REDUCTIVE DECHLORINATION OF POLYCHLORYNATED DIOXINS BY ZEROVALENT IRON IN SUBCRITICAL WATER

Kluyev N.A., Cheleptchikov A.A., Brodsky E.S., Soyfer V.S., Gilnikov V.G., Rudenko B.A[1].

Institute of Ecology and Evolution RAS, Leninsky pros. 33, 117701 Moscow, Russia, kluyv@glasnet.ru

[1] Institute of Geochemistry and Analytical Chemistry RAS, Kosigina st. 19, 117975, Moscow, Russia

Introduction

One of major ecological tasks is the creation of a method for remediation of polychlorinated organic pollutants contaminated soils and sediments. Incineration used for this purpose can result in significant air emissions[1]. Bioremediation can become one of the most cost-effective technologies, however here is still no data that microorganisms effectively destroying dioxins in natural matrixes are found. We suppose that one of the most perspective directions is the extraction under subcritical conditions. The solubility of most organic pollutants at 250°C is increased by 4-5 orders[2-4]. At temperatures 250-300°C, in some cases hydrothermal decomposition of PCDDs/PCDFs was observed[5-6]. Recently, it was been reported that zerovalent iron in subcritical water can reductive dechlorinated of PCBs[7].

In this work, we investigate an opportunity of the reduction of OCDD by zerovalent iron in subcritical water with subsequent extraction of PCDDs from soils.

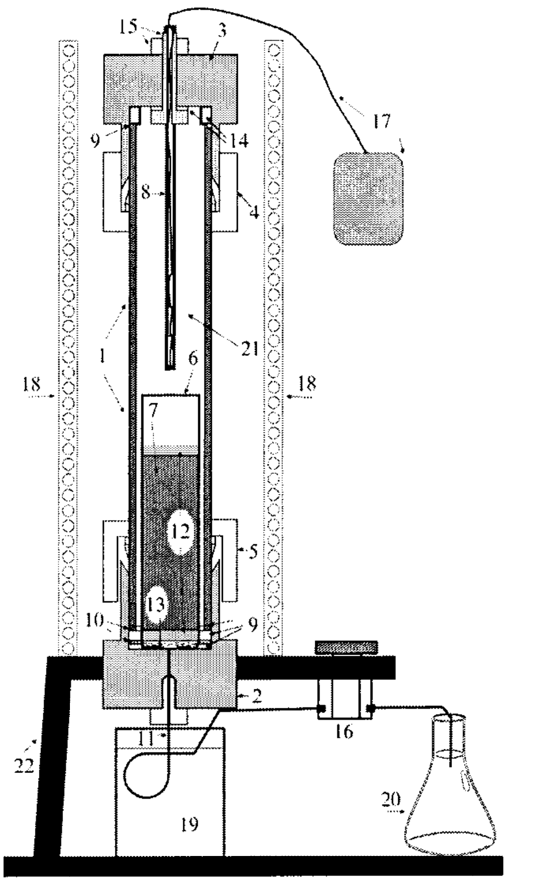
Methods and Materials

All the experiments were performed using a homemade apparatus for subcritical extraction under the equilibrium pressure (Fig. 1). Three types of matrixes were used throughout: SiO_2, sod-podzol soil and black earth. For each experiment, 6 g sample of SiO_2 and 4 g sample of soils were taken. All the matrixes were spiked with 1,11 mg OCDD in acetone and dried up on air; then iron powder (10 % of mass weight) was added. All the components were placed in to an extraction cartridge; newt the system was filled with water so that the system contained 1-2 ml of air. Systems 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). In the experiment with soils, the aqueous and solid (including internal surface of the apparatus) phase was analyzed separately. A mixture of ^{13}C labeled standards was added before the organic extraction. The extracts were cleaned-up in multilayer silica and alumina columns and analyzed by GC-HRMS. Also an experiment with iron powder without a matrix was carried out.

Results and discussion

Results are given in table 1. The data shows that metallic iron can cause stepwise reductive dechlorination of OCDD. The elimination of chlorine can occur both from 2,3,7,8 and from 1,4,6,9 positions, though the non-toxic congeners dominate in the products of the reaction; total TEQ is increased. The experiment without a matrix shows a higher performance, but, in this case, TEQ was also increased. In cases when OCDD was on a matrix a decrease in the reaction rate was observed, which can accounted for mass transfer. Also, we performed an experiment when a mixture of OCDD in SiO_2 and iron was placed between two layers (10 g each) of iron powder, but it does not reveal any significant changes. This indicates that dioxins don't migrate in the apparatus and do not a short contact during extraction when dioxins pass thought iron layer under this temperature is not enough for dechlorination. The accumulation of low chlorinated congeners can be explained by increasing energy when a PCDD molecule becomes less chlorinated. The similar situation were observed in the case of PCBs[7].

A significant part of spiked OCDD and formed less chlorinated congeners was found in the water fraction, which indicate a high potential of subcritical water extraction. Differences in PCDDs distribution between the water and soil might be caused by various contents of soil-insoluble organic matter and potential sorbents. The solubility of OCDD in the experiment with sod-podzol soil was 5,1 μg/l, that is 2 million fold over its solubility at ambient conditions[8].



1 - Stainless column, 25 cm long, 21 mm i.d.
2 - Bottom cap
3 - Upper cap
4 - Upper screw box
5 - Bottom screw box
6 - Extraction cartridge
7 - Sample
8 - Tube for the thermocouple
9 - Teflon ring
10 - Bronze ring
11 - Cooling capillary
12 - Quartz cotton filter
13 - Stainless grind
14 - Aluminum ring
15 - Thermocouple tube connector
16 - Valve
17 - Thermocouple
18 - Heater
19 - Water with ice
20 - Flask
21 - Solvent (water)
22 - Holder

Fig. 1. Apparatus for subcritical extraction.

Conclusion

It is found that the zerovalent iron can be applied for stepwise dechlorination of OCDD on various matrixes in water under 250°C and equilibrium pressure.

A significant part of residual OCDD and formed less chlorinated congeners are extracted with water in the given conditions. The solubility of OCDD was increased by a factor 2 million over its solubility at ambient conditions.

The dechlorination of OCDD results in the formation of high-toxic 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, which is necessary to take into account in developing the methods of extraction by subcritical water, when the matrix contains are rather strong reducers.

References

1. Tanaka M., Watanabe I., Hiraoka M., Takizawa Y., Masuda Y., Takeshita R. and Yagome K. (1989) Chemosphere. 18 (1-6), 321.
2. Miller D.J., Hawthorne S.B., Gizir A.M and Clifford A.A. (1998) J. Chem. Eng. Data , 43, 1043.

3. Yu Yang, Hawthorne S.B. and Miller D.J. (1997) Environ. Sci. Technol., 31, 430.
4. Yu Yang, Belghazi M, Lagadec A., Miller D.J., Hawthorne S.B. (1998) Journal of Chromatography A, 810, 149.
5. Yamaguch H. Shibuya E., Kanamaru Y., Uyama K., Nishioka M. and Yamasaki N. (1996) Chemosphere 32, (1), 203.
6. Windal I., Hawthorne S. and Pauw E. De. (1999) Organohalogen Compounds. 40, 591.
7. Yak H.K., Wenclawiak B.W., Cheng I.F., Doyle J.G. and Wai C.M. (1999) Environ. Sci. Technol. 33, 1307
8. Toxicological profile for chlorinated dibenzo-p-dioxins (1997), Research Triangle Institute, 600 p.

Table 1. Results of the reductive dechlorination of OCDD by zerovalent iron in subcritical water.

PCDD concentration, ng										
Time	30 min		90 min							60 min
Experiment condition	SiO_2	10% mass weigh iron powder								Iron powder
		SiO_2	SiO_2	black sand			sod-podzol soil			
Congener				aqueous phase	solid phase	Total	aqueous phase	solid phase	Total	
2,3,7,8-TCDD	**0.13**	**0.44**	**0.64**	**0.46**	**0.18**	**0.64**	**0.48**	**1.79**	**2.27**	**0.71**
Others TCDD	*0.63*	*2.42*	*15.42*	*0.09*	*0.22*	*0.31*	*1.83*	*0.96*	*2.79*	*1.09*
1,2,3,7,8-PeCDD	**0.08**	**1.12**	**4.30**	**0.15**	**<dl**	**0.22**	**0.79**	**0.33**	**1.12**	**0.82**
Others PeCDD	*<dl*	*2.82*	*32.81*	*0.73*	*0.12*	*0.85*	*9.11*	*0.21*	*9.32*	*1.95*
1,2,3,4,7,8-HeCDD	**0.15**	**1.80**	**4.32**	**0.33**	**0.18**	**0.51**	**1.56**	**0.42**	**1.99**	**3.90**
1,2,3,6,7,8-HeCDD	**0.17**	**3.59**	**9.44**	**0.70**	**0.29**	**0.99**	**8.53**	**2.00**	**10.53**	**0.30**
1,2,3,7,8,9- HeCDD	**0.15**	**2.99**	**10.00**	**0.66**	**0.42**	**1.09**	**7.63**	**1.00**	**8.63**	**0.59**
______ *HeCDD*	*<dl*	*30,98*	*98.31*	*11.04*	*4.69*	*15.73*	*112.7*	*13.02*	*125.7*	*6.91*
1,2,3,4,7,8,9-HpCDD	**4.08**	**86.36**	**85.58**	**42.97**	**18.65**	**61.62**	**150.4**	**4.41**	**154.8**	**0.10**
1,2,3,4,6,7,9-HpCDD	*8.97*	*121.3*	*84.83*	*59.99*	*32.90*	*92.89*	*198.4*	*0.57*	*199.0*	*0.28*
OCDD	**959.8**	**893.2**	**593.2**	**286.2**	**314.7**	**600.9**	**347.6**	**92.8**	**440.4**	**6.02**