

Application of zero-valent iron/peat permeable reactive barrier for in-situ remediation of lindane and chlorobenzenes

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ABSTRACT

Post pesticides production landfills are often a source of large uncontrolled contamination of groundwater. Therefore, there is a need to find suitable technologies to reduce the concentration and ecotoxicity of these pesticides. In this paper, both lab- and field-scale technology of permeable reactive barrier (PRB) for the treatment of hexachlorocyclohexanes (HCHs) and chlorobenzenes (CBs) at a site in Jaworzno, Poland are described. The results showed the high efficiency of the treatment process for hexachlorocyclohexane (90%) and chlorobenzenes (99%) in lab-scale which slowly decreased to 86% and 97%, respectively with the time of PRB operation (112 d). The efficiency of treatment of HCHs and CBs by PRB technology in pilot scale in the 8th day operation was ca. 82% and 60%, respectively during the first phase of operation and highly decreased after two months of operation due to the loss of sorption capacity of peat bed and the passivation process of iron chips. Based on the measured data, it could be determined that the treatment train in such barrier relies on subsequent reductive dehalogenation and adsorption. Therefore, the results obtained and presented in this paper could be useful for further design of full-scale permeable reactive barriers on sites with groundwater contaminated by similar organochlorine pesticides.

Keywords: Zero-valent iron; Hexachlorocyclohexane; Lindane; Chlorobenzenes; Groundwater treatment

1. Introduction

Post pesticides production landfills are often a source of a massive uncontrolled release of contaminants into the groundwater. Therefore, there is a need to find suitable technologies to reduce the concentration and ecotoxicity of these pesticides. Uncontrolled migration of pesticides in groundwater is a severe threat to drinking water resources. Among the pesticides, hexachlorocyclohexanes (HCH) were reported to be extremely toxic for humans [1–3]. Its synthesis procedure relies on the chlorine dissolution in

excess of benzene and exposing such a solution to UV irradiation. Subsequently, HCH resulting mixture (also called technical HCH) is washed and dried. The HCH insecticidal properties are almost entirely assigned to only one of the isomers (γ -HCH; Fig. S1a). While the first synthesis of HCH can be attributed to Michael Faraday in 1825 [1], the first one to isolate the γ -HCH at the beginning of 20th century was Van der Linden from whom γ -HCH was further named: lindane. Since the 1940s it was used for the control of flea beetle, different agricultural and horticultural pests, cockroaches, locusts, and others. Furthermore, it was used as a scabicide from the 1950s [4]. A few years after its

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first use, Danopoulos et al. [4] reported its possible toxic effect on humans. People after exposure to HCH informed about different symptoms (vertigo, myalgia, headaches, mental confusion and others). Recently, β -HCH exposition was associated with an Alzheimer's disease [5]. The γ -HCH use around the world has become a serious problem, and therefore it was banned in most of the countries [1]. However, the problem is larger because the other isomers formed during the lindane production are waste and were incorrectly disposed. Many countries have a background HCH contamination in surface water, groundwater and soil and also HCH waste hot-spots [1], for example, in Poland, contamination of 35,000 tons of HCH was estimated [1]. Moreover, treatment of HCH often generates other contaminants of concern - chlorobenzenes (1-CB (it is an example of CBs); Fig. S1b; [1]).

Application of permeable reactive barrier (PRB) for passive treatment of the contaminated groundwater is a modern technology involving engineered design but operated in a green manner [6–8]. Many authors presented the review of various types of PRB in terms of their construction, types of reagents and types of contaminants. The earliest and still most popular applications of PRB are those aimed at treatment of chlorinated contaminants and heavy metals using zero-valent iron (ZVI) as a reagent [9–11]. It is also common to use ZVI in nitrogen and phosphorus wastewater treatment [12–14]. Use of ZVI for treatment of groundwater contaminated with various compounds was reported also recently [15–17]. While PRB composed of ZVI was successfully applied for the treatment of inorganic cations, filling with solid-phase organic carbon was optimal for acid-mine drainage and anions [18]. Guerin et al. [19] presented the treatment of petroleum hydrocarbons with the use of peat in Australia. More examples of PRBs from both Australia and New Zealand are provided in a broad review by Thiruvengatchari et al. [20], including cleaning of groundwater contaminated by pesticides (atrazine, terbutryn, fenamiphos) in Perth. A combination of biological methods and PRBs was proposed by several authors [21,22]. Kalinovich et al. [23] and Zhang et al. [24] reported the use of this technology for the treatment of polychlorinated biphenyls (PCB) and chlorobenzenes (CB), respectively.

Some of PRBs are working with success for many years for chlorinated solvents and metals, like PRB in Elizabeth City, North Carolina, USA [9,25,26] or PRB in Monkstown, Northern Ireland [27].

The applications of PRBs for lindane and other HCH isomers treatment are rarely reported by the study of Vidal et al. [28]. One early example briefly mentioned in US EPA reports [29] is the Marzone site in Tifton, GA, USA where PRB was constructed to treat groundwater from CBs, dichlorodiphenyltrichloroethane (DDT) and lindane. In this system, groundwater was treated by activated carbon as a reactive material. Further related studies propose nano- and microparticles of iron for HCH treatment [30,31].

Recently, examples of lab experiments on lindane treatment by ZVI microparticles in both batch and column test scale [3], and physical lab model in <200 L scale [28] have been reported showing high degradation rates. Therefore, the current paper is presenting the next step, which is

testing the HCH degradation not only in lab, but also in field conditions at pilot scale.

This article is divided into two sections. The first section provides a result from lab-scale testing of peat/ZVI PRB setup for HCH and CBs contaminated water treatment. Section two elaborates the process of PRB up-scaling. The main aim of this study was to evaluate the effectiveness of such novel (peat/ZVI) *in situ* PRB setup for degradation of HCH isomers and CB congeners.

The two main HCH abiotic degradation pathways are metal-mediated dihaloelimination and dehydrohalogenation. Under acidic conditions, hydrogenolysis could occur, but it is rarely reported in the literature. Elliott et al. [32] reported the degradation trend of HCH isomers by nZVI, where they have observed dihaloelimination of γ -HCH as one of the possible pathways. It was also found that the vital reaction intermediate was 3,4,5,6-tetrachlorocyclohexene and traces of biphenyl and benzene [33]. On the other hand, Wang et al. [34] reported the possible lindane dechlorination pathways by ZVI. They have noticed benzene and chlorobenzene as possible products; however, benzene was reported as the primary end product.

Several important parameters, such as concentrations of HCH and its by-products as well as physicochemical parameters, were evaluated, to assess the PRB efficiency in degrading of these dangerous contaminants. The novelty of the article is the presents of the efficiency and the mechanisms of HCH removal from real contaminated groundwater in the pilot scale installation. The results obtained and shown in this paper could be useful for further designs of full-scale PRBs for sites with groundwater contaminated by organochlorine pesticides.

2. Materials and methods

2.1. Site description and history

The site is located in Jaworzno in southern Poland (Fig. 1) [35] where the Chemical Plant "Organika-Azot" produced lindane from 1965 till 1982.

The groundwater monitoring carried out since 2008 on the site has shown the HCH concentration in the groundwater. On the north of Wąwolnica stream, the HCH concentration ranges values between 10–100 $\mu\text{g/L}$ with the domination of β -HCH in the isomer mixture, characteristic for quite old contamination, as β -HCH is the most persistent of all the HCH isomers [36]. The concentration of the sum HCH even above 300 $\mu\text{g/L}$ was noticed on the south of the Wąwolnica stream, including α -HCH, γ -HCH and δ -HCH over β -HCH. Such isomer composition with a low β -HCH share is typical for relatively "fresh" contamination [36]. On the site, other persistent organic pollutants, including CBs, chlorophenols (CF), dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD), DDT, chloroethenes and chloromethane are also present in groundwater. Table 1 presents the chemical composition of groundwater from study area in Jaworzno.

Fig. 2 presents the pilot PRB at the study area and HCH and CB concentrations in the groundwater measured in July 2018.



Fig. 1. Localization of study area.

Table 1
The chemical composition of groundwater from area study in Jaworzno (mg/L)

Parameter	Min.	Median	Max.
Chemical oxygen demand	<10	13.25	79.1
Biochemical oxygen demand	<0.5	1.25	5.8
Calcium	32.1	61.9	89.2
Magnesium	7.61	35.35	83.3
Sodium	2.09	43.3	98.2
Potassium	1.97	18.05	98.9
Iron	0.012	12.1	78
Manganese	<0.003	1.15	12.3
Ammonium	<0.05	1.03	7.88
Chlorides	5.4	27.7	71.6
Sulphates	37.1	63.1	90.6
Bicarbonates	<24	70.2	97.6
Nitrates	<0.1	0.13	48.5
Nitrites	<0.02	<0.02	0.12

Data from 53 sampling points – sampling and analysis by Central Mining Institute in 2010.

2.2. Groundwater sampling

The research was carried out on a laboratory and pilot field scale. At first, groundwater samples from the area of planned pilot PRB were taken in January 2017 and used for tests in a laboratory. Then, the pilot PRB was constructed, and the field test was carried out in the period from January 2019 till the end of April 2019. Samples of groundwater in an inflow, in middle and in an outflow of the PRB system were taken after 8, 21, 36, 56, 64 and 112 d of treatment. Water samples were stored at 5°C before the analyzes.

2.3. Reagents and solutions

All of the chemicals used in the lab-scale experiments were analytical reagent grade. Reactive material used at the pilot PRB such as coarse sand, peat and iron chips was purchased from a local supplier. The parameters of materials: sand (particles sizes 0.5–1.0 mm), gravel (particles size: 0.5–1.0 cm), peat (particles size: 0.0–20.0 mm), iron chips

(variety of shape and dimensions from few millimeters to five centimeters).

2.4. Analytical and characterization

HCH and CB isomers were quantified by a gas chromatograph (Thermo TRACE 1310 combined with an MS Detector TSQ 8000 Triple Quadrupole). Headspace solid-phase microextraction (HS-SPME) was utilized for sample preparation and injection (PDMS SPME Fibers, Supelco). A TR-Pesticide chromatographic column, 30 m in length, 0.25 mm in diameter, was used for gas chromatography. For calibration, standard mixtures of HCH and CB (Neochema, Pesticide Mix 5 and Chlorobenzenes Mix 12) were employed along with deuterated γ -HCH (Ehrenstorfer GmbH) as an internal standard. Further details about the determination method for organochlorines can be found in a recent article [37].

The volatile organic compounds were determined in the full scan mode on gas chromatography/ion trap MS instrument [GC; Varian Saturn 3800, (CTC Analytics AG, Switzerland)], equipped with a VF-624ms column, 60 m in length, 0.32 mm in diameter and 1.8 μ m in film thickness. Helium was employed as a carrier gas with a flow rate of 1 mL/min.

Anions were determined on ion chromatograph Thermo Scientific™ Dionex™ ICS-2100 with Regent-Free™ IC (RFIC™) system, equipped with the conductivity detector.

The pH, ORP, and conductivity were measured by a WTW pH Meter equipped with SenTix pH electrodes (TMultiLine® Multi 3430 IDS, Weilheim, Germany).

Morphology of the ZVI after use was studied using scanning electron microscope (SEM, UHR FE-SEM ULTRA Plus, Carl Zeiss, Germany) working at an acceleration voltage of 0.5–2.5 kV.

2.5. Lab-scale experimental setup

Figs. S2a and b show the experimental configuration Column Test 1 (CT1, column dimensions: 50 cm \times 5.5 cm) used for performing column tests to determine a flow rate influence to the treatment efficiency. The groundwater containing a total concentration of 18.9 μ g/L of HCHs and 127 μ g/L of CBs was pushed through the columns by

a peristaltic pump; results are shown in Fig. S3. Columns were filled with different materials (sand, peat and iron chips), and the flow was changed from 0.8 to 16 mL/min to simulate different flow velocities from 2.3 to 45 m/d (Fig. 3).

Further, the water was collected at the column inlet and outlet and analyzed for different parameters (pH, ORP, conductivity and HCHs/CBs concentration). The experimental configuration was chosen, according to Kao et al. [38].

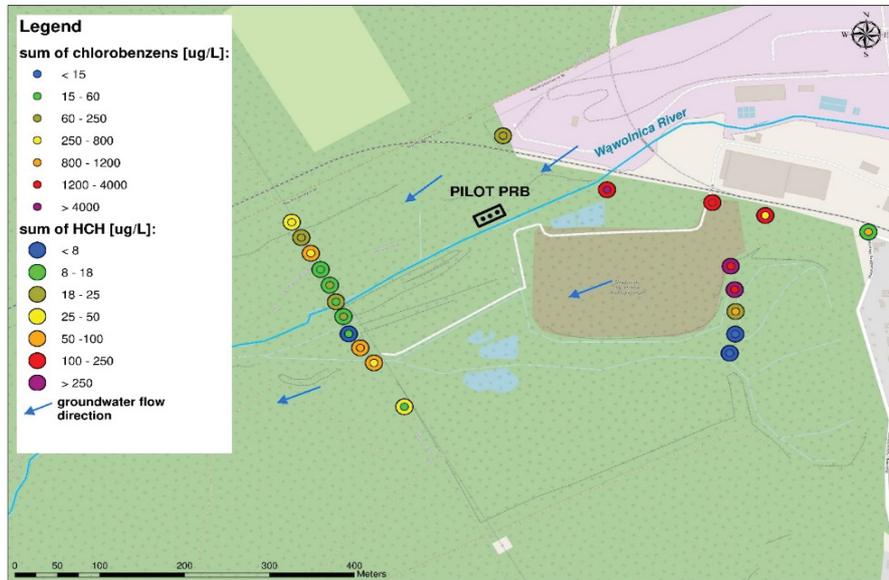


Fig. 2. Site background and localization of pilot PRB (groundwater contamination data from July 2018).

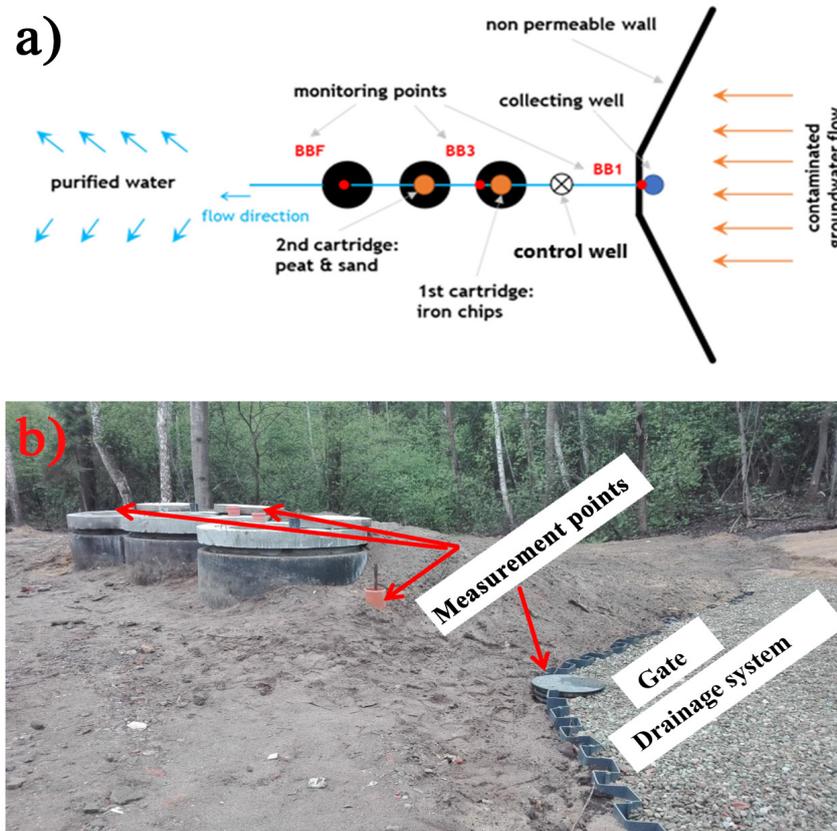


Fig. 3. (a) Construction of the pilot PRB system and (b) photograph of the pilot PRB system in Jaworzno.

The second experimental Column Test 2 (CT2, column dimensions: 8 cm × 1.8 cm) was aimed to evaluate contaminant removal efficiency as a function of a number of pore volumes flushed through the column [Eq. (1)]. Therefore, the experiments were performed with smaller columns (15 mL each; Fig. S2c). Columns were filled with peat or iron (the sand was not tested because of low efficiency) and run up to 550 pore volumes of flushed water. The measurement was similar to CT1.

Removal efficiency refers to a combination of degradation and adsorption phenomena [Eq. (1)].

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t is the concentration of contaminant at time 0 and t , respectively.

2.6. Location and construction of the pilot permeable reactive barrier

Due to the study's pilot character, the barrier was located in the northern plume area, where the concentration of sum HCH is below 50 µg/L (Fig. 2). This level of contamination is suitable for the optimization of passive methods like PRBs [39,40]. Moreover, this quite old contamination, dominated by persistent β-HCH, makes the selected area a typical example for passive clean-up technologies, as the last step in the remediation train.

The barrier is constructed by the “funnels and gates” concept with replaceable active materials. The groundwater is directed to the barrier by two non-permeable walls (7.5 m long each) with a depth of about 1 m below the top of the low permeable layer (about 7 m below ground level) to ensure vertical isolation (Fig. 3a). In groundwater flow direction ahead of the non-permeable walls, a drainage channel of the total length of 15 m (Fig. 3b) and the depth up to the level of loam (about 6 m below ground level) filled by gravel was constructed to direct groundwater into the collecting well. The treatment system consists of up to three cartridges filled with different types of active material chosen based on the lab-scale tests: sand, gravel, peat and iron chips. The cartridges were placed in a serial way inside the

reinforced concrete wells (Fig. 3a). The water flow through the system is by gravity according to the natural gradient of surrounding groundwater. The treated water is reverted into groundwater through a drainage system downstream the PRB. The three sampling points were: BioBarrier point 1 (BB1) – the inflow groundwater well, BioBarrier point 3 (BB3) – the point between cartridges, equipped with a pipe connected to the bottom of the cartridge, and BioBarrier out-Flow (BBF) – the outflow pipe for the sample collecting and flow measuring (Fig. 4).

The experimental system consisted then of two cartridges with the total volume of 140 L: the first cartridge filled with zero-valent iron (Fe⁰) (10 L of gravel at the bottom (170 kg), 100 L of Fe⁰ in the middle (39.1 kg) and 5 L of gravel at the top (85 kg) and the second filled with peat and sand (10 L of gravel at the bottom (170 kg), 20 L of sand (32 kg), 20 L of peat (3 kg), 5 L of gravel at the top (85 kg). The bulk density of the mixed sand-gravel-peat bed was 150 g/L. It wasn't measured the permeability of the mixed bed. The morphology of surface of the iron chips is presented in the supplementary materials (Fig. S5).

3. Results and discussion

3.1. Lab-scale operation

At first, the flow velocity influence on various parameters was investigated. Change of pH, ORP and conductivity as a function of various flow velocities and pore volumes flushed was evaluated (Fig. S4). Except for ORP and pH in columns filled with iron and peat, all the parameters showed no significant variation. When changing the flow velocity, pH appears constant and the flow would not seem to influence the pH value. Therefore, it can be concluded that the flow velocity does not influence pH value for the tested flow velocity range (only minimal displacement of the value recorded in sand and iron samples could be observed), whereas it is obvious that peat is acidifying the sample substantially. This could be primarily caused by the humic and flavic acids present in peat that could lower the pH value of the treated groundwater. The values recorded for column filled with sand have decreasing trend, that is, reduction of ORP value with increasing the flow velocity from 4 to 8 mL/min and a stabilization of this value at higher flow

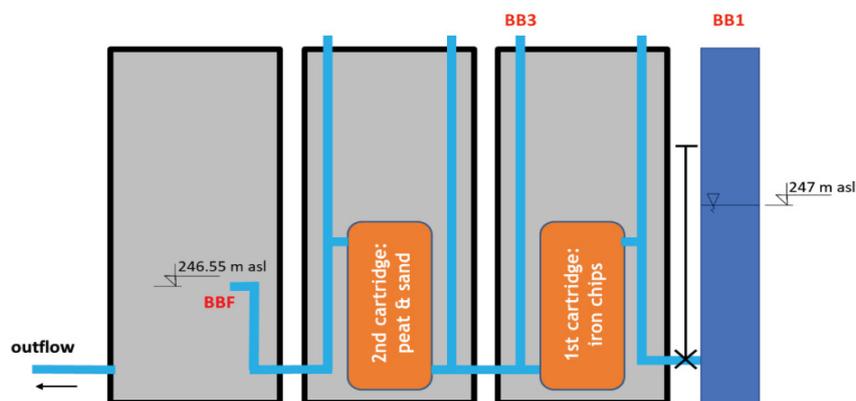


Fig. 4. Scheme of the pilot PRB construction.

velocities. In addition, the groundwater treated in the column filled with elemental iron have the lowest ORP values of all the experiments. This is due to the fact that iron is in its lowest possible oxidation state, possessing many electrons available for reduction of water and contaminants, similar observations were reported [41]. Moreover, the ORP value in this column seems to be not much influenced by changing the flow velocity. Contrariwise, the samples after treatment with peat are having very high ORP values, which is probably due to the acidic character of peat (electron accepting), and these values also do not vary a lot with changing the flow velocities. Furthermore, conductivity values of the treated groundwater as a function of different flow velocities were determined as well. All fillings seem to increase this parameter in groundwater with the increase of the flow velocity, however, the same trend is observed for the input samples, therefore, it can be concluded that the flow velocity does not influence substantially this parameter.

The effect of the flushed pore volumes on parameters such as pH, ORP, conductivity has been also investigated. The pH values recorded for the input exhibited values almost neutral with a minimal shift to alkaline pH by increasing the pore volumes. The pH value rises by increasing the pore volumes. It must be stressed that the change of the pH value is not extreme. On the other hand, the ORP values are fluctuating with the increase of the pore volumes in the peat and iron columns as well as in the input samples. Noticeably, the samples taken from the iron column had the lowest values of ORP. As for the conductivity values samples taken from the input of columns as well as output of the column filled with iron exhibited relatively stable and constant trend. Column filled with peat however, unveiled abnormal behavior of conductivity value in the groundwater. The conductivity dropped from ~1,200 to ~800 $\mu\text{S}/\text{cm}$ after flushing with 50 pore volumes. However, this value has increased after ~200 pore volumes to the similar one as recorded for groundwater treated with iron.

Fig. 5 shows the influence of flow rate on the effectiveness of HCH and CB removal for the columns with various fillings. The column filled with sand has the smallest decontamination efficiency for both groups of contaminants. In general, sand is considered as an inert material, and herein

we have employed it mainly as comparison for the reactive column fillings (peat and iron), then the results obtained from the sand column should be used only to compare the results of the peat and iron column. Nonetheless, at a low flow rate 0.8 mL/min the HCH and CB removal efficiency (calculated according to [Eq. (1)]) is 65% and 85%, respectively. This result is due to the longer contact time between the sand and the pollutants. Boucher and Lee reported that by increasing the time of contact between the sand and the contaminated water, the adsorption of lindane varies and that it is time and temperature-dependent [42]. Columns filled with iron and peat showed much higher efficiency of both HCH and CB removal. The column filled with iron seems to be more affected by the flow velocity (Fig. 5a). This can be due to different mechanisms of HCH removal. While peat sorbs the contaminants, on the ZVI surface, the oxidation-reduction processes convert the contaminant, and such processes have different kinetics. The surface reduction process is slower, and therefore the reaction is more sensitive to the flow rate.

Changing flow velocity does not affect CB decontamination efficiency by iron and peat (Fig. 5b). One should be aware that CB is the intermediate result of the reduction of HCH, while both HCH and CB are ideally, ultimately reduced to benzene molecules [1].

After testing the influence of flow rate, the effect of flushed pore volumes was evaluated (Fig. 6). In both columns, there is an effective removal of the HCH (decontamination efficiency ~90%), which seems to be not affected by the increasing volume of flushed water (up to 550 pore volumes). Similarly, both columns filled with peat and iron have very high efficiency in CB removal. Detailed analysis of the data showed a similar linear decrease; however, only by an amount of ca. 2% (from >99% to 97%). Based on the laboratory tests, one could conclude, that both peat and iron can be effectively used for the removal of HCH and CB and can be implemented as a filling in the PRB.

3.2. Pilot scale operation

The PRB constructed with iron chips in the first cartridge and peat and sand in the second was monitored for

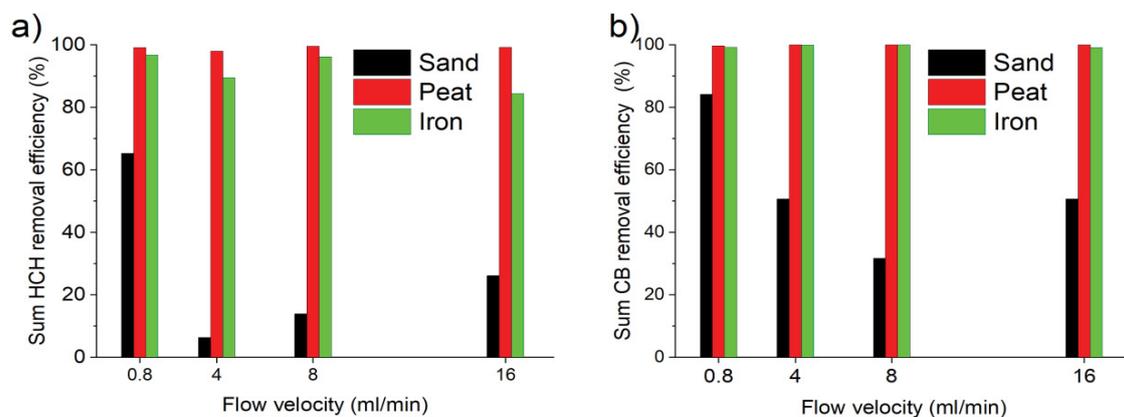


Fig. 5. Influence of the flow rate on (a) HCH and (b) CBs removal efficiency for columns filled with different materials (experimental setup: CT1; pore volumes: sand = 18.3 mL, peat = 18.4 mL, iron = 14.7 mL).

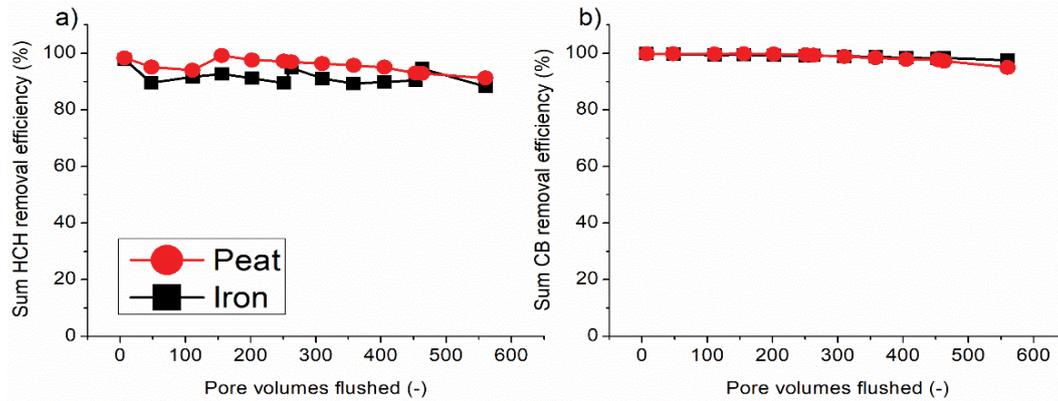


Fig. 6. Influence of the pore volumes flushed on (a) HCH and (b) CB removal efficiency (experimental setup: CT2).

112 d of operation. Similar to the lab determination, pH remained almost constant during the whole period of measurement and slightly increased compared to the inflow water. Conductivity as well remained stable throughout the process. However, the determined values are significantly (twice) higher than the samples used for the lab experiments, showing that water quality in the region where PRB is operating is different (Fig. 7).

The flow through the system was natural and uncontrolled. The flow rate showed no trend throughout the experiment but changes with a minimum of 226 L/d, a maximum of 467 L/d and a mean value of 380 L/d (Fig. 8a), reflecting the natural fluctuation. Such changes do not affect the efficiency of removing contaminants [40]. The laboratory tests showed that changing flow velocity (between 5 to 10 m/d) does not affect decontamination efficiency (Fig. 5). The inlet oxygen concentration showed values of 0.49 mg/L and 0.35 mg/L indicating anoxic conditions. Similarly, inside the system, the oxygen concentration remained between 0.33 and 0.57 mg/L, indicating anoxic conditions as well.

In Fig. 9, the efficiency of HCH and CB removal after treatment with only ZVI and the whole PRB system (ZVI + peat/sand) is shown. It seems that the adsorption capacity of peat plays a dominant role in HCH removal, as the treatment efficiency dramatically decreases in time as the empty capacity decreases. The removal ratio by iron itself is below 30% of inlet HCH, but its reactivity is significantly longer than peat. After 64 d, the removal efficiencies exchanged that the iron part of the PRB works still with an efficiency of around 30%, but overall efficiency is even lower. So, the peat capacity was oversaturated and HCH were released from the peat.

Different results were found for CB, where the overall efficiency mimics iron efficiency.

As the field experiment has its obvious limitations, such as lower number of measurements, it was not possible to perform detailed interpretation based on modelling (e.g., [43]). Therefore, simplified assessment had to be applied instead. The treatment capacity of the HCH removal system has been estimated as being proportional to the gap between the HCH load at the outflow and at the inflow (Fig. 8b). This gap gradually closes with time, as treatment capacity of the system is getting filled in by the contaminants removed

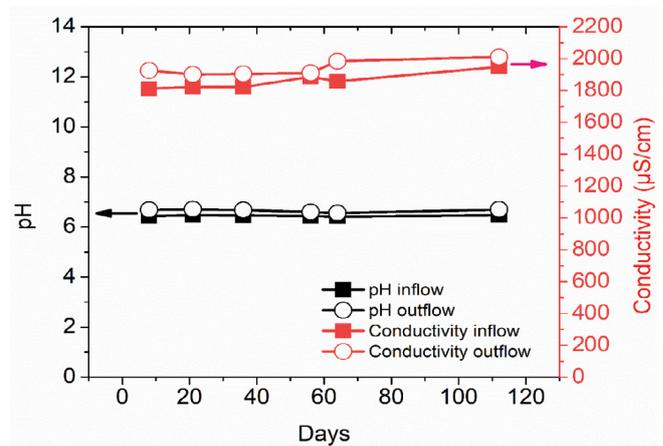


Fig. 7. The change of pH and conductivity of groundwater during PRB operation.

from groundwater. Simple estimation based on the assumption of the linear change of daily removed load of HCH in between the measurement days has given the total amount of HCH removed by the system equal to 127 mg till day 64 (in which the removal process in fact finished). However, a similar simple estimation for CBs (based on Fig. 8c) has given the total removed load of 1,550 mg CBs until day 64. This is an important lesson to remember while up-scaling in the future from the pilot to the full-scale PRB in Jaworzno.

Fig. 10 shows the removal efficiency of different HCH isomers. At the beginning of the PRB operation, γ -HCH and α -HCH seem to be the most susceptible to reduction (removal of 90% and 86%, respectively). These data are in accordance with the literature, where these isomers are reported to be the most unstable, following the trend $\gamma \approx \alpha > \beta > \delta$ as reported by Elliott et al. [32]. During the PRB operation, the efficiency of contaminant removal seems to be affected by the work time of the PRB. This can be caused by the passivation of iron [44] and by saturation of the active sites of peat. We have investigated the changes of ZVI after 112 d of service by SEM (Fig. S5). Indeed, the formation of nanoplates characteristic for ZVI oxidation was observed under high magnification (Fig. S5b), which indicates loss of

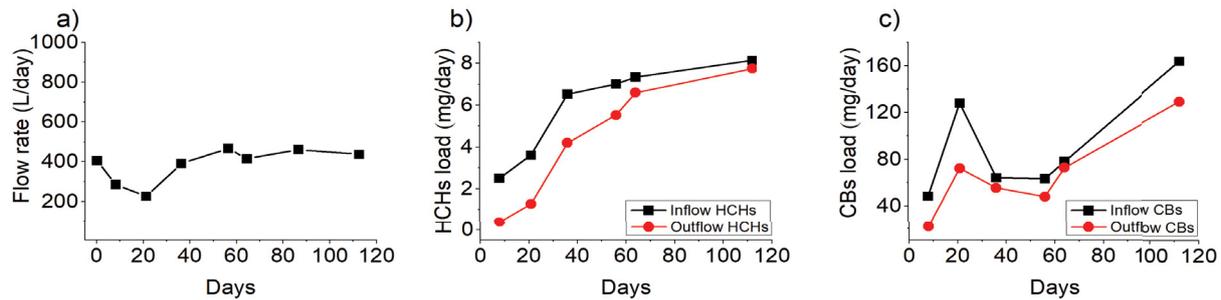


Fig. 8. Parameters of PRB, (a) the groundwater flow rate, (b) total HCHs and (c) CB inflow and outflow.

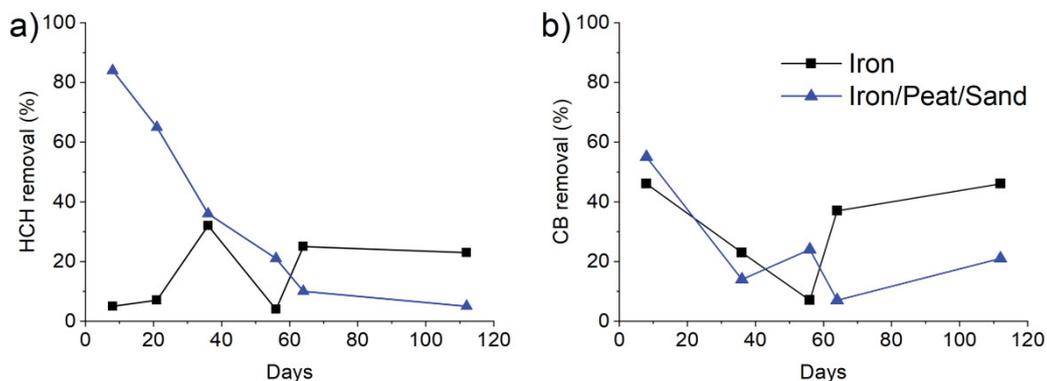


Fig. 9. The treatment efficiency of (a) HCHs and (b) CBs by using iron and peat/sand bed.

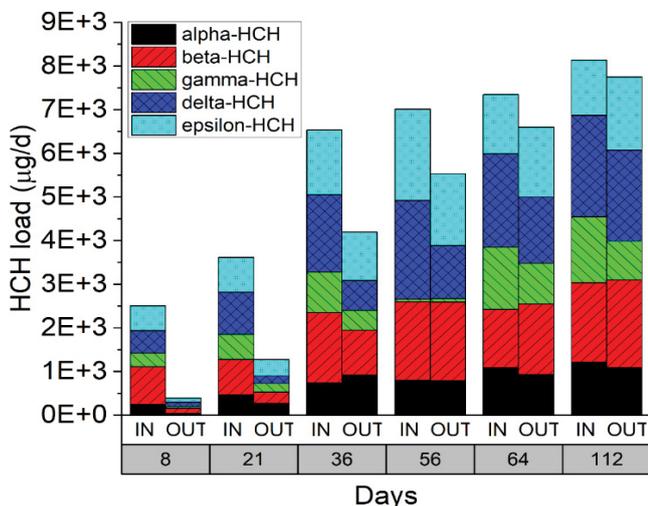


Fig. 10. Change of the concentration of individual HCH isomers in the inlet (IN) and outlet (OUT) of the PRB.

the reduction strength of the material. At the end (day 112) only γ -HCH was significantly affected by the PRB (removal of 42%).

Results of the study showed the process of the partial dechlorination of highly chlorinated benzenes present in the inlet like pentachlorobenzene (QCB), and tetrachlorobenzenes (TeCB) (Fig. 11). As shown in Fig. 11, biotransformation of HCH to chlorinated benzenes can occur, as well

as chemical reduction on Fe, which could be an additional source of (poly)chlorinated benzenes on-site [45]. According to Brahushi et al. [46], the main degradation pathway of CB under anaerobic and anoxic conditions is dichlorination, which causes the formation of lower-chlorinated benzenes. As a result, an increased proportion of dichlorobenzene (DCB) and trichlorobenzene (TCB) was observed in the effluent passing through PRB system (Fig. 11). In general, QCB and TeCB are almost completely removed, the portion of TCB is reduced only slightly and DCB dominated at the effluent (83% as an average over time). It was also observed, that TeCB and PCB completely disappeared from the treated water. According to Lu et al. [47] TeCB does not undergo hydrolysis due to the lack of hydrolyzable functional groups (SRC). The degradation of TeCB is therefore possible only in biological process. In order to ensure that the PRB treatment is a solution sustainable for a longer period, it is necessary to monitor and regulate the flow through the peat bed and periodically wash the bed to restore the sorbent capacity of the bed and to regulate the amount of biofilm formed.

Arvin et al. [48] has reported that in the anaerobic conditions the half-life of DCB can equal even to several years. Others presented that DCB are persistent in the environment and even after 12 months they could be detected in the column reactor throughout remediation tests [49].

Finally, monochlorobenzene and benzene were also detected during the treatment time, indicating complete dechlorination of the parent compounds. During the first 8 d of CB treatment, the effectiveness was high ca. 60% and

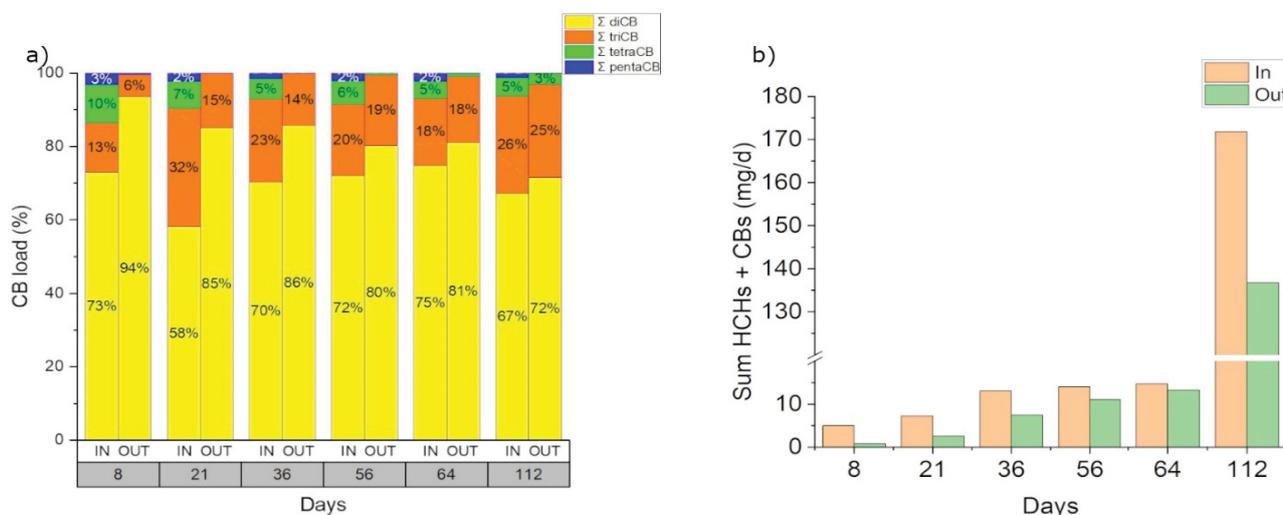


Fig. 11. (a) Change of the concentration of individual CB congeners in the inlet (IN) and outlet (OUT) of the PRB and (b) sum of HCHs and CBs in the inlet (IN) and outlet (OUT).

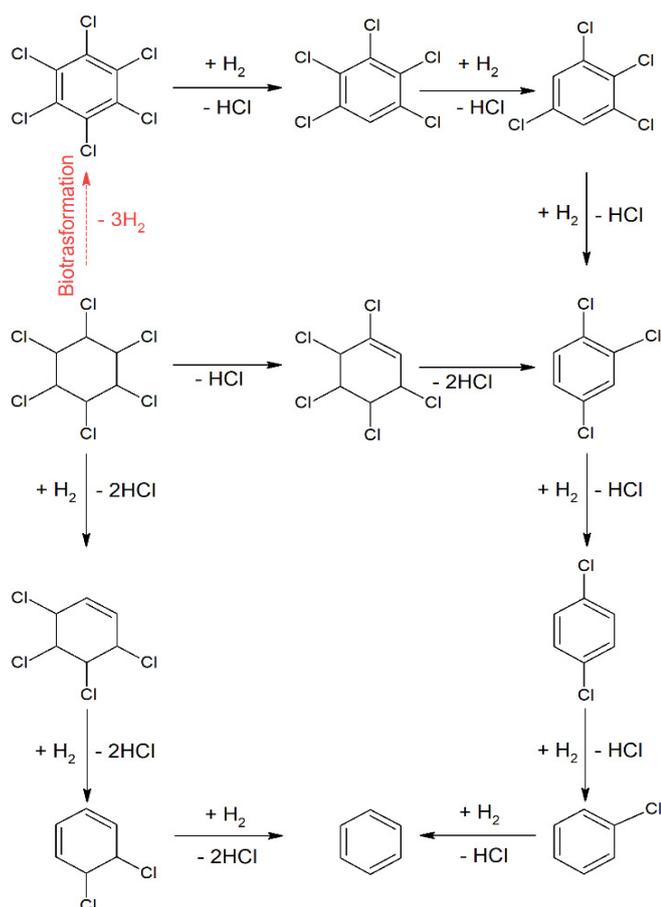


Fig. 12. Proposed transformation pathway of HCHs at the Jaworzno locality.

it was a result of the dechlorination process. According to Choi et al. [50], dechlorination prior to biodegradation turns out to increase the overall treatability.

Basing on our results, it can be concluded that the PRB consisting of iron and peat bed could be recommended for the treatment of groundwater polluted with chlorinated organic compounds such as CB.

HCH abiotic degradation includes two possible removal mechanisms (Fig. 12): dichloroelimination ($-2Cl$) and dehydrochlorination ($-HCl$) [51]. HCH by the dichloroelimination forms 3,4,5,6-tetrachlorocyclohexene, which can be further reduced to 3,4-dichlorocyclohexadiene and by a second dichloroelimination to benzene. The second pathway, dehydrochlorination, relies on a formation of 1,3,4,5,6-pentachlorocyclohexene, and further 1,2,3- and 1,2,4-trichlorobenzenes. The dechlorination goes finally to the same product – benzene [33]. Moreover, both of these pathways can be induced by Fe^0 . Our results showed the increasing concentration of less chlorinated cyclohexane with the time of process treatment induced by the adsorption process and dehalogenation in the reactor.

It should also be noted that biotic transformation of HCH to benzene may occur, as reported by Lian et al. [52].

4. Conclusions

This paper presents a rare example of various HCH isomers removal from groundwater by PRB filled with iron chips and peat. The laboratory experiments confirmed that both peat and iron can be successfully used for the treatment of HCH isomers *in situ*. The pilot system showed significant reduction efficiency of HCH at the beginning of the study, which gradually decreased to zero around day 64 of operation. The possible reason is that due to the complex contamination of groundwater, the PRB capacity gets reduced significantly faster compare to water contaminated with HCH only. This is an important lesson to remember while up-scaling from the pilot to full-scale PRB, so that the treatment capacity of full-scale installation should be adjusted not only to HCHs but also other organic contaminants (such as CB).

HCH degradation includes two possible removal mechanisms: dichloroelimination (-2Cl) and dehydrochlorination ($-\text{HCl}$), both induced by Fe^0 . The presence of benzene in the outlet indicated that biotic transformation of HCH to benzene may also occurred in the PRB system.

The results show also the passivation process of iron chips which caused the deactivation of zero-valent iron and decreasing of treatment efficiency. To improved the efficiency removal of HCH and CBs by zero-valent iron a pretreatment process may be required. Further research in this area should be done.

Nevertheless, the results of pilot-scale application of PRB at Jaworzno site in Poland are providing a sound quantitative base for future designs of full-scale PRB for sites with groundwater contaminated with organochlorine pesticides contamination.

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Supplementary information

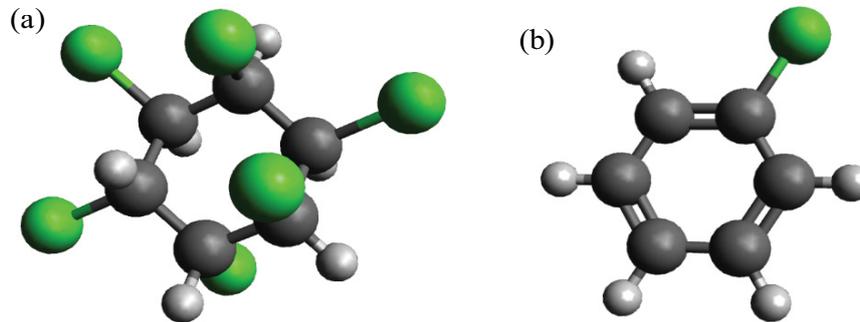


Fig. S1. 3D models of (a) lindane and (b) 1-CB (atoms: green – Cl, dark – carbon, white – hydrogen).

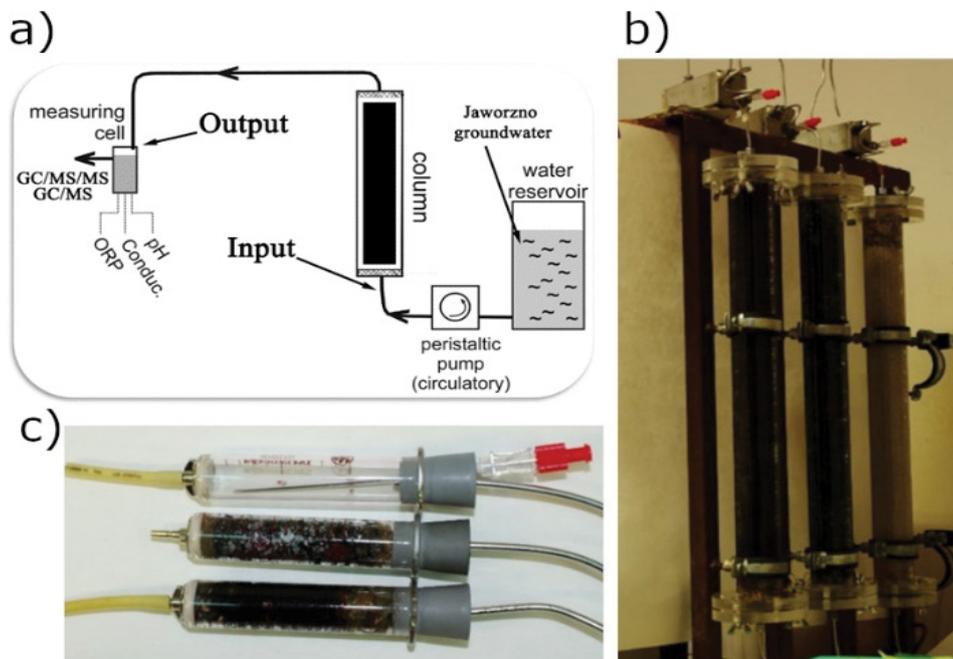


Fig. S2. (a) Experimental design of the column tests, (b) CT1, columns filled with (peat, iron and sand) and (c) CT2, smaller columns for the second set of experiments.

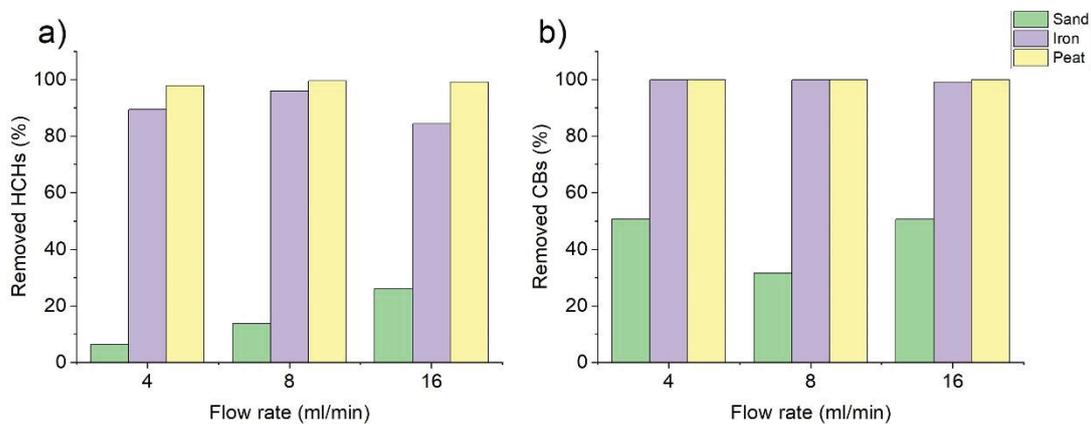


Fig. S3. (a) Removed HCHs and (b) removed CBs through different columns.

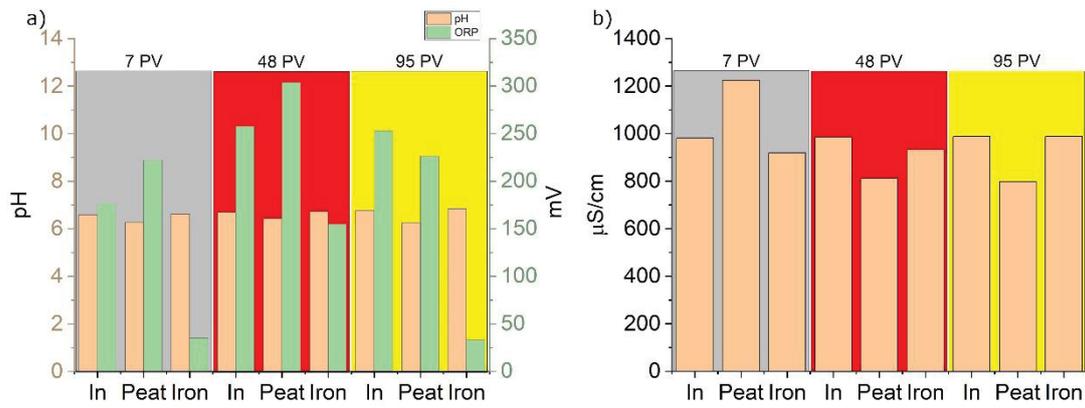


Fig. S4. Influence of (a) pH and ORP and (b) conductivity of the tested column.

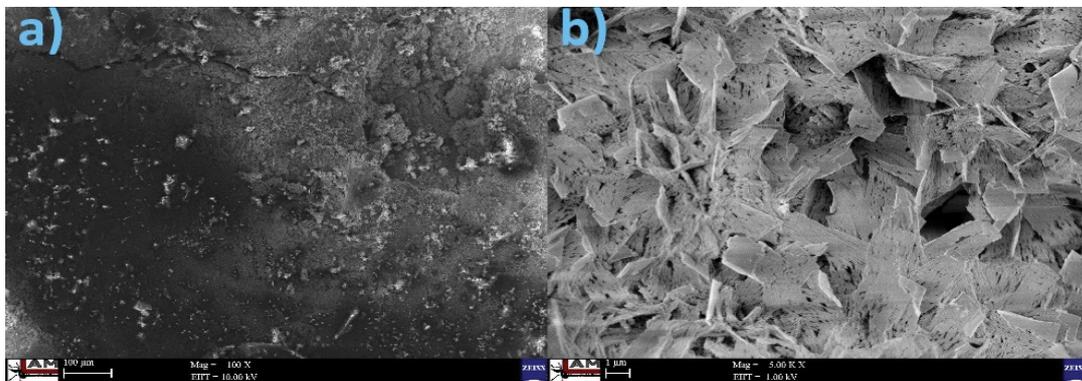


Fig. S5. SEM pictures of iron samples after use (112 d) with different magnifications (a) 100 X and (b) 5.00 K X.