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(54) Title: METHOD OF TREATING PERSISTENT ORGANIC POLLUTANTS

(57) Abstract: There is provided a method of treating persistent organic pollutants such as waste agrichemicals through indirect heating, according to which the pollutants decomposition efficiency can be improved, the burden on exhaust gas treatment can be greatly reduced, and treatment can be carried out safely, reliably, and at low cost. One aspect of the present invention relates to a method of treating a persistent organic pollutants comprising mixing together the organic pollutants, a solid medium, an alkali, and a high-boiling-point polar solvent. Moreover, another aspect of the present invention relates to a method of treating a persistent organic pollutants contained in a solid medium comprising mixing together the organic pollutants in the solid medium, an alkali, and a high-boiling-point polar solvent.



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DESCRIPTION

METHOD OF TREATING PERSISTENT ORGANIC POLLUTANTS

TECHNICAL FIELD

5 The present invention relates to a method of treating hazardous persistent organic pollutants. The present invention is useful for treating agrichemicals, in particular treating a persistent waste agrichemicals, and can be preferably applied to the decomposition of
10 organochlorines or drin waste agrichemicals, although can also be applied to the decomposition of organophosphorus or carbamate agrichemicals.

BACKGROUND ART

15 It is known that among agrichemicals whose use has been banned in Japan in the past, there are ones that were buried underground in containers so that toxic components persist as is even today. These include BHC, chlordane, DDT and so on, which are designated under international
20 treaties as persistent organic pollutants to be treated. As a method of treating these waste agrichemicals, one can envisage incineration as the simplest method. However, with incineration, a large amount of combustion exhaust gas is generated, and moreover high concentrations of hazardous
25 byproducts may be generated, and hence there are concerns of effects on the surrounding environment, and thus implementation is difficult in actual practice. Chemical treatment using a liquid reaction has advantages in that

hardly any exhaust gas is discharged, and should the treatment be insufficient, treatment can easily be carried out again; however, special treatment equipment is required.

In contrast with these treatment methods, a method
5 has been proposed in which a heating medium is used; the persistent organic pollutants to be treated is mixed with this heating medium and heating is carried out, whereby the organic pollutants is treated by being indirectly heated. With this method, there are advantages in that the amount
10 of exhaust gas can be reduced, and existing heating equipment such as a rotary kiln type heating furnace can be appropriated for use in the method. However, with this indirect heating treatment method, not all of the organic pollutants charged into the heating furnace together with
15 the heating medium can be decomposed, but rather some of the organic pollutants go into the exhaust gas still in an undecomposed state. Gas treatment to remove the persistent organic pollutants from the exhaust gas must thus be further carried out.

20 A method has been proposed in which organic pollutants are decomposed by being reacted with a reagent constituted from oxygen and the product of a reaction between an alkali metal hydroxide and a polyglycol (U.S. Patent No. 4400552). However, with this method, there are
25 disadvantages in that an excess of the reagent is required relative to the material to be treated, and moreover the reactivity of the reagent is poor.

A method has been proposed in which the material to

be treated is reductively dehalogenated by heating in the presence of an alkali and a catalyst (Japanese Patent No. 3025701). However, with this method, there is a problem in that the reactivity of the reagent is again poor, and the treatment takes a long time.

A method has been proposed in which a hydrocarbon, IPA and metallic sodium are added to the agrichemicals to be treated and a dechlorination reaction is carried out (Collection of Papers presented at the 14th Annual Conference of the Japan Society of Waste Management Experts, 2003, pages 1295 to 1297). However, with this method, there are problems in that the operation of separating the agrichemicals from the matrix requires much time, and moreover harmful substances such as benzene are produced as a reaction product.

A method has been proposed in which the material to be treated is finely dispersed or powdered so as to change the nature thereof and thus increase the chemical reactivity. For example, in the case of treating an organochlorine compound, a method has been proposed in which DCR treatment is carried out, and then an alkali and a catalyst are added to the dry powder thus produced and kneading is carried out to effect decomposition. However, with this method, there are problems such as the chemicals used being expensive, and large-scale waste gas treatment equipment being required due to moisture rapidly being removed through reaction and evaporation.

It is an object of the present invention to solve the

various problems of the prior art described above, and provide a method of treating persistent organic pollutants such as waste agrichemicals through indirect heating, according to which the pollutant decomposition efficiency
5 can be improved, the burden on exhaust gas treatment can be greatly reduced, and the treatment can be carried out safely, reliably, and at low cost.

BRIEF DESCRIPTION OF THE DRAWINGS

10 FIG. 1 is a drawing showing an example of the constitution of an organic pollutants-decomposing apparatus according to an aspect of the present invention.

FIG. 2 is a drawing showing an example of the constitution of another organic pollutants-decomposing
15 apparatus according to an aspect of the present invention.

DISCLOSURE OF THE INVENTION

As means for attaining the above object, the present inventors have invented a method of treating persistent
20 organic pollutants by mixing together the organic pollutants, a solid medium, an alkali, and a high-boiling-point polar solvent, and then heating the mixture, and have filed a patent application therefor (Japanese patent application No. 2004-166248).

25 In that method, a large excess of a solid heating medium (e.g. sand particles), i.e. 10 to 1000 times the amount of the organic pollutants to be treated, is made to be present, and an alkali and a high-boiling-point polar

solvent are added, and heating is carried out (indirect heating), thus reacting the organic pollutants with the alkali and hence decomposing the organic pollutants.

The present inventors carried out further studies relating to this art, and as a result accomplished the present invention upon discovering that in the case in particular that the amount of the solid medium (heating medium) is made to be not more than approximately five times the amount of the organic pollutants to be treated, the temperature of the reaction system is increased through the heat of reaction due to the reaction between the organic pollutants and the alkali itself, and hence the organic pollutants decomposition reaction proceeds rapidly even if heat is substantially not applied from the outside. That is, one aspect of the present invention relates to a method of treating persistent organic pollutants comprising mixing together the organic pollutants, a solid medium, an alkali, and a high-boiling-point polar solvent.

Examples of organic pollutants that can be treated according to the present invention are persistent waste agrichemicals, in particular organochlorine and drin waste agrichemicals. Examples of organochlorine agrichemicals that can be treated according to the present invention include BHC, hexachlorobenzene, DDT, chlordane, heptachlor and toxaphene, and examples of drin agrichemicals that can be treated according to the present invention include aldrin, dieldrin and endrin. Furthermore, according to the method of the present invention, organophosphorus

agrichemicals such as pyraclofos and propaphos, and carbamate agrichemicals such as carbaryl and ashram, and so on can also be treated. Furthermore, according to the present invention, any of various pesticides, herbicides, insecticides, microbicides, fungicides and so on can be treated, and moreover persistent organic pollutants such as organohalogen compounds such as chlorinated dioxins and PCB can be treated according to the present invention. Moreover, according to the present invention, polluted soil, polluted bottom sediment, sludge, deposit, waste, incinerated ash or the like polluted with any of various organic compounds as above can also be purified as the organic pollutants to be treated.

In the method of the present invention, the organic pollutants to be treated is added and mixed into a solid medium. The solid medium acts as a heating medium when thermally decomposing the organic pollutants. As the solid medium to be used with this objective, one having the form of a powder or granules is preferable, and moreover ability to hold the organic pollutants to some extent, heat resistance so as to be able to withstand heating process, abrasion resistance, durability to alkalis, and a sufficient relative density so as not to be easily scattered around are required. Specific examples of granular/powdery solid media that can be used in the present invention include natural minerals such as sand, gravel and stones, artificial minerals such as ceramics and beads, and metallic powders/granules such as iron powder,

Mn powder and Zn powder (granules). Regarding the particle size of the granular/powdery solid medium, so as to keep down dust, the particle diameter is preferably at least 0.1 mm.

5 In the present invention, at least one selected from alkali metal carbonates, bicarbonates or hydroxides or at least one selected from alkaline earth metal oxides or hydroxides (hereinafter referred to as an 'alkali') and a high-boiling-point polar solvent are further added and
10 mixed into the solid medium, and treatment of the organic pollutants is carried out. Examples of alkalis that can be used include alkali metals or alkaline earth metals such as metallic sodium or metallic potassium, hydroxides of alkali metals or alkaline earth metals such as sodium hydroxide,
15 potassium hydroxide, calcium hydroxide or magnesium hydroxide, carbonates or bicarbonates of alkali metals such as sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate, or oxides of alkaline earth metals such as calcium oxide or magnesium oxide.
20 These alkalis can be supplied as a solid or a liquid (aqueous solution). 'High-boiling-point polar solvent' refers to a polar solvent having a boiling point of at least 150°C, preferably at least 190°C; specifically, a glycol such as ethylene glycol, polyethylene glycol,
25 diethylene glycol, propylene glycol, dipropylene glycol or polypropylene glycol, or a glycol alkyl ether such as ethylene glycol diethyl ether, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether or dipropylene

glycol monopropyl ether, or the like can be used. With the method of the present invention, by adding the high-boiling-point polar solvent such as a glycol to the alkali, the alkali is efficiently dissociated, and hence the reactivity thereof with the material to be treated at room temperature or therearound is greatly improved.

With the method of the present invention, the organic pollutants, and the solid medium, the alkali and the high-boiling-point polar solvent as described above are mixed together. The mixing proportion of the organic pollutants will vary according to the ease/difficulty of decomposing the pollutants to be treated, the amount of heat generated through the reaction between the pollutants to be treated and the alkali, the thermal capacity of the material to be treated, the thermal capacity of the solid medium, and so on, but is generally preferably made to be 3 to 50 wt%, more preferably 3 to 35 wt%, yet more preferably 3.3 to 30 wt%, relative to the amount of the solid medium. Note that in the case that the organic pollutants to be treated is in a diluted state, for example in the case that the organic pollutants are in the form of preparation or the case of treating a polluted medium polluted with the persistent organic pollutants, this value means the percentage by weight of the component to be treated targeted for decomposition (the organic compound to be decomposed). In the case that the amount of the solid medium originally present is sufficiently great, it may not be necessary to newly add solid medium. Moreover, in the case of adding

the organic pollutants gradually to a solid medium to which the alkali and the high-boiling-point polar solvent have already been added and mixing as described later, the above amount of the organic pollutants relative to the solid
5 medium means the amount of the organic pollutants present in the reaction system. That is, upon adding the organic pollutants to the solid medium to which the alkali and the high-boiling-point polar solvent have been added and mixing, the organic pollutants are decomposed through reaction with
10 the alkali; in the case that organic pollutants are then further added, the amount of the organic pollutants in the above means the amount excluding that already decomposed.

Moreover, the alkali has a function of capturing the reactant in the organic pollutants and preventing
15 production of new harmful substances; for this objective, for example in the case that the reactant that is the material to be treated is an organohalogen compound, it is sufficient if the mixing proportion of the alkali is at least 1 mol per 1 mol of halogen in the material to be
20 treated, but this mixing proportion is preferably made to be 1.5 to 3.0 mol. Furthermore, the high-boiling-point polar solvent has a function of supplying sites for reaction by dissolving the organic pollutants and the alkali; for this objective, the mixing proportion of the
25 high-boiling-point polar solvent is preferably made to be 1 to 30 wt%, more preferably 1 to 20 wt%, relative to the amount of the solid medium. Note that to form a uniform mixture, it may be preferable to add the alkali and the

high-boiling-point polar solvent after dissolving them in water. Moreover, there are no particular limitations on the order of mixing in the solid medium, the alkali, the high-boiling-point polar solvent and the organic pollutants.

5 For example, it is possible to first add and mix the organic pollutants to be treated into the solid medium, and then add the alkali and the high-boiling-point polar solvent to the resulting mixture; alternatively, it is possible to use a mixture obtained by adding the alkali and
10 the high-boiling-point polar solvent to the solid medium as a treatment agent, and then add and mix the organic pollutants to be treated into this treatment agent. Note that when mixing in each component, it may be preferable to add a little water and knead.

15 With the method of the present invention, upon mixing together the solid medium, the alkali, the high-boiling-point polar solvent and the organic pollutants, the temperature of the reaction system rises through the heat of reaction generated through the reaction between the
20 organic pollutants and the alkali itself. Through the temperature rising, the reaction between the organic pollutants and the alkali is promoted, and hence close to 100% of the organic pollutants can be decomposed substantially without applying heat from the outside.

25 Moreover, with the method of the present invention, through adding the high-boiling-point polar solvent such as a glycol or a glycol alkyl ether to the alkali, the alkali is efficiently dissociated, and hence the reactivity thereof

with the material to be treated at room temperature or therearound is greatly improved.

There are no particular limitations on the order of mixing in the solid medium, the alkali, the high-boiling-point polar solvent and the organic pollutants. However, to control the amount of heat generated through the heat of reaction and thus maintain the temperature within a prescribed range as described later, the following method is most preferable: the high-boiling-point polar solvent is first uniformly dispersed in the solid medium, and then the alkali is added and kneading is carried out thoroughly until uniform to form a mixed medium; the organic pollutants to be treated is then added to the mixed medium a little at a time while controlling the amount added such that the temperature does not rise too much, and kneading is carried out. Note that the order of mixing in the solid medium, the alkali and the high-boiling-point polar solvent is not limited to the above method, but rather the mixing order can be changed. However, it is preferable to add and mix in the organic pollutants last. The reason for this is that the amount of the organic pollutants reacting is directly linked to the rise in temperature, and hence if the alkali is added last to a system into which the organic pollutants had already been mixed, then it may be difficult to control the reaction, for example the reaction may proceed explosively, and hence a large amount of gas may be produced all at once, or there may be a risk of ignition or the like. Moreover, if the alkali and the glycol or glycol

alkyl ether (high-boiling-point polar solvent) are added directly to the agrichemicals, then the composition or form will often be changed through an exothermic reaction. The organic pollutants and the alkali may become attached to the solid medium via diethylene glycol. In such a case in particular, so that the mixture can be kneaded easily and hence the rise in temperature can be made rapid, it is preferable to carry out kneading after adding a little water to the mixture.

Moreover, the alkali and the glycol or glycol alkyl ether (high-boiling-point polar solvent) may be added to a dispersion of the organic pollutants to be treated in the solid medium. In general, with an agrichemicals preparation, bentonite or the like is added to the technical product so as to dilute and disperse the technical product, thus improving the ease of handling and the sustainability of the effects. In the case that the concentration of the technical product in the agrichemical preparation is at least 10%, to increase the thermal capacity of the reaction system, a solid medium such as sand may be added to the preparation so as to dilute the technical product such that the concentration of the technical product becomes less than 10%, whereby the rise in temperature upon adding the alkali and the glycol or glycol alkyl ether (high-boiling-point polar solvent) can be kept down. With this method, it is preferable to add the alkali slowly while monitoring the temperature to a mixture obtained by kneading together the organic

pollutants, the solid medium and the high-boiling-point polar solvent, and in some cases also water, and carry out mixing while controlling the amount added of the alkali such that the temperature of the reaction system is
5 maintained within a range of 30 to 80°C.

Note that in the case, for example, that the organic pollutants to be treated are agrichemical preparations, the agrichemical component is often diluted with bentonite or the like, and in this case it may be sufficient to add a
10 solid medium to the system in only a very small amount, or it may not be necessary to add a solid medium at all.

With the method of the present invention, as described above, upon mixing the solid medium, the alkali, the high-boiling-point polar solvent and the organic
15 pollutants together, the temperature of the reaction system rises through the heat of reaction generated through the reaction between the alkali and the organic pollutants itself. The reaction can thus be made to proceed efficiently through the natural rise in temperature due to
20 heat generation by kneading the above components together at room temperature. However, if the temperature of the reaction system exceeds, for example, 100°C, then problems will occur such as moisture evaporating and a large amount of gas being generated. As described above, it is thus
25 preferable to add the organic pollutants a little at a time to a mixed medium obtained by mixing the solid medium, the alkali and the high-boiling-point polar solvent together while controlling the amount of the organic pollutants

added such that the temperature of the reaction system does not rise too much, and carry out kneading. In actual practice, it is preferable to control the amount of the organic pollutants mixed in such that the temperature of the reaction system is maintained within a range of 30 to 100°C, preferably 30 to 90°C, more preferably 40 to 80°C. Moreover, the reaction apparatus (mixing apparatus) may be provided with a cooler so that the reaction mixture can be cooled as required. Furthermore, in the case that the rise in the temperature of the reaction system due to the heat of reaction from the reaction between the organic pollutants and the alkali is low, heating from the outside may be carried out so as to maintain the temperature of the reaction system in a suitable range.

When treating the mixture, to prevent the generation of harmful byproducts, it is preferable to create an inert atmosphere through means such as supplying in nitrogen. The mixing time will vary according to the nature and amount of the organic pollutants to be treated, the temperature of the reaction system and so on, but is generally preferably made to be 5 to 120 minutes, preferably 15 to 100 minutes, more preferably 30 to 60 minutes.

After the organic pollutants have been decomposed, it is possible to take the solid medium out, leave the solid medium to cool down to room temperature as required, and then once again add organic pollutants and carry out treatment.

According to the method of the present invention, the temperature of the reaction system rises through the heat of reaction generated through the reaction between the organic pollutants to be treated and the alkali itself, whereby the decomposition reaction of the organic pollutants is promoted, and hence at least 97% of the organic pollutants can be decomposed substantially without applying heat from the outside. However, in the case, for example, of decomposing a substance listed under the POPs treaty, the permissible concentration in the environment is low, and hence when carrying out treatment to decompose the substance and thus make the substance harmless, a decomposition efficiency (removal rate) of at least 'six nines' (99.9999%) is required. In the case that the organic pollutants must be decomposed more completely in this way, it is possible to put the reaction mixture that has been treated using the method of the present invention into a heating reactor, and heat the reaction mixture so as to decompose the organic pollutants more completely.

When carrying out such decomposition treatment, for example with the method disclosed in Japanese patent application No. 2004-166248 filed by the present applicants, for example a mixture of 100,000 parts by weight in total obtained by adding 800 parts by weight of an alkali and 200 parts by weight of a high-boiling-point polar solvent to 1,000 parts by weight of BHC and then further adding 98,000 parts by weight of a solid medium (sand) is treated in a heating reactor. In contrast with this, with the method of

the present invention, for example a mixture of 5,000 parts by weight in total obtained by adding 800 parts by weight of an alkali and 200 parts by weight of a high-boiling-point polar solvent to 1,000 parts by weight of BHC and
5 then further adding 3,000 parts by weight of a solid medium (sand) is kneaded to subject the BHC to decomposition treatment, and then afterwards the mixture is put into a heating reactor and treated to completely decompose the BHC. Consequently, according to the method of the present
10 invention, the amount of the BHC to be decomposed in the heating reactor is overwhelmingly low, and hence the workload for the heating reactor is greatly reduced, and thus the overall cost can be reduced. Moreover, with the former method, the capacity of the heating reactor must be
15 such that 100,000 parts by weight of the mixture can be treated, whereas with the method of the present invention, a heating reactor with a capacity such that 5,000 parts by weight of the mixture can be treated is sufficient. Consequently, according to the method of the present
20 invention, the size of the heating reactor may be one twentieth, and hence the cost of the apparatus and operational costs can both be greatly reduced.

Moreover, the present invention also relates to an apparatus for adding organic pollutants as described above
25 a little at a time to a mixed medium obtained by mixing together a solid medium, an alkali and a high-boiling-point polar solvent as described above while controlling the amount of the organic pollutants added such that the

temperature of the reaction system does not rise too much, and kneading to decompose the organic pollutants. That is, another aspect of the present invention relates to an organic pollutants treatment apparatus comprising a mixing
5 reactor having a stirrer; storage tanks storing respectively a solid medium, a high-boiling-point polar solvent, an alkali, and organic pollutants to be treated; quantitative feeders that supply measured amounts of the solid medium, the high-boiling-point polar solvent and the
10 alkali from the respective storage tanks into the mixing reactor; a quantitative feeder that supplies a measured amount of the organic pollutants to be treated from the storage tank into the mixing reactor; a temperature measuring instrument that measures the temperature of the
15 mixture in the mixing reactor; and an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature
20 measured by the temperature measuring instrument. Moreover, yet another aspect of the present invention relates to an organic pollutants treatment apparatus comprising a mixing reactor having a stirrer; storage tanks storing respectively a solid medium, a high-boiling-point polar
25 solvent, an alkali, and organic pollutants to be treated; a mixer in which the solid medium, the high-boiling-point polar solvent and the alkali are mixed together in advance; quantitative feeders that supply measured amounts of the

solid medium, the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixer; a device for supplying the mixture of the solid medium, the high-boiling-point polar solvent and the alkali produced in the mixer into the mixing reactor; a quantitative feeder that supplies a measured amount of the organic pollutants to be treated from the storage tank into the mixing reactor; a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the temperature measuring instrument.

These apparatuses will now be described conceptually with reference to the drawings. FIG. 1 shows to the organic pollutants treatment apparatus according to one aspect of the present invention. A storage tank for sand as the solid medium, a storage tank for DEG (diethylene glycol) as the high-boiling-point polar solvent, and a storage tank for the alkali are each connected to a mixing reactor via a quantitative feeder, and the sand, the DEG and the alkali are supplied from the respective storage tanks into the mixing reactor, and are mixed together by the stirrer in advance to form a mixed medium. The material to be treated in a storage tank is then similarly supplied via a quantitative feeder into the mixed medium in

the mixing reactor. At this time, the temperature of the mixture is measured by a temperature measuring instrument installed in the reactor, and the amount supplied of the material to be treated is controlled by a controller such
5 that this temperature does not exceed a prescribed desirable range, for example 80°C. If necessary, the mixing reactor may also be provided with a cooler. The treated material can be discharged out from the mixing reactor as appropriate. Moreover, by continuously supplying in the
10 respective components, and discharging the mixture after the mixture has been in the mixing reactor for a prescribed residence time, the treatment can be carried out continuously. Exhaust gas is discharged from the reactor, and untreated organic pollutants, albeit only a small
15 amount, persists in this exhaust gas. After being cooled if necessary, the exhaust gas may thus be passed into a catalyst tank and an activated charcoal tank (not shown in the drawing) so that persistent organic pollutants in the exhaust gas can be further removed before the exhaust gas
20 is discharged into the atmosphere. According to the present invention, the persistent organic pollutants in the material to be treated can be decomposed and thus removed efficiently in the mixing reactor, and hence the burden on the catalyst tank and the activated charcoal tank can be
25 reduced. Examples of organic pollutants-decomposing catalysts that can be used in such a persistent organic s treatment system include precious metal catalysts, platinum oxide and vanadium oxide.

Moreover, as shown in FIG. 2, it is also possible to constitute the apparatus such that the sand, the DEG and the alkali are mixed together in a mixer in advance to form a mixed medium, and then this mixed medium is supplied into
5 the mixing reactor.

Note that in the case of treating organic pollutants having a small heat of reaction as the material to be treated using the present invention, it may be possible to not add a solid medium, but rather mix the technical
10 product as is with the alkali and the high-boiling-point polar solvent. This aspect is also included in the scope of the present invention.

Various aspects of the present invention are as follows.

15 1. A method of treating persistent organic pollutants comprising mixing together the organic pollutants, an alkali, and a high-boiling-point polar solvent.

2. A method of treating persistent organic pollutants comprising mixing together the organic pollutants, a solid
20 medium, an alkali, and a high-boiling-point polar solvent.

3. A method of treating persistent organic pollutants contained in a solid medium comprising mixing together the organic pollutants in the solid medium, an alkali, and a high-boiling-point polar solvent.

25 4. The method according to any of items 1 through 3 above, wherein the mixture is held under an inert atmosphere.

5. The method according to any of items 1 through 4

above, wherein the organic pollutants are solid or liquid agrichemicals.

6. The method according to any of items 2 through 5 above, wherein 3 to 50 wt% of the organic pollutants in terms of the weight of a pollutant component to be treated is mixed in relative to the solid medium.

7. The method according to any of items 2 through 6 above, wherein the solid medium is a natural mineral, an artificial mineral or a metallic powder.

8. The method according to any of items 1 through 7 above, wherein the alkali is at least one selected from alkali metal or alkaline earth metal hydroxides, alkali metal carbonates or bicarbonates, or alkaline earth metal oxides.

9. The method according to any of items 1 through 8 above, wherein the high-boiling-point polar solvent is a glycol or a glycol alkyl ether.

10. The method according to item 9 above, wherein the high-boiling-point polar solvent is ethylene glycol, polyethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, ethylene glycol diethyl ether, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether, or dipropylene glycol monopropyl ether.

11. The method according to any of items 2 through 10 above, wherein the alkali and the high-boiling-point polar solvent are added and mixed into the solid medium to form a mixed medium, and then the organic pollutants are added and

mixed into the mixed medium while controlling the amount added such that the temperature of the reaction system is maintained at not more than a prescribed value.

12. The method according to item 11 above, wherein
5 the temperature of the reaction system is maintained at not more than 100°C.

13. An organic pollutants treatment apparatus comprising a mixing reactor having a stirrer; storage tanks storing respectively a solid medium, a high-boiling-point
10 polar solvent, an alkali, and organic pollutants to be treated; quantitative feeders that supply measured amounts of the solid medium, the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixing reactor; a quantitative feeder that supplies a
15 measured amount of the organic pollutants to be treated from the storage tank into the mixing reactor; a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and an organic pollutants supply amount controlling device for
20 controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the temperature measuring instrument.

25 14. An organic pollutants treatment apparatus comprising a mixing reactor having a stirrer; storage tanks storing respectively a solid medium, a high-boiling-point polar solvent, an alkali, and organic pollutants to be

treated; a mixer in which the solid medium, the high-boiling-point polar solvent and the alkali are mixed together in advance; quantitative feeders that supply measured amounts of the solid medium, the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixer; a device for supplying the mixture of the solid medium, the high-boiling-point polar solvent and the alkali produced in the mixer into the mixing reactor; a quantitative feeder that supplies a measured amount of the organic pollutants to be treated from the storage tank into the mixing reactor; a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the temperature measuring instrument.

15. An organic pollutants treatment apparatus comprising a mixing reactor having a stirrer; storage tanks storing respectively a high-boiling-point polar solvent, an alkali, and organic pollutants to be treated; quantitative feeders that supply measured amounts of the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixing reactor; a quantitative feeder that supplies a measured amount of the organic pollutants to be treated from the storage tank into the

mixing reactor; a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the temperature measuring instrument.

16. An organic pollutants treatment apparatus comprising a mixing reactor having a stirrer; storage tanks storing respectively a high-boiling-point polar solvent, an alkali, and organic pollutants to be treated; a mixer in which the high-boiling-point polar solvent and the alkali are mixed together in advance; quantitative feeders that supply measured amounts of the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixer; a device for supplying the mixture of the high-boiling-point polar solvent and the alkali produced in the mixer into the mixing reactor; a quantitative feeder that supplies a measured amount of the organic pollutants to be treated from the storage tank into the mixing reactor; a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the temperature

measuring instrument.

17. The apparatus according to any of items 13 through 16 above, wherein the mixing reactor is provided with a cooler.

5

Following is a description of the present invention through examples; however, the present invention is not limited by the following description.

Example 1

10 0.5 kg of PCNB (pentachloronitrobenzene) and 1.2 kg of NaOH were put into a mixer (made by Mazelar, product name PM-33S) and mixing was carried out, and then while adding 1 kg of DEG (diethylene glycol) a little at a time, the temperature of the mixture was maintained at 50 to 65°C
15 through the heat of reaction, and the mixture was thoroughly kneaded for approximately 2 hours.

After leaving to cool, the mixture and the mixer were washed with a solvent (ethyl acetate), and the PCNB in the washings was analyzed, whereupon the percentage decomposed
20 (removal rate) was 90%.

Example 2

1.2 kg of PCNB (pentachloronitrobenzene) powder and 0.3 kg of NaOH were put into a mixer as in Example 1 and mixing was carried out, and then 0.5 kg of DEG (diethylene
25 glycol) was added. While thoroughly kneading the mixture, 23 kg of air-dried sand having an effective diameter of 0.45 mm and a uniformity coefficient of 1.3 was gradually added and mixed in. The temperature of the mixture rose

through the heat of reaction. The mixture was maintained at a temperature of 60 to 90°C for 1 hour, and was then left to cool, and then the sand and the mixer were washed with a solvent (ethyl acetate), and the PCNB in the washings was analyzed, whereupon PCNB was not detected (i.e. the amount of PCNB was below the detection limit). The PCNB removal rate was thus at least 99%.

Example 3

5 kg of PCNB (pentachloronitrobenzene) powder was put into a mixer as in Example 1, and then a mixture that had been obtained by thoroughly mixing 2 kg of KOH and 1.2 kg of polyethylene glycol together was added and kneading was carried out. Next, 15 kg of sand as in Example 2 was added gradually and mixed in. The temperature of the mixture rose through the heat of reaction. The mixture was maintained at a temperature of 75 to 95°C for 1 hour, and was then left to cool, and then the sand and the mixer were washed with a solvent (ethyl acetate), and the PCNB in the washings was analyzed, whereupon PCNB was not detected (i.e. the amount of PCNB was below the detection limit). The PCNB removal rate was thus at least 99%.

Example 4

1.5 kg of BHC (benzene hexachloride) powder, and 24 kg of sand as in Example 2 were put into a mixer as in Example 1, and 1.8 kg of polyethylene glycol was added and thorough kneading was carried out. Next, 1.6 kg of potassium hydroxide was gradually added. The temperature of the mixture rose through the heat of reaction. The

mixture was maintained at a temperature of 60 to 80°C for 2 hours, and was then left to cool, and then the sand and the mixer were washed with a solvent (ethyl acetate), and the BHC in the washings was analyzed, whereupon the BHC
5 removal rate was 99.3%.

Example 5

90 kg of sand as in Example 2 was put into a mixer as in Example 1, 4 kg of diethylene glycol was added, and then 8 kg of sodium hydroxide was added, and the mixture was
10 kneaded thoroughly until uniform. 10 kg of BHC powder was then added and mixed in slowly such that the temperature of the mixture, which rose through the heat of reaction, did not exceed 90°C, and then the temperature of the mixture was maintained at not less than 75°C for 0.5 hours. After
15 that, the mixture was left to cool, and then the sand and the mixer were washed with a solvent (ethyl acetate), and the BHC in the washings was analyzed, whereupon the BHC removal rate was 98.4%.

Example 6

20 0.5 kg of PCNB (pentachloronitrobenzene) and 1.2 kg of NaOH were put into a mixer as in Example 1 and mixing was carried out, and then while adding 1 kg of dipropylene glycol monopropyl ether a little at a time, the temperature of the mixture was maintained at 50 to 65°C through the
25 heat of reaction, and the mixture was thoroughly kneaded for approximately 2 hours. After leaving to cool, the mixture and the mixer were washed with a solvent (ethyl acetate), and the PCNB in the washings was analyzed,

whereupon the percentage decomposed (PCNB removal rate) was 93%.

Example 7

1.2 kg of PCNB (pentachloronitrobenzene) powder and
5 0.3 kg of NaOH were put into a mixer as in Example 1 and
mixing was carried out, and then 0.5 kg of dipropylene
glycol monopropyl ether was added. While thoroughly
kneading the mixture, 23 kg of air-dried sand having an
effective diameter of 0.45 mm and a uniformity coefficient
10 of 1.3 was gradually added and mixed in. The temperature
of the mixture rose through the heat of reaction. The
mixture was maintained at a temperature of 75 to 95°C for 1
hour, and was then left to cool, and then the sand and the
mixer were washed with a solvent (ethyl acetate), and the
15 PCNB in the washings was analyzed, whereupon PCNB was not
detected (i.e. the amount of PCNB was below the detection
limit). The PCNB removal rate was thus at least 99%.

Example 8

1.5 kg of BHC (benzene hexachloride) powder, and
20 24 kg of sand as in Example 2 were put into a mixer as in
Example 1, and 1.8 kg of ethylene glycol diethyl ether was
added and thorough kneading was carried out. Next, 1.6 kg
of potassium hydroxide was gradually added. The
temperature of the mixture rose through the heat of
25 reaction. The mixture was maintained at a temperature of
60 to 80°C for 2 hours, and was then left to cool, and then
the sand and the mixer were washed with a solvent (ethyl
acetate), and the BHC in the washings was analyzed,

whereupon the BHC removal rate was 98.3%.

Example 9

90 kg of sand as in Example 2 was put into a mixer as in Example 1, 4 kg of diethylene glycol diethyl ether was added, and then 8 kg of sodium hydroxide was added, and the mixture was kneaded thoroughly until uniform. 10 kg of BHC powder was then added and mixed in slowly such that the temperature of the mixture, which rose through the heat of reaction, did not exceed 90°C, and then the temperature of the mixture was maintained at not less than 75°C for 0.5 hours. After that, the mixture was left to cool, and then the sand and the mixer were washed with a solvent (ethyl acetate), and the BHC in the washings was analyzed, whereupon the BHC removal rate was 99.6%.

Example 10

90 kg of sand as in Example 2, and 8 kg of sodium hydroxide were put into a mixer as in Example 1, and the mixture was kneaded thoroughly until uniform. Next, 4 kg of tetraethylene glycol dimethyl ether was added, and 10 kg of BHC powder was added and mixed in slowly such that the temperature of the mixture, which rose through the heat of reaction, did not exceed 90°C, and then the temperature of the mixture was maintained at 75 to 85°C for 0.5 hours. After that, the mixture was left to cool, and then the sand and the mixer were washed with a solvent (ethyl acetate), and the BHC in the washings was analyzed, whereupon the BHC removal rate was 99%.

INDUSTRIAL APPLICABILITY

According to the present invention, persistent organic pollutants such as waste agrichemicals can be decomposed to a high degree in a solid medium. Moreover, the amount of the persistent organic pollutants in exhaust gas generated during the treatment is greatly reduced, and hence in the case of carrying out exhaust gas treatment, the exhaust gas treatment workload is reduced. Moreover, harmless substances produced through the treatment according to the present invention can be recovered and reused as resources. According to the method of the present invention, the majority of harmful substances can be decomposed into harmless substances through simple mixing without external heating; if necessary, heating may be further carried out to completely decompose remaining traces of harmful substances, and hence reliable treatment is possible. Moreover, in the case of carrying out such heating as a subsequent stage, because the amount of the solid medium used is less than with an ordinary indirect heating method, the heating apparatus can be made smaller, and the cost of the apparatus and operational costs can both be reduced.

CLAIMS

1. A method of treating persistent organic pollutants comprising mixing together the organic pollutants, an
5 alkali, and a high-boiling-point polar solvent.
2. A method of treating persistent organic pollutants comprising mixing together the organic pollutants, a solid medium, an alkali, and a high-boiling-point polar solvent.
3. A method of treating persistent organic pollutants
10 contained in a solid medium comprising mixing together the organic pollutants in the solid medium, an alkali, and a high-boiling-point polar solvent.
4. The method according to any of claims 1 through 3, wherein the mixture is held under an inert atmosphere.
- 15 5. The method according to any of claims 1 through 4, wherein the organic pollutants are solid or liquid agrichemicals.
6. The method according to any of claims 2 through 5, wherein 3 to 50 wt% of the organic pollutants in terms of
20 the weight of a pollutant component to be treated is mixed in relative to the solid medium.
7. The method according to any of claims 2 through 6, wherein the solid medium is a natural mineral, an artificial mineral or a metallic powder.
- 25 8. The method according to any of claims 1 through 7, wherein the alkali is at least one selected from alkali metal or alkaline earth metal hydroxides, alkali metal carbonates or bicarbonates, or alkaline earth metal oxides.

9. The method according to any of claims 1 through 8, wherein the high-boiling-point polar solvent is a glycol or a glycol alkyl ether.

10. The method according to claim 9, wherein the
5 high-boiling-point polar solvent is ethylene glycol, polyethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, ethylene glycol diethyl ether, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether, or dipropylene glycol
10 monopropyl ether.

11. The method according to any of claims 2 through 10, wherein the alkali and the high-boiling-point polar solvent are added and mixed into the solid medium to form a mixed medium, and then the organic pollutants are added and mixed
15 into the mixed medium while controlling the amount added such that the temperature of the reaction system is maintained at not more than a prescribed value.

12. The method according to claim 11, wherein the temperature of the reaction system is maintained at not
20 more than 100°C.

13. An organic pollutants treatment apparatus comprising:
a mixing reactor having a stirrer;
storage tanks storing respectively a solid medium, a
high-boiling-point polar solvent, an alkali, and organic
25 pollutants to be treated;

quantitative feeders that supply measured amounts of the solid medium, the high-boiling-point polar solvent and the alkali from the respective storage tanks into the

mixing reactor;

a quantitative feeder that supplies a measured amount of the organic pollutants to be treated from the storage tank into the mixing reactor;

5 a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and

an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the temperature measuring instrument.

14. An organic pollutants treatment apparatus comprising:

a mixing reactor having a stirrer;

15 storage tanks storing respectively a solid medium, a high-boiling-point polar solvent, an alkali, and organic pollutants to be treated;

a mixer in which the solid medium, the high-boiling-point polar solvent and the alkali are mixed together in advance;

quantitative feeders that supply measured amounts of the solid medium, the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixer;

25 a device for supplying the mixture of the solid medium, the high-boiling-point polar solvent and the alkali produced in the mixer into the mixing reactor;

a quantitative feeder that supplies a measured amount

of the organic pollutants to be treated from the storage tank into the mixing reactor;

a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and

5 an organic pollutants supply amount controlling device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the
10 temperature measuring instrument.

15. An organic pollutants treatment apparatus comprising:

a mixing reactor having a stirrer;

storage tanks storing respectively a high-boiling-point polar solvent, an alkali, and organic pollutants to
15 be treated;

quantitative feeders that supply measured amounts of the high-boiling-point polar solvent and the alkali from the respective storage tanks into the mixing reactor;

a quantitative feeder that supplies a measured amount
20 of the organic pollutants to be treated from the storage tank into the mixing reactor;

a temperature measuring instrument that measures the temperature of the mixture in the mixing reactor; and

an organic pollutants supply amount controlling
25 device for controlling the supply amount of the quantitative feeder that supplies a measured amount of the organic pollutants from the storage tank into the mixing reactor, in accordance with the temperature measured by the

temperature measuring instrument.

16. An organic pollutants treatment apparatus comprising:

a mixing reactor having a stirrer;

storage tanks storing respectively a high-boiling-
5 point polar solvent, an alkali, and organic pollutants to
be treated;

a mixer in which the high-boiling-point polar solvent
and the alkali are mixed together in advance;

quantitative feeders that supply measured amounts of
10 the high-boiling-point polar solvent and the alkali from
the respective storage tanks into the mixer;

a device for supplying the mixture of the high-
boiling-point polar solvent and the alkali produced in the
mixer into the mixing reactor;

15 a quantitative feeder that supplies a measured amount
of the organic pollutants to be treated from the storage
tank into the mixing reactor;

a temperature measuring instrument that measures the
temperature of the mixture in the mixing reactor; and

20 an organic pollutants supply amount controlling
device for controlling the supply amount of the
quantitative feeder that supplies a measured amount of the
organic pollutants from the storage tank into the mixing
reactor, in accordance with the temperature measured by the
25 temperature measuring instrument.

17. The apparatus according to any of claims 13 through
16, wherein the mixing reactor is provided with a cooler.

Fig. 1

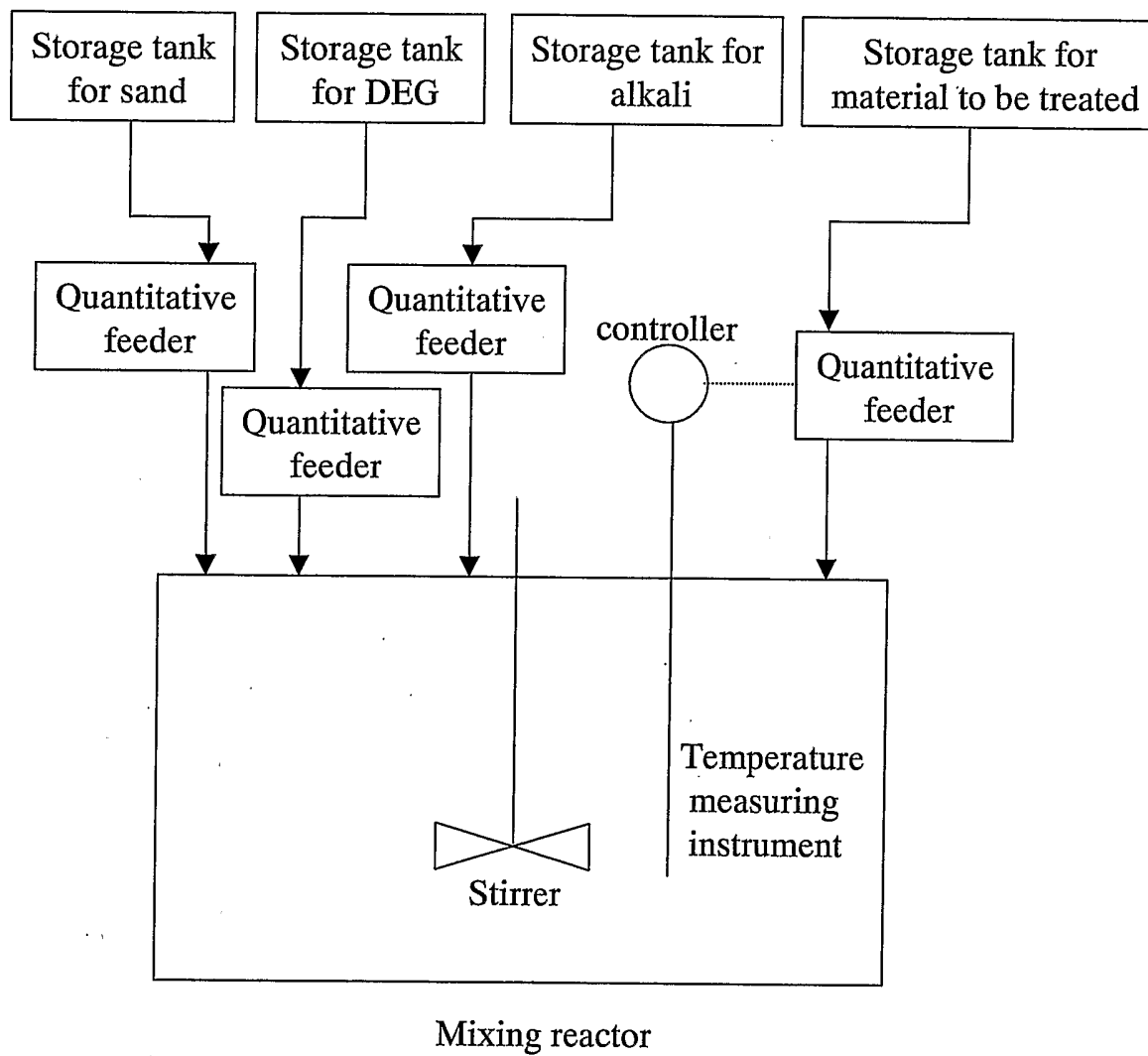


Fig. 2

