

SUBCRITICAL WATER REMEDIATION OF PCDD/PCDF CONTAMINATED SOIL AND SEDIMENT

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Introduction

Soils and sediments contaminated with polychlorinated organic pollutants threaten to human health. Incineration is the most effective remediation method but is expensive, destroys soil fertility, and generates concern about air emissions. Bioremediation can become one of the most cost-effective technologies; however here is still no data that microorganism effectively destroying dioxins in natural matrixes are found. Under normal conditions, water is too polar to dissolve most of the organic pollutants, but recently, it has been demonstrated that the drop in water's polarity at subcritical conditions (hot water under sufficient pressure to maintain the liquid state) dramatically enhances the solubility's of hydrophobic organics. For example at 250°C water solubility of polycyclic aromatic hydrocarbons are increased by 4-5 orders ¹⁻³. In addition to the drop in water's polarity that occurs with heating, both the viscosity and surface tension of water are substantially reduced to values similar to or below pure methanol or acetonitrile ². These factors have been used to perform the extraction of PAHs, PCBs, and other hydrophobic compounds from a variety of soils and sediments on the analytical scale ⁴⁻⁶. Also we reported about subcritical water extraction of PCDDs from spiked soils ⁷ and about reductive dechlorination of OCDD by zerovalent iron ⁸. Recently were reported that subcritical water has been used for the remediation of kilogram quantities of soils contaminated with several hundred mg/kg levels of polycyclic aromatic hydrocarbons (PAHs) and pesticides ⁹; also analogous work was executed for soils contaminated with high explosives (TNT, RDX and HMX) ¹⁰.

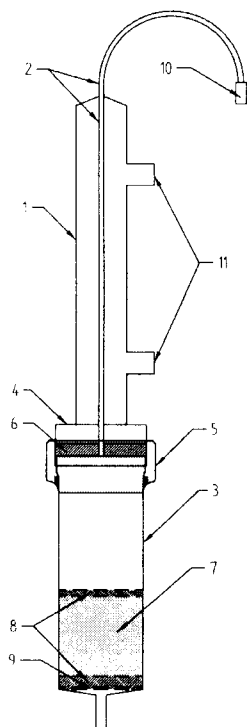
This work is devoted to the study of water in subcritical conditions as a possible solvent for the extraction of PCDDs and PCDFs from real extremely high-contaminated soil and sediment.

Methods and Materials

All the experiments were performed using a homemade apparatus for subcritical liquid extraction under the equilibrium pressure ⁸. Sample was placed into an extraction cartridge; than the system was filled with water so that the system contained 1-2 ml of air. The system heated to 250-260 °C and kept under this temperature for the required time. Next the valve was opened and water was removed (about 10 ml per minute). A mixture of ¹³C labeled standards was added to the analyzable phase before the organic extraction. The aqueous solutions were extracted by salted-out (50 ml acetone, 50 ml hexane and 71% ammonium sulphate). The solid samples were extracted by 150 ml hexane:acetone (1:1) mixture at 60 °C in special apparatus for contentious-flow extraction by hot solvents (Fig. 1). Samples were placed in to an extraction cell; next solvents are fed in continuously from reservoir by gas pressure (0,5-2 atm), flow rate 15-25 ml/min. This method utilized the same advantages, as the accelerated solvent extraction (ASE), but does not require usage of expensive high-pressure equipment. We designed it for fast extraction from matrices with

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low and medium sorption activity, such as soils, sediments, analytic-resins, air filters and others. Depending on the amount of the sample cells volumes 10, 30, 60, 150 can be set. The extracts were cleaned-up in multilayer silica and alumina columns and analyzed by GC-HRMS. Recovery was estimated to be 70-85%, 2-fluoro-6,7,8,9-tetrachlorodibenzo-p-dioxin was used as recovery standard.



- 1 - Heat exchanger*
- 2 - Tube for the solvent, 2 mm i.d.
- 3 - Extraction cartridge*
- 4 - Screw joint
- 5 - Screw box
- 6 - Teflon ring
- 7 - Sample
- 8 - Quartz cotton filter
- 9 - Stainless grind
- 10 - Connection for delivering a solvent from the tank
- 11 - Connection with a thermostat

* Heat exchanger and extraction cartridge are covered by heat-insulating material

Fig. 1. Apparatus for continuous flow hot solvent extraction.

Results and Discussion

Two different type of high-contaminated sample was used - vietnamese soil, contaminated by "Agent Orange" and sediment which was taken in chemical plant desilter contained products of burning of organochlorinated compounds. Experimental data, which are presented in tables 1 and 2, shows good recovery for vietnamese soil, which contain less 1 % soil-insoluble organic matter, and low recovery for chemical plant sediment, which is basically consists from organic matter. In both cases of the total concentration of PCDD/PCDF substances was considerable decreased. To confirm the observable phenomenon the additional experiments were carried out: soil sample was spiked by labeled 2,3,7,8-³⁷Cl₄DD and sediment was spiked by 1,2,3,7,8-PeCDD before heat treatment the similar hydrothermal decomposition were observed. At present time we cannot explain the mechanism of this process but we offer that the process of hydrolysis or oxidation, which catalyzed by anthropogenic components of a matrix takes place, as earlier at work with spiked matrixes of such phenomenon was not observed. In both cases hydrothermal destruction unaccompanied formation of low chlorinated congeners as it occurs at reductive dechlorination.

Table 1. Results of extraction of the chemical plant sediment, pg/g

Congener	Solvent Extraction (initial concentration)	Water extraction 150°C	Water extraction 200°C	Water extraction 250°C	28250 pg/g of 1,2,3,7,8-PeCDD were added before experiment		
					Water extraction 230° C	Solvent extraction	Total recovery, %
2,3,7,8-TCDD	ND	272	144	296	118	10	
1,2,3,7,8-PeCDD	ND	ND	10	70	1802	7408	33
1,2,3,4,7,8-HxCDD	75	16	ND	ND	ND	ND	
1,2,3,6,7,8-HxCDD	60	18	15	19	ND	ND	
1,2,3,7,8,9-HxCDD	42	16	ND	12	ND	ND	
1,2,3,4,6,7,8-HpCDD	5472	43	ND	41	112	998	20
OCDD	42095	26	33	346	571	24426	59
2,3,7,8-TCDF	223	ND	ND	ND	110	31	63
1,2,3,7,8-PeCDF	2148	25	85	1113	55	901	45
2,3,4,7,8-PeCDF	2228	37	38	683	40	558	27
1,2,3,4,7,8-HxCDF	11761	51	97	1266	227	4467	40
1,2,3,6,7,8-HxCDF	40028	38	27	328	454	10168	27
1,2,3,7,8,9-HxCDF	13435	26	15	378	253	2041	17
2,3,4,6,7,8-HxCDF	12823	21	16	618	206	2491	21
1,2,3,4,6,7,8-HpCDF	493793	184	88	2636	1508	97479	20
1,2,3,4,7,8,9-HpCDF	123354	43	13	252	282	14784	12
OCDF	1170041	157	113	3841	2940	397347	34

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Table 2. Results of extraction of the Vietnamese soil, pg/g

Experiment conditions	Experiment A				Experiment B				Experiment C						
	First water extraction 200-210 °C	Second water extraction 240-250 °C	Organic extraction	Total recovery, %*	Remediation effectuality, %**	First water extraction 250-260 °C	Second water extraction 250-260 °C	Organic extraction 250-260 °C	Total recovery, %	Remediation effectuality, %	Water extraction 250-260 °C, 3	Organic extraction	Total recovery, %	Remediation effectuality, %	Initial concentration
C congeners															
2,3,7,8-TCDD	116799	37863	1522	38	99.6	107847	5480	643	28	99.8	149295	7938	38	98.0	406761
1,2,3,7,8-PeCDD	483	396	31,6	118	95.9	1622	117	20,5	228	97.3	1663	138	233	82.1	772
1,2,3,4,6,7,8-HpCDD	27	164	182	134	34.3	63	8	149	79	46.2	300	306	219		277
OCDD	105	1255	3524	56	59.9	1593	136	1971	42	77.6	2144	2301	51	73.8	8797
1,2,3,7,8-PeCDF	2018	ND	6	57	99.8	1428	ND	9	12	99.7	126	48	5	98.7	3566
Other TCDDs	3743		31	74	99.4	4444		57	88	98.9	2727	276	59	94.6	5133
Other PeCDDs	9108		49	359	98.1	1984		7.9	78	99.7	783	203	39	92.0	2551
Other ICDFs	18214		2.8	88	100.0	16300		31	79	99.9	5994	609	32	97.1	20704
Other PeCDFs	19222		1294	56	96.5	46872		450	128	98.8	12529	2928	42	92.1	36955
Other HeCDFs	2244		209	41	96.5	5226		322	94	94.6	1752	506	38	91.5	5928

* The relation of the sum of concentration that were found at waters and organic extractions to initial concentration.

** 100% - the relation of amount of compound that was not removed during water extractions to initial concentration.