Removal of PCB and other halogenated organic contaminants found in Ex-Situ Structures

9-18-2007

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Recommended Citation

Clausen, Christian; Berger, Cristina; Coon, Christina; Filipek, Laura; Milum, Kristen; Quinn, Jacqueline; and Geiger, Cherie, "Removal of PCB and other halogenated organic contaminants found in Ex-Situ Structures" (2007). UCF Patents. Paper 780. http://stars.library.ucf.edu/patents/780

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Emulsified systems of a surfactant-stabilized, biodegradable water-in-solvent emulsion with bimetallic particles contained with the emulsion droplets are useful at removing PCBs from ex situ structures. The hydrophobic emulsion system draws PCBs through the solvent/surfactant membrane. Once inside the membrane, the PCBs diffuse into the bimetallic particles and undergo degradation. The PCBs continue to enter, diffuse, degrade, and biphenyl will exit the particle maintaining a concentration gradient across the membrane and maintaining a driving force of the reaction.
REMOVAL OF PCB AND OTHER HALOGENATED ORGANIC CONTAMINANTS FOUND IN EX SITU STRUCTURES

STATEMENT OF RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application Ser. No. 60/523,656 filed Nov. 17, 2003 and titled "MICRO-SCALE PARTICLE EMULSIONS AND THEIR APPLICATION FOR REMOVAL OF PCBs AND METALS FOUND IN EX-SITU STRUCTURES," which is commonly assigned.

STATEMENT OF GOVERNMENT INTEREST

The invention described herein was made in the performance of work under a NASA contract and by an employee of the United States Government and is subject to the provisions of Public Law 96-517 (35 U.S.C. § 202) and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefore. In accordance with 35 U.S.C. § 202, the contractor elected not to retain title.

TECHNICAL FIELD OF THE INVENTION

The present invention relates generally to the removal of contaminants and in particular to the removal of polychlorinated biphenyls (PCBs) or other halogenated contaminants from ex situ structures.

BACKGROUND OF THE INVENTION

The removal of contaminants from natural resources is an ongoing, significant problem. Numerous tactics have been considered with various degrees of success. In U.S. patent application Ser. No. 09/972,296 filed on Oct. 2, 2001 and issued Dec. 16, 2003 as U.S. Pat. No. 6,664,298, which is owned by the Assignee of the present invention and incorporated in the present application by express reference thereto, a method was disclosed for delivering the reactant material to the contaminant in situ. A method incorporated particles, surfactant, oil and water in a method of enhancing performance of work under a contract and by an employee of the United States Government and is subject to the provisions of Public Law 96-517 (35 U.S.C. § 202) and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefore. In accordance with 35 U.S.C. § 202, the contractor elected not to retain title.

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A second patent application, PCT/US 03/16610, was filed May 28, 2003, corresponding to U.S. patent application Ser. No. 10/449,907, also filed on May 28, 2003 and issued Mar. 7, 2006 as U.S. Pat. No. 7,008,964 which patent also is owned by the Assignee of the present invention and is incorporated into the present application by reference thereto. This second patent application is directed, among other features, to a zero-valent metal emulsion containing zero-valent metal particles doped with a catalytic metal to remediate halogenated aromatic compounds, such as polychlorinated biphenyls (PCBs), from natural resources, i.e., in the ground.

PCBs have been used in many industrial applications because of their robust physical and chemical properties such as their resistance to acids, bases and oxidation, their excellent dielectric characteristics and their thermal stability at high temperatures (up to 350° C.). PCBs were abundantly used as a stabilizer in paints in the late 1960s. When PCBs were released into the environment, they were sorbed to particulate matter that was then dispersed over large areas. PCBs can be introduced into the food chain by the uptake of contaminated soils by biota and humans can directly inhale or absorb PCBs by dermal contact. Although the United States Environmental Protection Agency (EPA) has banned the manufacture of PCBs since 1979, PCBs are still present in the environment posing possible adverse health affects to both humans and animals. In fact, PCBs can still be found in the paints located on NASA property at a number of the Centers. The PCB levels in painted structures on the Kennedy Space Center (KSC) have been documented to be as high as 31,000 ppm.

Currently, only land filling or smelting operations are available for complete treatment of ex situ structures containing PCBs. Sandblasting or water blasting operations can be utilized to remove contaminated coatings from structures; however, this material must also be thermally treated or land-filled in a Toxic Substances Control Act (TSCA) regulated landfill. As will become clear here below, the present invention expands on the concept described in the previously cited applications to effectively treat PCBs found in painted structures or other ex situ facilities. For the reasons stated above, and for other reasons stated below that will become apparent to those skilled in the art upon reading and understanding the present specification, there is a need in the art for alternative methods and compositions for the removal of PCBs from ex situ structures.

SUMMARY

The various embodiments of the invention provide an emulsified system of a surfactant-stabilized, biodegradable water-in-solvent emulsion with nano or microscale bimetallic particles contained with the emulsion droplets. The hydrophobic emulsion system draws PCBs through the solvent/surfactant membrane. Once inside the membrane, PCBs diffuse to the bimetallic particles and undergo degradation. The PCBs continue to enter, diffuse, degrade, and biphenyl or other benign byproduct will exit the particle maintaining a concentration gradient across the membrane and maintaining a driving force of the reaction.

For one embodiment, the invention provides a water-in-solvent emulsion. The emulsion includes a solvent phase having a solvent and a surfactant and a water phase having water and nano or microscale bimetallic particles. The bimetallic particles include a zero-valent metal component and a catalytic component that are milled together prior to forming the emulsion. The solvent can be toluene, d-limonene, hexanes or the like. The water phase may further include a surfactant and/or a hydrophilic solvent, such as methanol.

For another embodiment, the invention provides a water-in-solvent emulsion. The emulsion includes a solvent phase having a solvent and a surfactant and a water phase having water and nano or microscale bimetallic particles. The solvent is toluene, d-limonene, hexanes or the like. The water phase may further include a surfactant and/or a hydrophilic solvent, such as methanol. The bimetallic particles include a zero-valent metal component and a catalytic component.

For a further embodiment, the invention provides a method of removing contaminants from an ex situ structure. The method includes applying a water-in-solvent emulsion...
to the structure, where the emulsion includes a solvent phase having a solvent and a surfactant and a water phase having water and nano or microscale bimetallic particles. The bimetallic particles include a zero-valent metal component and a catalytic component. The water phase may further include a surfactant and/or a hydrophilic solvent.

The invention further includes methods of varying scope.

**BRIEF DESCRIPTION OF THE DRAWING**

The FIGURE is a conceptual depiction of an emulsified system in accordance with the invention.

**DETAILED DESCRIPTION OF THE INVENTION**

In the following detailed description of the preferred embodiments, the embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be utilized and that logical, mechanical and chemical changes may be made without departing from the spirit and scope of the present invention. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined only by the appended claims and equivalents thereof.

The present invention provides an in-situ PCB remediation process that is applicable for the treatment of ex situ structures containing metal and PCB compounds within externally applied coatings such as paint, caulking material, elastomeric coating, etc. While it is known that zero-valent iron (Fe) is very effective in the treatment of chlorinated hydrocarbons, such as dissolved trichloroethylene (TCE), zero-valent iron, by itself, is unable to completely dechlorinate PCBs dissolved in aqueous solutions. As described herein, a catalyst, such as palladium (Pd), can be added to the zero-valent iron or other zero-valent metal particle, such as zero-valent magnesium (Mg). While the Pd/Fe bimetallic particles can be not effectively remove dissolved phase PCBs, the use of Pd/Fe and/or Pd/Mg particles to treat impregnated PCBs would be minimized by the coating material itself. As will be explained below, the emulsion technology of the present invention can be used to remediate PCB-containing coatings that have historically been applied to ex situ support structures. As will be explained, a dense, reactive emulsion applied to ex situ structures functions to disassociate the PCBs from the coating, i.e., paint, and degrades the chlorinated aromatics into biphenyl, or other benign by-product. In addition, the invention describes a method for ball milling carbon-supported noble metals and transition metals together to form a very effective and economical catalytic system.

The present invention is directed to an emulsified system consisting of a surfactant-stabilized, biodegradable water-in-toluene or water-in-d-limonene emulsion with nano or microscale bimetallic particles contained within the emulsion droplets. The hydrophobic emulsion system draws PCBs through the solvent/surfactant membrane (solvents may include but are not limited to d-limonene and toluene and a food-grade surfactant may be chosen). Once inside the membrane, the metals and PCBs diffuse to the bimetallic particles and undergo degradation in the case of chlorinated compounds. The PCBs continue to enter, diffuse, degrade, and biphenyl or other benign byproduct will exit the particle maintaining a concentration gradient across the membrane and maintaining a driving force of the reaction. Microscale magnesium (Mg) coated with a very small amount of palladium (Pd) was chosen as the media for the PCB degradation. Other catalysts may be used instead of Pd. These active catalysts include zinc (Zn), nickel (Ni), copper (Cu) and others.

The present invention uses an emulsion system to degrade PCBs into benign end products. The unique emulsion may be formulated as follows: 40 ml toluene, 80 ml water, 20 g bimetallic metal, 12 g surfactant. The bimetallic metal may comprise either microscale magnesium or iron, e.g., approximately 0.1-10 microns or smaller, ball milled with 1-10% palladium supported on carbon. The mass percent palladium by weight ranges from approximately 0.01-15%, and more preferably 0.08-8%. While toluene is utilized as the solvent, the present invention may use d-limonene, hexanes or other similar solvents.

As an alternative to ball milling, the metal particles, e.g., Fe or Mg, may be coated with a catalytic metal, e.g., Pd, via solution. For one example, approximately 100 g of microscale zero-valent iron particles, such as those available through Alfa Aesar, Inc. or BASE2, Inc., are weighed and placed in a Buchner Funnel. The microscale zero-valent iron particles are then washed with 100 ml of a 5% hydrochloric (HCl) or sulfuric (H2SO4) solution (5 mL HCl or H2SO4 and 95 mL of deoxygenated de-ionized water) and maintain a driving force of the reaction. Microscale zero-valent iron particles are then filtered. Then, 0.19 g of K2PdCl4 is dissolved in 100 mL of deoxygenated de-ionized water. The filtered microscale zero-valent iron particles are then placed in an Erlenmeyer flask and the K2PdCl4 solution added. The resulting mixture is stirred in the flask using a magnetic stirrer for 5 minutes. The solution is then allowed to settle and filtered until dry. Using a procedure as described, the resulting bimetallic microscale particles had a palladium coating of approximately 0.06% Pd/Fe. For another example, microscale zero-valent iron may be coated with palladium (Pd) using a 40 g/L Pallamerse solution. The Pallamerse solution is made up of 10.0% potassium dinitrosulfito palladate (II), K2(Pd(NO3)6−SO3). The following procedure indicates one such method for coating 2.5 g of microscale zero-valent iron particles. The microscale zero-valent iron particles are washed in a Buchner Funnel with 10 mL of 10% H2SO4 solution. The microscale zero-valent iron particles are then rinsed with 10 mL of deoxygenated de-ionized water. Then, 5 mL of the Pallamerse solution is added and the mixture is allowed to sit for 2 minutes before filtering. After the mixture is filtered, the microscale zero-valent iron particles are washed with 10 mL of deoxygenated de-ionized water. The material is then filtered until dry. The resulting bimetallic microscale particles had a palladium coating of approximately 7% Pd/Fe.

The FIGURE is a conceptual depiction of an emulsified system in accordance with the invention. The emulsified system has a solvent phase 105 and a water phase 110 contained in the solvent phase and separated by an interface 115. Droplets of the water phase 110 contain bimetallic particles 120. Bimetallic particles 120 contain a zero-valent metal component 125 and a catalytic component 130.

The solvent phase 105 contains a hydrophobic solvent, such as toluene, d-limonene, hexanes and the like, suitable for transport of the PCBs or other halogenated organic contaminants to droplets of the water phase 110. The solvent phase 105 further includes a surfactant chosen to promote a water-in-solvent emulsion. The water phase 110 may also include a surfactant or a hydrophilic solvent, such as methanol, to reduce surface tension of the droplet and to promote transport of the PCBs or other halogenated organic contaminants to the bimetallic particles 120 contained within the water phase 110.
Choice of surfactants for the solvent phase and water phase is generally well understood in the art. To produce a water-in-solvent emulsion, the surfactant system must generally be more hydrophobic than hydrophilic. The surfactant system can include more than one surfactant.

For one embodiment, the zero-valent metal component contains iron or magnesium. For a further embodiment, the catalytic component contains a noble or transition metal catalyst. Some example catalysts include Pd, Zn, Ni or Cu.

Experimental Results

The reaction rates are divided into two independent categories: the rate at which the emulsion can extract the PCBs from the paint and the rate at which the PCBs can be degraded by the bimetal and water reactants.

It is noted that a GC/MS (gas chromatograph/mass spectrometer) was utilized for evaluation of the results presented herein. However, an ECD (electron capture detector) tracking a specific congener simplifies the analysis. Data values presented are area counts except for retention time, which is expressed in minutes.

From Emulsion Extracts

(An Evaluation of how Much PCB can be Extracted into an Emulsion—not a Measurement of PCB Degradation)

<table>
<thead>
<tr>
<th>Retention Time (minutes)</th>
<th>Area Counts</th>
<th>PCB Area Count in the Paint Chip after 4 hr Exposure to Emulsion</th>
<th>Initial Area Counts</th>
<th>Paint Chip to Paint Chip (Area Counts)</th>
<th>60 ppm Aroclor</th>
<th>6 ppm Aroclor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Area Counts</td>
<td>Area Counts</td>
</tr>
<tr>
<td></td>
<td>15.554</td>
<td>45947</td>
<td>28377</td>
<td>39920</td>
<td>2718</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.905</td>
<td>86164</td>
<td>51833</td>
<td>57038</td>
<td>3740</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.944</td>
<td>83936</td>
<td>45846</td>
<td>47023</td>
<td>3047</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.323</td>
<td>35695</td>
<td>21800</td>
<td>20459</td>
<td>1014</td>
<td></td>
</tr>
</tbody>
</table>

A Measurement of the Amount of Removal of PCB From Paint Chip After Exposure To Emulsion

(PCB Content in Paint Chip After Exposure to Emulsion)

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Paint Chip Initial Area Counts</th>
<th>PCB Area Count in the Paint Chip after 4 hr Exposure to Emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.542</td>
<td>45947</td>
<td>5162</td>
</tr>
<tr>
<td>16.893</td>
<td>86164</td>
<td>57038</td>
</tr>
<tr>
<td>17.93</td>
<td>83936</td>
<td>47023</td>
</tr>
<tr>
<td>18.323</td>
<td>35695</td>
<td>20459</td>
</tr>
</tbody>
</table>

The present invention has significant commercial application to government and industry in removing PCBs from paints and similar materials covering ex situ structures. Numerous NASA Centers have older metal structures upon which paints containing polychlorinated biphenyls (PCB) were applied. These painted structures are posing worker and ecological health hazards and, in several instances, are now considered a TSCA-level (Toxic Substance Control Act) waste. Some of the impacted structures could be refurbished and utilized for new Programs, but because the paint currently on the structures is heavily laden with PCBs, the Programs are unable to reuse or even discard these structures without significant cost. The embodiments of the invention detail a new and innovative solution to the removal of PCBs from painted structures using a "paint on and wipe off" bimetallic emulsion that extracts only the PCBs from the paint, and leaves the structure virtually unaltered.

Polychlorinated biphenyls (PCBs) are a group of synthetic aromatic compounds with the general formula C₁₂H₁₀₇Cl₃, that were historically used by industry because of their excellent dielectric properties and their resistance to heat and chemical degradation. Although the US Environmental Protection Agency (EPA) has banned the manufacture of PCBs since 1979, they currently can be detected at every NASA Center. PCBs have been introduced into the NASA work environment via improper disposal and accidental leaks from transformers, heat exchangers, and hydraulic systems. Formerly, PCBs were also extensively used in paints, as their properties enhanced structural integrity, reduced flammability and boosted antifungal properties. Because of the serious health problems associated with the bioaccumulation of PCBs in animals, including humans, and the desire for NASA Programs to have a quick and nondestructive means of removing PCBs from existing structures,
the development of a “paint-on/wipe-off” emulsion for the removal of PCBs found in older painted structures is considered highly desirable.

In 2003, KSC initiated the development of a water-in-toluene emulsion containing a bimetallic reactant for the treatment of PCBs found in painted structures. The emulsion droplet has two functions. First and foremost, the exterior component is selected from the group consisting of noble metals and transition metals. The water and bimetal initiate an abiotic, reductive dehalogenation reaction that completely degrades the PCBs to benign end-products that diffuse out of the emulsion membrane. The emulsion developed in 2003 was applied to pieces of paint obtained from the abandoned Apollo Program’s Launch Umbilical Tower (LUT). LUT paint chips were immersed in the PCB-removal emulsion for various periods of time extending from two hours to four days. Emulsion kinetics were evaluated from two perspectives; effective rate of PCB removal from the paint, and the kinetic degradation of the PCBs once interior to the emulsion droplet and in contact with the bimetallic reactant. Initial data indicates that complete PCB extraction and degradation from paint chips containing as high as 700 ppm total PCBs could be achieved in as little as 48 hours of exposure.

CONCLUSION

An emulsified system of a surfactant-stabilized, biodegradable water-in-solvent emulsion with bimetallic particles contained with the emulsion droplets have been described for the removal of PCBs from coated surfaces. The hydrophobic emulsion system draws PCBs through the solvent/surfactant membrane. Once inside the membrane, the PCBs diffuse to the bimetallic particles and undergo degradation. The PCBs continue to enter, diffuse and degrade to nonchlorinated products such as biphenyl, which then exits the emulsion droplet, maintaining a concentration gradient across the membrane and maintaining a driving force of the reaction.

Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that any arrangement that is calculated to achieve the same purpose may be substituted for the specific embodiment shown. This application is intended to cover any adaptations or variations of the present invention. Therefore, it is manifestly intended that this invention be limited only by the claims and the equivalents thereof.

What is claimed is:

1. A water-in-solvent emulsion, comprising:
   a solvent phase comprising a solvent and a surfactant; and
   a water phase comprising water and bimetallic particles; wherein the bimetallic particles comprise a zero-valent metal component and a catalytic component; and wherein the zero-valent metal component is milled with the catalytic component prior to forming the emulsion.

2. The emulsion of claim 1, wherein the water phase further comprises a surfactant and/or a hydrophilic solvent.

3. The emulsion of claim 2, wherein the hydrophilic solvent is methanol.

4. The emulsion of claim 1, wherein the catalytic component is selected from the group consisting of noble metals and transition metals.

5. The emulsion of claim 4, wherein the catalytic component is palladium.

6. The emulsion of claim 1, wherein the bimetallic particles are nano or microscale particles.

7. The emulsion of claim 1, wherein the zero-valent metal component has a particle size of less than about 10 microns prior to milling.

8. The emulsion of claim 1, wherein the zero-valent metal component is selected from the group consisting of iron and magnesium.

9. The emulsion of claim 1, wherein the catalytic component is supported on a carbon support structure.

10. The emulsion of claim 1, wherein the catalytic component comprises approximately 0.01-15% by mass of the bimetallic particles.

11. The emulsion of claim 1, wherein the catalytic component comprises approximately 0.08-8% by mass of the bimetallic particles.

12. The emulsion of claim 1, wherein the solvent is selected from the group consisting of toluene, d-limonene and hexanes.

13. The emulsion of claim 1, wherein the surfactant is a food-grade surfactant.

14. A water-in-solvent emulsion, comprising:
   a solvent phase comprising a solvent and a surfactant; and
   a water phase comprising water and bimetallic particles; wherein the solvent is selected from the group consisting of toluene, d-limonene and hexanes; and wherein the bimetallic particles comprise a zero-valent metal component and a catalytic component.

15. The emulsion of claim 14, wherein the water phase further comprises a surfactant and/or a hydrophilic solvent.

16. The emulsion of claim 15, wherein the hydrophilic solvent is methanol.

17. The emulsion of claim 14, wherein the catalytic component is selected from the group consisting of noble metals and transition metals.

18. The emulsion of claim 17, wherein the catalytic component is palladium.

19. The emulsion of claim 14, wherein the bimetallic particles are nano or microscale particles.

20. The emulsion of claim 14, wherein the zero-valent metal component has a particle size of less than about 10 microns prior to forming the bimetallic particles.

21. The emulsion of claim 14, wherein the zero-valent metal component is selected from the group consisting of iron and magnesium.

22. The emulsion of claim 14, wherein the catalytic component comprises approximately 0.01-15% by mass of the bimetallic particles.

23. The emulsion of claim 14, wherein the surfactant is a food-grade surfactant.

24. The emulsion of claim 14, further comprising: wherein the solvent comprises approximately 15-50% by weight; wherein the surfactant comprises approximately 1-15% by weight; wherein the water comprises approximately 20-60% by weight; and wherein the bimetallic particles comprise approximately 1-20% by weight.

* * * * *