

REMOVAL OF ULTRATRACES PCDD/PCDF FROM VINYLCHLORIDE PRODUCTION WASTE WATER

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Introduction

The actual situation on purification of waste water especially in Russia develops in such a manner that the biological treatment is now a most widespread method of removal organic contamination's from waste water. Dioxins removal by biological process happens by adsorption to the biological material only. The analysis of the purified water discharged from biological treatment plant "Khimprom", the city of Ufa has shown that up to 99,7 % of PCDD/PCDF are adsorbed by the suspended solid. The insufficient degree of purification from the suspended particles can be accounted for by the out-of-date equipment, irregular submission of waste water, insufficient aeration, that results in air flotation of active sludge and increase of carrying out the suspended particles with the purified waters. Thus, only observance of norms for discharge of the suspended particles with the purified waste water will allow to reduce the contents of PCDD/PCDF in water. On the other hand, it is necessary to inspect dioxins input with waste water to biological purification plant. The local waste water treatment polluted by PCDD/PCDF is necessary.

In the present work the results of investigation of unit of the preliminary treatment of vinyl chloride-monomer production waste water, at the Kaustic plant, Sterlitamak in Russia are presented. Production of vinyl chloride-monomer includes two stages: ethylene oxychlorination at the temperature of 250°C in presence of copper-aluminum catalyst and dichloroethane pyrolysis at 500°C. The formation of PCDD/PCDF is possible both at the first, and at the second stages. Under water hardening of pyrolysis gases by water PCDD/PCDF pass partially in to water and can be in the dissolved or suspended state depending on pH and the amount of the carried out catalytic dust and organohalogen compounds. In production of vinyl chloride-monomer a unit for waste water purification from heavy metals is used. The waste water from production of vinyl chloride-monomer discharged to the purification unit, contains impurities of non-ferrous and heavy metals - Cu, Al, Fe, which can be in water both in the dissolved form and as suspension. The waste water, after the water hardening and washing technological processes contains also impurities as dichloroethane, vinyl chloride-monomer and other organohalogen compounds up to 0,001 % of weight.

Materials and Methods

For the analysis the samples of waste water before and after purification unit were collected. The samples were taken in specially prepared vessel in volume 10 litres. Sampling and sample preparation for analysis were performed in compliance with recommendations of US EPA 1613, as reported¹⁾. For control of sample preparation process isotope-labelled standards ³⁷Cl-2,3,7,8-TCDD, ¹³C₁₂-2,3,7,8-TCDF, ¹³C₁₂-1,2,3,4,6,7,8-HpCDF and ¹³C₁₂-OCDD were introduced into all samples. Water samples were extracted with three portions of hexane. The water filter was extracted in a Soxhlet extractor with toluene. Toluene was substituted by hexane. The extracts were cleaned by silica gel and charcoal columns. The analysis was performed using a mass-spectrometer Incos 50 equipped with a chromatograph Varian 3400 and a capillary column DB-5MS in the mode of se-

lective ion-determination. The internal ^{13}C -labelled standards $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD were used for calculation of mass-chromatograms. Analysis error was 60%.

Results and Discussion

The data of the analysis of waste water show that the contents of PCDD/PCDF in waste water had levels 0,39-3,02 ng/l-TEQ (table 1). The sample № 3 was collected when the production vinyl chloride-monomer did not work, but the residuals of water were pumped to the purification unit. The high contents of PCDD/PCDF - 9,40 ng/l-TEQ – is accounted for probably to a breach of technological parameters - temperature and time of contact under stop of vinyl chloride-monomer production. The congener profile of PCDD/PCDF is represented mainly by high-chlorinated furans, but in samples № 2 and № 3 high-chlorinated dioxins and 2,3,7,8-TCDF appear.

Table 1.

Concentration of PCDD/PCDF in samples of waste water of vinyl chloride-monomer productions, ng/l.

Isomers PCDD/PCDF	Sample No					
	1997				1998	
	1	2	3	4	5	6
1,2,3,7,8-PeCDD	ND	ND	1,90	ND	ND	ND
1,2,3,6,7,8-HeCDD	ND	ND	0,76	ND	ND	ND
1,2,3,4,6,7,8- HpCDD	ND	ND	2,03	ND	0,79	1,54
ОХДД	ND	2,11	11,39	ND	3,24	11,61
2,3,7,8-TCDD	ND	0,31	5,70	ND	ND	ND
1,2,3,7,8-PeCDF	ND	ND	3,99	ND	ND	0,61
1,2,3,4,7,8-HxCDF	16,52	ND	15,61	ND	ND	5,56
1,2,3,4,6,7,8-HpCDF	65,72	11,86	103,14	7,09	35,89	40,73
OCDF	712,50	430,64	3182,68	31,88	574,30	389,15
TEQ, ng/l	3,02	0,580	9,40	0,39	0,94	1,41

The purpose of waste water treatment - to receive satisfactory according to the specification outcomes of the residual metal's contents in the treated waste water by the settling of hydroxides of metals. It is achieved by acidification, alkalization and filtration of formed solid phase. On inspection of purification unit it found that PCDD/PCDF are adsorbed on the solid phase and are removed from waste water in this way. The concentration of PCDD/PCDF in the purified waste water after the purification unit had levels of 0,01-0,04 ng/l-TEQ. The range of PCDD/PCDF concentration depends on the structure of formed solid phase and on conditions of the filtration, which

should exclude a solid phase passage through filtering material. In sample №11 contents of PCDD/PCDF in water - 0,035 ng/l-TEQ, in solid phase - 0,60 ng/l-TEQ, in sample №12 the total contents of PCDD/PCDF had level of 0,136 ng/l-TEQ, owing to solid phase passage through the filtering material (table 2).

The analyses of sludge after waste water filtration evidently shows, that PCDD/PCDF formed during production of vinyl chloride-monomer are concentrated in sludge. The congener profile of PCDD/PCDF is represented mainly dibenzofurans of a different degree of chlorinating. Table 3 shows that from the moment of start-up and improvement of the technological process of production vinyl chloride-monomer the contamination sludge by PCDD/PCDF has decreased by 15,23 ng/g-TEQ to the average value - 0,86 ng/g-TEQ. The most significant decrease is observed for lower chlorinated PCDF. At a quota of sludge formation - 1 kg on 1 m³ waters the PCDD/PCDF contents in sludge is about 6% of total PCDD/PCDF emission of vinyl chloride-monomer production including waste incinerators.

Table 2

Concentration of PCDD/PCDF in samples of waste water of vinyl chloride-monomer productions after preliminary treatment, ng/l

Isomers PCDD/PCDF	Sample No.						
	1997 г.				1998 г.		
	7	8	9	10	11 (liquid)	11 (solid phase)	12
2,3,7,8-TCDF	ND	ND	ND	0,36	0,30	ND	ND
1,2,3,7,8-PeCDF	ND	ND	ND	ND	ND	0,39	ND
1,2,3,4,7,8-HxCDF	ND	ND	ND	ND	ND	2,06	ND
1,2,3,4,6,7,8-HpCDF	ND	ND	ND	ND	ND	15,43	1,01
OCDF	28,04	18,37	10,13	3,82	3,22	217,96	125,94
TEQ, ng/l					0,035	0,60	
TEQ, ng/l	0,028	0,018	0,01	0,04	0,635		0,136

Table 3.

Concentration of PCDD/PCDF in samples of sludge after preliminary treatment, ng/g

Isomers PCDD/PCDF	Sample No.							
	1997						1998	
	13	14	15	16	16	17	18	19
1,2,3,4,6,7,8-HpCDD	ND	2,51	ND	ND	ND	ND	ND	ND
OCDD	ND	8,75	0,90	ND	ND	0,64	ND	ND
2,3,7,8-TCDF	12,75	3,66	ND	0,20	0,43	0,17	ND	ND
1,2,3,7,8-PeCDF	13,78	12,25	0,35	0,36	0,96	1,22	ND	ND
1,2,3,6,7,8-HxCDF	46,38	47,96	1,53	2,00	0,76	1,83	1,28	3,49
1,2,3,4,6,7,8-HpCDF	121,17	125,64	11,95	13,48	15,05	20,06	13,72	16,09
OCDF	1214,1	764,98	684,39	695,15	36,63	440,6	795,9	277,8
TEQ, ng/g	15,23	7,83	0,98	1,07	0,35	0,90	1,06	0,79

Conclusion

The preliminary purification of waste water from impurity of metal's allows to reduce the PCDD/PCDF contents. It is demonstrated by analysis data that maximum formation of PCDD/PCDF in the vinyl chloride-monomer production occurs during startup and shutdown.

References

1. Khizbullin F, Muslymova I, Khasanova I, Chernova L and Abdraschitov Ja; *Organohalogen Compounds*. **1998**, 36, 225.