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(54) Title: PROCESS

(57) Abstract: The present invention provides a process for the extraction of an organic heavy metal compound from an aqueous medium comprising the step of contacting the aqueous medium containing the organic heavy metal compound with an ion exchanger.

Process

The present invention relates to a process for the extraction of an organic heavy metal compound from an aqueous medium.

5

Organic heavy metal compounds have been used in a wide variety of industrial applications in recent years. For example, lead tetraethyl and lead tetramethyl have been used in large quantities as anti-knock compounds in fuels for four-stroke engines. In view of the reported toxicity and carcinogenic properties of lead alkyls and their decomposition products, their use has been kept to a minimum in Europe, and in a number of other regions. Nevertheless, in a number of countries lead alkyls have continued in use as anti-knock compounds.

In lead alkyls manufacturing facilities, leakage has allowed considerable quantities of lead alkyls to flow into the soil, and subsequently this has been washed into the groundwater through the action of rainwater.

There has been a slow breakdown of lead alkyls from tetra- to tri- and di-compounds over the years in the soil and in the groundwater, leading to the formation of inorganic lead, in accordance with the following scheme:

20



where R represents methyl or ethyl, and L represents an inorganic acid residue such as CO_3^{2-} or SO_4^{2-} .

25

Lead alkyls have been reported to act primarily on the human central nervous system, and may cause states of agitation or epileptic convulsions as well as leading to Parkinson's disease. The chronic effects may also produce the symptoms of lead poisoning. Contamination of the soil and thus of groundwater therefore presents a considerable problem, because the contaminants may easily pass into humans over the long term through drinking water. It is therefore necessary to remove lead alkyl contamination.

30

Until now relatively little experience has been acquired in the purification of water contaminated with lead alkyls, and initially processes were only available which avoid additional contamination of the water, for example through the use of halogens, i.e. fluoride, chlorine and bromide (Schulze, Chem. Ztg. 64, 47, 1940.

5

The oxidation of lead alkyls through the use of oxygen and exposure to UV light, was described by Willemsens, L.C. in Intern. Lead Zinc Res. Org. Inc. New York, 1967.

A similar process is disclosed in EP-A-0714712, in which lead alkyls contained in water are decomposed by the action of UV light, in the presence of H_2O_2 , to release oxygen and ferric salt (Fenton's reagent), and are subsequently precipitated with flocculators. In one form of this method, contaminated water is purified by the use of active carbon or inorganic silicates, e.g. zeolite. The disadvantage of this method is that adsorption only removes those dialkyls which are insoluble in water. Tri- and dialkyls that are easily soluble in water are either not adsorbed or are only adsorbed to a very small extent. As a result of the initial oxygen treatment, only water-soluble tri- and dialkyls are found in the water, and consequently this method is not a practical one and the decontamination is found to be unsatisfactory.

The treatment of lead tetraethyl using ozone in sewage in the presence of silica gel as a catalyst is known from Linch et al., Am. Ind. Hyg. Assoc. J. 25, 1964. It may be assumed that, in the aforementioned process, the adsorbents are not used for that purpose but as catalysts to promote the oxidation of the tetraethyl lead. However, the problem still remains in the aforementioned process that the decomposition products are dissolved in water.

Prior art processes require considerable expenditure of energy in order to purify waste water, and are also expensive. Moreover they only provide complete decomposition of lead alkyls at temperatures in excess of $50^{\circ}C$. Moreover, the concentrations of lead alkyls in contaminated groundwater typically present in concentrations between a tenth and a thousandth that of the processes described in the prior art. Thus the cost of operating prior art processes to decontaminate ground water would be unacceptably high.

A process for reducing lead organic compounds, especially lead tetraethyl in contaminated, natural media, is described in US-A-5656489. This documents relates to the use of micro-organisms which decompose the named compounds to form inorganic lead compounds. The disclosed process is technically complicated and un-economic, because the population of the relevant micro-organisms has to reach a certain size in order to be able to decompose the lead compounds within an acceptable period of time. However, even within the parameters stated in US-A-5656489, the process is long and drawn out, in which the micro-organisms require a constant supply of additional nutrients in order to maintain their population at the necessary level. Moreover the lead is not removed completely from the soil, but is only converted into a less toxic form, and consequently the benefits are reduced.

US-A-6030467 teaches a process for purifying sludge and soil, for example, in which lead organic compounds are flushed using an aqueous solution of a surface-active substance. This process is not suitable for removing contamination that is already in the groundwater. Moreover the cost in the case of wide scale contamination is very high.

The present invention aims to provide a process that enables organic heavy metal compounds, such as lead alkyls, to be extracted simply, at a reasonable cost and almost entirely from contaminated water, especially groundwater.

The present invention alleviates the problems of the prior art.

In one aspect the present invention provides a process for the extraction of an organic heavy metal compound from an aqueous medium comprising the step of contacting the aqueous medium containing the organic heavy metal compound with an ion exchanger.

In a further aspect the present invention provides a use of an ion exchanger for the extraction of an organic heavy metal compound from an aqueous medium.

We have surprisingly found that not only are ionic heavy metal organic compounds, such as low alkylised lead organics PbR_3^+ and PbR_2^{2+} , bonded by means of ion exchange, but also the uncharged heavy metal organic compounds including highly alkylised compounds PbR_4 , are bonded, with the result that the present process is believed to consist of a combination of adsorption and ion exchange processes.

It is an advantage that, through the use of this process, 99% of heavy metal organic compounds such organic lead contaminants in the groundwater, may be removed from the aqueous medium. This produces a substantial advantage in that the vast majority of
5 the heavy metal organic compound, e.g. inorganic lead, remains in the ion exchanger.

In one preferred aspect the ion exchanger is a cation exchanger.

In a preferred aspect the ion exchanger is an organic ion exchanger.

10

Preferably the ion exchanger is an organic cation exchanger.

One skilled in art would selected an ion exchanger to meet the requirements of the organic heavy metal compound to be extracted from the aqueous medium. When the
15 aqueous medium is ground water, typically the ion exchanger will also be carefully selected to ensure that it only eliminates heavy metals from the water. When the ion exchanger is a cation exchanger preference is given to cation exchangers containing chelate-forming groups, for example the cation exchanger TP 207 from Bayer AG, as well as ion exchangers that reduce water hardness, such as Amberlite from Messrs.
20 Rohm & Haas.

By the term "organic heavy metal compound" it is meant a compound comprising a hydrocarbyl group and a heavy metal.

25 The term "hydrocarbyl group" as used herein means a group comprising at least C and H and may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo, alkoxy, nitro, an alkyl group, a cyclic group etc. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one
30 C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the hydrocarbyl group may contain hetero atoms. Hetero atoms may include, for instance, sulphur, nitrogen and oxygen.

35 A typical hydrocarbyl group is a hydrocarbon group. Here the term "hydrocarbon" means

any one of an alkyl group, an alkenyl group, an alkynyl group, which groups may be linear, branched or cyclic, or an aryl group. The term hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either
 5 the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

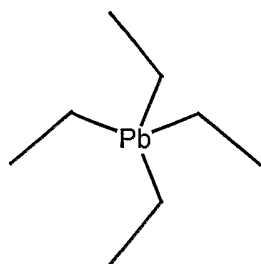
By the term "heavy metal" it is meant a metal in accordance with the definition of the European Environment Agency, namely a "metal or metalloid which is stable and which
 10 have a density greater than 4.5 g/cm³. Particular heavy metals are lead, copper, nickel, cadmium, platinum, zinc, mercury and arsenic.

In a preferred aspect the heavy metal of the organic heavy metal compound is lead.

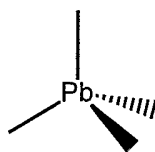
15 In a preferred aspect the organic heavy metal compound is a heavy metal alkyl. Preferably the heavy metal alkyl is a heavy metal C₁-C₁₀ alkyl, preferably a heavy metal C₁-C₆ alkyl, preferably a heavy metal C₁-C₃ alkyl, more preferably a heavy metal ethyl or heavy metal methyl.

20 In a preferred aspect the organic heavy metal compound is a lead alkyl. Preferably the heavy metal alkyl is a lead C₁-C₁₀ alkyl, preferably a lead C₁-C₆ alkyl, preferably a lead C₁-C₃ alkyl, more preferably a lead ethyl or lead methyl.

In a highly preferred aspect the organic heavy metal compound is selected from



tetraethyl lead



tetramethyl lead

25 and combinations thereof

The extraction process of the present invention may be used to extract organic heavy metal compounds from aqueous medium which has been intentionally or unintentionally contaminated with the compound. For example the aqueous medium may be for

example water from the environment, such as groundwater, which has unintentionally been contaminated with organic heavy metal compounds. In one alternative the aqueous medium may have resulted from the washing of a material which contained the organic heavy metal compound. For example the aqueous medium may have resulted from the a
5 decontamination process performed on contaminated soil (earth), sludge or other industrial waste.

In one highly preferred aspect the ion exchanger is an organic cation exchanger, the heavy metal compound is a lead methyls or a lead ethyls and the aqueous medium is
10 groundwater. Thus in this aspect the present invention provides a process for the extraction of a lead methyl and/or a lead ethyl from groundwater comprising the step of contacting the groundwater with an organic cation exchanger.

The ion exchanger of the invention may be subsequently regenerated after use to extract
15 the heavy metal compound. Typically the ion exchanger is regenerated by contact with one of the group selected from acids, sodium chloride solution, water having a temperature of greater than 60°C and combinations thereof.

In a preferred embodiment the eluate from the regeneration is treated with ozone at an
20 elevated temperature, preferably a temperature of greater than 60°C. We have found that in this preferred aspect substantial quantities of the organic compounds are converted into inorganic compounds. The inorganic compounds can in turn can be precipitated as a sulphide. In a preferred embodiment the heavy metal compound is precipitated from the eluate in the form of sulphide, and is optionally separated.

25

The present invention will now be described in further detail in the following example.

EXAMPLE

30 Groundwater is extracted from a depth of 3 m from premises which were used for the production of the antiknock compound lead tetraethyl. 350 l of this water was purified using 1 l of a selective exchanger resin TP 207 supplied by Bayer AG. The exchanger resin was of the Na⁺ form.

35 The following results were obtained:

Contaminant	Contamination				Regeneration with 5 litres HNO ₃ + NaCl soln. (µg/l)	
	Contaminant Concentration (µg/l)					
	Original sample	Following passage of (l) of eluate				
20		170	350			
Pb ⁺⁺	670	175	144	290	37520	
PbR ₄	60	<10	<10	<10	3100	
PbR ₃	960	13	12	12	51700	
PbR ₂ ⁺⁺	89	<10	<10	<10	4880	

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims

Claims

1. A process for the extraction of an organic heavy metal compound from an aqueous medium comprising the step of contacting the aqueous medium containing the organic heavy metal compound with an ion exchanger.
5
2. A process according to claim 1 wherein the ion exchanger is a cation exchanger.
3. A process according to claim 1 or 2 wherein the ion exchanger is an organic ion
10 exchanger.
4. A process according to claim 1, 2 or 3 wherein the ion exchanger is an organic cation exchanger.
- 15 5. A process according to any one of the preceding claims wherein the heavy metal is selected from lead, copper, nickel, cadmium, platinum, zinc, mercury and arsenic.
6. A process according to claim 5 wherein the heavy metal is lead.
- 20 7. A process according to any one of the preceding claims wherein the organic heavy metal compound is a heavy metal alkyl.
8. A process according to claim 7 wherein the heavy metal alkyl is selected from lead methyls, lead ethyls and combinations thereof.
25
9. A process according to any one of the preceding claims wherein the aqueous medium is groundwater.
10. A process according to any one of claims 1 to 8 wherein comprising the prior step
30 of contacting water with a material containing the organic heavy metal compound to provide the organic heavy metal compound containing aqueous medium.
11. A process according to claim 10 wherein the material is soil, sludge or industrial waste.
35

12. A process according to claims 1 wherein the ion exchanger is an organic cation exchanger, the heavy metal compound is a lead methyls or a lead ethyls and the aqueous medium is groundwater.
- 5 13. A process according to any one of the preceding claims comprising the further step of regenerating the ion exchanger.
14. A process according to claim 13 wherein the ion exchanger is regenerated by contact with one of the group selected from acids, sodium chloride solution, water having
10 a temperature of greater than 60°C and combinations thereof.
15. A process according to claim 14 wherein the eluate from the regeneration is treated with ozone at an elevated temperature.
- 15 16. A process according to claim 15 wherein the fact that the elevated temperatures is a temperature of greater than 60°C.
17. A process according to claim 14, 15 or 16 wherein the heavy metal compound is precipitated from the eluate in the form of sulphide, and is optionally separated.
20
18. Use of an ion exchanger for the extraction of an organic heavy metal compound from an aqueous medium.
19. Use according to claim 18 characterised by the features of any one of claims 2 to
25 17.
20. A process as substantially hereinbefore described with reference to the Examples.
- 30 21. A use as substantially hereinbefore described with reference to the Examples.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03215

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C02F1/42 B09C1/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C02F B01J B09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 491 533 A (WESTINGHOUSE ELECTRIC CORPORATION) 24 June 1992 (1992-06-24) page 2, line 1 - line 7 page 3, line 30 - line 33; claims 1,3 page 4, line 14 - line 16 ---	1-6, 10, 11, 13, 18-21
X	WO 00 01459 A (KX INDUSTRIES) 13 January 2000 (2000-01-13) claims 15-17 ---	1, 2, 5, 6, 9, 18-21
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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INTERNATIONAL SEARCH REPORT

Internati	Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 4 592 843 A (L.G. GUILBAULT) 3 June 1986 (1986-06-03) column 2, line 52; claim 1	1-9, 12-14, 18-21
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