2003-503197

Disclosure of the Invention

Problems to be Solved by the Invention

[0008]

The present invention has been made in view of the above problems resided in the prior arts, and an object thereof is to provide a method of purifying soil and/or groundwater capable of easily applying to a system of purifying soil/groundwater polluted by persistent organic compounds at in situ without affecting the ambient environment, ecosystems, and the like, capable of accomplishing effective purification in short period of time and in safety, and further capable of purifying highly concentrated pollution.

Means for Solving the Problems

[0009]

As a result of the intensive studies to solve the above problems, the present inventors have finally found that a method comprising adding a biodegradable chelating agent to a purification object to produce an iron ion complex and then adding an oxidizer, and preferably further adding a pH buffering agent is capable of accomplishing effective purification while preventing secondary pollution caused by elution of heavy metals, as well as preventing precipitation of iron ions as a catalyst for decomposition reaction of pollutants, and have completed the invention.

According to an aspect of the invention, there is provided a method of purifying soil and/or groundwater characterized in that it comprises: a step of addition of a

biodegradable chelating agent wherein a dicarboxymethylamine biodegradable chelating agent selected from the group consisting of methylglycine-diacetic acid, glutamate diacetic acid and salts thereof is added to a purification object in a molar ratio of 0.5 to 4.0 to iron ions being present in the purification object to thereby form a complex of biodegradable chelating agent and iron ion; and a step of addition of an oxidizer wherein an oxidizer is added after forming the complex while maintaining the pH value of the purification object at 5 to 10.

The present disclosure provides a method of purifying shown in the following (1) to (7).

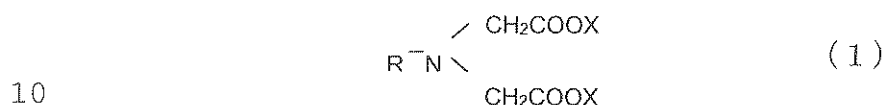
(1) A method of purifying soil and/or groundwater characterized in that it comprises:

a step of addition of a biodegradable chelating agent wherein a dicarboxymethylamine biodegradable chelating agent represented by the following general formula (1) is added to a

purification object in a molar ratio of 0.5 to 4.0 to iron ions being present in the purification object to thereby form a complex of biodegradable chelating agent and iron ion; and

a step of addition of an oxidizer wherein an oxidizer is added after forming the complex while maintaining the pH value of the purification object at 5 to 10.

[Chemical formula 1]



(R represents an organic group not containing nitrogen atoms, and X represents H or an alkali metal)

(2) The method of purification according to (1), characterized in that said R in the general formula (1) represents $-\text{CH}(\text{CH}_3)\text{COOX}$, $-\text{CH}(\text{COOX})\text{C}_2\text{H}_4\text{COOX}$, $-\text{CH}(\text{COOX})\text{CH}_2\text{COOX}$, or $-\text{C}_2\text{H}_4\text{SO}_3\text{X}$ (X is H or an alkali metal).

(3) The method of purification according to (1) or (2), characterized in that in said step of addition of an oxidizer, said oxidizer is added while maintaining the pH value of the purification object at 7 to 9.

(4) The method of purification according to any one of (1) to (3), characterized in that, in said step of addition of an oxidizer, at least one pH buffering agent selected from a group consisting of sodium carbonate, potassium carbonate, calcium carbonate, magnesium carbonate, sodium hydrogen carbonate, and potassium hydrogen carbonate.

(5) The method of purification according to any one of (1) to (4), characterized in that said oxidizer is hydrogen peroxide.

(6) The method of purification according to any one of (1) to (5), characterized in that, preliminary to the step of addition

of a biodegradable chelating agent, it further comprises a step of pretreatment wherein the pH of the purification object is decreased from 6 or more to not less than 5 but less than 6 so as to allow the iron ions in soil to dissolve into groundwater.

- 5 (7) The method of purification according to any one of (1) to (6), characterized in that, preliminary to the step of addition of a biodegradable chelating agent, it further comprises a step of pretreatment wherein iron ions are added to the purification object.

10

Advantages of the Invention

[0010]

The method of purification according to the present invention has the following advantages.

- 15 (1) It is possible to decompose pollutant organic compounds in a high pH range within which elution of heavy metals does not occur, at a particularly high speed of decomposition without inhibiting reaction of a decomposition agent (an oxidizer and an iron-chelate complex as a catalyst).
- 20 (2) It is possible to effectively prevent generation and precipitation of hydroxide formed from metallic ions such as iron as a catalyst in a high pH range, whereby a purification process can be carried out without occurrence of blocking of a passage or piping for soil and/or groundwater caused by the precipitation
- 25 of metal components.
- (3) It is possible to use agents having a low environmental load, that is, agents used in the present invention are a biodegradable chelating agent, hydrogen peroxide as an oxidizer, and carbonate as a pH buffering agent.

(4) It is possible to accomplish purification of highly concentrated pollution.

Thus, according to the present invention, it is possible to safely purify soil and/or groundwater polluted by organic
5 compounds in short period of time. Further, it is possible to accomplish purification in situ without greatly affecting the ambient environment such as ecosystems and the like.

Best Mode for Carrying Out the Invention

10 [0011]

Soil and/or groundwater to be purified in the present invention are assumed to be polluted by persistent organic matters. Examples of the organic matters include agrichemicals, preservatives, aromatic compounds contained in petroleum and any
15 fraction thereof, chlorinated organic compounds, and the like. Examples of the aromatic compounds contained in petroleum and any fraction thereof include toluene, benzene, and the like. Examples of the chlorinated organic compounds include trichloroethylene (TCE), tetrachloroethylene (PCE), and the
20 like.

Hydroxyl radicals generated by reaction of hydrogen peroxide and iron ions in the present invention have a strong oxidizing power and therefore can be applied not only to the chlorinated organic compounds but also to toluene, benzene,
25 oil-based soil pollution.

[0012]

A method of purification according to the present invention comprises:

a step of addition of a biodegradable chelating agent

wherein a biodegradable chelating agent is added to a purification object in a molar ratio of 0.5 to 4.0 to iron ions being present in the purification object to thereby form a complex of biodegradable chelating agent and iron ion; and

5 a step of addition of an oxidizer wherein an oxidizer is added after forming the complex while maintaining the pH value of the purification object at 5 to 10.

(1) Step of addition of a biodegradable chelating agent:

Iron ions being present in a purification object have a
10 function of reacting with an oxidizer to generate hydroxyl radicals to oxidatively decompose organic pollutants in the purification object. Therefore, it is only necessary for the iron ions to be contained in the purification object at a concentration sufficient for effective oxidative decomposition.
15 The concentration of the iron ions in a purification object is preferably about 15 to 100 mg/L, depending on the pollution level.

In the case where a suitable amount of the iron ions is originally present in groundwater and/or soil, further addition of the iron ions is not required. However, depending on a
20 condition such as purification period, preliminary addition of iron ions to the purification object as a pretreatment can improve the effect and reduce a required purification period. In the case of adding iron ions, a compound that can supply iron ions may be added to a purification object. Examples of the compound
25 that can supply iron ions include an iron salt such as ferrous sulfate, ferrous chloride and the like. The use amount of the iron salt is not particularly limited and determined case by case depending on the pollution level. In general, the amount of iron salts to be added is 0 to 0.1 % by weight in terms of ferrous

sulfate based upon the total amount of a purification object. The iron salt can be supplied to soil and/or groundwater in the form of aqueous solution by a facility such as a well dug in the soil. The concentration of iron salt aqueous solution is
5 preferably 0 to 10 % by weight.

[0013]

The step of addition of a biodegradable chelating agent in the present invention is preferably to be carried out without involving a decrease of the pH value of a purification object
10 (while maintaining the pH value at 5 or more) in order to prevent elution of heavy metals. However, in the case where the pH value of a purification object is 6 or more, pretreatment may be carried out to decrease the pH value of the purification object to not less than 5 but less than 6 so as to allow the iron ions in soil
15 to dissolve into groundwater. More specifically, an acid component including, e.g., mineral acids such as hydrochloric acid and sulfuric acid and organic acids such as acetic acid is added to soil and/or groundwater to decrease the pH thereof to not less than 5 but less than 6 so as to allow the iron ions in
20 soil to dissolve into groundwater, followed by addition of the biodegradable chelating agent. As described above, by previously controlling the pH value to not less than 5 but less than 6 in the case where the pH value of a purification object is 6 or more, the required amount of iron ions can be supplied
25 to groundwater. That is, in the case where the amount of iron ions in groundwater is insufficient, the pH of a purification object is made somewhat acidic. This allows the iron ions in soil to dissolve into groundwater to thereby ensure a required iron ion concentration without need of adding iron salts from

outside.

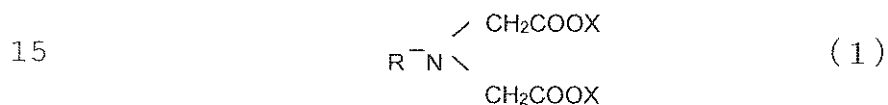
The acid component used for pretreatment can be supplied to soil and/or groundwater in the form of aqueous solution by a facility such as a well dug in the soil. The concentration of the acid component solution is preferably 0 to 10 % by weight.

[0014]

The biodegradable chelating agent to be added is one certified as biodegradable in a biodegradability test and intrinsic biodegradability test specified by OECD Guidelines. In the present invention, dicarboxymethylamine-based chelating agents represented by the following general formula (1) are used.

[0015]

[Chemical formula 2]



(R represents an organic group not containing nitrogen atoms, and X represents H or an alkali metal)

[0016]

Examples of the alkali metal represented by X include sodium (Na) and potassium (K).

Preferably, R is an organic group not containing nitrogen atoms and having the carbon number of 1 to 10, more preferably the carbon number of 1 to 4. More preferably, R is an organic group not containing nitrogen atoms and containing at least one selected from a group consisting of -COOX and -SO₃X. Even more preferably, R is an organic group not containing nitrogen atoms, having the carbon number of 1 to 4, and containing at least one selected from a group consisting of -COOX and -SO₃X.

Among the dicarboxymethylamine-based biodegradable chelating agents represented by the above general formula (1), particularly suitable examples include one wherein R in the above general formula (1) represents $-\text{CH}(\text{CH}_3)\text{COOX}$, $-\text{CH}(\text{COOX})\text{C}_2\text{H}_4\text{COOX}$, $-\text{CH}(\text{COOX})\text{CH}_2\text{COOX}$, or $-\text{C}_2\text{H}_4\text{SO}_3\text{X}$ (X is H or an alkali metal).

Examples of the dicarboxymethylamine-based biodegradable chelating agents include methylglycine diacetic acid, glutamate diacetic acid, aspartic acid diacetic acid, 2- aminoethanesulfonic acid diacetic acid, and sodium salts thereof. The addition of the chelating agent generates a complex of iron ion being present in a purification object to prevent precipitation and generation of ferrihydrite.

An insufficient addition of the chelating agent causes precipitation of ferrihydrite and excessive addition thereof inhibits purification. Thus, the chelating agent is preferably used in a molar ratio of 0.5 to 4.0 based upon 1 mol of iron ions. In particular, a molar ratio of 1.0 to 2.0 based upon 1 mol of iron ions provides a higher effect and thus preferable. The chelating agent can be supplied to soil and/or groundwater in the form of aqueous solution by a facility such as a well dug in the soil. The supply of the chelating agent can be carried out continuously or intermittently. The concentration of the chelating agent aqueous solution is preferably 50 to 5000 mg/L.

[0017]

(2) Step of addition of an oxidizer:

In the purification method according to the present invention, an oxidizer is added after the formation of a complex while maintaining the pH value of the purification object at 5 to 10 (oxidizer addition process). Since organic pollutants are

decomposed after the formation of a complex of biodegradable
chelating agent and iron ion while maintaining the pH value of
the purification object at a high pH value, it is possible to
prevent elution of heavy metals, as well as prevent generation
5 and precipitation of ferrihydrite.

Examples of the oxidizers to be used include hydrogen
peroxide, percarbonate salt, percarbonate, perborate salt,
perborate, peracetic acid, peracetic salt and the like. Hydrogen
peroxide is most preferable in terms of damages to the environment,
10 operationality, cost, and versatility. Although varying
according to the pollution level and the amount of water to be
injected or pumped into soil, the injection concentration of
hydrogen peroxide is preferably 0.5 to 5 % by weight based upon
the amount of water to be injected. In general, the use amount
15 of hydrogen peroxide is not particularly limited and determined
case by case depending on the pollution level, ambient
environment, and the purification period. The oxidizer can be
supplied to soil and/or groundwater in the form of aqueous
solution by a facility such as a well dug in the soil. The supply
20 of the oxidizer can be carried out continuously or intermittently.
The concentration of the oxidizer aqueous solution is preferably
0 to 35 % by weight.

[0018]

The addition of an oxidizer is preferably carried out in
25 a pH range within which the effect of the chelating agent
satisfactorily appears in the above oxidizer addition process,
so that it is necessary to maintain the pH range of the
purification object at 5 to 10, preferably 7 to 9. However, there
may be a case where the addition of an oxidizer accelerates

decomposition of organic pollutants in the purification object to cause a decrease of pH of the purification object. Therefore, it is preferable to add a pH buffering agent that can maintain the above pH range.

5 As the pH buffering agent, carbonic acids, phosphoric acids, acetic acids and the like are appropriately selected for use. Among them, the carbon acid buffering agents are preferable considering that it can maintain the pH of the purification object at 7 to 9 within which the effect of the chelating agent most
10 satisfactorily appears and in terms of environmental load. Examples of the carbonic acid buffering agents include sodium carbonate, potassium carbonate, calcium carbonate, magnesium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate and the like. Examples of the phosphoric acid
15 buffering agents include disodium hydrogen phosphate, sodium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium dihydrogen phosphate and the like. Examples of the acetic acid buffering agents include acetic acid, sodium acetate, and the like.

20 Among them, it is preferable to use sodium hydrogen carbonate independently or in combination with sodium carbonate in terms of cost, solubility, and pH level. Alternatively, it is also preferable to use acetic acid in combination with sodium acetate.

25 Even if decrease of pH occurs, it is not always necessary to add a pH buffering agent as long as the pH range of a purification object is 5 to 10. However, in order to reduce the purification period, it is desirable to add a pH buffering agent to control the pH value at 7 to 9. The buffering agent can be

supplied to soil and/or groundwater in the form of aqueous solution whose pH value has been controlled at the intended range by a facility such as a well dug in the soil.

[0019]

5 Although the purification method according to the present invention is basically assumed to be applied to purification of soil and/or groundwater in situ, the present invention is not limited to this configuration, but may also be applied to secondary processing performed ex situ.

10

Examples

[0020]

 Some examples carrying out the present invention will be described below. Note that the following examples do not limit
15 the present invention.

[0021]

<Examples 1 to 6, Comparative examples 1 to 9>

 15 mg-Fe/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and an equal molar amount of a chelating agent to iron ion were previously added in a 134 ml
20 vial to generate an iron chelate complex. Subsequently, simulated polluted water wherein tetrachloroethylene (PCE) had been dissolved as a volatile organic compound at a concentration of 19 to 28 mg/L, 680 mg/L (in the case where pH range is 5 to 6), 63 mg/L (in the case where pH range is 7 to 8), or 660 mg/L
25 (in the case where pH range is 9 to 10) of hydrogen peroxide, and a buffering agent for maintaining the pH of the reaction liquid at a constant value which is a combination of sodium hydrogen carbonate/sodium carbonate or a combination of acetic acid/sodium acetate were poured into the vial. The vial was then

sealed, and a purification test was carried out. After elapse of a certain time (1h) from the start of reaction, the PCE concentration in the liquid was measured so as to check the progress of purification.

The test results wherein methylglycine diacetic acid (sodium salt; product name "Trilon M" (registered trademark) provided by BASF Japan Ltd.) or L-glutamate diacetic acid (sodium salt; reagent, manufactured by Tokyo Kasei Co., Ltd.) was used as a chelating agent were shown in Examples 1 to 6 in Table 1.

The test results wherein the chelating agent was not added or gluconic acid or ethylene diamine disuccinic acid each of which has biodegradability but falls outside the scope of the present invention was used were shown in Comparative Examples 1 to 9 in Table 1.

[0022]

[Table 1]

	pH range	Initial concentration of hydrogen peroxide solution [mg/L]	Chelating agent	Initial PCE concentration [mg/L]	Residual PCE concentration [mg/L]	PCE decomposition rate [%]
Example 1	5-6	680	Methylglycine diacetic acid	26.2	13.5	48.5
Example 2			Glutamate diacetic acid	21.7	11.8	45.6
Comparative Example 1			Not added	26.2	25.5	2.7
Comparative Example 2			Gluconic acid Na	26.2	25.5	2.7
Comparative Example 3			Ethylene diamine disuccinic acid	21.7	19.5	10.0
Example 3	7-9	60	Methylglycine diacetic acid	18.7	4.9	73.6
Example 4			Glutamate diacetic acid	18.7	5.6	70.0
Comparative Example 4			Not added	36.8	36.8	0.0
Comparative Example 5			Gluconic acid Na	24.4	22.9	6.1
Comparative Example 6			Ethylene diamine disuccinic acid	36.1	21.9	39.2
Example 5	8-10	660	Methylglycine diacetic acid	22.6	8.0	64.6
Example 6			Glutamate diacetic acid	22.6	5.7	75.0
Comparative Example 7			Not added	24.7	24.5	0.8
Comparative Example 8			Gluconic acid Na	27.9	27.3	2.2
Comparative Example 9			Ethylene diamine disuccinic acid	30.6	25.0	18.3

[0023]

In the case where the chelating agent falling within the scope of the present invention is used as shown in Examples 1 to 6, 45% or more of PCE decomposition was obtained, and acceleration effect of PCE decomposition reaction due to addition of the chelating agent was exhibited in the pH range from 5 to 10. However, in the case where the chelating agent is not added as shown in Comparative examples 1, 4, and 7 and in the case where the chelating agent falling outside the scope of the present invention is added as shown in Comparative examples 2, 5, and 8, the PCE decomposition reaction hardly proceeded. In the case where the chelating agent falling outside the scope of the present invention is added as shown in Comparative examples 3, 6, and 9, although the PCE decomposition reaction proceeded, the PCE decomposition amount was less than about half to that in the case where the chelating agent falling within the scope of the present invention was used under the same pH conditions. The above results reveal that addition of the biodegradable chelating agent specified by the present invention is highly effective for decomposition of a chlorinated organic compound in the pH range from 5 to 10.

[0024]

<Examples 7 to 14, Comparative example 10 to 16>

15 mg-Fe/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and a chelating agent were previously added in a 134 ml vial to generate an iron chelate complex. The additive amount of the chelating agent was varied as a molar ratio of the chelating agent to iron ions added. Subsequently, simulated polluted water wherein tetrachloroethylene (PCE) had been dissolved as a volatile

organic compound at a concentration of 26 to 52 mg/L, a buffering agent for maintaining the pH of the reaction liquid at a constant value (from 7 to 9) which is a combination of sodium hydrogen carbonate/sodium carbonate, and 65 mg/L of hydrogen peroxide were poured into the vial. The vial was then sealed, and a purification test was carried out. After elapse of a certain time (1h) from the start of reaction, the PCE concentration in the liquid was measured so as to check the progress of purification.

The test results wherein methylglycine diacetic acid or glutamate diacetic acid was used as a chelating agent were shown in Examples 7 to 11 and 12 to 14 in Table 2.

The test results wherein the chelating agent was added in a molar ratio falling outside the scope of the present invention were shown in Comparative Examples 10 to 12 in Table 2.

The test results wherein ethylene diamine tetraacetic acid which is persistent and is outside the scope of the present invention was used were shown in Comparative Examples 13 to 16 in Table 2.

[0025]

[Table 2]

	Chelating agent	Molar ratio of chelating agent to be added [mol/mol-Fe]	Initial PCE concentration [mg/L]	Residual PCE concentration after 1h [mg/L]	PCE decomposition rate after 1h [%]	Precipitation of Fe (presence/absence*)
Example 7	Methylglycine diacetic acid	1	30.7	9.8	68.2	○
Example 8		0.5		12.0	60.8	○
Comparative Example 10		0.25		18.9	38.5	×
Example 9	Methylglycine diacetic acid	1	25.9	8.2	68.3	○
Example 10		2		9.5	63.3	○
Example 11		4		17.1	33.7	○
Comparative Example 11	Glutamate diacetic acid	8	36.2	22.1	14.6	○
Example 12		1		16.0	55.7	○
Example 13		2		15.2	58.1	○
Example 14		4		27.4	24.4	○
Comparative Example 12		8		35.1	3.0	○
Comparative Example 13		1	52.4	32.0	38.9	○
Comparative Example 14	Ethylene diamine tetraacetic acid	2		46.7	10.8	○
Comparative Example 15		4		46.5	11.2	○
Comparative Example 16		8		48.2	8.1	○

*) Fe precipitation ○: not precipitated, ×: precipitated

[0026]

In Examples 7 to 11 using methylglycine diacetic acid, the molar ratio of the chelating agent was 0.5 to 4.0 to iron ions, within which the residual PCE concentration was low. That is, decomposition of PCE satisfactorily proceeded. However, in Comparative examples 10 to 11, the molar ratio of the chelating agent is outside the range from 0.5 to 4.0 to iron ions. In this case, the residual PCE concentration was high, which exhibits that decomposition of PCE did not sufficiently proceed. Further, although precipitation of ferrihydrite did not occur in Examples 7 to 11 and Comparative example 11, it was clearly observed in Comparative example 10.

In Examples 12 to 14 using glutamate diacetic acid, the residual PCE concentration was low within the additive molar ratio within the scope of the present invention and thus decomposition of PCE satisfactorily proceeded, as in the case where methylglycine diacetic acid was used. In particular, in the case where the additive molar ratio of the chelating agent to iron ions was 2 or less, decomposition rate as high as 5% or more was exhibited. However, with the additive amount of the chelating agent which falls outside the scope of the present invention, a decrease in the PCE decomposition rate was observed (Comparative example 12).

[0027]

In Comparative examples 13 to 16 using ethylene diamine tetraacetic acid, the precipitation of ferrihydrite was not observed. However, in the case where the additive molar ratio of the chelating agent to iron ions is 2 or more in Comparative examples 14 to 16, the PCE decomposition reaction hardly

proceeded, which reveals that excessive addition of the chelating agent inhibited the decomposition reaction.

As shown in the above results, the chelating agent having a structure and properties defined in the present invention is
5 highly effective for decomposition of chlorinated organic compounds with the additive molar ratio to iron ions in the range from 0.5 to 4.0 which falls within the scope of the present invention.

10 Industrial Applicability

[0028]

According to the present invention, after generation of a complex of biodegradable chelating agent having an extremely low environmental load and iron ion, an oxidizer is added while
15 maintaining the pH of a purification object at a high pH value. This process prevents secondary pollution caused by elution of heavy metals, as well as effectively prevents blocking of a passage or piping caused by generation and precipitation of ferrihydrite.

20 Thus, it is possible to effectively and safely purify soil and/or groundwater polluted with organic compounds in a short period. In particular, it is possible to accomplish purification in situ without greatly affecting the ambient environment such as ecosystems and the like. Further, the present invention is
25 extremely effective for purification of highly concentrated pollution.

C L A I M S

1. A method of purifying soil and/or groundwater
characterized in that it comprises:

5 a step of addition of a biodegradable chelating agent wherein
a dicarboxymethylamine biodegradable chelating agent selected from
the group consisting of methylglycine-diacetic acid, glutamate
diacetic acid and salts thereof is added to a purification object
in a molar ratio of 0.5 to 4.0 to iron ions being present in the
10 purification object to thereby form a complex of biodegradable
chelating agent and iron ion; and

a step of addition of an oxidizer wherein an oxidizer is added
after forming the complex while maintaining the pH value of the
purification object at 5 to 10.

15

2. The method of purification according to claim 1,
characterized in that

in said step of addition of an oxidizer, said oxidizer

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25

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is added while maintaining the pH value of the purification object at 7 to 9.

3. The method of purification according to any one of claims
5 1 to 2, characterized in that

in said step of addition of an oxidizer, at least one pH buffering agent selected from a group consisting of sodium carbonate, potassium carbonate, calcium carbonate, magnesium carbonate, sodium hydrogen carbonate, and potassium hydrogen carbonate.

10

4. The method of purification according to any one of claims 1 to 3, characterized in that said oxidizer is hydrogen peroxide.

5. The method of purification according to any one of claims
15 1 to 4, characterized in that,

preliminary to the step of addition of a biodegradable chelating agent, it further comprises a step of pretreatment wherein the pH of the purification object is decreased from 6 or more to not less than 5 but less than 6 so as to allow the iron ions in soil
20 to dissolve into groundwater.

6. The method of purification according to any one of claims 1 to 5, characterized in that,

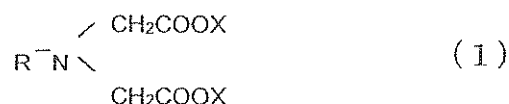
preliminary to the step of addition of a biodegradable
25 chelating agent, it further comprises a step of pretreatment wherein iron ions are added to the purification object.

Method Of Purifying Soil And/Or Groundwater

A B S T R A C T

An object of the present invention is to provide an effective purification method having a low environmental load, in the purification of soil and/or groundwater polluted by persistent organic compounds. There is provided a method comprising adding a dicarboxymethylamine-based biodegradable chelating agent represented by the following general formula (1) to a purification object in a molar ratio 0.5 to 4.0 to iron ions being present in the purification object to generate a complex of biodegradable chelating agent and iron ion and adding an oxidizer while maintaining the pH value of the purification object at 5 to 10, preferably using a pH buffering agent.

[Chemical formula 1]



(No Figure)