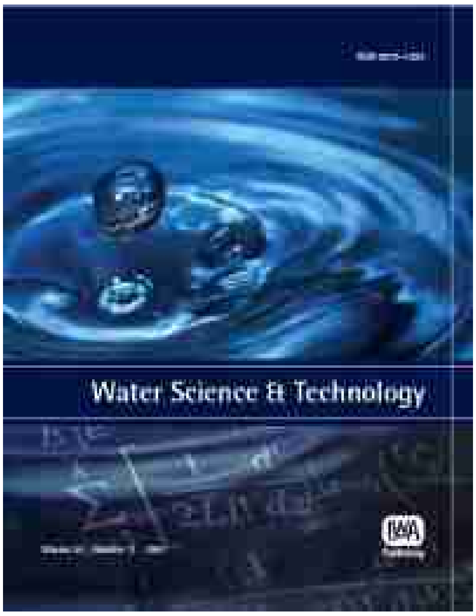

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Technico-economic assessment of groundwater treatment by palladium-on-zeolite-catalyst in comparison to GAC fixed bed adsorbers

P. Bayer and C. Schüth

ABSTRACT

A technico-economic comparison between palladium-on-zeolite (Pd/Y), and granular activated carbon (GAC) based methods of groundwater clean-up is presented. The treatment concepts are assessed by means of process-based cost functions that can be applied to a broad range of case-specific conditions. The analysis accounts for variability in cost and performance parameters and reduces the interplay of multiple factors to expressive indifference curves that can be used for identifying a favorable technology. The findings for the treatment of halogenated hydrocarbons reveal that the Pd/Y offers advantages compared to GAC use in case of high contaminant concentrations and for the treatment of lower halogenated compounds such as cis-Dichloroethene.

Key words | cost, economic analysis, granular activated carbon (GAC), indifference curves, palladium

P. Bayer (corresponding author)
Engineering Geology,
ETH Zurich,
Sonneggstrasse 5,
8092 Zurich,
Switzerland
E-mail: *bayer@erdw.ethz.ch*

C. Schüth
Institute of Applied Geosciences,
Hydrogeology Group,
Technical University of Darmstadt,
D-64287 Darmstadt,
Germany
E-mail: *schueth@geo.tu-darmstadt.de*

INTRODUCTION

Halogenated hydrocarbons (HHCs), such as perchloroethene (PCE) and trichloroethene (TCE), are among the most prevalent contaminants in groundwater. Many HHCs are toxic and not easily degraded in natural systems, therefore frequently requiring remedial action. The improvement of existing and the development of new HHC groundwater remediation technologies over the last three decades has made it possible to choose from a variety of options in selecting remediation measures. However, to maximize the benefit for the capital spent, a profound knowledge of the different methods is required. The long term performance of a system, as well as its costs, needs to be carefully analysed. The fundamental technological differences between clean-up techniques make it difficult to compare them and remediation decisions are frequently based on experience rather than on impartial criteria. This is often the major obstacle preventing emerging technologies from being considered as treatment alternatives, although they might be more cost effective.

A standard concept for the treatment of HHC contaminated groundwater is still the extraction of the groundwater from the subsurface through wells and its treatment above ground (pump-and-treat). Treatment is typically achieved using sorption on granular activated carbon (GAC). As an alternative to sorption from the water phase, sorption from the gas phase after air stripping is often applied, especially for volatile organic compounds (VOCs). Stripping can be achieved using strip towers in which the water, entering from the top, comes into contact with air fed from the bottom in counterflow.

As sorption is a non-destructive process and any sorbent has a limited sorption capacity, this concept implies that the GAC has to be replaced after it is exhausted and disposal or regeneration is necessary. On the contrary, destructive methods ideally transform the contaminants to harmless products and no after-treatment is necessary. For HHCs, abiotic reductive dehalogenation can be achieved using zero valent iron (ZVI) through a corrosion reaction

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(Gillham & O'Hannesin 1994; Bayer & Finkel 2005; Kouznetsova *et al.* 2006). While ZVI typically has half-lives of several hours for HHC reduction, using palladium-based catalysts and dissolved hydrogen gas as the reductant was found to dechlorinate HHCs much more quickly (Schreier & Reinhard 1995; Schüth & Reinhard 1998) and catalytic reductive dechlorination has been proposed as a treatment technology. We recently demonstrated the effectiveness and long-term stability of a catalyst system based on palladium on a hydrophobic zeolite-Y support (Pd/Y) for the reduction of HHCs in a small scale field application (Schüth *et al.* 2000, 2004). However, only a limited number of field tests were performed with such catalytic systems (McNab *et al.* 2000; Schüth *et al.* 2000) and the technology is still not considered as a technically mature treatment option, preventing its commercialization. Davie *et al.* (2008) extrapolated the findings of a field experiment with Pd/Y and concluded that the innovative treatment concept is technically and economically competitive to traditional technologies. For this study, cost numbers reported from other case-studies were compared to those estimated for a Pd/Y system.

Although the two technologies, sorption of HHC using GAC, and catalytic destruction of HHCs using Pd/Y, have fundamental differences, they are, in principal, alternatives for the same target (e.g. Bayer & Finkel 2006). In this study we therefore evaluate them in terms of their economic viability for water treatment. Although the overall cost of a groundwater clean-up measure is affected by numerous technology- and site-specific factors, the treatment step itself, e.g. the removal of the HHCs from the extracted groundwater or their direct destruction, can generally be well predicted based on a few parameters. For the techno-economic comparison of the two systems we therefore limit the calculations to the requirements for the treatment steps, e.g. the consumption of GAC, and the costs of the Pd-catalyst including necessary replacement and auxiliary materials, to specific but identical conditions. The technologies are evaluated in terms of treatment costs for the removal of PCE, TCE, and cis-dichloroethene (cis-DCE) from water. These compounds were selected as they are typical targets for the technologies and represent a range of chemical-physical properties that influence treatment performance.

CONCEPT OF TECHNICO-ECONOMIC COMPARISON

Framework

Costs that have to be spent to achieve a desired clean-up objective are ideally quantified by cost functions that incorporate site conditions, technological performance and prices as input parameters. Here these functions are used to determine how the type of contaminant, its concentration in the groundwater and the volumetric throughput rate of a treatment system influence the expenditures for the different technologies. Performance ranges for sorption capacities and degradation rates are considered as well as price ranges instead of fixed values. This enables an objective cost comparison for a wide range of conditions.

When absolute costs of different technological options are estimated and compared with each other, the results are strictly valid only for one specific situation. Showing only absolute numbers easily hides the controlling factors, particularly when calculated based upon the interplay of multiple parameters. As a remedy, here relative cost calculations are preferred. This means that, instead of absolute values, ratios between the calculated costs for two technologies are examined. Factors that equally influence both costs cancel down. Unity represents indifference, for which both technologies are on a par. As will be shown, such a perspective enables the calculation of expressive economic indifference curves, which trace options of equal costs for different technologies. In a diagram an indifference curve therefore separates those application windows which are economically more attractive for the one or the other technology.

To calculate the total expenses E_{tot} over a specified time period T, annual expenses E_t for each year t are summarized after discounting to net present value:

$$E_{\mathrm{tot}} = \sum_{t=0}^{T} \frac{E_t(1+p)^t}{(1+d)^t} \tag{1}$$

It is assumed that the annual inflation rate is constant at $p = 2\%$, which reflects a common value in modern economies. The discount factor d is set fixed at a moderate value of 7% (e.g. NRC 1997). Usually, costs are not only paid annually, in which case t represents time steps that are not full years. If for instance GAC is replaced each half year, then $t = 0.5$, 1, 1.5, etc. Different intervals apply to different elements or activities of the treatment system.

Model assumptions

For cost comparison the two technologies have to decrease the same contaminant concentration C_w in the groundwater to a specified target level, C_{MCL}, over a specific time period of operation, T. During this time, concentration and throughput rate, Q, are assumed to be constant. In addition, no temporal variations in treatment performance and prices for media and auxiliary materials are considered. Setting such steady-state conditions is supposed to be a valid approximation for commonly more dynamic field situations (Clark 1987).

Expenditures for the design, installation and operation of a treatment system can typically be subdivided into major cost building blocks, e.g. planning costs, installation costs, energy costs, or maintenance costs, which can be calculated with different levels of reliability. Highest uncertainty is often associated with the most essential part of a system, i.e. the treatment step itself, where contaminants are removed from the aqueous phase by the selected technology. For example, the sorption capacity of GAC is highly dependent on the type and concentration of a contaminant and the water throughput of the system. In addition, groundwater chemistry might alter the effectiveness of a system, which can have a major impact on the costs of the treatment.

In this study we therefore focus on the treatment step by analyzing the specific demand of treatment media and auxiliary materials for different technologies. As the two major technological variants for the treatment with GAC, sorption from the aqueous phase and after stripping from the gas phase are compared. Subsequent calculations assume that the contact time within the treatment unit is sufficiently long and that kinetic sorption limitations can be neglected (Bayer *et al.* 2005*a*,*b*). In practice, such conditions are achieved for instance by sequential use of multiple vessels. Note that this assumption simplifies the calculation of required GAC mass, which becomes independent of the target level, C_{MCL}.

Linear cost functions are assumed, for example, by ignoring the effect of economy of scale. Costs are exclusively calculated for the operation, that is the consumption of GAC for sorptive treatment, and the material continuously consumed for Pd/Y application. For the latter this means that the continuous costs for catalyst and H_2O_2 for iterative purge are summed up. The findings from a preceding sensitivity analysis concur with experience in the field, where further technical cost elements for the Pd/Y-system are only of minor importance (Schüth *et al.* 2004). This applies to the fees for H_2 supply (a hydrogen generator is used), which is needed as electron acceptor. Also the expenses for container, conduits, flow controller and energy consumption are relatively low. Therefore, neglecting these here seems to be a valid assumption without loss of generality. For the comparison with the alternative treatment media, this can even be regarded as a conservative assumption. GAC commonly is used at significantly higher volumes, thus requiring larger technical equipment and multiple, sizeable vessels. These are not accounted for here. Also, the comparatively high charges for the stripping unit (supply and operation of stripping tower, heater, blower) are not added here.

Sorption on GAC

Sorptive removal of contaminants from water is typically achieved on site in flow-through column reactors filled with GAC. In general, sorption of organic compounds on GAC increases as hydrophobicities of the compounds increase and water solubilities decrease. Typically, sorption isotherms are determined for a single contaminant although competitive effects can be observed for contaminant mixtures (Schaefer *et al.* 2000). The equilibrium loading of the GAC, which depends on both GAC and contaminant type as well as on the concentration of the contaminant in the extracted ground water, can then be described by a nonlinear Freundlich isotherm (Grathwohl 1998):

$$\frac{M_S}{M_{\mathrm{GAC}}} = K_{F,w} \cdot C_w^{n_{F,w}} \tag{2}$$

where M_s is the sorbed contaminant mass and M_{GAC} is the GAC mass. The Freundlich sorption coefficient $K_{F,w}$ and the Freundlich exponent $n_{F,w}$ quantify the equilibrium sorption capacity of a certain contaminant on a specific type of GAC in the aqueous phase. For each value of C_w, a partitioning coefficient $K_{d,w}$ can be computed:

$$K_{d,w} = K_{F,w}\, C_W^{n_{F,w}-1} \tag{3}$$

At a constant groundwater throughput rate, Q, and aqueous concentration, C_w, the sorbed contaminant mass within time period ΔT_{GAC} is given by $M_S = \Delta T_{\mathrm{GAC}}\, Q C_W$. The consumed mass of GAC is derived by:

$$\frac{M_{\mathrm{GAC}}}{\Delta T_{\mathrm{GAC}}} = \frac{Q}{K_{F,w}} C_W^{1-n_{F,w}} \tag{4}$$

This equation ignores the contaminant mass in aqueous phase, i.e. assumes that all mass input to the reactor gets sorbed. This is a common assumption for description of GAC, because mass in the aqueous phase is very small compared to mass on solid phase (e.g. Bayer & Finkel 2006).

Sorption capacities of GAC for VOCs from the gas phase are substantially higher compared to the water phase, as competing effects from other groundwater solutes can be excluded. Contaminant concentration in the gas phase is determined by the dilution according to the air-to-water ratio (AW) in the stripping tower (Hand *et al.* 1986; Dvorak & Schauble 2001). Applying Freundlich sorption isotherms for the vapor phase, the sorption coefficient $K_{d,v}$ for a specific aqueous concentration is calculated equivalent to Equation (3):

$$K_{d,v} = K_{F,v}\left(\frac{C_w}{\mathrm{AW}}\right)^{n_{F,v}-1} \tag{5}$$

Analogous to Equation (4), the GAC mass demand is calculated by

$$\frac{M_{\mathrm{GAC}}}{\Delta T_{\mathrm{GAC}}} = \frac{\mathrm{AW}\cdot Q}{K_{F,v}}\left(\frac{C_w}{\mathrm{AW}}\right)^{1-n_{F,v}} = \mathrm{AW}^{n_{F,v}}\frac{Q}{K_{F,v}} C_w^{1-n_{F,v}} \tag{6}$$

Assuming a fixed interval of ΔT_{GAC} (e.g. 0.5 years) until the sorption capacity of GAC is exhausted and has to be replaced, total costs for GAC add up to

$$E_{\mathrm{GAC}} = \varepsilon_{\mathrm{GAC}} M_{\mathrm{GAC}} \sum_i \left(\frac{1+p}{1+d}\right)^i \tag{7}$$

for time steps of $i = 0, \Delta T_{\mathrm{GAC}}, 2\Delta T_{\mathrm{GAC}}, \ldots, T - \Delta T_{\mathrm{GAC}}$

The price of GAC is expressed by $\varepsilon_{\mathrm{GAC}}$. Regeneration of GAC is not considered here but could be included across the board by a modified value of $\varepsilon_{\mathrm{GAC}}$.

Catalytic hydrodechlorination using a Pd/Y catalyst

Palladium-based catalysts rapidly dechlorinate many HHCs with dissolved hydrogen gas (H_2) as the reductant. Due to the high reactivity of the palladium, small scale on site flow-through column reactors filled with the pelletized catalyst are feasible (Schüth *et al.* 2004). As a catalyst is not used up in the reaction, theoretically no catalyst replacement is necessary over time. However, due to the complex groundwater chemistry, deactivation of noble metal catalysts is observed in field applications (McNab *et al.* 2000). We showed that by using a hydrophobic zeolite Y-200 (SI/Al ratio is 200) as the palladium support (Pd/Y) and flushing the catalyst periodically with a dilute hydrogenperoxide (H_2O_2) solution, fairly stable degradation rates could be obtained over about 2 years (Schüth *et al.* 2000).

For cost calculation of the Pd/Y system, several components crucial for the treatment step have to be considered. These are the catalyst itself, H_2O_2 for iterative purge and a continuous H_2 source. The composite catalyst can be divided into the noble metal (Pd) and the support material (zeolite Y). Their relative masses are described by their weight ratios w_{Pd} and $(1 - w_{\mathrm{Pd}})$, respectively. Since degradation of contaminants using Pd/Y typically follows a first-order mechanism (Schüth *et al.* 2000, 2004), the mass M_{pdY} of the composite catalyst is derived by

$$M_{\mathrm{PdY}} = \frac{Q\rho_{\mathrm{PdY}}}{k n_{\mathrm{PdY}}} \ln\left(\frac{C_w}{C_{\mathrm{MCL}}}\right) \tag{8}$$

where k is the degradation rate, ρ_{PdY} is the density and n_{PdY} is the effective porosity of the catalyst.

Provided that the lifetime, Δt_{Pd}, of the catalyst is limited, depleted Pd/Y is iteratively replaced. Consequently, the expenses ε_{Y} for the zeolite cumulate to

$$E_{\mathrm{Y}} = \varepsilon_{\mathrm{Y}} M_{\mathrm{PdY}} \sum_i \left(\frac{1+p}{1+d}\right)^i \tag{9}$$

for time steps of $i = 0, \Delta T_{\mathrm{PdY}}, 2\Delta T_{\mathrm{PdY}}, \ldots, T - \Delta T_{\mathrm{PdY}}$

The cost coefficient ε_{Y} represents the price of zeolite. Due to the very small portion of Pd, the weight ratio of the zeolite is assumed to be 100% ($1 - w_{\mathrm{pd}} \approx 1$) here. The right factor in Equation (9) includes discounting of future costs according to Equation (1).

The used precious Pd is recycled (Barakat *et al.* 2006), so that only for the first fill (time $t = 0$) the full price, $\varepsilon_{\mathrm{Pd}}$, has to be paid. The total costs can be calculated by

$$E_{\mathrm{Pd}} = \varepsilon_{\mathrm{Pd}} M_{\mathrm{PdY}} \left[1 + w_{\mathrm{Pd}} \mathrm{rec}_{\mathrm{Pd}} \sum_{i} \left(\frac{1+p}{1+d} \right)^{i} \right] \quad (10)$$

for time steps of $i = 0, \Delta T_{\mathrm{PdY}}, 2\Delta T_{\mathrm{PdY}}, \ldots, T - \Delta T_{\mathrm{PdY}}$

where $\mathrm{rec}_{\mathrm{pd}}$ denotes the cost ratio when recycling Pd. This means that, if the net charge for Pd is e.g. 35% of that for virgin Pd, this is expressed by $\mathrm{rec}_{\mathrm{pd}} = 0.35$.

To ensure stability of the Pd/Y catalyst, the system has to be flushed with hydrogen peroxide (H_2O_2) in intervals of 2 days ($\Delta T_{H_2}O_2$) (Schüth *et al.* 2004). Its demand is supposed to be not more than two pore volumes, at a concentration of $C_{H_2}O_2 = 10\,\mathrm{g/L}$, which yields a total mass of H_2O_2 per flushing event of

$$M_{H_2O_2} = 2 \frac{n_{\mathrm{PdY}} M_{\mathrm{PdY}}}{\rho_{\mathrm{PdY}}} C_{H_2O_2} \quad (11)$$

Assuming annual refill of H_2O_2 bottles, total costs for H_2O_2 can be calculated by

$$E_{H_2O_2} = \varepsilon_{H_2O_2} M_{H_2O_2} \sum_{i=0}^{T-1} \left(\frac{1+p}{1+d} \right)^{i} \frac{365\mathrm{days}}{\Delta T_{H_2O_2}}. \quad (12)$$

COST COMPARISON

Input parameters

The calculation and comparison of treatment costs for different scenarios requires definition of performance ranges for the two technologies and prices for the media and auxiliary materials used. For GAC, sorption isotherms can be used as a performance measure. We consider typical ranges for the Freundlich parameters as are found in the literature. The Freundlich sorption coefficients vary by a factor of 3 to 5 between different GAC types for one compound (see Table 1).

In the case of the Pd/Y system, degradation rates are independent from the type of chlorinated contaminant as the reaction is mass transfer limited rather than reaction limited. Degradation rates for flow through column experiments were reported previously (Schüth *et al.* 2000, 2004). Using original groundwater from a contaminated site,

Table 1 | Freundlich isotherm parameters for sorption of chlorinated ethenes on GAC from aqueous and gaseous phasesss

GAC type	Concentration range (mg/L)	$K_{F,w}$ (mg/g)/(mg/L)^{nF,w}	$n_{F,w}$
PCE			
F400*	NA	143	0.52
PE*	NA	236.3	0.51
H71*	1–40	116	0.38
F300†	NA	50.8	0.6
F400†	NA	84.1	0.4
Norit†	NA	51	0.56
Filtrasorb TL830‡	NA	106.2	0.52
Unspecified§	NA	309	0.22
Unspecified‖	NA	442.4	0.16
TCE			
F100*	0.01–20	67	0.52
H71*	0.005–50	58	0.44
HKW1*	0.01–20	54	0.45
F300†	NA	26.2	0.5
Witcarb950†	NA	28.2	0.4
Norit†	NA	28	0.62
Filtrasorb TL830‡	NA	48.4	0.59
Unspecified§	NA	204	0.39
Unspecified‖	NA	289	0.29
cis-DCE			
F400*	NA	11.7	0.59
PE*	NA	19.6	0.71
Norit†	NA	12	0.59
Filtrasorb 300†	8.4	0.5	
Norit†	NA	6.5	0.7
Filtrasorb TL830‡	12.7	0.53	
Unspecified§	NA	82	0.42
Unspecified‖	NA	170	0.26

*ETDOT.

†ADS guide (Mertz *et al.* 2000).

‡Tiehm *et al.* (2000).

§GUTmbH, online isotherm parameters accessed at http://gutmbh.de/aktivkohlevortrag3.htm

‖Prantner GmbH Verfahrenstechnik. The latter references do not further specify respective GAC types ("unspecified").

first-order rate constants were estimated to be about 0.7 min^{-1} (half life ~1 minute) in a laboratory setup. Rates in a corresponding field application over a time period of about 2 years were on average slightly slower, although for extended periods of time HHC concentrations were below the detection limit in the outflow, indicating half lives of less than 1.5 min^{-1} (Schüth *et al.* 2004). Slightly faster rates were observed in a field test by McNab *et al.* (2000) with a Pd on alumina catalyst of similar size. Substantially faster rates ($>$1.5 min^{-1}) were reported for a more than 100 day field trial by Davie *et al.* (2008). Based on these four studies it can be concluded that a first-order rate of 0.7 min^{-1} is a realistic lower boundary value for long term treatment using these materials.

It was also shown that degradation rates are dependent on the catalyst grain size (Schüth *et al.* 2004). The size of the Pd/Y catalyst pellets (~1.5 × 3.0 mm) can be significantly reduced without critically increasing the flow resistance (back pressure) in the system. To show this effect for the Pd/Y system, we performed column experiments according to the experimental setup described in Schüth *et al.* (2000) with crushed catalyst pellets. Figure 1 shows the linear dependency of the first-order rate constants on grain size. For the smallest tested grain size (~0.5 mm) showing no significant back pressure during operation, a maximum rate of 19.7 min^{-1} was measured.

Based on the published field studies and our laboratory experiments, rates of 0.7 min^{-1} and 19.7 min^{-1} were taken as lower and upper limits for cost comparison, respectively, with a rate of 3.7 min^{-1} representing the geometric mean.

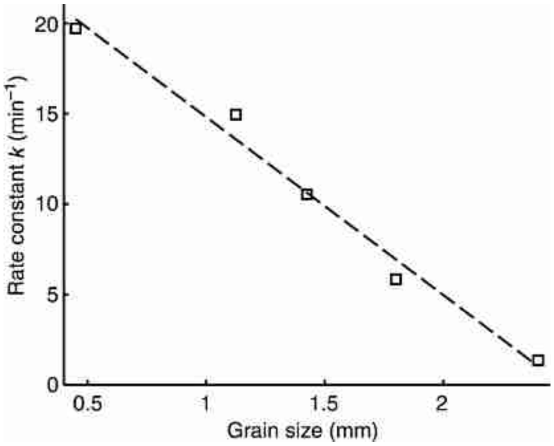

Figure 1 | Dependency of Pd/Y reactor first-order rate constants on grain size of pellets.

Besides the degradation rates the lifetime of the catalyst, from installation to replacement, has to be defined. We reported fairly stable degradation rates over a time period of about 2 years (Schüth *et al.* 2004). However, a first replacement of the catalyst was necessary after 5 years of operation (data not published). For cost comparison we therefore define a lifetime of 3 years for the catalyst until replacement, which is a conservative assumption.

Material properties, prices and technical parameters are compiled according to information from vendors, literature and documented field applications (see Table 2). For GAC only the cost for the material itself have to be considered, i.e. 2 €/kg and 0.60 €/kg, respectively. For the Pd/Y system, the price for Pd (300 $/ounce), for the zeolite support (100 €/kg), and for H_2O_2 (1.50 €/kg) have to be taken into account. The ranges of uncertainty and/or variability inherent to the material parameter values listed in Table 2 cannot accurately be reflected and instead medium values are taken. However, to examine the role of uncertainty, we selected the assumed cost values for the Pd/Y system, for which, in contrast to the established GAC, least experience from field applications exists. Prices for the components of the Pd/Y system were varied within defined boundaries.

In our hypothetical treatment scenarios, two decisive input parameters were held constant. Firstly, the volumetric flow rate Q was set to 1 m^3/h as changes would have a linear effect on the costs of both technologies, and therefore does not affect their relative performance. Secondly, the treatment goal C_{MCL} was set to a concentration of 0.01 mg/l, reflecting a typical drinking water standard for (higher) chlorinated ethenes. The other crucial parameters, inflow concentration to be treated, time period looked at, and the type of contaminant, were varied as these parameters have distinctive effects on the different technologies.

Comparison Pd/Y and GAC

In Figure 2 the temporal development of the cumulative costs (E_{tot}) for the Pd/Y system and GAC over a time scale of 15 years and an inflow concentration of 1 mg/l are presented. For the Pd/Y system the average first-order rate of 3.7 min^{-1} is assumed as well as costs for palladium,

Table 2 | Parameter specifications for cost comparison

Material property and demand	Fixed values (medium)	Ranges (low/high)
Pd/Y reactor		
Density Pd/Y	$\rho_{PdY} = 0.5\,g/cm^3$ ($500\,kg/m^3$)	
Effective porosity Pd/Y	$n_{PdY} = 50\%$	
Weight ratio of Pd	$w_{pd} = 0.004$	
Rate constant ranges	$k = 3.7\,min^{-1}$	
Lifetime until replacement	$\Delta t_{PdY} = 3$ years	
H_2O_2 flushing interval	$\Delta t_{H_2O_2} = 2$days	
H_2O_2 concentration during flushing	$C_{H_2O_2} = 10\,g/L$	
Cost parameters		
Pd	$\varepsilon_{Pd} = 300$ \$/oz (7,720 €/kg)	200–400 \$/oz (5,140–10,290 €/kg)
Cost ratio for recycling of Pd	$rec_{pd} = 35\%$ (referred to ε_{Pd})	20–50%
Zeolite Y	$\varepsilon_Y = 100$ €/kg	80–120 €/kg
H_2O_2	$\varepsilon_{H_2O_2} = 1.50$ €/kg	1–2 €/kg
GAC unit cost	$f_{GAC} = 2.00$ €/kg	No ranges considered
Rate of price increase	$p = 2\%$	
Discount rate	$d = 7\%$	
Total operation time	$T = 15$ years	

the zeolite, and H_2O_2. The costs roughly follow a step function of 3-year intervals reflecting periodic refill of the catalyst. The successive decrease of the step sizes over time is due to the discount rate. Apparently, the expenditures for the zeolite dominate and account for about 80% of the total costs, whereas those for Pd and H_2O_2 supply are only in the range of ca. 10% each. Due to first-order degradation, E_{tot} would be equal for cases with different concentrations but with same ratio C_w/C_{MCL}.

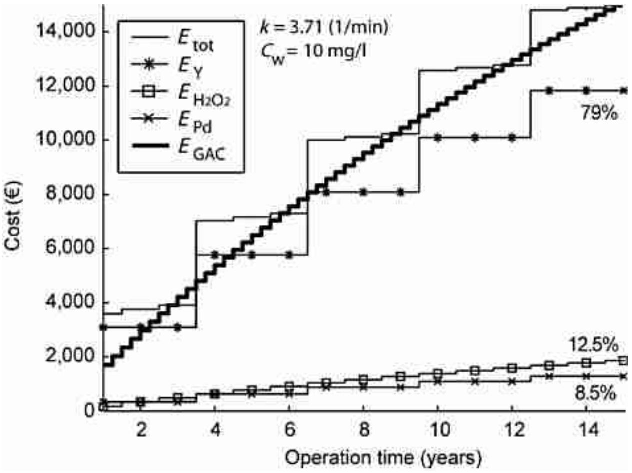

Figure 2 | Development of total expenditures (E_{tot}) and costs for individual Pd/Y reactor elements assuming a three-year exchange interval and medium system cost. After 15 years, the costs are equal for GAC use (sorption from water phase) if the linear sorption coefficient is $K_{d,w} = 12.6$ (mg/g)/(mg/L).

Costs for GAC treatment (E_{GAC}) are highly dependent on the sorption capacity, i.e. GAC type and contaminant. To enable a direct comparison between Pd/Y and GAC therefore the sorption capacity is determined that results in identical costs for both systems after 15 years of operation, assuming a GAC price of 2 €/kg. This is achieved using a threshold value of the linear sorption coefficient $K_{d,w}$ of 12.6 (mg/g)/(mg/L). The step cost function for GAC indicates about quarterly replacement of exhausted GAC. The step size is solely dependent on the assumed reactor size (i.e. GAC mass) but does not influence overall costs.

Due to constant operational costs and using the same discount values, E_{tot} and E_{GAC} differ only marginally in the three-year turn. Slight differences are caused by higher charges for fresh Pd in the first year than successive use of recycled Pd. As a result, the estimated threshold value of $K_{d,w}$ is virtually independent of operation time. Also, $K_{d,w}$ is independent of the flow rate Q, since both Pd/Y-system and GAC costs are expressed as linear functions of Q.

Since the cost comparison between Pd/Y and GAC is mainly governed by the degradation rate for the catalyst, k, and the influence of C_w on $K_{d,w}$, these relationships are subsequently elaborated in detail. For GAC, the relationship between $K_{d,w}$ and C_w is shown in Figure 3, using the range of isotherm parameters for PCE, TCE and cis-DCE listed in Table 1. The ranges produce areas in the $K_{d,w} - C_w$ diagram which are typical for the contaminants (here: the same in Figure 3(a–c)). Due to the nonlinearity of the isotherms, $K_{d,w}$ values decrease with an increase in C_w. Since different GAC types and references are considered, overlaps of the areas can be found. For example, for $C_w = 1$ mg/L sorption capacities for PCE and TCE are reported that both are about $K_{d,w} = 60$ (mg/g)/(mg/L).

Each value of $K_{d,w}$ denotes a certain consumption of GAC. The higher $K_{d,w}$ the higher the associated treatment costs. The calculation of the costs enables a direct comparison of the Pd/Y system with GAC. As demonstrated in Figure 2, for a given concentration C_w and a degradation rate k of the Pd/Y system, a $K_{d,w}$ threshold value can be calculated for GAC that yields same costs for both systems. Consequently, it is possible to trace systems of same cost along indifference curves within the range of C_w. This is shown for minimum, average and maximum values of k in Figure 3(a–c). All GAC-specific values of $K_{d,w}$ that lie above this indifference curve yield lower costs for GAC than Pd/Y and vice versa.

When comparing the ranges of $K_{d,w}$ for the ethenes with the position of the indifference curves, the Pd/Y-system turns out to be increasingly favorable for rising contaminant concentration and less chlorinated ethenes. If the rate constant for the Pd/Y system is rather high ($k = 19.7\,\mathrm{min}^{-1}$), GAC treatment is only favorable for low PCE concentrations. Even if price ranges for the Pd/Y system are considered (Table 2, Figure 3: dotted lines), the catalyst is preferable for all cases with concentrations above 10 mg/l. As depicted in the diagram for $k = 3.7\,\mathrm{min}^{-1}$, these advantages for the catalyst disappear with declining degradation rate. However, for cis-DCE, the GAC fixed bed is in general more expensive. Only for the lowest assumed k ($0.7\,\mathrm{min}^{-1}$) does Pd/Y not appear to be a favorable option.

Particularly for the lower chlorinated ethenes such as cis-DCE, stripping and successive sorption on GAC from the gaseous phase yields significantly higher sorption capacities. A critical design parameter is the air to water ratio AW (Equation (5)). Higher AW ratios would result in lower gas-phase contaminant concentrations and therefore less contaminant loading on the GAC at breakthrough. Assuming 100% removal efficiency, the AW is fixed at 30 (see Equation (5)) for the cost comparison, reflecting the lower range of common operation conditions for stripping of chlorinated ethenes (Dvorak & Schauble 2001). Figure 4 shows that sorption from the gaseous phase now makes GAC competitive in comparison to the catalyst. Only the assumption of high first-order rate constants for the catalyst and high contaminant concentrations in the aqueous phase results in a better cost performance of the Pd/Y system.

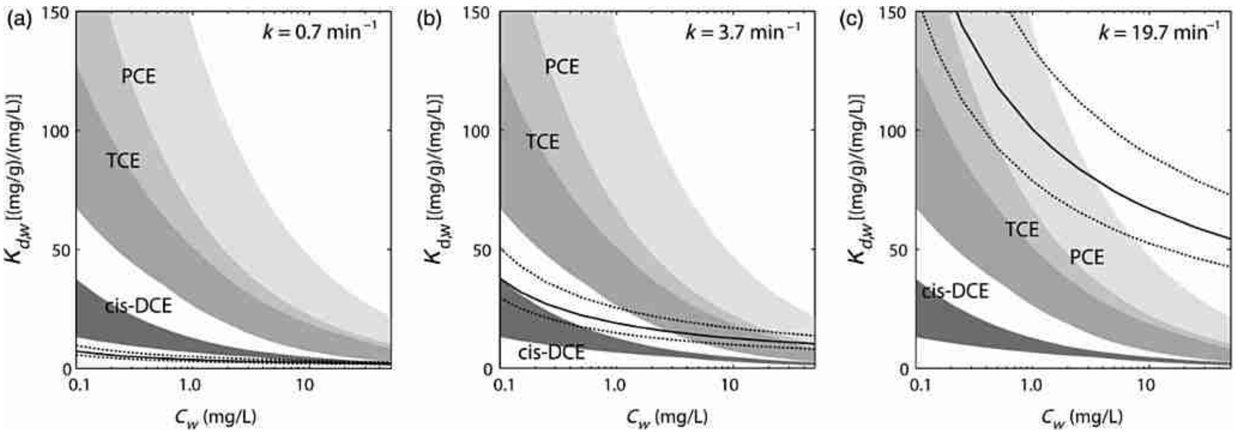

Figure 3 | Areas denote contaminant-specific (partly overlapping) ranges of linear sorption coefficients $K_{d,w}$ for GAC (aqueous phase). Solid line in a)–c) displays indifference curves for Pd/Y reactor costs compared with GAC (i.e. the threshold value of $K_{d,w}$ as a function of C_w). Dotted curves demarcate variability of the threshold value if the ranges for cost functions are considered.

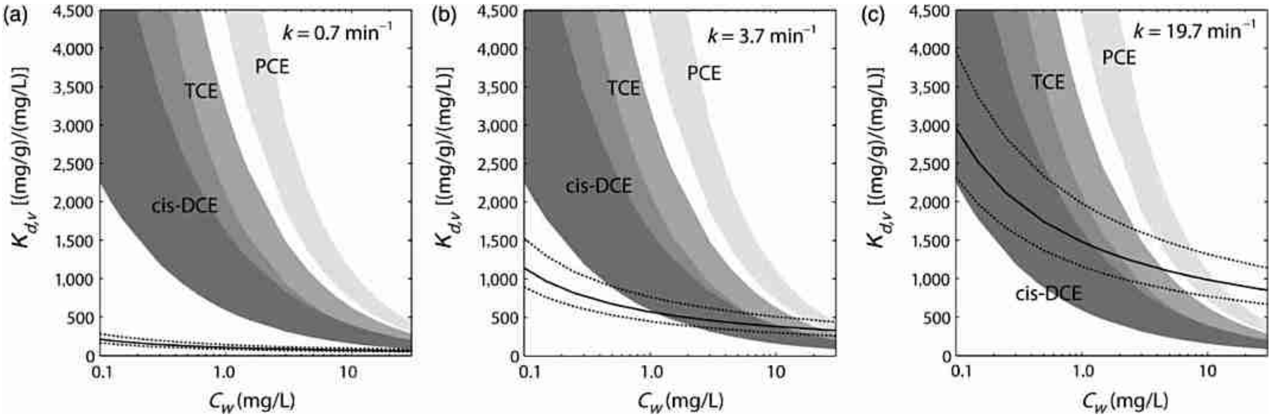

Figure 4 | Areas denote contaminant-specific (partly overlapping) ranges of linear sorption coefficients $K_{d,v}$ for GAC (gas phase). Solid line in a)–c) displays indifference curves for Pd/Y reactor costs compared with GAC (i.e. the threshold value of $K_{d,v}$ as a function of C_w). Dotted curves demarcate variability of the threshold value if the ranges for cost functions are considered.

In order to further investigate the role of k for the outcome of the comparison of the catalyst to GAC, subsequently average sorption isotherms are taken for each ethene. As a further constraint, the abovementioned base case ($Q = 1\,\mathrm{m}^3/\mathrm{h}$, $T = 15$ years, medium prices) is chosen to compute absolute cost contours for Pd/Y in a k-C_w-plot. These are shown in Figure 5, for convenience scaled with respect to the half life times $t_{1/2} = \ln(2)/k$. Please note that, as mentioned above, the total costs are directly proportional to Q. Therefore, the role of this parameter is not examined in detail.

In Figures 3 and 4, it was possible to delineate indifference curves for ranges of the GAC sorption capacity. On the Pd/Y cost contours of Figure 5, we can equally trace the contaminant specific costs for GAC, E_{GAC}, along decreasing concentrations. Similar to those in Figures 3 and 4, these lines represent curves of indifference: if $t_{1/2}$ is higher and accordingly rate k lower, total costs rise and GAC is favorable. In contrast, higher rates which represent the entire area under these curves denote benefits for the catalyst.

The rising indifference curves delineate the trend identified above: Pd/Y becomes more competitive with growing contaminant concentration. Moreover, when comparing Figure 5(a and b), the economic advantage of stripping is highest for cis-DCE. For the other ethenes, stripping does not appear to be recommendable at high concentrations

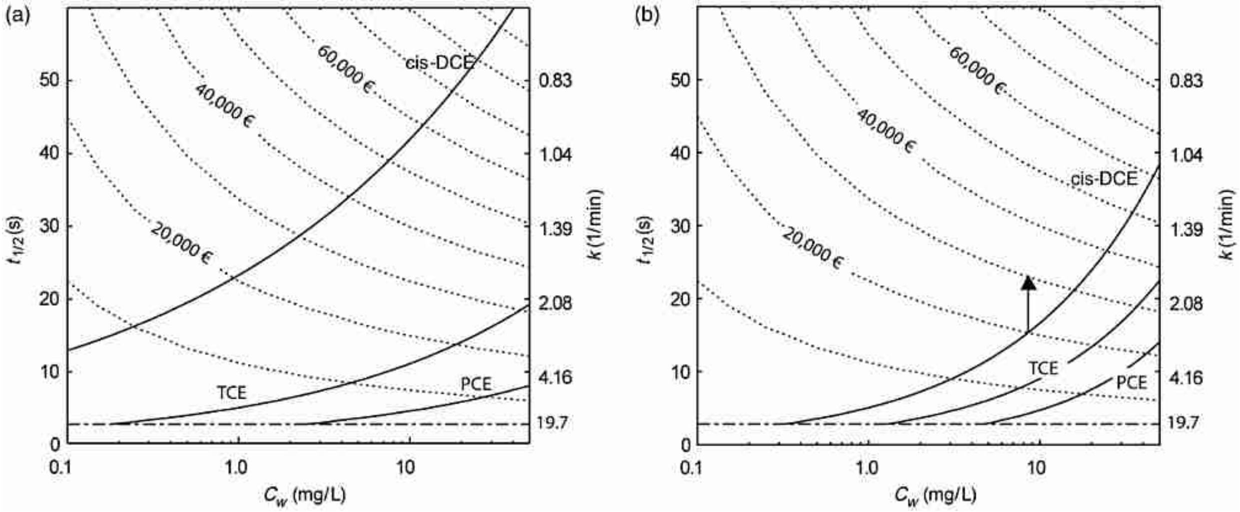

Figure 5 | Isoline plots of calculated costs for Pd/Y with curves of indifference when compared with sorption on GAC from a) water and b) vapor. Arrow marks shift of curve when fixed costs of 10,000 € for the stripping system have to be considered.

($C_w >$ approx. 10 mg/L). This is due to steeper indifference curves for stripping compared to sorption directly from water, a fact which basically reflects the differences in the Freundlich exponents. In practice, however, there may be other technical decision criteria for preferring adsorption from the gaseous phase than only the costs for the GAC. For example, much smaller contact times in the fixed bed are required for adsorption from the gaseous phase (in the order of seconds) than from water (ca. 20 min) to approach sufficient equilibrium conditions (Bayer *et al.* 2005*b*).

For the assumed prices and measured degradation rates, there exist contaminant-specific minimum values of C_w, above which the Pd/Y-system can perform better at all. In the plots (Figure 5), these values are represented by the intersection between indifference curve and lowermost line demarcating the highest practical value of $k = 19.7\,\text{min}^{-1}$. This is for example 0.2 mg/l and 1.0 mg/l for TCE when sorption occurs from water and air, respectively. For cis-DCE, such a minimum value only exists for sorption after stripping ($C_w = 0.3$ mg/l). In contrast, very low values of k, which yield half life times about 60 sec, always yield a better economic result for GAC.

Especially when stripping is considered, the cost for supply and maintenance of the treatment plant may be important to consider. This refers to the operation of a stripping tower, heater, etc. Such costs can be incorporated into the diagrams of Figure 5 by adding the respective net present value costs to the case of interest. For example, consider a cis-DCE contamination of $C_w = 9$ mg/l. For sorption from air, we compute a threshold for $K_{d,v}$ of $2.6\,\text{min}^{-1}$ ($t_{1/2} = 16$ sec) at total costs of 20,000 €. If additional costs for the treatment plant surmount to 10,000 €, the threshold for $K_{d,v}$ shrinks to $1.8\,\text{min}^{-1}$ ($t_{1/2} = 23$ sec, arrow in Figure 5(b)). The same procedure of vertically shifting the indifference curves can be applied to any other case, where site specific demands are known.

CONCLUSIONS

Due to the multiple factors involved, general cost-based comparison of different water treatment technologies is often not possible. In order to establish a more general framework for cost comparison than offered by unique case-specific cost calculations, we develop economic indifference curves. The principle is to reverse the perspective and identify those case-specific conditions, for which technologies have the same price. This enables to rank technologies according to cost-efficiency. It also facilitates to characterize the role of the influencing factors on this ranking and consequently the robustness of ranking: the more distant the actual conditions are from the indifference curve in the diagram, the less will the optimal choice be influenced by parameter variability or uncertainty.

The concept is applied to identify potential application window of innovative Pd on zeolite (Pd/Y) catalysts for contaminant groundwater treatment in comparison to the more established technology with granular activated carbon (GAC). The findings for the two technologies are solely based on a relative cost comparison of the treatment step itself using performance parameters that are inherent to the methods. Other cost parameters, e.g. planning cost and personal costs, are neglected. This is in our opinion justified as these can hardly be captured in such a general framework. Accordingly, the parameters have to be calculated on a case by case basis.

The resulting indifference curves illustrate application windows that can be used to support the decision for a specific technology. In general, high concentrations favor destructive methods with first-order degradation kinetics compared to e.g. sorptive removal. Especially lower chlorinated ethenes are efficiently removed by the Pd/Y method as its performance is independent of at least the contaminants studied here.

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