REMEDIATION OF HEXACHLORO-1,3-BUTADIENE CONTAMINATED GROUNDWATER

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ABSTRACT. Hexachloro-1,3-butadiene (HCBD) is an industrial by-product that is produced during the manufacturing of various chlorinated hydrocarbons like vinyl chloride, trichloroethene or tetrachloroethene. HCBD is toxic and considered harmful for the environment and especially for aquatic ecosystems. Various processes have been investigated for the abatement of chlorinated hydrocarbons in aqueous solutions. In this study, the physical and chemical remediation of HCBD contaminated groundwater was investigated. On the basis of the results, the costs for the treatment of a contaminated water flow of 200 m³/h were compared. The results show that in the investigated application, a dechlorination reactor would be less expensive than an adsorber.

Keywords: Hexachloro-1,3-butadiene, groundwater, dechlorination, adsorption, Central Europe

1. INTRODUCTION

Hexachloro-1,3-butadiene (HCBD) is an industrial by-product that is produced during the manufacturing of various chlorinated hydrocarbons like vinyl chloride, trichloroethene or tetrachloroethene. HCBD is toxic and considered harmful for the environment and especially for aquatic ecosystems (Gillham, 1996; Taylor et al., 2003; Lecloux, 2004). Various processes have been investigated for the abatement of chlorinated hydrocarbons in aqueous solutions. Lee et al. (2017) investigated different oxidative processes using O_3, H_2O_2 and UV photolysis. For the degradation of chlorinated volatile organic compounds in groundwater zero valent iron (ZVI) can also be used (Gillham and O'Hannesin, 1994; Rodrigues et al., 2017). Thereby, ZVI can also be installed in the form of permeable reactive barriers (Blowes et al., 2000; Henderson and Demond, 2007). Alternatively, activated carbon (AC) can be used for the removal of chlorinated hydrocarbons mainly through sorption (Peng et al., 2003; Pavoni et al., 2006).

In this study, the physical and chemical remediation of HCBD contaminated groundwater was investigated. As a first step, laboratory studies on the kinetics and reduction capacity of different types of ZVI materials and adsorbents (activated carbon, zeolithes) were performed as basis for a pre-selection of the materials for the field tests.

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These were performed using two types of ZVI for dechlorination and two types of C-based adsorbents in column tests to determine the reaction parameters and the adsorption isotherms. On this basis, the costs for the treatment of a contaminated water flow of 200 m³/h were compared. The results show that in the investigated concentration range, a dechlorination reactor would be more efficient and less expensive than an adsorber.

2. MATERIALS AND METHODS

2.1. Materials
2.1.1. Water samples
The groundwater samples investigated in this study were obtained from an HCBD contaminated area. The HCBD concentration is usually in the range of 150 to 250 µg/L.

2.1.2. ZVI and AC samples
Two different ZVI materials were used in this study: sponge iron and iron shavings. The sponge iron was supplied by a steel mill, while the iron shavings were obtained from a workshop. The latter material was carefully cleaned prior to use by washing with acetone and subsequently drying.

The AC pellets (4 mm) have a specific surface area of 1100 m²/g and an iodine value of >1050 mg/g. Other adsorbents like zeolithes were exluded from the study in the pre-selection phase (Obiri-Nyarko et al., 2014).

2.2. Methods
2.2.1. Batch tests
The batch tests for degradation were performed in 1 L glass bottles in a overhead shaker. A defined mass of ZVI was filled into the bottle. After adding some deionized water, the bottles were placed in a ultrasonic bath for 20 minutes to drive the air out from the pores. Subsequently, the water sample containing HCBD was poured into the bottle until it was overflowing with water. Then the bottle was covered with aluminium foil and screwed closed. The samples were shaken for 3 to 48 hours. The blank test sample was also shaken for 48 hours.

The adsorption batch tests were also performed in an overhead shaker in 1 L glass bottles. Different amounts from 0.0 to 50 g of AC were filled into the bottles. The procedure for filling the bottles was similar for both tests. The shaking time was 2.5 hours.

2.2.2. Column tests
Columns with a length of 1.0 m and an inner diameter of 9.0 cm were filled with ZVI or AC. The porosity of the filling with iron shavings, sponge iron and AC was 0.90, 0.75 and 0.66, respectively. The columns were equipped with five sampling ports installed at different heights on the column. The column experiments were performed onsite at the area where the contaminated groundwater was extracted. The feed of

HCBD contaminated water to each column was approximately 1.0 mL/min during the ZVI tests. In the adsorption test, the feed flow was 0.9 L/min. The degradation tests were operated for more than two months, while the adsorption tests were stopped after approximately 300 hours when break-through of HCBD was observed.

2.2.3. Sample preparation and HCBD analysis

A volume of 15 mL of water sample was poured into 22 mL headspace vials using a syringe. Before the bottle was closed, 2 mg of a standard solution (Br_2ClCH and C7 in ethanol) were added.

The samples were analysed by GC using a HP 6890 chromatograph equipped with a CB-624 column (60 m × 0.32 i.d., with a 1.7 μm film thickness). After the column, the sample was split-up 1:1 and supplied to two detectors in parallel, a FID and an ECD. Hydrogen was chosen as carrier gas at 2.4 mL/min flow rate. The samples were heated at 80°C for 20 min, and headspace gas was introduced 3.6 s into the injector chamber at 250°C (1:5 split ratio). The oven was maintained at 0°C for 2 min and, then, ramped to 220°C at 6°C/min with a hold for 11 minutes at this final temperature. The flame ionization detector (FID) temperature was maintained at 250°C with a He makeup at a flow rate of 25 mL/min. Combustion in the FID was carried out with H_2 (30 mL/min) and air (400 mL/min).

3. RESULTS AND DISCUSSIONS

3.1. Degradation using ZVI

A pseudo-first-order equation is usually used for the description of the degradation of chlorinated organic compounds (Johnson et al., 1996; Rodrigues et al., 2017). This model was also used in the study to describe HCBD degradation,

$$-\frac{dC}{dt} = k_{de} \cdot C \qquad (1.1.)$$

where   C is the concentration in HCBD (µg/L) at time t (h) and
                         k_{de} is the pseudo-first-order rate constant (1/h).
                         C_0 is the concentration of HCBD at the start of the test.
The rate constants obtained in the batch tests are shown in Table 1.

Table 1. *Pseudo-first-order rate constants for HCBD degradation*

Iron carrier	Mass of iron	C_0 HCBD	k_{de}	r^2
	g/L	µg/L	h^{-1}	-
Iron shavings	10	170	0.024	0.96
Sponge iron	10	170	0.018	0.95
Sponge iron	20	180	0.022	0.93

Figure 1 shows the average HCBD concentrations as a function of the residence time obtained in the sponge iron column experiment. The reduced efficiency of the first section might be caused by shortcomings in the distribution of the feed flow. The variation of the data indicated by the error bars (n = 8) is assumed to be partly caused by the variation of the ambient temperature.

3.2. Adsorption by AC

In the batch adsorption tests, the Freundlich adsorption isotherm of the AC for HCBD was determined.

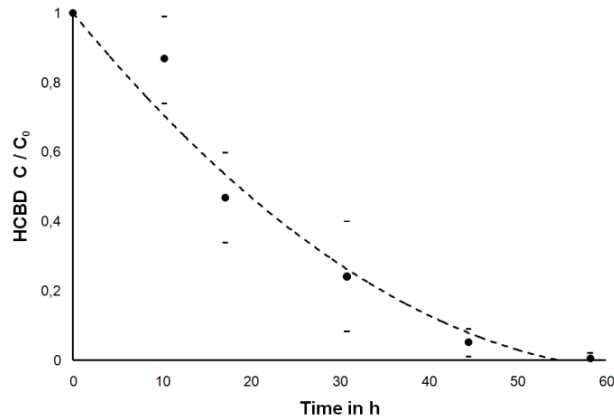$$q_e = K_F \cdot C_e^{1/n} \tag{1.2.}$$

where

q_e is the amount of the adsorbate on the adsorbent at equilibrium (mg/g),

C_e is the equilibrium concentration of the adsorbate,

K_F is the Freundlich coefficient and

$1/n$ is the adsorption intensity.

The parameters obtained in the experiments were $n = 0.98$ and $K_F = 2.61$ ($r^2 = 0.97$).

Fig. 1. Evolution of HCBD concentration versus residence time in the column experiment with sponge iron

In the column test, breakthrough was reached when the percentage of pollutant remaining in solution exceeded 5% of the starting concentration. The limits used for the determination of the length of the mass transfer zone (MTZ) C/C_0 were 0.05 and 0.95. Figure 2 shows the evolution of the HCDB concentration profile along the column.
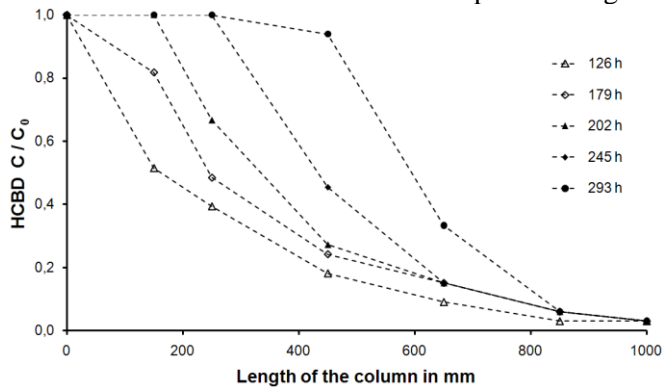

Fig. 2. HCBD concentration profiles versus operation time in the column experiment with AC

The calculated length of the MTZ was 600±60 mm. This value is rather high compared to the result (83 mm) reported by Pavoni et al. (2006). The larger size of the AC particles of 4 mm and the higher velocity (3.5 mm/s) in this study compared to a size of approximately 1 mm and a velocity of 0.77 mm/s might explain the difference.

3.3. Comparison of the two processes

The results of the column experiments were used in the comparison of the estimated costs for the treatment of a contaminated water flow of 200 m³/h. For the adsorption variant, a solution with an operation of 3 adsorber vessels out of 4 was selected. For the degradation variant, the effectivity of the ZVI material was assumed for at least 15 years (Blowes et al., 2000; Henderson and Demond, 2007; Obiri-Nyarko et al., 2014). Basic assumptions for the cost estimation were: cost of sponge iron: 300 €/t; cost of AC: 1,500 €/t; disposal cost for used AV: 280 €/t; investment cost for vessels: 100 €/m³. The cost for pumps and pipings as well as for electrical and measuring equipment were not considered in this estimate, because they would be similar for both variants. Depreciation was assumed to be 15 years with an interest rate of 6%.

Figure 3 shows a comparison of the relative annual costs of both variants. The investment costs, and therefore the resulting depreciation, are much higher for the degradation with sponge iron compared to the the adsorption variant. This is a result of the larger volume required for degradation. However, the cost of replacing used AC and the cost of its disposal are substantially higher.
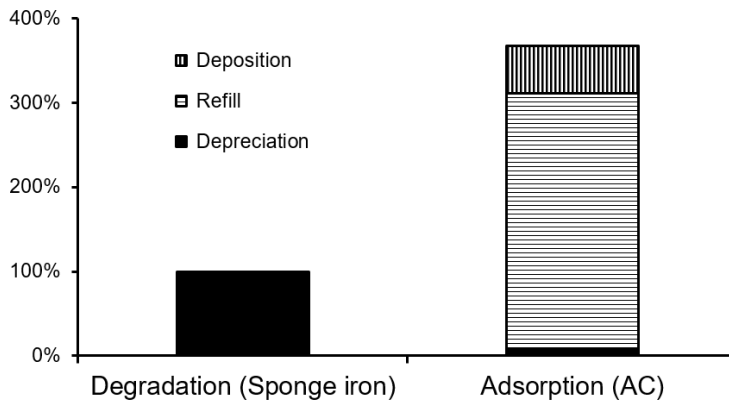
Fig. 3. Comparison of annual costs

4. CONCLUSIONS

The results show that in the investigated application for the treatment of HCBD contaminated water, a dechlorination reactor with ZVI would be much more cost effective compared to an adsorber with AC. This is because of the high cost of the required replacement of the used adsorbent.

ACKNOWLEDGEMENTS

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