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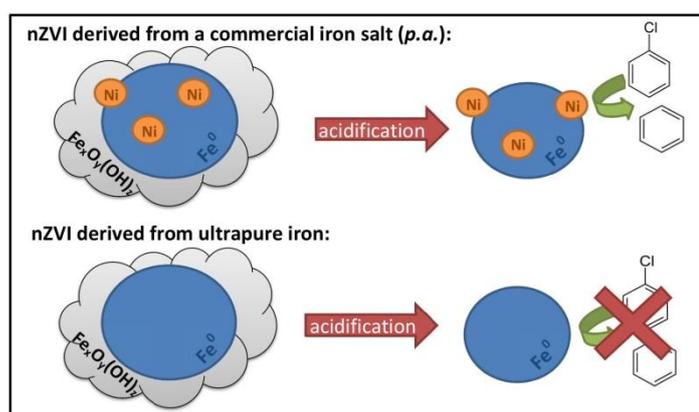
The role of nickel traces in fine chemicals for hydrodechlorination reactions with zero-valent iron

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Abstract

Two different types of nanoscale zero-valent iron (nZVI) were synthesized according to the same standard procedure: reduction of dissolved Fe(II) with sodium borohydride – one starting from a



commercial iron salt having *pro analysi* (*p.a.*) purity, and another from microscale iron with an extraordinary degree of purity, derived from the decomposition of iron pentacarbonyl. The ZVI samples exhibited similar hydrodechlorination activities towards hexachlorobenzene as an example for higher chlorinated aromatics and carbon tetrachloride as an aliphatic model substance. However, only the sample derived from the iron salt (*p.a.*) was able to dechlorinate monochlorobenzene (MCB) at a measurable rate whereas the nZVI derived from the very pure precursor (nZVI_{pure}) did not show this ability. Closer inspection lead us to the finding

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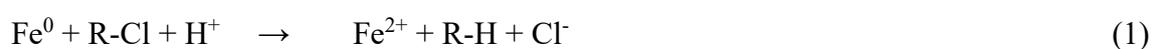
that the observed activity could be attributed to a Ni content as small as 0.005 wt.-% of the former nZVI sample which was named nZVI_{impure} accordingly. It was demonstrated that such a small amount of Ni develops its catalytic activity for the hydrodechlorination of MCB only under acidic conditions. Although acidic conditions might not be common for studies with ZVI, higher Ni contents (e.g. of reagent grade iron sources) could have an influence under ambient conditions.

Keywords

Hydrodechlorination, zero-valent iron, nickel traces, monochlorobenzene

1. Introduction

For more than two decades, zero-valent iron (ZVI) has been used as a versatile reducing agent for a broad spectrum of chemicals in groundwater [1-5]. To maximize the reduction efficiency, many variations of ZVI have been investigated, e.g. nanoscale particles with larger specific surface areas [3, 6-14], ZVI combined with sorbents such as activated carbon [15-20] or doped with catalytically active noble metals or Ni [15, 20-27]. One of the major target groups are chlorinated organic compounds which react with ZVI according to equation (1):



Regarding the reactivity of ZVI towards organic compounds, there has to be distinguished between aliphatic and aromatic substances. It is known that the cleavage of aromatic carbon-chlorine bonds driven by electron transfer proceeds with more difficulty than that of aliphatic ones [28]. Therefore, chlorinated aromatic compounds are commonly degraded with bimetallic particles because the desired reaction is catalyzed by metals which provide hydrogenation activity, such as Pd, Pt and Ni [6, 21, 22, 24, 27, 29, 30]. Their mode of action is based on two processes: first, those metals exhibit higher standard redox potentials (E^0) than iron, hence they function as a cathode whereas ZVI acts as an anode. Thus, a local galvanic cell is formed and the corrosion of the reactive metal is enhanced. Second, the noble metals can stabilize reactive intermediates, e.g. atomic hydrogen, through surface adsorption [31]. While all of the above has been elaborately described over the years, we still came across some peculiarities when evaluating results from published studies: there are publications which state the observation of the complete dechlorination of aromatic rings with undoped nanoscale ZVI (nZVI) [6, 13, 32-34]. Especially the work of Poursaberi *et al.* [33] attracted our attention because they explored the reactivity of nZVI under quite unusual conditions: their application of an initial pH of 2 rapidly consumes the metal by dissolution but might also provide a highly reactive iron surface. Under these conditions, Poursaberi *et al.* [33] reported the complete dechlorination of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane

(DDT) within 4 h where 1,1-diphenylethane was the only product detected. This and other publications motivated us to investigate the key question: is pure nZVI – without any additives – able to reduce chloroaromatic compounds in which only one chlorosubstituent is connected to the benzene ring (Cl-C_{aromatic})? To closely investigate this query, we examined two different nZVI samples: ZVI_{impure} derived from a commercial iron salt (analytical grade) and ZVI_{pure} derived from a microscale iron with an extraordinary degree of purity (from the decomposition of iron pentacarbonyl). To characterize their hydrodechlorination activities, the degradation of carbon tetrachloride (CCl₄) as an aliphatic model substance, hexachlorobenzene (C₆Cl₆, HCB) as an example for higher chlorinated aromatics and monochlorobenzene (C₆H₅Cl, MCB) as a representative for lower chlorinated aromatics was explored in batch reactions. As our research aim is rather fundamental, our experiments include strongly acidic conditions, which are usually not appropriate for the application of ZVI.

2. Materials and Methods

2.1. Chemicals

Ferrous sulfate heptahydrate (99.5 %, *p.a.*), nickel(II)-sulfate heptahydrate (≥ 99 %), ultrapure iron (> 99 %), sodium borohydride (≥ 98.0 %), sodium hydroxide (> 99 %, *p.a.*), nitric acid (60 wt-%, ultrapure), hydrochloric acid (30 wt-%, ultrapure), methanol (99.8 %), acetone (gas chromatographic grade, SupraSolv[®]), benzene (gas chromatographic grade, SupraSolv[®]) and toluene (99.8 %) were obtained from Merck, Germany. Monochlorobenzene (MCB) (≥ 99.5 %) was purchased from Fluka, Germany. Carbon tetrachloride (≥ 99.9 %), hexachlorobenzene (HCB) (99 %) and pyrene (99 %) were obtained from Sigma-Aldrich, Germany. 1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) (99.3%) was from Institute of Organic Chemistry (ANOPOL 6, Warsaw, Poland). Ultrapure sulfuric acid (95 %) was obtained from Chemsolute, Germany, and diluted to the desired concentration with high-purity water (conductivity $0.05 \mu\text{S cm}^{-1}$) prepared with the Simplicity[®] ultrapure water system from Merck, Germany.

2.2. Preparation of the nZVI particles and batch experiments

The nanoscale iron particles were prepared as previously described in literature [6] with slight modifications. Primary differences compared to the previous method were that shaking was used rather than magnetic stirring and NaBH_4 was added in a solid form rather than as an aqueous solution. In this study, 50 mL of a 0.36 M solution of ferrous sulfate were mixed with the triple molar amount of NaBH_4 and shaken until the hydrogen and heat evolution subsided. The resulting nZVI suspension was centrifuged and the precipitate was washed once with deoxygenated, deionized water. Due to noticeable heavy metal impurities of the precursor material, this type of nZVI is marked “nZVI_{impure}” in the following. For nZVI with a lower content of impurities, called “nZVI_{pure}”, ultrapure iron, produced by the decomposition of iron pentacarbonyl, was dissolved in sulfuric acid diluted with high-purity water. After the adjustment of the pH value with NaOH, the ferrous solution was processed as described

beforehand. To generate nZVI with a defined Ni content, an aliquot of an aqueous NiSO₄ solution was added to the dissolved iron precursor prior to the reduction with borohydride. In each case, 1.2 g of the freshly synthesized nanoscale particles were transferred in the wet state under argon flow to a screw neck bottle with 200 mL of deoxygenated high-purity water and 40 mL of argon headspace. These batch reactors were closed with a Mininert[®] valve (Supelco) and placed in an ultrasonic bath for 10 min in order to dissipate agglomerated iron particles. MCB and carbon tetrachloride were dissolved in methanol; DDT and HCB were dissolved in acetone. To start the dechlorination reaction ($t = 0$), an aliquot of the particular stock solution was added to the reaction mixture and the vessels were continuously shaken at ambient temperature, either on an end-to-end rotary shaker with 11 revolutions per minute (rpm) or on a horizontal shaker with 240 motions per minute (mpm). At the beginning of the reaction, the pH of the aqueous nZVI suspension was 8.8 ± 0.1 . For experiments in the lower pH range, the reaction mixture was acidified with sulfuric acid (50 wt.-%). Blank experiments were conducted without any iron particles. All dechlorination experiments were conducted at least twice.

2.3. Analytical methods

The morphology of the nZVI samples was analyzed with a Zeiss Orion NanoFab helium ion microscope. The beam current amounted to 0.7 pA, the ion landing energy was 25 kV. For imaging secondary electrons were collected using an Everhard-Thornley detector.

The concentrations of educts and products were measured by means of gas chromatography-mass spectrometry (GC-MS). The GCMS-QP2010 (Shimadzu) used was equipped with a HP-5MS column (30 m \times 0.32 mm \times 0.25 μ m). For sufficiently volatile compounds (Henry's law coefficients $K_H > 0.1$, CCl₄ and C₆H₅Cl), 25 μ L gas samples from the headspace above the reaction suspension were injected into the GC ($T_{\text{injector}} = 150$ °C, $T_{\text{column}} = 60$ °C). For higher-chlorinated compounds with lower K_H values (HCB and DDT), the aqueous suspension was extracted for 30 min with 10 mL toluene using pyrene as an internal GC standard.

Furthermore, the iron was completely dissolved in H_2SO_4 (5 wt-%) in order to release adsorbates enclosed in the iron oxide/hydroxide surface layer of the particles. As the acidic extraction was performed in the presence of the extracting agent, it was assumed that the target compounds (HCB and DDT) were instantly absorbed by the extractant and thus protected against further reaction. 2 mL of the extract were then concentrated to around 100 μL , of which 1 μL was injected into the GC-MS at $T_{\text{injector}} = 280\text{ }^\circ\text{C}$. The separation was carried out with the following temperature program: from 60 $^\circ\text{C}$ (3 min) to 280 $^\circ\text{C}$ (10 min) at a heating rate of 20 K min^{-1} .

The pH value was measured with a glass electrode (InLab[®] Micro, Mettler Toledo) and a pH meter (MP225, Mettler Toledo). Fig. 1 shows the experimental setup in order to follow the pH development of the nZVI suspension under inert conditions on the horizontal shaker over time.

In order to keep the nZVI suspension oxygen-free during pH measurements, the pH electrode (a) was immersed through an air-tight septum (c) into the reaction vessel (b) which was put on a horizontal shaker (d). The pH electrode was also fastened (e) on the horizontal shaker and moved with the same frequency as the vessel. On the end-to-end rotator, the setup had to be changed: the batch reactor was periodically shortly paused from shaking and opened in order to insert the pH electrode.

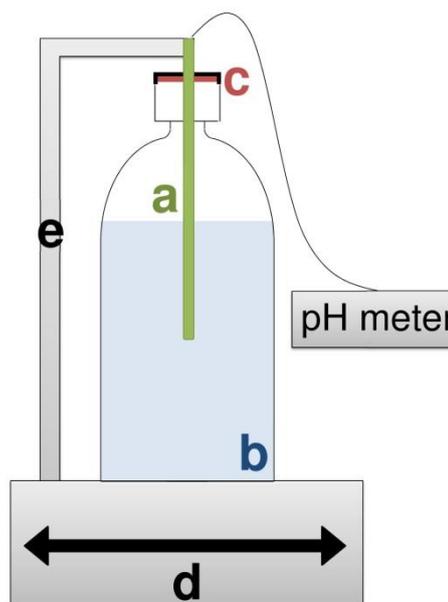


Fig. 1. Experimental setup for the time-resolved measurement of the pH evolution of the nZVI suspension under inert conditions. Symbols (a) to (e) are elucidated in the text.

Dissolved Fe species were measured photometrically 30 min after acidification when the pH was neutral again. For sampling, the particulate iron was precipitated with a magnet and an aliquot of the clear solution was withdrawn, diluted and mixed with Spectroquant[®] for

bivalent and trivalent iron (Merck). The absorption of the violet iron complex was measured with a GENESYS 20 photospectrometer (Spectronic) at a wavelength of 562 nm.

Contents of metal impurities of the two mainly used nZVI types (“pure” and “impure”) were determined by means of mass spectrometry with inductively coupled plasma excitation (ICP-MS) using the Element XR (Thermo). For this purpose, 300 μL nitric acid (60 wt-%) and 900 μL hydrochloric acid (30 wt-%) were added to 50 mg of the dry nZVI sample. A blank sample consisted of the acids only. These samples were further diluted with an acid mixture containing 0.2 wt-% HNO_3 , 0.12 wt-% HCl and 0.0006 wt-% HF to a total volume of 5 mL and treated in an ultrasonic bath for 20 min. Afterwards, the iron concentration was further decreased to 1 g L^{-1} by adding the diluted acid mixture specified above. For calibration, indium was used as an internal standard.

3. Results and Discussion

3.1. Reactivities of the different nZVI samples – pure and impure

At first, the morphology of the two nZVI types – “pure” and “impure” – was characterized by means of helium ion microscopy (Fig. 2). Both samples look very similar: they consist of

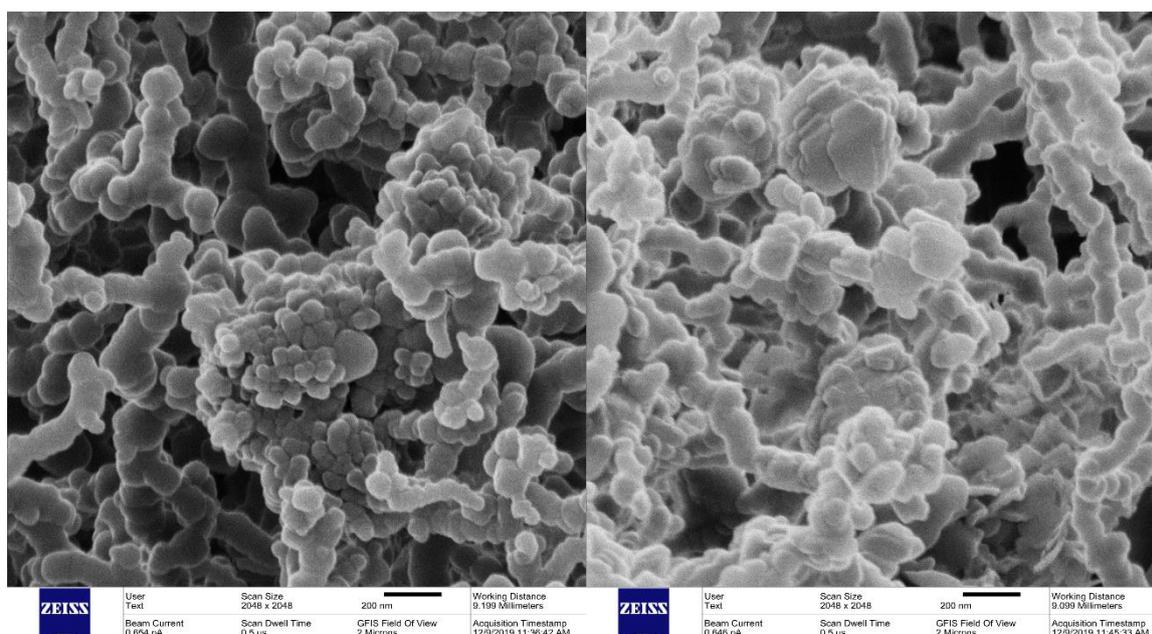


Fig. 2. Helium ion microscopy of nZVI_{impure} (left) and nZVI_{pure} (right)

rather spherical primary particles which form chain-like aggregates. The mean diameter of the observed primary particles is (91 ± 24) nm for nZVI_{impure} and (92 ± 15) nm for nZVI_{pure} respectively. This kind of morphology and size range is well known from literature [6, 7, 9, 10, 13, 24, 30, 35].

The hydrodechlorination activities of the two nZVI samples were initially investigated by the degradation of CCl₄ as an aliphatic model substance. For the kinetic evaluation, a pseudo-first order model was chosen as it is common in literature for reactions of chlorinated organic substances with ZVI [2, 5, 9, 10, 18, 26, 29, 35-37]. The observed rate constants k_{obs} were 1.3 h^{-1} for nZVI_{impure} and 1.1 h^{-1} for nZVI_{pure} and thus in the same range for both nZVI types (Fig. S1). The reactivities towards HCB as an example for a higher chlorinated aromatic compound were about 4 orders of magnitude lower: after 16 days, only 6 % of HCB was converted to pentachlorobenzene by both nZVI samples (Fig. S2). The large difference in dechlorination rates of CCl₄ and HCB was expected due to the different dechlorination mechanisms. Aliphatic compounds undergo a dissociative electron transfer, meaning the latter occurs concerted with the C-Cl bond cleavage. The dehalogenation of aromatic compounds, however, proceeds according to a two-step mechanism where a radical anion results after the electron transfer as a true intermediate [28].

Furthermore, it is noticeable from Fig. S2 that no traces of tetrachlorobenzene were detected. This could be assigned in part to the deactivation of nZVI after longer contact times due to the formation of an iron oxide/hydroxide layer [29, 37]. Another explanation for the stoppage of dechlorination beyond pentachlorobenzene is the decreasing electron affinity of the chlorobenzenes with decreasing number of chlorosubstituents [38, 39]. At this point, it is important to state that the two nZVI samples behaved very similarly in the preceding experiments. Obviously, trace contaminants do not play a significant role here. The nZVI reactivities towards less chlorinated aromatics were tested by means of dechlorination experiments with MCB. The latter can be considered as the least reactive probe compound in

the group of chlorinated aromatics. The electron affinity of MCB ($\text{Ph-Cl} + e^- \rightarrow [\text{Ph-Cl}]^-$) is about -0.14 eV [38, 39]. It increases with increasing number of chlorine substituents at the benzene ring up to $+0.98$ eV for HCB. Even the monochlorinated biphenyls have significantly higher electron affinities ($+0.19$ to $+0.24$ eV) than MCB [38, 39]. If one assumes that the transfer of the first electron is the rate-determining step in the dechlorination reaction of aromatics, MCB is clearly the least reactive compound in this substrate group.

At the ambient pH value (8.8) of the nZVI suspensions ($c_{0,\text{nZVI}} = 6 \text{ g L}^{-1}$), no benzene formation was detected when monitored over at least eight days for both nZVI samples (limit of detection for $c_{\text{Benzene}}/c_{\text{MCB}} \leq 10^{-5}$, data not shown here). In order to increase the reactivity of nZVI, the reaction medium was acidified with sulfuric acid in the following experiments. This should lead to an increase of the hydrodechlorination activity as well as the iron corrosion rate [37].

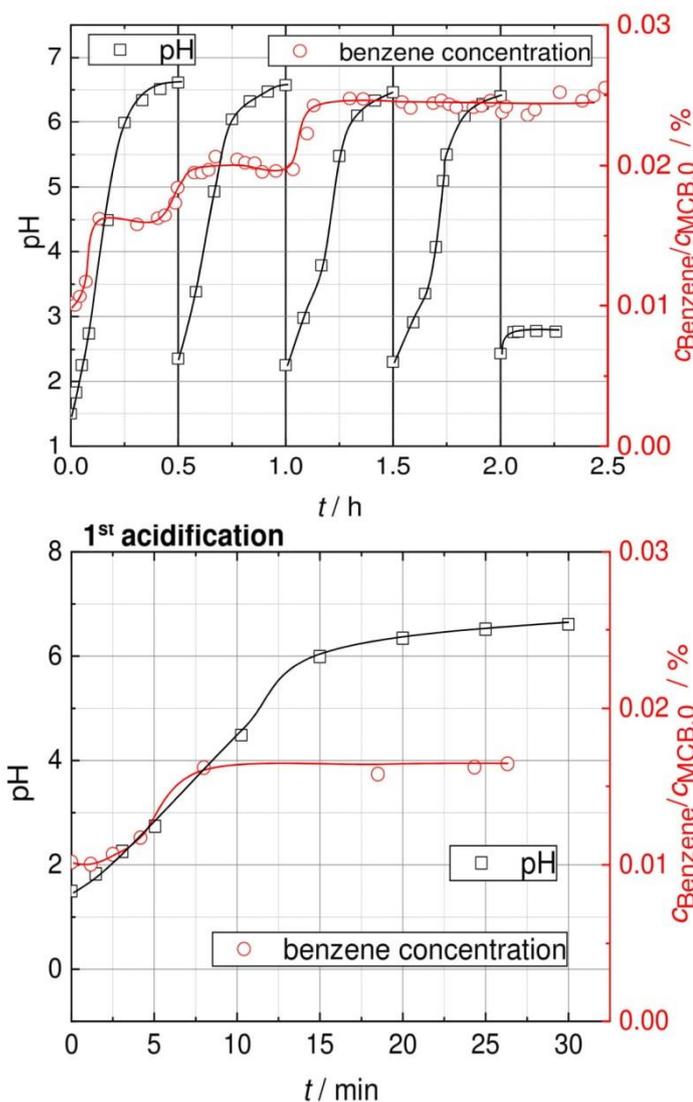


Fig. 3. *Top:* Formation of benzene during the reaction of MCB with $\text{nZVI}_{\text{impure}}$ depicted along with the pH value; half-hourly acidifications to $\text{pH} \approx 2$ were performed with H_2SO_4 , (represented by the vertical lines); curved lines are a guide for the eyes only; $c_{0,\text{MCB}} = 100 \text{ mg L}^{-1}$, $c_{0,\text{nZVI}} = 6 \text{ g L}^{-1}$, $1.5 < \text{pH} < 6.6$, horizontal shaker 240 rpm
Bottom: Higher time-resolution of the first acidification.

As the pH rose rapidly after acidification due to iron dissolution, the suspension was re-acidified periodically every half hour. In order to gain a closer insight into the correlation between the pH value and hydrodechlorination rates, these two parameters were closely investigated for nZVI_{impure}. From Fig. 3 it can be seen that 0.015 % of the initial MCB was dechlorinated to benzene during the first three acidic periods in the presence of nZVI_{impure} (please note the trace impurity of 0.01 % of benzene of the MCB used). After the 4th acidification, no additional benzene was formed although the nZVI was not completely dissolved until the 5th acidification step as can be deduced from the exhausted buffer capacity. This observation indicates that the formation of benzene is not ensured in the presence of nZVI. Furthermore, the benzene evolution strongly correlates with the pH value: benzene is formed only under acidic conditions in the pH window from about 2 to 4.5, whereas a stagnation of the dechlorination reaction was observed at higher pH values and a lag period below pH 2. In order to investigate this observation further, an experiment was conducted where the reaction suspension was acidified only to pH₀ = 3 in the first acidification and probed for product formation. However, no significant benzene formation was observed under these conditions (data not shown here). We conclude that a kind of ‘surface cleaning’ of the nZVI could be necessary for its hydrodechlorination activity. Apparently, pH < 3 is necessary for such a cleaning step. Above pH ≈ 4.5, presumably the precipitation of iron oxide and hydroxide species covers the particle surface again and inhibits further hydrodechlorination. The favored pH range (2 - 4.5) was only available during a short time window when the nZVI suspension was shaken vigorously on the horizontal shaker.

In order to prolong the time frame where the pH increases from 2 to 4.5, the shaking intensity was decreased. This was realized on an end-to-end rotator in order to avoid precipitation of nZVI agglomerates. In this setup, the pH indeed rose more slowly than on the horizontal shaker (Fig. 4). The

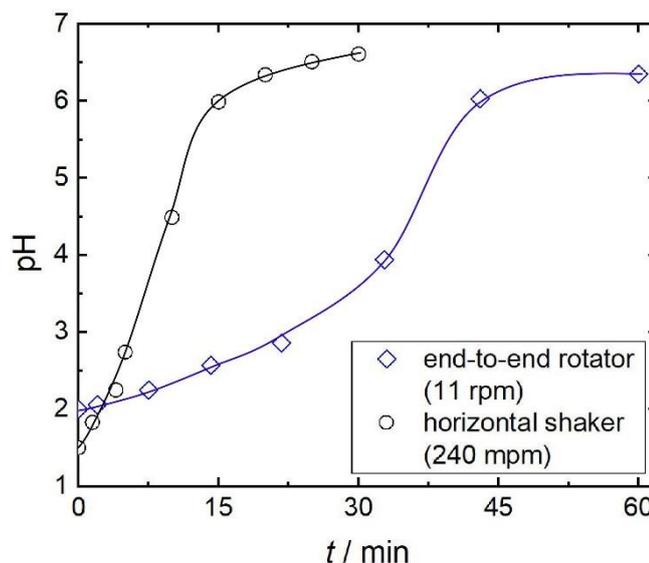


Fig. 4. Rise of the pH value after acidification of the suspension with H_2SO_4 , where the batch reactor was fixed on either a horizontal shaker (240 mpm) or an end-to-end rotator (11 rpm); lines are a guide for the eyes only; $c_{0,\text{nZVI}} = 6 \text{ g L}^{-1}$.

time span for the pH range from 2 to 4.5 expanded from about 7 min to 35 min. This elongation effected a significantly higher benzene yield of

0.25 % already after the first acidification, which increased to almost 2 % after 4 acidification steps (Fig. 5, left).

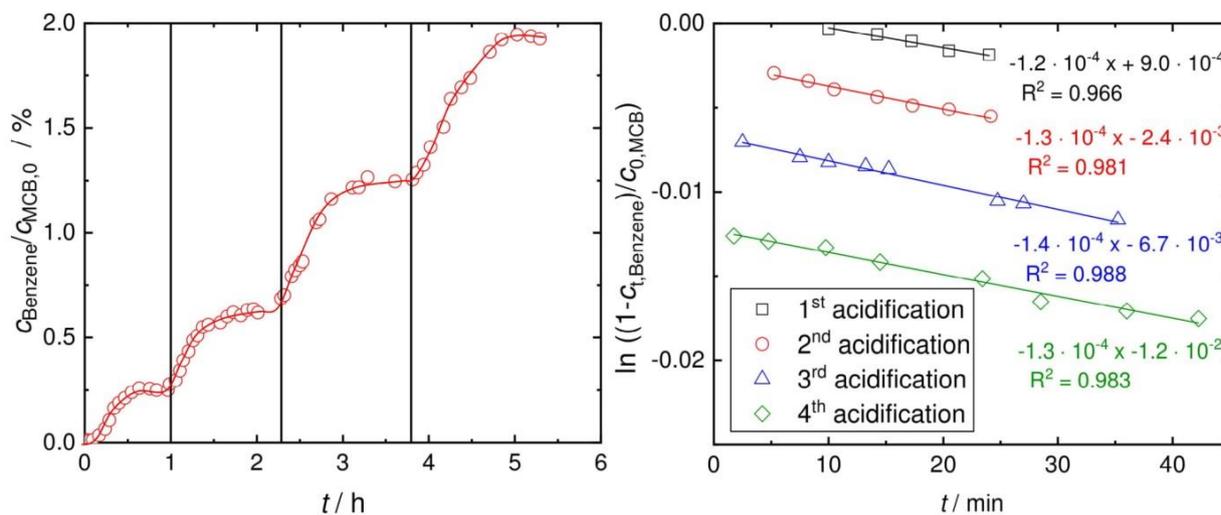


Fig. 5. *Left:* Benzene formation during the reaction of MCB with $\text{nZVI}_{\text{impure}}$; acidifications to $\text{pH} \approx 2$ with H_2SO_4 , are represented by the vertical lines;

Right: First order kinetics of the benzene formation with $\text{nZVI}_{\text{impure}}$ in four subsequent acidification steps to $\text{pH} \approx 2$ with H_2SO_4 ;

$c_{0,\text{MCB}} = 100 \text{ mg L}^{-1}$, $c_{0,\text{nZVI}} = 6 \text{ g L}^{-1}$, $1.5 < \text{pH} < 6.6$, end-to-end rotator 11 rpm.

As depicted in Fig. 5, the experimentally obtained rate constants for the benzene formation are $(1.3 \pm 0.1) \cdot 10^{-4} \text{ min}^{-1}$, i.e. identical throughout all four acidification steps. The apparent constancy of the dechlorination rates is remarkable taking into account that (i) the nZVI concentration decreased from the first to the fourth reaction period and (ii) the proton concentration decreased within every reaction period by more than two orders of magnitude. The amount of nZVI consumed per acidification step was determined photometrically and is

shown in Fig. 6. After the first acidification, 1.3 g L^{-1} iron can be found as dissolved species in the nZVI suspension. However, during the following acidifications, including the 4th one, the dissolved Fe content in the solution does increase only slightly. Therefore, it is

assumed that part of the initially dissolved Fe precipitates again as iron-

(hydr)oxide species at neutral pH. After the last acidification the Fe^0 content of the particles presumably is so low that the pH does not increase above 3 anymore (cf. Fig. 3) and thus the iron species remain in the dissolved state. Unfortunately, it was not possible to determine the Fe^0 content of the iron particles with this procedure.

Nevertheless, the apparent independence of the hydrodechlorination rates of the proton concentrations over two-and-a-half pH units (Fig. 5, right) is a curious observation which deserves closer inspection. Possible rate-controlling steps for the observed hydrodechlorination reaction are an electron transfer or a hydrogen attack from the ZVI

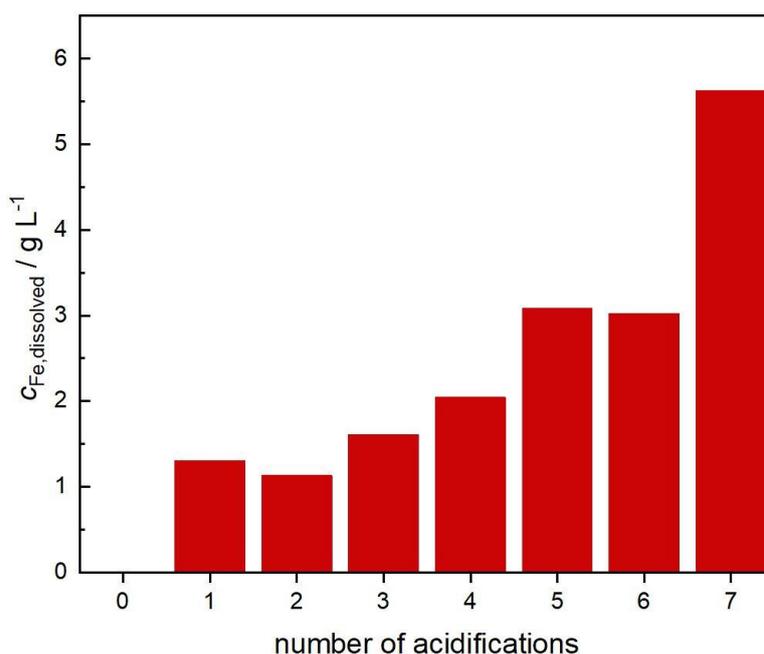


Fig. 6. Dissolved Fe content after stepwise acidification of the $\text{nZVI}_{\text{impure}}$ suspension; $c_{0,\text{nZVI}} = 6 \text{ g L}^{-1}$, $1.5 < \text{pH} < 6.6$ (sampling at $\text{pH} = 6.6$), end-to-end rotator 11 rpm.

surface to the adsorbed substrate molecule. It is assumed that surface-bound hydrogen species (H^*_{surface}) play a key role for the hydrodechlorination of aromatic substrates [25, 34, 40] however in our case their precursors $H^+_{\text{dissolved}}$ do not affect the reaction rate. This can possibly be explained by a saturation phenomenon: All reactive surface sites are most likely charged to capacity by H^* in the investigated pH range. This assumption, as well as the observation that the benzene formation is not guaranteed in the presence of $nZVI_{\text{impure}}$ (cf. Fig. 3, 4th acidification step), both indicate that additional active surface sites other than the iron-based ones must be responsible for the observed reactivity of $nZVI_{\text{impure}}$. In addition, the analogue of the experiment shown in Fig. 3, performed with MCB and $nZVI_{\text{pure}}$, showed no significant benzene formation beyond the range of background scattering ($(0.011 \pm 0.002)\%$, Fig. 7). This leads to the conclusion that pure $nZVI$ is not able to dechlorinate MCB in aqueous suspension, irrespective of the applied pH conditions. The low but significant hydrodechlorination activity of $nZVI_{\text{impure}}$ indicates that one or several of the trace impurities in this $nZVI$ sample are key components for the observed dechlorination reaction. This is known for noble metals such as palladium and platinum, which however can be ruled out as impurities according to the manufacturer's information on the $FeSO_4 \cdot 7 H_2O$ used as iron precursor. From literature it is known that also the implemented boron content due to the applied $nZVI$ synthesis (reduction with $NaBH_4$) can promote the hydrogenation activity of the generated $nZVI$ [10]. However, in the present work both $nZVI$ samples were prepared in the same way therefore the boron content is not a plausible reason for different chemical activities.

Other metal impurities were determined by means of ICP-MS analysis. Tab. 1 shows that the foreign metal contents of $nZVI_{\text{pure}}$ are indeed very low, as they are all ≤ 2 ppm. On the contrary, $nZVI_{\text{impure}}$ contains significantly higher amounts of metal impurities. From the three main detected contaminants, Ni is known for its hydrogen activation and hydrodechlorination activity [36, 41] and is therefore suspected to be the active component in the observed hydrodechlorination reaction.

Tab. 1. Trace metal contents of the synthesized $nZVI$ samples (pure and impure) determined by ICP-MS and specified in $\mu\text{g g}^{-1}$.

	$nZVI_{\text{pure}}$	$nZVI_{\text{impure}}$
[Mn]	0.74	410
[Co]	0.02	10
[Ni]	2	45

To check if a small content of around 50 ppm Ni can develop the observed

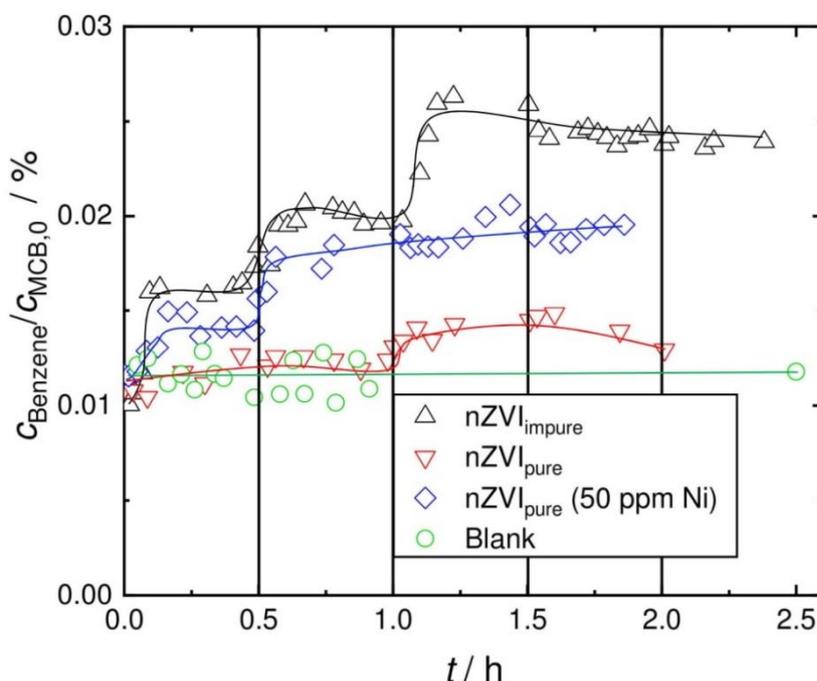


Fig. 7. Formation of benzene during the reaction of MCB with $nZVI_{\text{impure}}$, $nZVI_{\text{pure}}$ and $nZVI_{\text{pure}}$ (+50 ppm Ni) depicted along with a blank sample without any $nZVI$; half-hourly acidifications to $\text{pH} \approx 2$ were performed with H_2SO_4 , (represented by the vertical lines); solid lines are a guide for the eyes only; $c_{0,\text{MCB}} = 100 \text{ mg L}^{-1}$, $c_{0,nZVI} = 6 \text{ g L}^{-1}$, $1.5 < \text{pH} < 6.6$, horizontal shaker 240 rpm.

hydrodechlorination activity, a defined amount of NiSO_4 was added to the precursor solution of $nZVI_{\text{pure}}$ prior to the reduction with NaBH_4 (cf. section 2.2). As depicted in Fig. 7, a

significant dechlorination activity of nZVI_{pure} (+50 ppm Ni) was observed, which was in the same order of magnitude as for nZVI_{impure}. Based on this finding, the observed hydrodechlorination activity of nZVI_{impure} towards MCB is assigned to the small Ni content of this nZVI sample derived from its precursor salt. It is clear that the herein described conditions, under which the activity of a contamination of 50 ppm Ni was observed, might not be relevant for most of the nZVI applications. However, higher Ni contents (e.g. of reagent grade iron sources) could have an influence even under ambient pH conditions. As described in literature, already an amount of 0.5 wt.-% of Ni related to the Fe shows a significant catalytic effect on the hydrodechlorination of PCBs under ambient conditions [42].

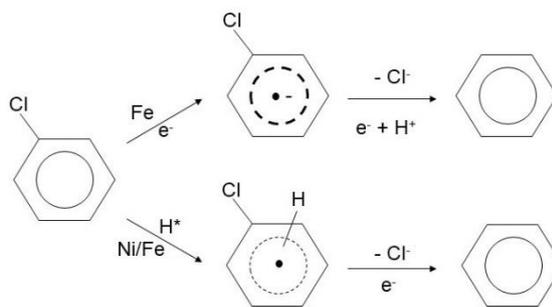
3.2. Reconsidering findings from literature studies

Based on the preceding findings, it might also be useful to reconsider literature reports on interactions between ZVI and chlorinated aromatic compounds. Most of the literature studies were conducted with polychlorinated biphenyls (PCBs). The obtained results are, however, quite divergent. Characteristic examples are the two studies by Lowry and Johnson [9] and by Sevcu *et al.* [13]. They used the same type of nZVI (dissolved ferrous iron reduced with borohydride; specific surface area $\approx 35 \text{ m}^2 \text{ g}^{-1}$) to degrade similar substrates (trichlorobiphenyls) in a comparable experimental setup (batch experiments in the presence of co-solvents). However, the difference in surface-normalized dechlorination rate constants amounts to 7 orders of magnitude, i.e. $k_{\text{SA}} = 4 \cdot 10^{-9} \text{ L m}^{-2} \text{ h}^{-1}$ and $6 \cdot 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$, respectively. This difference could be due to the different iron sources used. While Lowry and Johnson [9] utilized a high purity iron salt (99.4 % from Fisher), Sevcu *et al.* [13] did not specify source nor purity of their iron salt ($\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$). Thus, possible Ni contamination cannot be evaluated. One has to take into consideration that Ni is a kind of ‘natural’ contamination for iron sources due to the close relation of the two elements.

We have to state that we could not reproduce the findings of Poursaberi *et al.* [33], who detected the complete hydrodechlorination of DDT ($c_0 = 3 \text{ mg L}^{-1}$) to 1,1-diphenylethane with

nZVI (30 mg L^{-1}) in acidic suspension within 4 h. In our experiments, 1,1-diphenylethane was detected only at a trace level (0.01 % of the initial DDT concentration, Tab. S1) with nZVI_{impure}.

In this study, the observed main product was DDD, which results from



Scheme 1. Hydrodechlorination of chlorinated aromatic compounds by ZVI in the absence and presence of Ni.

hydrodechlorination in the aliphatic part of the molecule. However, the diverging findings of Poursaberi *et al.* [33] could possibly be explained by the iron sources used: while our nZVI precursor was analytical grade, they used a reagent grade iron salt without further specification. The latter could have contained a significantly higher Ni content which may catalyze the hydrodechlorination at the benzene ring of DDT. The ability of Ni to enhance the reactivity of ZVI for hydrodechlorination reactions is well known and extensively described in the literature [4, 22, 25, 30, 35, 36, 42, 43]. A possible mechanistic explanation of the Ni effect is illustrated in Scheme 1: because of the ability of Ni to adsorb and stabilize hydrogen atoms at the particle surface [43] the unfavorable electron transfer from ZVI to a monochlorinated aromatic ring [38, 39] could be replaced by a more favorable H transfer as initial step of the hydrodechlorination reaction.

Recently, Birke *et al.* [44] investigated the impact of trace elements and impurities in technical ZVI brands on the reductive dechlorination of tetrachloroethene (PCE). The varying content of trace elements such as Cr, Mn, Co, Ni, Cu and S of the examined ZVI types significantly influenced their reactivities. Compared to various technical ZVI brands, ultrapure carbonyl ZVI showed a very low reactivity for the reductive dechlorination of PCE which was assigned to the absence of impurities [44]. Birke *et al.* [44] did not involve chlorinated aromatics in their study as they investigated technical ZVI samples for the application in permeable reactive barriers. In contrast, our study was of a more general

interest regarding especially the group of aromatic chlorocompounds. Nevertheless, one aspect of our findings is quite similar: while Birke *et al.* [44] showed that the technical ZVI brand should be chosen with care for the application in groundwater remediation, we came across a comparable finding when working with fine chemicals on a lab scale: it is important to consider contaminants in the ZVI and its precursor, as even a very small amount of 0.005 wt.-% of Ni can change the hydrodechlorination properties of a ZVI sample substantially.

4. Conclusions

This study showed that pure nZVI is not capable to completely dechlorinate chlorinated aromatic rings in aqueous suspension. Furthermore, it was observed that even minor Ni impurities (50 ppm) of the nZVI, derived from a commercial precursor (analytical grade purity), can catalyze the hydrodechlorination of aromatics under certain conditions. Thus, the Ni content of ZVI is an issue for the hydrodechlorination of aromatic rings with a low degree of chlorination, such as monochlorobenzene. Apparently, it is not essential or less significant for the reactivity of ZVI towards more reactive, highly chlorinated compounds, such as carbon tetrachloride and hexachlorobenzene. Based on these findings, it might be possible to re-evaluate some literature studies which reported the cleavage of all carbon-chlorine bonds at the aromatic ring with putatively undoped nZVI. Future research on ZVI reactivity should have a closer look at the trace-level contaminations of the final ZVI as well as of the iron source used.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

References

- [1] R.W. Gillham, S.F. Ohannesin, Enhanced degradation of halogenated aliphatics by zero-valent iron, *Ground Water* 32 (1994) 958-967.
- [2] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, *Environ. Sci. Technol.* 28 (1994) 2045-2053.
- [3] W.L. Yan, H.L. Lien, B.E. Koel, W.X. Zhang, Iron nanoparticles for environmental clean-up: recent developments and future outlook, *Environ. Sci. Process Impacts* 15 (2013) 63-77.
- [4] F.L. Fu, D.D. Dionysiou, H. Liu, The use of zero-valent iron for groundwater remediation and wastewater treatment: a review, *J. Hazard. Mater.* 267 (2014) 194-205.
- [5] S.P. Singh, P. Bose, Degradation of soil-adsorbed DDT and its residues by nZVI addition, *RSC Adv.* 5 (2015) 94418-94425.
- [6] C.B. Wang, W.X. Zhang, Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs, *Environ. Sci. Technol.* 31 (1997) 2154-2156.
- [7] S. Choe, S.H. Lee, Y.Y. Chang, K.Y. Hwang, J. Khim, Rapid reductive destruction of hazardous organic compounds by nanoscale Fe, *Chemosphere* 42 (2001) 367-372.
- [8] W.X. Zhang, Nanoscale iron particles for environmental remediation: an overview, *J. Nanopart. Res.* 5 (2003) 323-332.
- [9] G.V. Lowry, K.M. Johnson, Congener-specific dechlorination of dissolved PCBs by microscale and nanoscale zerovalent iron in a water/methanol solution, *Environ. Sci. Technol.* 38 (2004) 5208-5216.
- [10] Y.Q. Liu, S.A. Majetich, R.D. Tilton, D.S. Sholl, G.V. Lowry, TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties, *Environ. Sci. Technol.* 39 (2005) 1338-1345.
- [11] K.D. Grieger, A. Fjordboge, N.B. Hartmann, E. Eriksson, P.L. Bjerg, A. Baun, Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: risk mitigation or trade-off?, *J. Contam. Hydrol.* 118 (2010) 165-183.
- [12] Y.S. El-Temsah, A. Sevcu, K. Bobcikova, M. Cernik, E.J. Joner, DDT degradation efficiency and ecotoxicological effects of two types of nano-sized zero-valent iron (nZVI) in water and soil, *Chemosphere* 144 (2016) 2221-2228.
- [13] A. Sevcu, Y.S. El-Temsah, J. Filip, E.J. Joner, K. Bobcikova, M. Cernik, Zero-valent iron particles for PCB degradation and an evaluation of their effects on bacteria, plants, and soil organisms, *Environ. Sci. Pollut. Res.* 24 (2017) 21191-21202.
- [14] T. Phenrat, G.V. Lowry, P. Babakhani, NZVI for environmental decontamination: A brief history of 20 years of research and field-scale application, in: T. Phenrat, G.V. Lowry (Eds.) *Nanoscale zerovalent iron particles for environmental restoration*, Springer International Publishing AG, Basel, 2019, pp. 1-44.
- [15] H. Choi, S. Agarwal, S.R. Al-Abed, Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: mechanistic aspects and reactive capping barrier concept, *Environ. Sci. Technol.* 43 (2009) 488-493.

- [16] H. Tang, D.Q. Zhu, T.L. Li, H.N. Kong, W. Chen, Reductive dechlorination of activated carbon-adsorbed trichloroethylene by zero-valent iron: carbon as electron shuttle, *J. Environ. Qual.* 40 (2011) 1878-1885.
- [17] K. Mackenzie, S. Bleyl, A. Georgi, F.-D. Kopinke, Carbo-Iron - an Fe/AC composite - as alternative to nano-iron for groundwater treatment, *Water Res.* 46 (2012) 3817-3826.
- [18] F.-D. Kopinke, G. Speichert, K. Mackenzie, E. Hey-Hawkins, Reductive dechlorination in water: interplay of sorption and reactivity, *Appl. Catal. B-Environ.* 181 (2016) 747-753.
- [19] Z.G. Liu, F. Zhang, S.K. Hoekman, T.T. Liu, C. Gai, N.N. Peng, Homogeneously dispersed zerovalent iron nanoparticles supported on hydrochar-derived porous carbon: simple, in situ synthesis and use for dechlorination of PCBs, *ACS Sustain. Chem. Eng.* 4 (2016) 3261-3267.
- [20] K. Mackenzie, A. Georgi, NZVI synthesis and characterization, in: T. Phenrat, G.V. Lowry (Eds.) *Nanoscale zerovalent iron particles for environmental restoration*, Springer International Publishing AG, Basel, 2019, pp. 45-95.
- [21] C. Grittini, M. Malcomson, Q. Fernando, N. Korte, Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system, *Environ. Sci. Technol.* 29 (1995) 2898-2900.
- [22] W.X. Zhang, C.B. Wang, H.L. Lien, Treatment of chlorinated organic contaminants with nanoscale bimetallic particles, *Catal. Today* 40 (1998) 387-395.
- [23] Y. Fang, S.R. Al-Abed, Partitioning, desorption, and dechlorination of a PCB congener in sediment slurry supernatants, *Environ. Sci. Technol.* 41 (2007) 6253-6258.
- [24] Y.H. Shih, Y.C. Chen, M.Y. Chen, Y.T. Tai, C.P. Tso, Dechlorination of hexachlorobenzene by using nanoscale Fe and nanoscale Pd/Fe bimetallic particles, *Colloids Surf. A* 332 (2009) 84-89.
- [25] H. Tian, J.J. Li, Z. Mu, L.D. Li, Z.P. Hao, Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles, *Sep. Purif. Technol.* 66 (2009) 84-89.
- [26] Y. Zhuang, S. Ahn, A.L. Seyfferth, Y. Masue-Slowey, S. Fendorf, R.G. Luthy, Dehalogenation of polybrominated diphenyl ethers and polychlorinated biphenyl by bimetallic, impregnated, and nanoscale zerovalent iron, *Environ. Sci. Technol.* 45 (2011) 4896-4903.
- [27] X. Chen, X.Y. Yao, C.N. Yu, X.M. Su, C.F. Shen, C. Chen, R.L. Huang, X.H. Xu, Hydrodechlorination of polychlorinated biphenyls in contaminated soil from an e-waste recycling area, using nanoscale zerovalent iron and Pd/Fe bimetallic nanoparticles, *Environ. Sci. Pollut. Res.* 21 (2014) 5201-5210.
- [28] C.P. Andrieux, J.M. Saveant, K.B. Su, Kinetics of dissociative electron-transfer - direct and mediated electrochemical reductive cleavage of the carbon halogen bond, *J. Phys. Chem.* 90 (1986) 3815-3823.
- [29] T. Phenrat, T.S.T. Le, B. Naknakorn, G.V. Lowry, Chemical reduction and oxidation of organic contaminants by nanoscale zerovalent iron, in: T. Phenrat, G.V. Lowry (Eds.) *Nanoscale zerovalent iron particles for environmental restoration*, Springer International Publishing AG, Basel, 2019, pp. 97-155.
- [30] Y. Han, W. Li, M. Zhang, K. Tao, Catalytic dechlorination of monochlorobenzene with a new type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant, *Chemosphere* 72 (2008) 53-58.
- [31] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, Enhanced corrosion-based Pd/Mg bimetallic systems for dechlorination of PCBs, *Environ. Sci. Technol.* 41 (2007) 3722-3727.
- [32] C.J.G. Jou, S.C. Hsieh, C.L. Lee, C.T. Lin, H.W. Huang, Combining zero-valent iron nanoparticles with microwave energy to treat chlorobenzene, *J. Taiwan Inst. Chem. E.* 41 (2010) 216-220.

- [33] T. Poursaberi, E. Kono, S. Mohsen, H. Amir, M. Hassanisadi, F. Hajifathli, Application of nanoscale zero-valent iron in the remediation of DDT from contaminated water, *Chem. Sci. Trans.* 1 (2012) 658-668.
- [34] J. Yang, Y.L. Guo, D.C. Xu, L.M. Cao, J.P. Jia, A controllable Fe-C permeable reactive barrier for 1,4-dichlorobenzene dechlorination, *Chem. Eng. J.* 203 (2012) 166-173.
- [35] J. Feng, T.T. Lim, Pathways and kinetics of carbon tetrachloride and chloroform reductions by nano-scale Fe and Fe/Ni particles: comparison with commercial micro-scale Fe and Zn, *Chemosphere* 59 (2005) 1267-1277.
- [36] J.P. Fennelly, A.L. Roberts, Reaction of 1,1,1-trichloroethane with zero-valent metals and bimetallic reductants, *Environ. Sci. Technol.* 32 (1998) 1980-1988.
- [37] Y.Q. Liu, G.V. Lowry, Effect of particle age (Fe-0 content) and solution pH on nZVI reactivity: H₂ evolution and TCE dechlorination, *Environ. Sci. Technol.* 40 (2006) 6085-6090.
- [38] J.R. Wiley, E.C.M. Chen, E.S.D. Chen, P. Richardson, W.R. Reed, W.E. Wentworth, The determination of absolute electron-affinities of chlorobenzenes, chloronaphthalenes and chlorinated biphenyls from reduction potentials, *J. Electroanal. Chem.* 307 (1991) 169-182.
- [39] K. Rajeshwar, J. Ibanez, *Environmental electrochemistry - fundamentals and applications in pollution abatement*, Academic Press, San Diego, 1997.
- [40] J. Wang, J. Farrell, Investigating the role of atomic hydrogen on chloroethene reactions with iron using tafel analysis and electrochemical impedance spectroscopy, *Environ. Sci. Technol.* 37 (2003) 3891-3896.
- [41] E.T. Martin, C.M. McGuire, M.S. Mubarak, D.G. Peters, Electroreductive remediation of halogenated environmental pollutants, *Chem. Rev.* 116 (2016) 15198-15234.
- [42] Z. Zhang, S. Hu, S. Baig, J. Tang, X. Xu, Catalytic dechlorination of Aroclor 1242 by Ni/Fe bimetallic nanoparticles, *J. Colloid Interface Sci.* 385 (2012) 160-165.
- [43] B. Schrick, J.L. Blough, A.D. Jones, T.E. Mallouk, Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoparticles, *Chem. Mater.* 14 (2002) 5140-5147.
- [44] V. Birke, C. Schuett, H. Burmeier, H.-J. Friedrich, Impact of trace elements and impurities in technical zero-valent iron brands on reductive dechlorination of chlorinated ethenes in groundwater, in: R. Naidu, V. Birke (Eds.) *Permeable reactive barrier: sustainable groundwater remediation*, CRC Press, Taylor & Francis Group, Boca Raton, 2015, pp. 86-98.