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Modelling of sequential groundwater treatment with zero valent iron and granular activated carbon

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Abstract

Multiple contaminant mixtures in groundwater may not efficiently be treated by a single technology if contaminants possess rather different properties with respect to sorptivity, solubility, and degradation potential. An obvious choice is to use sequenced units of the generally accepted treatment materials zero valent iron (ZVI) and granular activated carbon (GAC). However, as the results of this modelling study suggest, the required dimensions of both reactor units may strongly differ from those expected on the grounds of a contaminant-specific design. This is revealed by performing an analysis for a broad spectrum of design alternatives through numerical experiments for selected patterns of contaminant mixtures consisting of monochlorobenzene, tetrachloroethylene, trichloroethylene (TCE), *cis*-1,2-dichloroethylene (*cis*-DCE), and vinyl chloride (VC). It is shown that efficient treatment can be achieved only if competitive sorption effects in the GAC unit as well as the formation of intermediate products in the ZVI unit are carefully taken into account. Cost-optimal designs turned out to vary extremely depending on the prevailing conditions concerning contaminant concentrations, branching ratios, and unit costs of both reactor materials. Where VC is the critical contaminant, due to high initial concentration or extensive production as an intermediate, two options are cost-effective: an oversized ZVI unit with an oversized GAC unit or a pure GAC reactor.

Keywords: Groundwater remediation; Permeable wall; Zero valent iron; Granular activated carbon

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1. Introduction

The use of zero valent iron (ZVI) has been established as an effective method for groundwater treatment predominantly applied in passive systems such as continuous permeable reactive walls or funnel-and-gate systems (Gillham and O'Hannesin, 1994; Starr and Cherry, 1994). However, the range of applications with respect to the type of contaminants is somewhat limited. Besides the implementation for the treatment of inorganic compounds, ZVI has been used particularly as a reducing agent for the degradation of organic solutes. This is practical for a broad range of contaminants, especially for most of the chlorinated compounds that often dominate environmental pollutions. Others, like aromatics such as BTEX, require a different method since the carbon occurs in a relatively reduced form. One approach is accomplished by oxidation through the supply of an oxidant (Barker et al., 1993) or an oxygen-releasing compound (ORC™; Bianchi-Mosquera et al., 1994). Several other approaches are based on microbial degradation, many of these with promising results for specific contaminant patterns (e.g., Devlin and Barker, 1994). For a wide range of contaminated sites, where plumes consist of multiple contaminants of different types, groundwater treatment by means of a single technology may not be efficient or feasible. In these cases, a sequence of two or more treatment technologies must be applied. For mixtures of BTEX and chlorinated solvents, a treatment with reductive and oxidative reactors or reaction zones, respectively, has been proposed (Morkin et al., 2000; Xie and Barcelona, 2001). An alternative to completely redox-driven methods is the use of a classical means of water clean-up: granular activated carbon (GAC), applied either on its own or in addition to another treatment technology. Sorption of organic contaminants onto GAC is the conventional method for on-site treatment and recently has also been used in funnel-and-gate systems (O'Brien and Keyes, 1997). Köber et al. (2001) suggested using a combination of ZVI and GAC for permeable walls for complex contaminant mixtures (Fig. 1). Through column tests with trichloroethylene (TCE) and monochlorobenzene (MCB) they showed that (i) the life time of the GAC could be extended by a factor of four within the given framework if a GAC reactor is coupled with a pre-treatment unit filled with ZVI, and that (ii) the sequential use of ZVI followed by GAC is superior to mixing the substances. In their conclusions they emphasized the generality of their findings, and thus comparable results are expected for similar contaminant mixtures.

The auspicious results of Köber et al. (2001) initiated this study on accordant treatment systems by means of numerical experiments. Since the degradation of chlorinated compounds by ZVI is associated with the production of intermediate chlorinated ethylenes (O'Hannesin and Gillham, 1998; Arnold and Roberts, 2000), we have expanded the

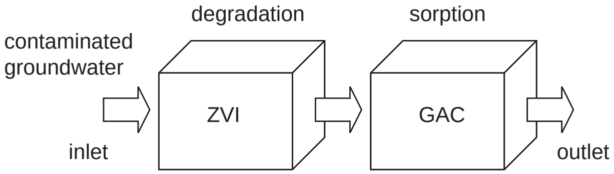

Fig. 1. Concept of treatment train combining contaminant degradation by ZVI and successive sorption on GAC.

examination to five compounds: MCB, tetrachloroethylene (PCE), TCE, *cis*-1,2-dichloroethylene (*cis*-DCE), and vinyl chloride (VC). The consideration of the lower chlorinated daughter products such as *cis*-DCE and VC is in fact a major issue even if they do not occur within the contaminant plume. In particular, the production of VC, which is highly toxic and has therefore to be limited to a rather low target concentration at the reactor outlet, while also having a low sorptivity, might be a striking decision criterion for the set-up of the reactor.

The major goals of this modelling study are (i) to examine the technical appropriateness and economical feasibility of ZVI–GAC reactors and (ii) to offer valuable clues for optimal dimensioning of the reactor units. The latter is based on a systematic analysis of the performance of ZVI–GAC reactors for various scenarios that differ with respect to the influent contaminant concentrations as well as to the extent of byproduct formation.

2. Reactor models

2.1. First order kinetic model for zero valent iron

The abiotic dehalogenation of dissolved organic compounds is generally described by pseudo-first order kinetics with respect to the concentration C_i (μmol L^{-1}) of the organic compound i in the solution (Johnson et al., 1996; O'Hannesin and Gillham, 1998):

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = -k_i C_i = -k_{\mathrm{SA}} \rho_{\mathrm{a}} C_i. \tag{1}$$

The reaction rate constant k_i (h^{-1}) is expressed by the specific rate constant k_{SA} (L m^{-2} h^{-1}) and the surface area concentration of ZVI ρ_{a} (m^2 mL^{-1}). This reflects the dependency of the degradation velocity on the available reactive surface area of ZVI, which varies among different iron types.

Wüst et al. (1999) describe the transition of pseudo-first order to zero order degradation kinetics with increasing influent concentrations, which can be explained by a filling-up of the reactive iron surface. For the present study, low contaminant concentrations are considered, assuming that the degradation reactions are not surface limited. For the modelled concentration spectrum, intra- and interspecies competition of contaminants for reactive sites on the ZVI surface is also not expected. As argued by Schäfer et al. (2003), who compared a TCE–*cis*-DCE system to the respective single component systems, considerable implications from interspecies competition are expected only if contaminants are present at high concentrations. In cases where interspecies competition cannot be ruled out, models as used by Arnold and Roberts (2000) or Schäfer et al. (2003) must be applied. As an alternative, Hand (2003) proposes a model based on the pore surface diffusion model (PSDM, see next section), extended by a degradation step.

The physical and chemical mechanisms of the degradation of chlorinated ethylenes are described by Arnold and Roberts (2000). They subdivide two reaction paths, hydrogenolysis with sequential dechlorination of the solvents and reductive β-elimination including the formation of chlorinated acetylenes. Both paths are not separable and make up a unidirectional reaction network of 19 individual steps that result in the formation of ethene and finally ethane. In our approach, we simplify the network as we do not distinguish the degradation pathways through which compounds degrade or are generated. Aside from this, the highly reactive intermediates of the β-elimination path as well as the dichloroethylene isomers that are produced to a lesser extent (Liang et al., 1997) are not considered. This yields a reaction path with knots represented by the contaminants of interest (PCE, TCE, *cis*-DCE, VC). The mole percent conversion of a contaminant to one or more less chlorinated compounds is described by the yield coefficient $\kappa_{ij}*$. Accordingly, the production rate of uncritical products such as ethene, ethane, and C_4-compounds from the β-elimination path is determined by $1-\kappa_{ij}*$. In the network the degradation step of each compound j is expressed by

$$\frac{\mathrm{d}C_{w,i}}{\mathrm{d}t} = -k_i \cdot C_{w,i} + \sum_j \kappa_{ji}* \cdot k_j \cdot C_{w,j} \tag{2}$$

with i referring to all educts.

The resulting differential equation series is approximated numerically by the finite difference technique. Assuming a constant flow velocity v (m/s) and considering exclusively advective transport, the plug flow reactor can be divided into $x_{\max}/\Delta x$ reactor sections, given that $x_{\max}$ (m) is the total reactor length in the flow direction and Δx (m) is the discretization interval. The concentration of contaminant compound j in some section w is obtained by

$$C_{w,i}(x) = C_{w,i}(x-\Delta x) \cdot e^{-k_i \frac{\Delta x}{v}} + \sum_j \kappa_{ji} \cdot C_{w,j}(x-\Delta x) \cdot e^{-k_j \frac{\Delta x}{v}}. \tag{3}$$

The contaminant transport from one section to the next is conceptually analogous to the degradation in time step $\Delta t = \Delta x / v$. The numerical solution (Eq. (3)) is stable independently of the chosen discretization. However, the discretization needs to be properly adjusted to the given problem to achieve accurate results. Preliminary model runs showed that the relative change in concentration over Δx must be limited to $\Delta C_w / C_w(x) < 1\%$ for every compound.

Despite a presumably larger computational time for the calculation, we prefer this traditional numerical procedure over analytical solution techniques (e.g., Eykholt, 1999) because of the superior programming flexibility with regard to modifications, e.g. extensions such as the incorporation of further reaction steps or variations in incorporating κ (Kouznetsova et al., 2003b).

2.2. Pore surface diffusion model for GAC

The pore surface diffusion model (PSDM) presented by Crittenden et al. (1986) is a comprehensive dynamic adsorption mass transfer model. It serves as a kernel of the AdDesign™ software, which is part of the commercially available ETDOT package (Mertz et al., 1994) used in this study. The PSDM incorporates mass transfer by advective flow, liquid phase film transfer, pore and surface diffusion into the immobile liquid phase (intraparticle pores), and local equilibrium adsorption. These processes are expressed by a set of partial differential equations, which are solved numerically by orthogonal collocation. The accuracy of this method to simulate concentration profiles is optimised by solving the equations sequentially for reactor subsections (axial elements), which are connected in series so that the effluent concentrations of one section provides the influent concentration of the next section. Starting with the first sub-section at the inlet of the GAC unit, a PSDM run is processed for each sub-section. The number of sections used varies with the total volume of GAC that is required to meet the target concentrations for all five compounds. Multicomponent sorption is described in the PSDM by the ideal adsorbed solution theory (IAST; Radke and Prausnitz, 1972). Assuming Freundlich isotherms for every single compound i

$$q_i = K_{\mathrm{F},i} C_i^{n_{\mathrm{F},i}} \tag{4}$$

the IAST isotherm is stated as

$$C_i = \frac{q_i}{\sum_{k=1}^{m} q_k} \left(\frac{\sum_{k=1}^{m} \frac{q_k}{n_{\mathrm{F},k}}}{\frac{K_{\mathrm{F},i}}{n_{\mathrm{F},i}}} \right)^{\frac{1}{n_{\mathrm{F},i}}}, \tag{5}$$

where q (μmol g^{-1}) is the contaminant concentration on the solid phase, K_{F} [(μmol g^{-1})(L μmol^{-1})$^{n_{\mathrm{F}}}$] is the Freundlich constant, and n_{F} is the Freundlich exponent with indices for the components i and k, respectively. Index k refers to all components counted from 1 to m. Note that Eq. (5) assumes ideal adsorbing compounds, which is theoretically limited to a low loading of the GAC but has proven to be a good approximation for a broad concentration range (Crittenden et al., 1985).

For the purpose of a general evaluation, no performance loss due to fouling of the GAC reactor or to mineral precipitation in the ZVI section shall be assumed. Optionally, this aspect can be included for the GAC model by applying a timely variant K_{F} and adequately for the ZVI reactor by simulating the development of mineral coatings or the reduction of the reactive iron surface by a decreasing ρ_{a} over the total operation time.

3. Contaminant patterns and reactor specification

3.1. Patterns of contaminant concentrations considered

Contaminant mixtures of aromatic and chlorinated hydrocarbons in groundwater occur in very different compositions. Concentration patterns that could be considered representative therefore do not exist. However, the patterns that are chosen here have been found to be suitable to demonstrate the key issues of sequential ZVI–GAC treatment design. Two main patterns of influent concentrations (subsequently denoted as I and II) of the five compounds are considered (Table 1). In the first pattern, MCB dominates, in the second, the higher chlorinated ethylenes PCE and TCE dominate. Since emphasis shall be given to intermediate products, the main patterns are further sub-divided with respect to the influent concentrations of the lower chlorinated ethylenes. In the a-patterns (Ia, IIa) the

Table 1
Pattern-specific influent concentrations C_i (μg L^{-1}) and maximum contaminant levels C_{MCL} (μg L^{-1})

C_i	Pattern				C_{MCL}
	Ia	Ib	IIa	IIb	
MCB	500	500	200	200	10
PCE	200	200	500	500	10
TCE	200	200	500	500	10
cis-DCE	10	0.1	10	0.1	10
VC	2	0.1	2	0.1	2

The values of C_{MCL} represent typical Northern American and European standards.

concentrations of *cis*-DCE and VC are set to the given maximum concentration levels C_{MCL}, while the patterns Ib and IIb represent conditions nearly free of *cis*-DCE and VC.

3.2. Model parameters for reactor specification

There is a remarkable discordance in regard to degradation rate constants given in the literature (e.g. Johnson et al., 1996; O'Hannesin and Gillham, 1998; Su and Puls, 1999; Arnold and Roberts, 2000; Vogan et al., 1999), which reflects the sensitivity of the ZVI performance to a variety of influencing factors, such as the given lab or field conditions and the ZVI-specific characteristics of the degradation mechanism. The degradation rate constants of this study are taken from Johnson et al. (1996), who provided values of k_{SA} for common chlorinated solvents that have been compiled from previous studies on commercial iron performance (Table 2). Their investigations are correlative to our own laboratory results (Kouznetsova et al., 2003a) for multi-component systems where high degrees of halogenation favour relatively rapid reduction. The surface area concentration of ZVI is set to $\rho_a = 3.5 \cdot 10^3$ m^2 L^{-1} (Tratnyek et al., 1997) without loss of generality, as will be discussed in the section on economic considerations further below.

Similar to the degradation rate constants, the values of the yield coefficients k^*_{ij} provide no consistent picture. Su and Puls (1999) conclude from their laboratory experiments for a range of commercial iron types, that the intermediate production is highly variable. Reported values usually vary in a range of 0.5% to over 5% (Orth and Gillham, 1996; Liang et al., 1997; O'Hannesin and Gillham, 1998; Arnold and Roberts, 2000; Farrell et al., 2000).

Table 2
Degradation rate constants and Freundlich parameters of reactor models (Johnson et al., 1996; Tiehm et al., 2000)

	k_{SA} (L m^{-2} h^{-1})	K_F (μmol g^{-1})(L $\mu mol^{-1})^{n_F}$	n_F
MCB	–	341.0	0.40
PCE	$2.1 \cdot 10^{-3}$	310.0	0.52
TCE	$3.9 \cdot 10^{-4}$	111.0	0.59
cis-DCE	$4.1 \cdot 10^{-5}$	38.0	0.53
VC	$5.0 \cdot 10^{-5}$	6.5	0.64

For the purpose of a general evaluation (e.g., Starr and Cherry, 1994) we assume that every chlorinated ethylene degrades by the same proportions to the less chlorinated contaminants i.e. intermediates are produced as equal shares (Fig. 2) of a reference value κ:

$$\kappa = \sum_i \kappa_{ij}*. \tag{6}$$

Although this assumption rigorously limits the variability of κ_{ij}^* in the reaction network, it allows us to transparently define the production of intermediates within this study by only one value (κ). Specific reactors, however, require an individual adjustment of the values of κ_{ij}^*. The appropriateness of the reaction model (Fig. 2) has been verified by Kouznetsova et al. (2003a), who successfully calibrated it using data from column tests. They investigated different weightings of κ in the network and concluded that there is a considerable range of best fit values of κ_{ij}^* depending on the degradation rate constants.

Taking into account the ambiguity of the reported values of branching factors, we perform calculations with different values of κ (0.5%, 2.5%, 5%) in order to examine the importance of the evolvement of critical intermediates.

For the GAC reactor model analogous to the assumptions for the ZVI model, short-lived intermediates are neglected. Also, the nontoxic end products of the degradation, ethane and ethene, are not considered due to their low sorptivity and the exiguous effect on the sorptivity of the contaminants. The Freundlich isotherm parameters (Table 2) are taken from Tiehm et al. (2000) who investigated the sorption characteristics of TL 830 GAC (Chemviron Carbon). Additional data for the PSDM (e.g. pore and surface diffusion coefficients) were taken from the database of the AdDesign™ software.

The operation time of the sequenced in-situ reactor is set to 10 years. In this case the retardation of MCB in the ZVI reactor (retardation factor of 40) observed by Köber et al. (2001) can be neglected (the resulting retardation time span reaches about 10 days depending on the ZVI volume). The hydraulic boundary conditions are held constant throughout the investigation of this study, assuming a discharge rate of 10^{-3} m^3/s and a pore velocity of $v = 2 \cdot 10^{-3}$ m/s (area of reactor cross section perpendicular to flow is set

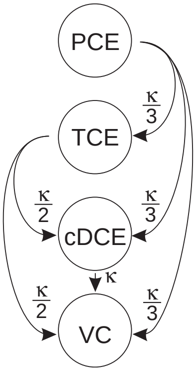

Fig. 2. Weighting of connections in reaction network of contaminants (weighting of degradation to non-toxic end-products is $1-\kappa$).

to 1 m^2, effective porosity of the ZVI reactor is set to 50%). In accordance with the accuracy criterion given for Eq. (3), a model discretization of $\Delta x = 0.01$ m has been chosen.

For the application of the PSDM, the GAC reactor is divided into sub-sections of 0.01 m^3. Sub-sections are added and processed until C_{MCL} is met for all contaminants during the total operation time of 10 years. By this procedure, the required GAC volume is determined through the number of GAC sub-sections needed. The concentration thresholds C_{MCL} are selected according to North American and European standards but vary based on regional regulations. They are used as design criterions for the combined reactor in this study, although at several sites rigorous treatment to C_{MCL} at the reactor outlet may not be required. Natural attenuation can lead to a further decrease of contaminant concentrations so that at distant points of compliance or at downgradient receptors, desired standards can be achieved by setting significantly higher concentration thresholds for the reactor design. However, required volume of ZVI and GAC is predominantly controlled by the ratio between influent and target contaminant concentrations rather than the absolute values. Consequently, even if the selected absolute concentrations and threshold values are only valid for one particular system, the modelling results can reveal general controlling factors specific for the sequential treatment.

4. Results and discussion

4.1. Pre-Dimensioning of the ZVI reactor for degradation of chlorinated ethylenes

The minimum ZVI volume $V_{ZVI,MCL}$ that is required to guarantee concentrations of the chlorinated ethylenes at or below C_{MCL} at the ZVI reactor outlet serves as a reference value for the subsequent analysis. The calculated values of $V_{ZVI,MCL}$ (Table 3) exhibit the significance of both influent concentrations and intermediate production. The influence of κ is illustrated in Fig. 3 for pattern Ia. Given a small κ (0.5%), a slight but continuous decrease of the concentration of *cis*-DCE over the reactor profile is observed. C_{MCL} is met for all contaminants at $V_{ZVI} = V_{ZVI,MCL} = 15.6$ m^3, and the critical dimension-relevant contaminant is TCE. Compared to that, a high κ (5%) aggravates the degradation of the chlorinated intermediates to C_{MCL}. In this case VC determines $V_{ZVI,MCL}$, which is tripled compared to the previous scenario. For all patterns (Table 3) $\kappa = 0.5\%$ results in a sufficient

Table 3
Critical contaminants and volumes of single ZVI reactor to guarantee C_{MCL} of ethylenes at outlet

κ (%)	0.5		2.5		5	
	$V_{ZVI,MCL}$ (m^3)	Critical contaminants	$V_{ZVI,MCL}$ (m^3)	Critical contaminants	$V_{ZVI,MCL}$ (m^3)	Critical contaminants
Ia	15.6	TCE	29.6	VC	48.1	VC
Ib	15.57	TCE	15.63	TCE	28.9	VC
Iia	20.4	TCE	53.4	VC	77.9	VC
Iib	20.4	TCE	38.8	VC	68.9	VC

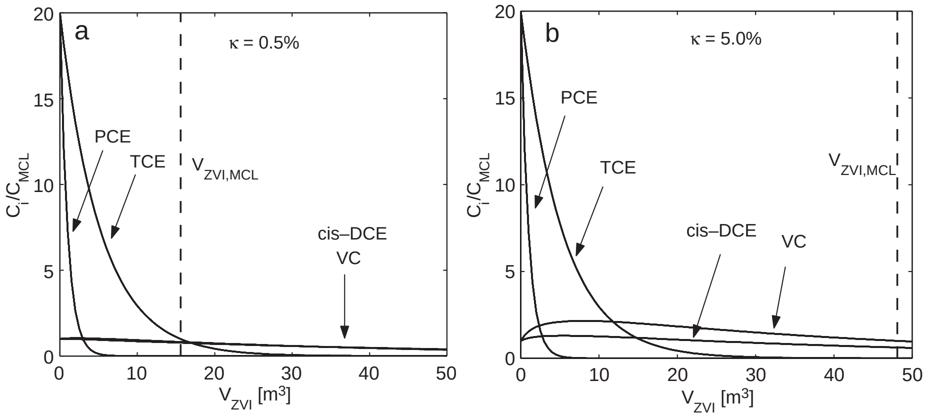

Fig. 3. Concentration profiles through ZVI reactor for pattern Ia.

degradation of the intermediates, whereas for higher values of κ relatively high volumes $V_{\mathrm{ZVI,MCL}}$ are required due to the production of relatively stable intermediates. Here, VC reveals itself to be the most problematic contaminant of the reaction chain. This is also true if VC occurs only in very low concentrations in the influent water (patterns Ib, IIb) due to degradation of TCE and PCE. If TCE is the critical contaminant, $V_{\mathrm{ZVI,MCL}}$ remains nearly unaffected by the value of κ, indicating a relatively low production and simultaneously a rapid degradation of TCE. However, if VC becomes critical, $V_{\mathrm{ZVI,MCL}}$ shows a steep increase which illustrates that it is significantly influenced by the boundary conditions.

4.2. Designing the sequenced reactor

In order to assess the performance of sequenced ZVI–GAC reactors, an array of feasible reactor configurations is compiled. Feasibility, in this context, means that the requirement of keeping the concentration of all contaminants at or below C_{MCL} at the reactor outlet over the life time of 10 years is fulfilled. For a range of V_{ZVI}, the GAC volumes $V_{\mathrm{GAC},i}$ that would be necessary to meet C_{MCL} of the individual contaminants i of the mixture are calculated. The maximum of all $V_{\mathrm{GAC},i}$ determines $V_{\mathrm{GAC,bulk}}$, the GAC volume of feasible reactor configurations. $V_{\mathrm{GAC,bulk}}$ is represented by the envelope of the array of $V_{\mathrm{ZVI}}-V_{\mathrm{GAC},i}$ curves in Figs. 4 and 5. It is shown that the critical contaminant that affect $V_{\mathrm{GAC,bulk}}$ vary with V_{ZVI}.

$V_{\mathrm{GAC,MCB}}$ is nearly independent of V_{ZVI}. For both patterns, $V_{\mathrm{GAC,MCB}}$ is calculated to about 6 m^3 for a broad range of V_{ZVI} values. Approximately the same value is ascertained when assuming MCB to be the one and only contaminant in the influent. This signifies that the sorption of MCB, because of its relative high sorptivity, is only slightly influenced by the occurrence of the halogenated ethylenes. Only if these are barely degraded due to small volumes $V_{\mathrm{ZVI}}<5\ \mathrm{m}^3$, a competitive effect can be identified and a slightly higher volume $V_{\mathrm{GAC,MCB}}$ is required. Yet, even if the preceding ZVI section is properly dimensioned ($V_{\mathrm{ZVI}}=V_{\mathrm{ZVI,MCL}}$) to degrade the halogenated ethylenes, the ethylenes show up to be significant for the GAC section as well. As the retardation of TCE, *cis*-DCE, and

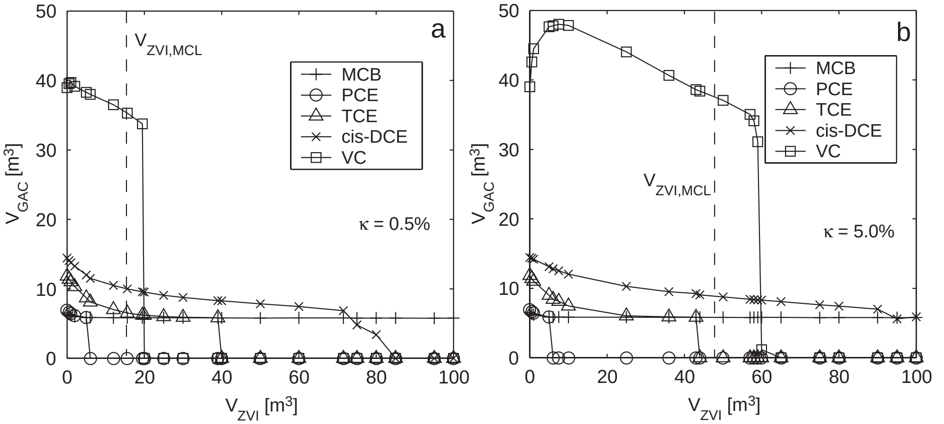

Fig. 4. Sequenced reactor configurations for each individual contaminant that comply with the particular C_{MCL} (pattern Ia).

especially VC is much lower compared to MCB, it is obvious that the volumes can be much larger than $V_{GAC,MCB}$. For the concentration patterns examined, especially for a high value of κ (Figs. 4b and 5b), GAC volumes would have to be applied that exceed $V_{GAC,MCB}$ by a factor of up to 6. Competitive sorption among the contaminants is responsible for this phenomenon. The occurrence of relatively strong sorbing compounds such as PCE and MCB causes a displacement of previously sorbed compounds with a relatively low sorptivity (TCE, *cis*-DCE, and especially VC). This leads to an accumulation of these relatively weak sorbing contaminants in the liquid phase ahead of the concentration fronts of PCE and MCB, which act like brooms sweeping the GAC clean of TCE, *cis*-DCE, and VC. As a consequence, the concentration of TCE, *cis*-DCE and VC in the mobile liquid phase of the GAC unit exceeds the influent concentration and rises continuously with increasing travel distance in the GAC unit. The concentration

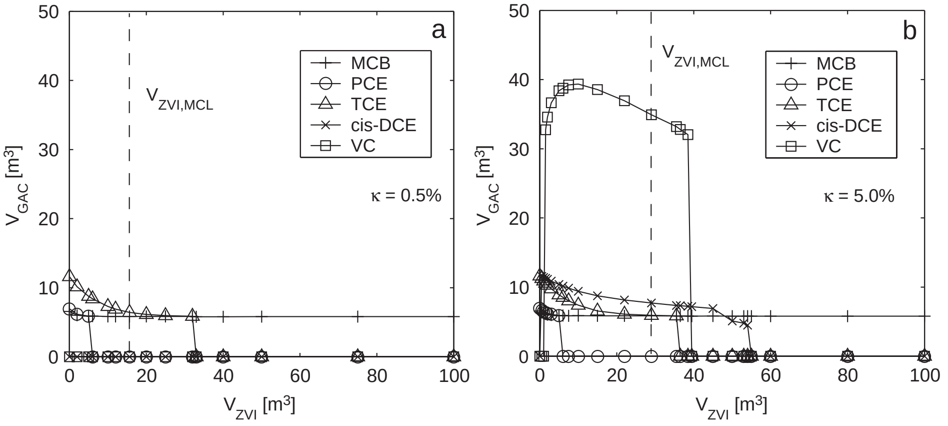

Fig. 5. Sequenced reactor configurations for each individual contaminant that comply with the particular C_{MCL} (pattern Ib).

history of the displaced compounds shows a distinct peak, which gradually changes into a plateau with increasing accumulation time (Fig. 6). The time of breakthrough, as well as the size of the peak or plateau, depends on the isotherm parameters of the particular contaminant. The lower the sorptivity of the contaminant, the faster a plateau will be formed. The sorptivity also determines the height of the peaks (plateaus) reflecting the load of contaminants in the GAC before displacement due to competition with better sorbing compounds. Early breakthrough of all 'above C_{MCL}'-peaks at the outlet can be avoided by increasing V_{GAC} in order to obtain a feasible reactor design. For pattern Ia and $\kappa = 5\%$ (Fig. 4b), for example, $V_{\mathrm{GAC}} = 37$ m^3 would delay the breakthrough of VC at the outlet of the GAC unit over the expected operational time of 10 years.

Another strategy is to enlarge the ZVI unit in order to further degrade TCE, *cis*-DCE, and VC so that the emergence of 'above C_{MCL}'-peaks of one or more contaminants can be circumvented. The benefit that can be obtained from here is demonstrated in Fig. 4b. The

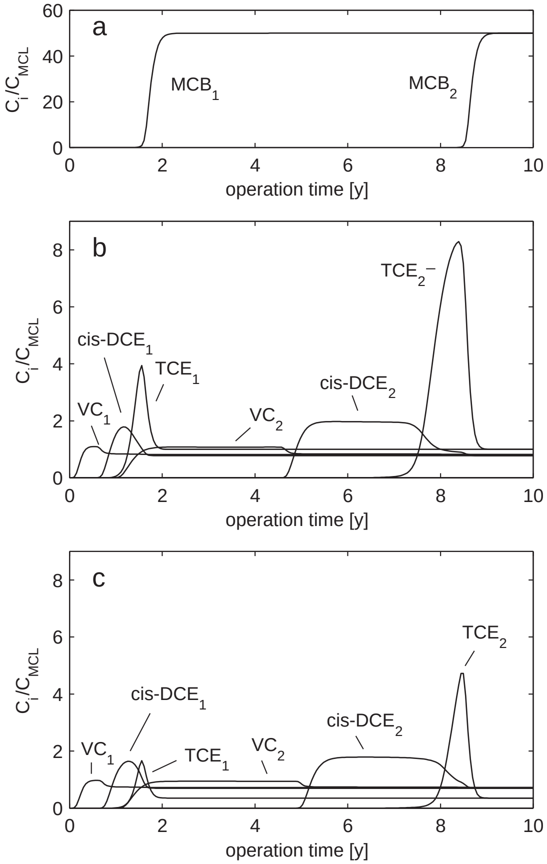

Fig. 6. Concentration breakthrough curves (BTC) at the reactor outlet for pattern Ia at $\kappa = 5\%$); comparison for $V_{\mathrm{GAC}} = 1$ m^3 (index 1) and 5 m^3 (index 2): (a) BTC of MCB, (b) BTC of chlorinated ethylenes if $V_{\mathrm{ZVI}} = V_{\mathrm{ZVI,MCL}} = 48.1$ m^3, (c) BTC of chlorinated ethylenes if $V_{\mathrm{ZVI}} = 61$ m^3. *Remark: BTC of PCE is not shown because it is almost completely degraded.*

steep decline of the $V_{\mathrm{GAC,VC}}$ curve at $V_{\mathrm{VZI}}=61$ m^3 indicates the ZVI volume required to keep the concentration of VC in the GAC unit below C_{MCL}. For $V_{\mathrm{VZI}}>61$ m^3, not VC but *cis*-DCE is dimension-relevant, and the required GAC volume can be considerably decreased to $V_{\mathrm{GAC},cis\text{-}\mathrm{DCE}}=8$ m^3. The diminishing effect of an over-sized ZVI unit also illustrates comparison of the size of the concentration peaks in Fig. 6b and c. Note that a similar situation may occur even for a very low concentration of *cis*-DCE and VC in the influent of the ZVI unit if κ is relatively high (pattern Ib, $\kappa=5\%$; Fig. 5b).

An important feature that has to be considered for a high κ is the increase of $V_{\mathrm{GAC},cis\text{-}\mathrm{DCE}}$ and $V_{\mathrm{GAC,VC}}$ at low values of V_{ZVI} (Figs. 4b and 5b). This is due to the fact that the degradation of *cis*-DCE and especially VC cannot compensate their production, which leads to increasing concentrations in the ZVI unit (see concentration profiles in Fig. 3b). For pattern Ib (Fig. 5b), it seems desirable not to even use a ZVI unit, since the necessary volume of GAC increases from 12 m^3 (if no ZVI is used) to a maximum of nearly 40 m^3 for $V_{\mathrm{ZVI}}=10$ m^3. In this case, a benefit from the application of a ZVI unit in terms of a reduction of the required V_{GAC} is only obtained if the ZVI unit is enlarged to $V_{\mathrm{ZVI}}\geq 40$ m^3.

The observations for the contaminant patterns used here facilitate a glimpse into cases that are characterized by other patterns and degradation mechanisms in the ZVI unit. If VC is absent at the reactors' interface, then the shape of the design curve changes remarkably as either TCE or *cis*-DCE becomes critical. In these cases, over-sizing the ZVI unit appears to be impractical since only small GAC savings can be achieved. This especially applies to TCE (Fig. 5a) but is also relevant for *cis*-DCE (e.g. Figs. 4 and 5b, assuming that no VC is present).

At several field sites, instead of PCE and TCE, high concentrations of secondary contaminants such as *cis*-DCE can be found. If we assume high *cis*-DCE concentrations in the influent water while leaving the other model settings unchanged, *cis*-DCE will especially control the reactor configuration due to a potential production of VC. This is similar to the effects observed for higher-chlorinated ethylenes. Since *cis*-DCE, however, is assumed to have significantly higher half-life times than PCE or TCE, degradation by the use of ZVI is principally not a suitable technology.

4.3. Results for variable operation time

The reactor design criterion has been set in order to guarantee that C_{MCL} is met at the reactor outlet over the entire time of operation. Thus the maximum concentration $C_{i,\max}$ of each contaminant must be held below C_{MCL} at any point of time within this period. Due to the above mentioned accumulation (see Fig. 6) the maximum concentrations $C_{\mathrm{TCE,max}}$, $C_{cis\text{-}\mathrm{DCE,max}}$, and $C_{\mathrm{VC,max}}$ vary with the travel time through the GAC unit, and thus depend not only on V_{ZVI} but also on V_{GAC}. It is therefore relevant to know whether a limitation of the travel time within the GAC reactor, i.e. a shorter GAC operation time, may prevent an accumulation leading to concentrations beyond C_{MCL}. As such, it might be beneficial to use a smaller GAC unit with the filling regenerated at least once during the operation time. To account for the role of the preceding ZVI reactor, we examine two scenarios: (i) there is no preceding ZVI unit at all, and (ii) the ZVI unit is inadequately over-sized ($V_{\mathrm{ZVI}}=19.5$ m$^3>V_{\mathrm{ZVI,MCL}}$). Pattern Ia ($\kappa=0.5\%$) is considered as an example.

The first scenario is representative for all cases where degradation in the ZVI unit is insufficient $(V_{\mathrm{ZVI}} < V_{\mathrm{ZVI,MCL}})$ to avoid $C_{i,\max}$ of the least sorbing compound i (here: VC) reaching or exceeding C_{MCL} at the interface of the reactors. The desorption in the GAC causes an immediate increase of C_i in the reactor profile (Fig. 7a). Contaminant i is critical for V_{GAC} independent from the desired reactor life time, which due to the constant flux is linearly related to V_{GAC} (Fig. 7b). Thus the consumption of GAC cannot be reduced by using a smaller unit and regularly exchanging the GAC filling.

A different situation arises if the ZVI unit is reasonably dimensioned but not sufficiently over-sized. Here, in accordance with Fig. 4a, the volume V_{GAC} required to achieve a life time of 10 years is still determined by the occurrence of chlorinated ethylenes, especially VC. Therefore, although the $C_{i,\max}/C_{\mathrm{MCL}}$ ratios are significantly lowered (Fig. 7c), the GAC volume required for a life time of 10 years does not decrease remarkably in comparison with the “non-ZVI” scenario (Fig. 7b, d). However, as the

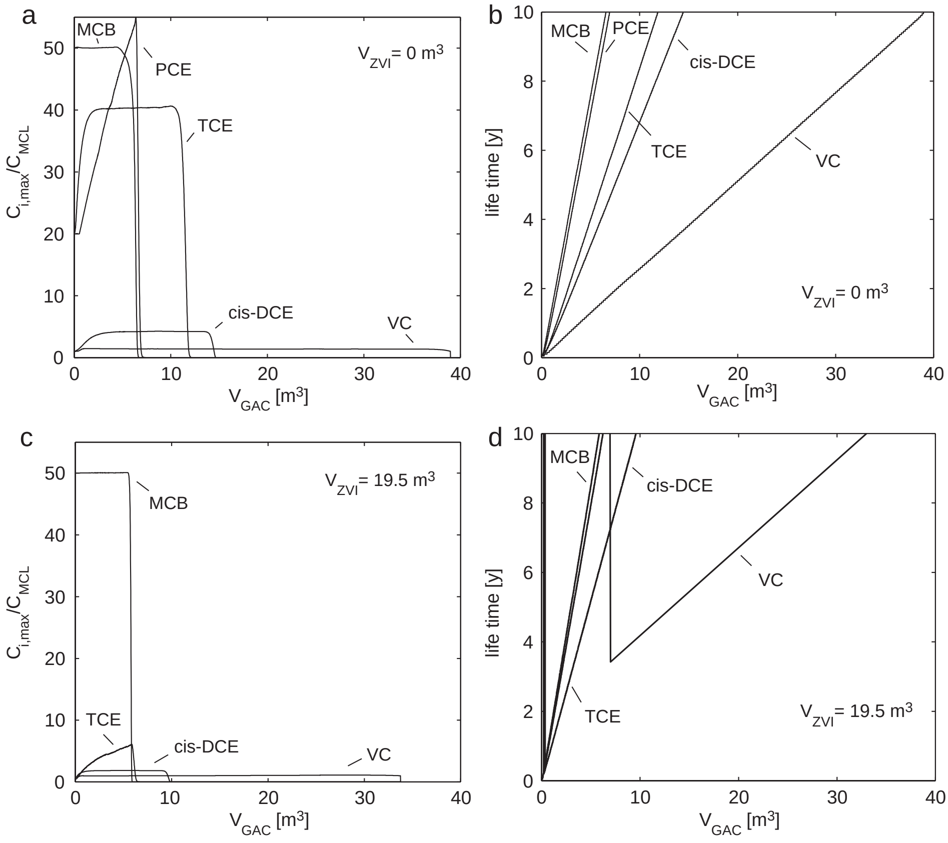

Fig. 7. Maximum contaminant concentrations $C_{i,\max}$ at the GAC reactor outlet within a time period of 10 years referred to $C_{i,\mathrm{MCL}}$ (a, c) and life time of GAC unit (b, d) as functions of GAC volume V_{GAC} for two scenarios: (a, b) no preceding ZVI unit (V_{ZVI}=0 m^3), (c, d) insufficiently over-sized ZVI unit (V_{ZVI}=19.5 m^3).

critical contaminant changes with V_{GAC} (*cis*-DCE for $V_{\mathrm{GAC}}<7$ m^3, VC for $V_{\mathrm{GAC}}>7$ m^3), there is no linear relationship between the volume and the life time of one filling (Fig. 7d). Employing smaller GAC units yields a savings in the total GAC volume required: a GAC unit of 5 m^3, for example, will have a life time of about 5 years so that a total operation time of 10 years can be achieved with a volume of only 10 m^3 instead of 32 m^3 when no refilling is planned.

4.4. Economic considerations

Having created an array of feasible reactor configurations, the question arises which of these settings is preferred from an economic point of view? In order to provide a reasonable assessment, it is assumed that the differences of the reactor configurations with respect to total costs (capital and running costs) are primarily due to the required amount of reactor filling materials. Any volume-dependent installation or disassembly costs that may be incurred are neglected. Using this concept, the economic assessment of a given reactor configuration can be done on the basis of only three variables: V_{ZVI}, V_{GAC} and the unit cost ratio r_{C} relating the unit costs of GAC per m^3 reactor volume to those of ZVI. The unit costs may include both purchasing and disposal costs provided that present values are considered. Moreover, r_{C} is assumed to be independent of the volumes applied i.e. no quantity discounts are used. Therefore no matter what the real unit costs are, we have to give up $1/r_{\mathrm{C}}$ unit volumes of GAC to apply one unit volume of ZVI in order to keep a certain cost level. This implies that any cost level is represented in a V_{ZVI} vs. V_{GAC} diagram by a straight line with a negative slope of $1/r_{\mathrm{C}}$. By superimposing these isolines of costs on the curves representing feasible reactor configurations ($V_{\mathrm{GAC,bulk}}$ as a function of V_{ZVI}) we can identify cost-optimal reactor designs. Fig. 8 shows appropriate diagrams for the concentration patterns IIa and IIb and two different cost ratios.

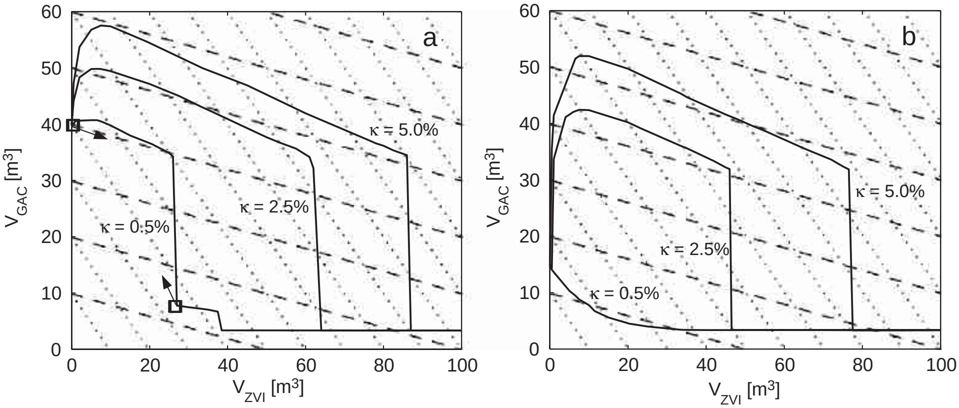

Fig. 8. Feasible reactor configurations for patterns IIa (a) and IIb (b) with isolines of ZVI–GAC unit cost ratios $r_{\mathrm{C},1}=1$ (dotted) and $r_{\mathrm{C},2}=5$ (dashed). Square markers and arrows indicate cost-efficient reactor configurations for selected cases: IIa, $\kappa=2.5\%$; and IIb, $\kappa=0.5\%$.

Patterns IIa and IIb lead to similar design curves as shown above for patterns Ia and Ib, reflecting that competitive sorption plays a role even if MCB is present at lower concentration than PCE and TCE. However, due to the higher influent concentrations of PCE and TCE for patterns IIa and IIb, the production of VC and *cis*-DCE is higher, resulting in an even more pronounced rise of V_{GAC} at $V_{\mathrm{ZVI}} < 10\ \mathrm{m}^3$. The base line of the design curves refers to $V_{\mathrm{GAC}} = 4\ \mathrm{m}^3$, the volume required to sufficiently retard MCB in the GAC unit.

The definition of the cost-optimal design depends on the shape characteristics of the curve representing feasible designs. If VC is the critical contaminant, and design curves show a characteristic sharp decline of required GAC volume at a certain value V_{ZVI}, the choice is reduced to only two priority options: not to use a ZVI unit at all, or to appropriately oversize V_{ZVI} so that VC becomes uncritical. Which option is to be preferred depends on the cost ratio r_{C}, as exemplified by the markers in Fig. 8a for $\kappa = 2.5\%$. At a cost ratio of $r_{\mathrm{C},1} = 1$ a pure GAC reactor ($V_{\mathrm{ZVI}} = 0\ \mathrm{m}^3$, $V_{\mathrm{GAC}} = 40\ \mathrm{m}^3$) is identified as cost-optimal option. If ZVI can be purchased at a rather low price ($r_{\mathrm{C},2} = 5$), a sequenced treatment system ($V_{\mathrm{ZVI}} = 64\ \mathrm{m}^3$, $V_{\mathrm{GAC}} = 4\ \mathrm{m}^3$) with a ZVI unit that is oversized compared to the contaminant-specific design ($V_{\mathrm{ZVI,MCL}} = 53.4\ \mathrm{m}^3$) is optimal. The cost ratio threshold r_{C}^* that shifts the decision from a pure GAC reactor to a sequenced system increases with κ ($r_{\mathrm{C}}^* = 0.8$ for $\kappa = 0.5\%$, $r_{\mathrm{C}}^* = 1.8$ for $\kappa = 2.5\%$, $r_{\mathrm{C}}^* = 2.4$ for $\kappa = 5\%$) indicating that the intermediate production penalizes the use of ZVI. In this context, it is important to mention that the V_{ZVI} values quantified in this study are based on the assumption that ZVI's surface area concentration amounts to $\rho_{\mathrm{a}} = 3.5 \cdot 10^3\ \mathrm{m}^2\ \mathrm{L}^{-1}$. V_{ZVI} must be rescaled if other values of ρ_{a} apply, leading to lower V_{ZVI} values at higher ρ_{a} values and vice versa. To simplify matters we can also adjust the unit price of ZVI or the cost ratio, respectively. Correspondingly, this would change the threshold values r_{C}^*.

As discussed above, situations where TCE or *cis*-DCE are critical exhibit design curves with a completely different shape (Fig. 8b, $\kappa = 0.5\%$). Here, cost-optimal designs refer to the entire range of the design curve. With increasing cost ratio, cost-optimal design gradually changes from a pure GAC reactor towards a sequenced system. The higher the r_{C}, the larger the appropriate V_{ZVI} and the lower the required V_{GAC}. However, due to the slight slope of the design curves, cost-optimal V_{ZVI} is below $V_{\mathrm{ZVI,MCL}}$ even in case of rather high cost ratios (for the example given in Fig. 8b with $r_{\mathrm{C}} = 5$ and $\kappa = 0.5\%$: cost-optimal $V_{\mathrm{ZVI}} = 19.5\ \mathrm{m}^3$, $V_{\mathrm{ZVI,MCL}} = 20.4\ \mathrm{m}^3$). Reconsideration of TCE- and *cis*-DCE-specific design curves in Figs. 4 and 5 reveals the similarity of the design task even if different conditions apply.

It should be clarified that the economic considerations above are mainly intended to provide a wider perspective of the task of this study, thereby giving a means to judge the relevance of the results from the analysis of combined ZVI–GAC reactors' performance. They are not intended to replace a detailed cost analysis, which will certainly be necessary for a definitive economic assessment, but which was beyond the scope of this paper. For example, this refers to the fact that the results apply to a given operation time of 10 years, assuming that both reactor units are being operated without any exchange of the reactor fillings. Both issues, the total operation time as well as the life time of one filling, are relevant when a cost-optimal design is sought for an individual case. In general, a longer operation time will tend to support the application of a preceding ZVI unit since its costs are supposed to be not as time-dependent as the GAC costs, provided that the deactivation of ZVI over time is reasonably low.

5. Conclusions

The presented generic study is based on several assumptions with respect to sorption as well as degradation parameters of each of the five compounds being considered. In reality these parameter values may vary significantly with prevailing site conditions and have to be newly specified for each individual system planned. Therefore the results presented cannot replace site-specific analysis and pre-testing but reveal important features of the main processes influencing the performance of combined ZVI–GAC reactors. In this way the study provides practical hints for the design of such reactors.

In particular, two processes appear to be most important: production of intermediates (byproducts) in the ZVI reactor and competitive sorption in the GAC reactor. Assuming first order kinetics for the degradation of the chlorinated solvents, the ZVI reactor design is governed by the contaminant concentrations at the reactor inlet, the target concentrations at the outlet, and the contaminant-specific degradation rate constants. If the half-life times in the reactor decrease with the chlorination, then intermediate production may lead to the occurrence of critical lower chlorinated compounds. If VC is produced at considerable rates, compliance with its target concentrations usually becomes the main reactor design criterion due to its normally high half-life.

In this study, the crucial point revealed by the numerical experiments is that even if concentrations of chlorinated hydrocarbons are below MCL values at the ZVI reactor outlet, they still can be the main factor for the proper adaptation of the subsequent GAC reactor. This is due to the relative low sorptivity of these compounds, particularly of the lower chlorinated solvents. Being accumulated on the GAC in a first phase of reactor operation, they tend to desorb as a consequence of competition when better sorbing chemicals such as monochlorobenzene (MCB), and subsequently propagate through the GAC reactor. As a consequence, the concentrations of the desorbed compounds may exceed their inlet concentrations and the desired MCLs. In this case, the required GAC volume is determined by these compounds, although they are not a problem at the inlet.

The findings indicate that the sequential use of a ZVI and a GAC reactor is not just a combination of both. It is not sufficient to design both reactor types individually and then operate them in series. As has been shown in this study, the optimal combination of both reactors can be derived from non-linear ZVI-volume/GAC-volume trade-offs. By considering simple relationships of unit costs of both reactor materials it is possible to decide whether a combination of both makes sense. For the contaminant patterns and descriptive parameters considered here, either an over-designed ZVI–GAC combination has to be used or a GAC reactor exclusively. However, if e.g. the ZVI degradation rate constants of the compounds have a reverse order and decline with chlorination, different design rules are expected. In this case, a combined use of ZVI and GAC to treat mixtures of aromatic and chlorinated compounds should complement one another due to the opposite contaminant treatability trends of both reactors.

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