

Permeable Adsorbing Barrier for Groundwater Protection from Single-Compounds and Multicomponent Contamination by Chlorinated Organic Compounds

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This work deals with the application of a Permeable Adsorbing Barrier (PAB) for the remediation of an aquifer contaminated by Tetrachloroethylene (PCE) and Trichloroethylene (TCE). Based on a hydrological and geotechnical characterization of the entire polluted aquifer, the design and optimization of the barrier parameters (location, orientation and dimensions) are defined by an iterative procedure using a CFD (Computational Fluid Dynamics) approach. Laboratory adsorption tests on binary system (i.e. PCE+TCE) on a commercial activated carbon are carried out to support the PAB design. A site located near a solid waste landfill in the metropolitan area North of Naples (Italy), where PCE and TCE are simultaneously present, is considered as a case study. Model results show that the PAB designed is effective for the remediation of the contaminated aquifer, both for single-compound and binary contamination, since the concentration of pollutants flowing out of the barrier is everywhere always lower than the concentration limits provided for Italian regulations on groundwater quality.

1. Introduction

The *in-situ* treatment of contaminated groundwater is gaining growing interest as an alternative to the classical depuration methods based on *pump and treat* technology. The accidental discharge at industrial sites can lead to groundwater contamination both by inorganic and organic compounds. In particular, due to their widespread use and subsequent disposal, chlorinated hydrocarbons, such as Tetrachloroethylene (PCE) and Trichloroethylene (TCE), are commonly found at hazardous waste disposal sites, especially in urban industrial areas. They are persistent in nature and produce toxic and carcinogenic intermediate products; furthermore, the contamination often involves the simultaneous presence of many pollutants that can affect the efficiency of common adopted decontamination strategies.

The large extent of groundwater contamination with these compounds has led to use of various innovative remediation technologies. The most important techniques currently available for the *in-situ* decontamination of polluted groundwater include Air Sparging, Soil Vapor Extraction, Chemical Oxidation, Permeable Reactive Barrier (PRB), etc. A PRB is a wall of reactive material whose hydraulic conductivity is higher than that of the surrounding soils, so that the contaminated groundwater is forced to pass through the barrier itself, moving under natural hydraulic gradient. Even if a fair comparison among the depuration technologies is strictly site-dependent, a PRB allows the minimisation of operating and maintenance costs and it is specifically intended for the treatment of large volumes, with diffuse contamination and low pollutant concentrations (D'Andrea et al., 2005). The mechanism of action of a PRB depends on the choice of the reactive material used to build the barrier itself. The most widely used reactive material for the treatment of groundwater polluted by chlorinated organic compounds is zero-valent iron (Jun et al., 2009), in which pollutants are degraded through a series of reduction reactions. Alternatively, adsorbing media can be used to build the barrier which, in this case, is referred herein as Permeable Adsorbing

Barrier (PAB). Adsorption can be efficiently used for the removal of both organic and inorganic pollutants with different chemical properties (Di Natale et al., 2009); in particular, activated carbons are unselective porous solids which allow the simultaneous capture of many pollutants (Erto et al., 2011b).

The design of adsorption treatments mainly depends on sorbent adsorption capacity in equilibrium conditions but, despite the large knowledge about single-compound systems available in the pertinent literature, the multicomponent competitive interaction has received scarce attention. It is worth to observe that the assessment of the adsorption capacity of a compound in the presence of other solutes can be hardly derived from its single-compound adsorption properties. Even if some attempts for the definition of appropriate theoretical models for multicomponent adsorption have been recently made (Erto et al., 2012), the investigations in the field of concentrations typical of groundwater still remain partially unexplored. Similarly, the applications of a PAB to the capture of single compounds have been successfully achieved both for inorganic and organic compounds (Di Natale et al., 2008), but the extension to multicomponent systems has still to be correctly addressed.

In this work, the design of a PAB for the remediation of an aquifer contaminated by PCE and TCE is presented. A comparison between single compound (i.e. PCE or TCE) and binary (i.e. PCE and TCE) treatment is carried out, in order to explore the concrete possibility to extend the use of a PAB to the capture of multicomponent contamination. Laboratory tests are performed to characterize the equilibrium adsorption properties of the activated carbon in PCE/TCE containing aqueous solutions, with concentrations typical of polluted groundwater. The design procedure is based on the use of Computational fluid dynamic (CFD) codes for the simulation of groundwater flow and pollutant capture inside the barrier.

2. Permeable Adsorbing barrier design

The design of a PAB consists in the identification of the barrier location and orientation, in the definition of its dimensions (length, height, and width) and, finally, in the determination of the amount of adsorbing material (Erto et al. 2011a). A preliminary characterization of the adsorbing media must be achieved to support a correct barrier design. In particular, the physical properties (porosity, density, etc.) and the adsorption capacity both in single and multicomponent systems have to be defined.

Simultaneously, a complete knowledge of all the hydraulic, geotechnical and contaminant properties of the polluted groundwater is a fundamental step to understand the dynamics of an aquifer and, hence, for barrier design and optimization (Erto et al., 2011a).

Once the geometrical properties of the barrier together with the adsorbing material have been chosen, the barrier performance must be checked by evaluating the evolution in time of the pollutant plume over the calculation domain considering that the pollutant concentrations downstream the barrier ($C_{OUT, i}$) have to be everywhere lower than the fixed limit values ($C_{lim, i}$) for the whole barrier lifetime.

The design of the barrier requires the use of an iterative procedure by the application of a *trial and error* approach; the whole methodology can be effectively assisted by CFD (Computational Fluid Dynamics). In this work, a commercial 2D model flow, MODFLOW™ is used to describe convection and dispersion inside the aquifer, while a Visual Basic Application code, developed on purpose by Authors, is used to describe capture phenomena inside the barrier.

2.1 Aquifer/PAB modelling equations

Generally, in the saturated zone of an aquifer, the advection and dispersion phenomena determine the solute contaminant transport. In a two-dimensional system, for a porous media with a uniform porosity distribution, the mass transport equation can be written as in the following (Bear, 1979):

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C_k) + \sum_{k=1}^N R_h \quad (1)$$

where C_k is the concentration of the pollutant (e.g. PCE or TCE) dissolved in groundwater, t is the time, x_j is the distance along the respective coordinate axis, D_{ij} is the hydrodynamic dispersion coefficient, v_j is the seepage or linear pore water velocity, while $\sum_{k=1}^N R_h$ is a chemical reaction rate.

The hydrodynamic dispersion coefficient, D_{ij} , is a second-rank tensor consisting in the sum of mechanical dispersion tensor and the molecular diffusion coefficient (a scalar).

The linear pore water velocity, v_j , can be calculated by the Darcy equation, which can be written as:

$$v_j = K_{ij} \cdot \frac{\partial h}{\partial x_j} \quad i, j = 1, 2, 3 \quad (2)$$

where K_{ij} is the hydraulic conductivity of the porous medium (a second-order tensor), and h is the hydraulic head, that can be calculated starting from Laplace equation. A complete description of the equations set for aquifer/PAB modelling has been reported in Erto et al. (2011a)

In a PAB, where adsorption phenomena take place, the chemical reaction term of Eq(1) is represented by adsorption and can be expressed as follows:

$$\sum_{k=1}^N R_h = \frac{\rho_b}{n_b} \frac{\partial \omega}{\partial t} = K_c a [C - C^*(\omega)] \quad (3)$$

where ω represents the pollutant concentration on solid, ρ_b the dry bulk density of the adsorbing material, n_b its porosity, $C^* = C^*(\omega)$ is the pollutant liquid concentration at thermodynamic equilibrium with adsorbing solid; C^* derives from the adsorption isotherm and defines the mass transfer driving force in the transport model equation, a is the specific surface area of the adsorbent, K_c is the global mass transfer coefficient. Throughout the entire flow domain, the initial PCE/TCE concentrations in the groundwater are known and they are assumed to be zero on the surrounding soil.

2.2 Adsorption material characterization

Laboratory tests to support the PAB design procedure have been carried out at the temperature $T=10^\circ\text{C}$ using a granular activated carbon (GAC), the Aquacarb 207EATM (provided by Sutcliffe Carbon). This GAC has the following characteristics: a BET surface area of $950 \text{ m}^2 \text{ g}^{-1}$, an average pore diameter of 26 \AA , a dry bulk density (ρ_b) of 500 kg m^{-3} , a porosity (n_b) of 0.4 and a hydraulic conductivity of about 0.001 m s^{-1} . PCE (Erto et al., 2009) and TCE (Erto et al., 2010) adsorption isotherms in single compound systems on the selected GAC were reported in previous works. In Figure 1, the PCE and TCE adsorption isotherms in binary system on Aquacarb 207EATM GAC at 10°C are reported.

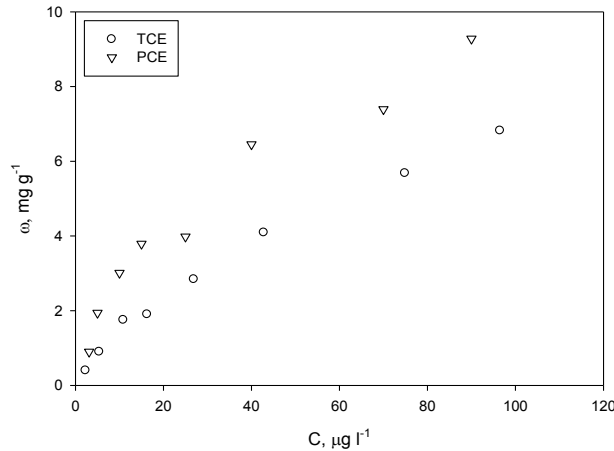


Figure 1. PCE and TCE adsorption isotherms in binary system. $T=10^\circ\text{C}$, $\text{pH}=7$

Experimental data reveal that the PCE adsorption capacity is the highest in the investigated equilibrium concentration range. Moreover, a comparison with single-compound data previously available shows that PCE adsorption capacity is almost independent on the presence of TCE (Erto et al., 2009), while TCE adsorption is slightly reduced in presence of PCE (Erto et al., 2010). These results are consistent with those reported in previously available studies on the same mixture and in similar experimental conditions (Erto et al., 2011b). However, for low concentration values of the two compounds, such as those usually found in polluted groundwater, the competitive effect is lower and, for this reason, the multi-component Langmuir model Eq(2) satisfactorily interprets the experimental data.

$$\omega_i = \frac{\omega_{\max,i} K_i \cdot C_i^*}{1 + K_i \cdot C_i^* + K_j \cdot C_j^*} \quad (4)$$

where ω_i is the adsorption capacity of either PCE or TCE, $\omega_{i, MAX}$ the correspondent maximum value and C_i , C_j and K_i , K_j are equilibrium concentrations and adsorption constants, respectively. The Langmuir model parameters obtained by regression of single-compound data reported in Erto et al. (2009) and Erto et al. (2010) are: $\omega_{1, MAX} = 1.944 \text{ mol kg}^{-1}$; $\omega_{2, MAX} = 5.512 \text{ mol kg}^{-1}$; $K_1 = 4.60 \cdot 10^4 \text{ L mol}^{-1}$; $K_2 = 1.98 \cdot 10^4 \text{ L mol}^{-1}$ (with 1=TCE; 2=PCE).

The complete experimental procedure for binary adsorption tests have been reported in Erto et al. (2011b).

3. Application of PAB design algorithm

The PAB design procedure has been applied to a PCE/TCE-contaminated aquifer near a solid waste landfill in Giugliano in Campania, in the metropolitan area North of Naples (Italy). In this area (2.25 km²), several solid landfills are located and an enormous amount of solid wastes was deposited in the last decades. A complete characterization of the aquifer was previously made (Di Nardo et al., 2010) and the main properties are reported in Table 1.

Table 1. Case study: aquifer characteristic and PAB properties

Aquifer characteristic	
Polluted area total extent, A	1.1 km ²
Transversal site extension, Y	996 m
Piezometric gradient, J	0.01 m m ⁻¹
Porosity, n_s	0.25
Dry soil bulk density, ρ_s	1,500 kg m ⁻³
Hydraulic conductivity, K_s	$5 \cdot 10^{-5} \text{ m s}^{-1}$
PCE maximum concentration	30.0 $\mu\text{g L}^{-1}$
TCE maximum concentration	6.4 $\mu\text{g L}^{-1}$
PAB properties	
Reactive media	Activated carbon
Dry bulk density, ρ_b	520 kg m ⁻³
Porosity, n_b	0.4
Hydraulic conductivity, K_b	0.01 m s ⁻¹
Barrier width, W	3 m
Barrier length, L	900 m
Distance from contaminant plume, E	6 m

The soil can be considered as made of a single mineral type (Neapolitan yellow tuff), with a hydraulic conductivity of $5 \cdot 10^{-5} \text{ m s}^{-1}$. Throughout the entire flow domain, the pollutant concentration onto soil can be considered to be zero due to its very low adsorption capacity towards organic compounds (Leone et al., 2012). The PCE and TCE concentrations are variable into the area and a maximum value of 30.0 $\mu\text{g L}^{-1}$ and 6.4 $\mu\text{g L}^{-1}$ for PCE and TCE can be registered. These values result higher than the correspondent Italian regulatory limits for groundwater quality, established at 1.1 $\mu\text{g l}^{-1}$ and 1.5 $\mu\text{g L}^{-1}$ for PCE and TCE.

4. Numerical results

The design procedure has been applied to all the polluted area and it has repeated, separately, hypothesising either single compound (i.e. PCE or TCE) or binary (i.e. PCE+TCE) contamination. However, simulation results in terms of pollutant concentrations flowing out of the barrier ($C_{out, PCE}$ and $C_{out, TCE}$) have been reported only in correspondence of the points where the maximum concentration of PCE (Point S) and TCE (Point P) have registered, respectively. As a matter of fact, these points represent the most critical situations and the barrier width that assure the abatement of PCE/TCE concentration under the regulatory limits in correspondence of these points can be considered as efficacious for all the domain. The numerical simulations led to the determination of pollutant concentrations flowing out of the barrier as a function of the barrier width (W). In Figure 2, the results are reported separately for PCE and TCE, and for single-compound and binary systems, together with the current Italian regulatory limits.

As expected, for both the compounds, an increase in the barrier width determines a reduction of the concentration flowing out of the barrier. In particular, it can be observed that, due to the higher initial concentration of PCE and its lower regulatory limit, a wider barrier is necessary for PCE capture. In particular, a 3 m wide barrier, also inclusive of a safety coefficient, provides the best results for PCE remediation, while for TCE a 2 m wide barrier would be largely sufficient. Of course, in a binary system

contamination, the optimal width of the barrier corresponds to the higher of the two values which allows complying with the regulatory limits simultaneously for PCE and TCE. Furthermore, it is interesting to observe that the same width (3 m), that assure the respect of regulatory limit under the hypothesis of single-compound PCE contamination, can be adopted for a successful treatment of the same aquifer simultaneously contaminated by PCE and TCE. This result highlights the high potentialities of PAB, and in particular of the activated carbon used as reactive media, for the *in-situ* treatment of a multicomponent contaminated groundwater.

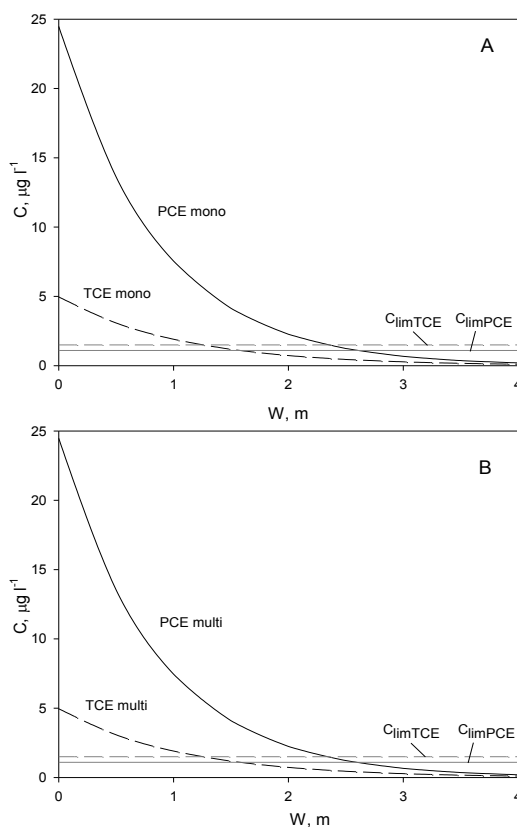


Figure 2. Single-Compound (A) and binary (B) TCE and PCE concentrations flowing out the barrier ($C_{\text{out, PCE}}$ and $C_{\text{out, TCE}}$) as a function of barrier width

Finally, in Figure 3, PCE and TCE concentrations, at the points S and P of the barrier respectively, have been represented as a function of barrier operating time, and in correspondence of a barrier width of 3 m. It is confirmed that, over an observation time of about 60 years, the inbound PCE and TCE concentrations change, assuming values significantly higher than their respective regulatory limits. Furthermore, results in Figure 3 show that a barrier 3 m wide can assure the simultaneous respect of the regulatory limits for both PCE and TCE, over the entire run time.

5. Conclusions

In this work, a procedure for the design of a Permeable Adsorbing Barrier made of activated carbon has been presented. The procedure has been applied to a real case-study represented by an aquifer simultaneously contaminated by Tetrachloroethylene (PCE) and Trichloroethylene (TCE). Model results showed that, for both the compounds, an increase in the barrier width determines a reduction of the concentrations downstream the barrier. In particular, a 3 m wide barrier provides the best results for PCE single-compound remediation, while for TCE a 2 m wide barrier should be adopted. Furthermore, a comparison of the optimal barrier dimensions between single compound and binary contamination has been carried out. In this case, the model results showed that the same width (3 m) that assure the respect of regulatory limit under the hypothesis of single-compound PCE contamination can be adopted for a successful treatment of the same aquifer simultaneously contaminated by PCE and TCE. This result

highlights the high potentialities of PAB for the in-situ treatment of a multicomponent contaminated groundwater.

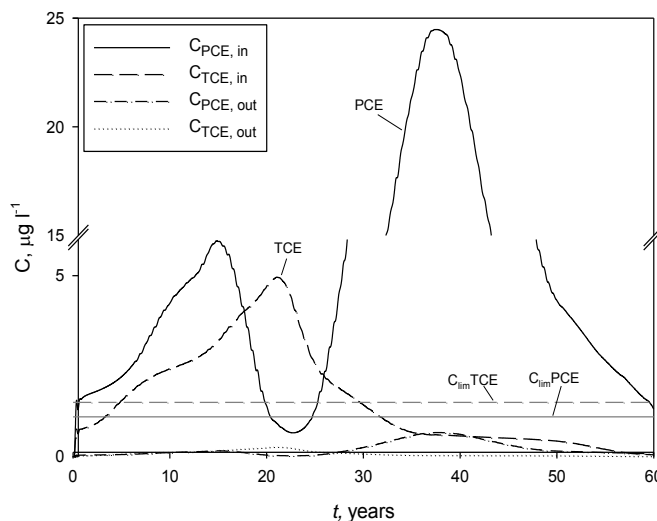


Figure 3. PCE and TCE concentrations in binary system at points S (for PCE) and P (for TCE) of the barrier, as a function of operating time. $W=3$ m. Regulatory limits for PCE ($C_{lim,PCE}$) and TCE ($C_{lim,TCE}$) are also indicated.

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