



Groundwater protection from cadmium contamination by permeable reactive barriers

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ABSTRACT

This work studies the reliability of an activated carbon permeable reactive barrier in removing cadmium from a contaminated shallow aquifer. Laboratory tests have been performed to characterize the equilibrium and kinetic adsorption properties of the activated carbon in cadmium-containing aqueous solutions. A 2D numerical model has been used to describe pollutant transport within a groundwater and the pollutant adsorption on the permeable adsorbing barrier (PRB). In particular, it has been considered the case of a permeable adsorbing barrier (PAB) used to protect a river from a Cd(II) contaminated groundwater. Numerical results show that the PAB can achieve a long-term efficiency by preventing river pollution for several months.

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1. Introduction

The presence of toxic pollutants in groundwater brings about significant changes in the properties of water resources and has to be avoided in order to preserve the environmental quality. Heavy metals are among the most dangerous inorganic water pollutants, they can be related to many anthropogenic sources and their compounds are extremely toxic. Many heavy metals, such as mercury, chromium and cadmium, accumulate in the aquatic food web reaching human beings through the food chain, and causing several pathologies [1]. The presence of heavy metals in groundwater is due to water exchange with contaminated rivers and lakes or to leaching from contaminated soils by rainfall infiltration.

Hence, the removal of heavy metals from groundwater is a major challenge for environmental engineering. One of the most promising technologies to conventional remediation methods, such as pump-and-treat, is the in situ treatment of groundwater contaminants by means of permeable adsorbing barriers (PRBs) [2–11]. Since 1990s both laboratory and full-scale studies have been carried out on these systems to show the potential of PRBs technology.

The main advantage of a reactive barrier is the passive nature of the treatment: the contaminated groundwater moves under natural hydraulic gradient through the permeable reactive zone

where the pollutant is degraded or immobilized. The use of reactive materials whose hydraulic conductivity is higher than that of the surrounding soils ensures that groundwater spontaneously flows through the barrier without any external energy input.

The reactive material used in the barrier varies according to the type of contaminants being treated. Most of the installed PRBs are made of zero-valent iron, Fe⁰, to remove heavy metals by redox reaction and precipitation [2–4] and to degrade chlorinated hydrocarbons, sulphates and nitrates [5–8]. A weak point of Fe⁰ barriers is that accumulation of precipitates may limit barrier longevity by reducing porosity and conductivity [4]: preferential flow paths in the barrier may form leading to a reduction of the contact time of the contaminated water with the reactive material [10].

Current research is focused on the use of alternative materials and physical chemical processes for PRBs [11–23]. Adsorption is a very promising physical process for removing heavy metals and chlorinated solvents from natural and industrial waters [24]. Adsorption phenomena include mass transfer from fluid bulk to a solid surface of adsorbing material and the formation of bonds between molecules in the fluid and atoms of the surface. Several materials exhibit good adsorption properties, such as zeolites [14,25,26], organic humic materials [13,27], by-products of industrial processes [17–20,27–30], industrial or natural activated carbons [15,31–34]. In this sense, the use of a permeable adsorbing barrier (PAB) can be considered as a special case of PRB application.

The selection of the adsorbing medium is a critical step for proper barrier designing and is strictly related with the specific pol-

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Nomenclature

Notation

a	specific surface area (m^2/m^3)
c	concentration (mg/l)
c°	solute concentration before sorbent addition (mg/l)
k	hydraulic conductivity (m/s)
k_c	mass transfer coefficient (m/s)
K	Langmuir model parameters (l/mol)
n	porosity
u_b	groundwater flow velocity (m/s)
x, y	horizontal and vertical coordinates (m)
$[x]$	molar concentration of the species x (mg/l)

Greek letters

α_L, α_T	longitudinal and transversal dispersivity (m)
Θ	temperature ($^\circ\text{C}$)
ρ_b	dry bulk density (kg/m^3)
ω	adsorption capacity (mg/g)
ω_{\max}	Langmuir model parameters (mg/g)

lutant to be treated. Adsorption isotherms and breakthrough curves must be experimentally determined to assess the equilibrium and kinetic characteristics of the adsorption process, and the assessment of a descriptive adsorption model is of the utmost importance for the reactor scale-up.

Furthermore, the design of a permeable reactive barrier has to account for hydrologic and geotechnical considerations in order to establish the spatial and temporal distribution of the contaminant plume, groundwater velocity and soil characteristics. Hence, the project of a permeable reactive barrier typically requires in situ analyses of the hydrological and the geotechnical conditions and geochemical properties of the polluted groundwater.

Computational fluid dynamic (CFD) codes for the simulation of reactive solute transport in groundwater flows can assure a successful PRB design in different working conditions. In particular, for a given polluted site, it is possible to analyse the effect of inflow pollutant concentration as well as to test the efficiency of different PRB configurations (continuous trench, funnel and gate, etc.). However, while hydraulic parameters can be properly estimated by in situ aquifer characterization and by properly calibrated models, a significant description of the adsorption dynamics is not currently available and strictly depends on the specific pollutant and on the selected sorbent.

The aim of this work is to investigate the potential application of active carbon in PAB for the removal of cadmium. The adsorption isotherms of the material are experimentally determined and a theoretical model is proposed for the interpretation of experimental results. An example of application of a PAB is presented, using a granular activated carbon for cadmium adsorption. To evaluate barrier performance a commercial 2D model flow, SEEPTM, is used to analyse the groundwater flow, while a Fortran code has been developed to describe convection, dispersion, and adsorption phenomena involving the pollutant.

2. Experimental analysis—determination of adsorption isotherms

2.1. Sorbent characteristics

Aquacarb 207EATM is a commercially available non-impregnated granular activated carbon, produced by Sutcliffe

Carbon starting from a bituminous coal. This material has a BET surface area of $950 \text{ m}^2/\text{g}$ and an average pore diameter of around 26 \AA . Sorbent particles with average diameter between 1 and 1.2 mm have been used in this work.

The sorbent is slightly alkaline ($\text{pH}_{\text{pZC}} 8$) and its surface functional groups, obtained with the Boehm's titration analysis, are mainly represented by basic activated sites and by lactones and phenols acid sites. Morphological and chemical properties of the GAC are reported in Di Natale et al. [34]. Before each experimental run, the sorbents have been carefully rinsed with distilled water and oven dried for 48 h at 80°C .

2.2. Sorption procedure

The stock solutions of test reagent are prepared by dissolving $\text{Cd}(\text{NO}_3)_2$ in bi-distilled water to obtain total cadmium concentration levels ranging from 5 to 50 mg/l . Solution pH is initially adjusted by adding HNO_3 (0.1 M) or KOH (0.1 M) and then it is not altered during the experimental runs. Solution salinity has been modified by adding NaNO_3 or NaCl . The experimental runs have been carried out in batch mode at constant temperature in a P.I.D. controlled thermostatic oven. Each sample consists of a 200 ml aqueous solution at the desired cadmium concentration, put in contact with a mass of sorbent ranging between 0.5 and 2 g.

Preliminary tests show that a contact time of 60 h is required to reach equilibrium conditions without additional stirring. At equilibrium conditions, both the cadmium concentration in solution and the cadmium amount on the carbon surface have been measured. The solution is filtered in a Hirsch funnel ceramic filter with the aid of a vacuum pump. The filtered solution is then analysed for pH and total cadmium concentrations while the carbon is leached to allow a direct measurement of the cadmium uptake on the solid surface. The accuracy of the experimental runs is checked by allowing a maximum error of 5% in the cadmium material balance.

2.3. Analytical methods

The total cadmium concentration in solution has been measured by means of air/acetylene flame atomic absorption spectrophotometry (AAS-F) by using a Varian SpectrAA-220 spectrophotometer, with cadmium standard solution provided by Sigma-Aldrich. Dilutions, where required, are carried out with 1 M HNO_3 water solution.

The amount of adsorbed cadmium is measured by leaching the solid material with 100 ml nitric acid aqueous solution (HNO_3 , 1 M) for 24 h, which assures a complete desorption of cadmium from the carbon surface. Then, the solution is analysed by means of AAS-F.

To establish the accuracy, reliability and reproducibility of the collected data, all batch isotherm tests are recorded in triplicate and average values only are reported. Blank tests are carried out in parallel. All the lab-ware used in the study is previously soaked in 1 M HNO_3 , triply rinsed with distilled water and oven dried. All the chemicals are AR grade supplied by Sigma-Aldrich.

2.4. Experiments

The typical adsorption isotherms for cadmium capture on the Aquacarb 207EATM are reported in Fig. 1 for experimental runs carried out at 20°C and equilibrium pH levels between 2.5 and 7.5.

Experimental results show that the adsorption capacity increases with cadmium concentration and strongly depends on the working conditions. The shape of the adsorption isotherm is typical of a Langmuir-like behaviour. Furthermore, adsorption isotherms clearly show that adsorption capacity monotonically increases by increasing pH.

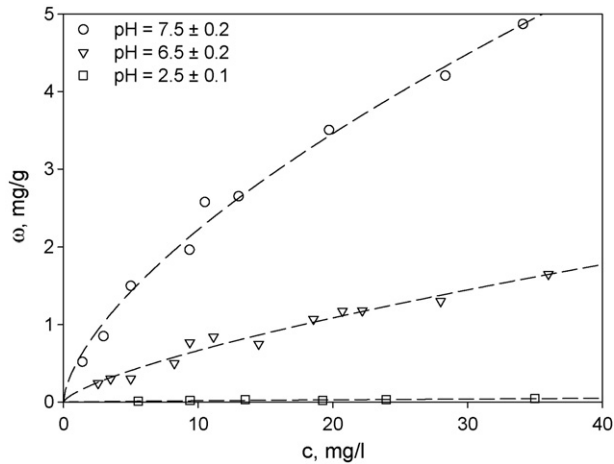


Fig. 1. Cadmium adsorption isotherms in distilled water at different pH; $T = 20^\circ\text{C}$.

The effect of solution pH on cadmium capture is further analysed by considering eight solutions with the same cadmium concentration, c_0 , and carbon dosage, m/V , and different initial pH values. Experimental results (reported in Fig. 2 as adsorption capacity as a function of the equilibrium pH) show that the GAC has a max adsorption capacity at a pH of about 7.5. At higher pH values, due to the precipitation of cadmium hydroxide, the determination of reliable adsorption isotherms is not possible.

The effect of solution pH can be referred to the well-known competition phenomena among cadmium ions (mainly represented by Cd^{2+} and CdOH^+ cations) and H^+ , as described, for example, by Benjamin [33].

The influence of solution salinity on cadmium adsorption capacity is important to estimate carbon effectiveness in real waters. To this purpose, some experiments have been carried out by using NaNO_3 or NaCl to modify salinity level. The results of this experiment (Fig. 2) point out that the adsorption capacity constantly decreases by increasing sodium nitrate concentration. The reduction of adsorption capacity at increasing solution salinity may be directly ascribed to the competitive effect of Na^+ ions with cadmium cations.

The adsorption of metallic ions onto activated carbon occurs through parallel and consecutive reactions that involve the active

Table 1

Mean value and standard error of parameters in Eq. (1) from data regression analysis

Parameter	Mean	Error (%)
ω_{\max} (mg/g)	11.80	24.4
$K_{\text{Cd}^{2+}}$ (l/mol)	3.09×10^3	20
K_{H^+} (kJ/mol)	7.67×10^6	22
K_{Na^+} (kJ/mol)	3.20×10^1	26

sites on carbon surface and ionic species of the dissolved metal, while the adsorption of molecular species is usually neglected [24,33,35]. The dependence of equilibrium adsorption capacity on the process parameters is strictly correlated with their influence on the concentration of ionic species in solution as well as on the sorbent properties.

The concentration of ionic species in solution is the driving force of adsorption phenomena and the speciation analysis of the equilibrium solution is the first mandatory step to describe the experimental data.

Cadmium speciation is evaluated by using mass and electric charge balance equations coupled with the equations representing chemical equilibria. Davies's formula [24,33] is used for the evaluation of the activity coefficients of the ionic species. Speciation analysis of cadmium nitrate solutions [24,36] shows that in all the investigated conditions cadmium is almost completely dissociated as Cd^{2+} for pH values below 7. For alkaline systems, almost all the cadmium precipitates as $\text{Cd}(\text{OH})_2$. Experiments show that, for the concentration range investigated, the precipitation of $\text{Cd}(\text{OH})_2$ occurs at $\text{pH} > 8$.

The multicomponent Langmuir model [33] has been applied to the description of cadmium ion adsorption mechanisms. The isotherm for cadmium adsorption involves the ionic species Cd^{2+} , H^+ and Na^+ and is expressed by Eq. (1):

$$\omega = \omega_{\max} \frac{K_1 [\text{Cd}^{2+}]}{1 + K_1 [\text{Cd}^{2+}] + K_{\text{H}^+} [\text{H}^+] + K_{\text{Na}^+} [\text{Na}^+]} \quad (1)$$

The ion concentrations of Cd^{2+} , H^+ and Na^+ are correlated with the cadmium adsorption capacity by means of Eq. (1) for the whole set of experimental data. The values of the regression parameters with their error of determination are reported in Table 1. The value of the correlation factor R^2 for the whole set of experimental data is 0.85.

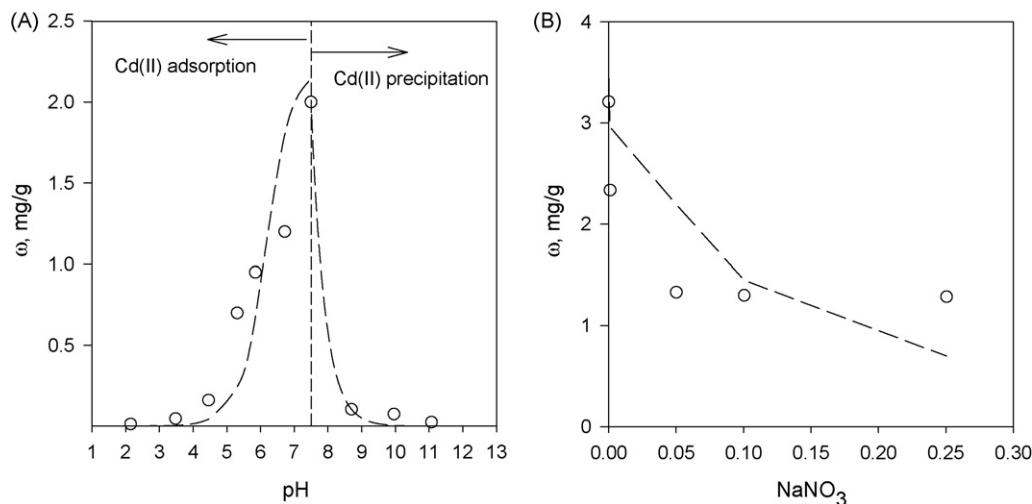


Fig. 2. (A) Effect of solution pH ($c_{\text{Cd}}^0 = 25 \text{ mg/l}$; carbon dosage: 7.5 g/l) and (B) solution salinity ($\text{pH} 7.3 \pm 0.2$; $c_{\text{Cd}}^0 = 25 \text{ mg/l}$; carbon dosage: 5 g/l) on cadmium adsorption; $T = 20^\circ\text{C}$: (○) experiments; (---) model Eq. (1).

The comparison between experimental data at different pH and salinity and the model results are reported in Figs. 1 and 2.

3. Permeable reactive barrier design—model setup

A successful barrier design requires the definition of many different parameters, such as: an appropriate hydraulic and geotechnical site characterization; the assessment of the contaminant properties, distribution and tracking; the choice of the reactive medium; the definition of the most cost-effective barrier location, orientation and dimensions. The variability of all these parameters gives rise to a variety of scenarios in which the barrier efficiency must be tested, therefore mathematical modelling is an essential tool to predict barrier performance in different working conditions.

3.1. Description of the case study

In this paper the case of a topsoil layer contaminated by cadmium and located near a river bank is simulated by solving the groundwater contaminant transport and adsorption equations in a 2D case study.

A 1 m deep and 100 m wide horizontal topsoil containing a cadmium concentration as high as $c_s = 10 \mu\text{g/g}$ lies above a clean free surface aquifer, confined at the depth of 7.0 m below soil surface by an horizontal aquitard, characterized by such a small hydraulic conductivity as to be considered as an impervious soil layer. Groundwater flows under natural hydraulic gradient towards a nearby river. To protect the river from the pollution due to the cadmium leachate by rainfall infiltration, the hypothesis of placing a barrier downstream the polluted aquifer is considered (Fig. 3).

In order to test the barrier deputation efficiency a critical case study is considered, consisting in an extreme rainfall event causing an infiltration height of 100 mm with a total duration of 24 h. The soil is characterized by a dry bulk density $\rho_b = 1600 \text{ kg/m}^3$, a high-hydraulic conductivity ($k = 0.001 \text{ m/s}$) and by the absence of adsorption or chemical reactions with the cadmium ions dissolved in the groundwater.

Assuming a moderately rainy climate (mean annual rainfall height around 1000 mm), rainfall events with some tens of millimetres of infiltration height in 24 h may happen several times every year. Assuming an average cadmium concentration in the rainfall leachate of the order of 0.1 mg/l, it takes 100 years to achieve a complete deputation of the topsoil. During these rainfalls, the concentration of the contaminated plume reaching the river may attain dangerous values.

The barrier is a continuous trench penetrating the aquifer at full-depth perpendicular to the groundwater flow to ensure that the most efficient capture of the plume is obtained.

A first choice of barrier dimensions is made by considering the capability to retain intense concentration peaks and the long-term performances.

For the first requirement, the residence time of the contaminated flow travelling through the barrier should be long enough for adsorption process to take place. Therefore, barrier width W

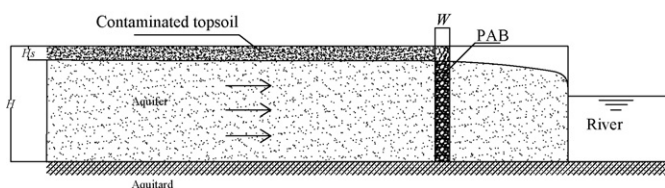


Fig. 3. Sketch of the geometry of the example of PAB application.

Table 2
Summary of PAB application example parameters

Aquifer characteristics	
Aquifer bed depth, H	7.0 m
Piezometric gradient, J	0.001 m/m
Porosity, n_s	$0.4 \text{ m}^3/\text{m}^3$
Hydraulic conductivity, k_s	0.001 m/s
Longitudinal dispersivity, α_L	1.0 m
Transverse dispersivity, α_T	0.2 m
Dry soil bulk density, ρ_s	1600 kg/m^3
Topsoil characteristics	
Contaminated depth, H_s	1.0 m
Mean Cd concentration in soil, ω_s	$10 \mu\text{g/g}$
Event characteristics	
Infiltration height, h	100 mm
Infiltration duration, T_s	24 h
Leachate pH	7.0
PAB characteristics	
Adsorbing medium	Aquacarb 207EA activated carbon
Dry bulk density, ρ_b	600 kg/m^3
Porosity, n_b	$0.4 \text{ m}^3/\text{m}^3$
Hydraulic conductivity, k_b	0.001 m/s
Barrier width, W	2.0 m
Numerical model parameters	
Horizontal space step, Δx	0.2 m
Vertical space step, Δy	0.2 m
Time step, Δt	100 s

must satisfy the following inequality (Eq. (2)):

$$\frac{W}{u_b} > (k_c a)^{-1} \quad (2)$$

In the above equation u_b represents groundwater flow velocity through the barrier, k_c the overall mass transfer coefficient for adsorption reactions and a represents the external specific surface of the adsorbent particles.

For intermittent contaminant sources, the second requirement may be addressed by considering the occurrence of desorption phenomena within the barrier. The rainfall infiltration mobilizes the contaminants stored in the soil and the barrier reduces their concentration by adsorption until it is saturated. However, whereas the polluted PAB is crossed by clean groundwater, adsorbed species are removed from the solid matrix giving rise to a contaminated plume at the exit of the barrier. A wider barrier ensures the gradual release of the adsorbed species so as to avoid intolerable outgoing concentration, virtually extending barrier life indefinitely.

At a first glance, the barrier width has been considered as large as 3.4 m. Once approximate dimensions have been defined, the optimal design for a permeable adsorbing barrier can be obtained by evaluating the barrier performance with numerical simulation at different working conditions. The characteristics of the simulated site are sketched in Table 2.

3.2. Pollutant transport and adsorption equations

The contaminant migration in a porous medium is due to advection–dispersion processes; therefore, considering a two-dimensional system, the dissolved cadmium mass balance equation may be written with indicial notation, as follows [37]:

$$\frac{\partial c_{Cd}}{\partial t} + \frac{\rho_b}{n} \frac{\partial \omega}{\partial t} + \frac{\bar{u} \nabla c_{Cd}}{n} - D_{ij} \frac{\partial^2 c_{Cd}}{\partial x_j^2} + S = 0 \quad (3)$$

In Eq. (3) c_{Cd} represents cadmium mass concentration in fluid, \bar{u} the unit flux vector, ω the cadmium concentration on solid, ρ_b the dry adsorbing material bulk density, n the soil porosity, and S represents a source of cadmium concentration (i.e. leakage from topsoil).

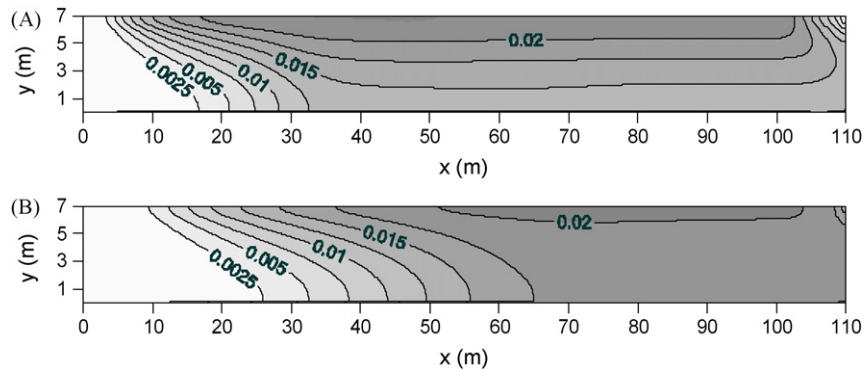


Fig. 4. Simulated Cd^{2+} concentration (mg/l) distribution in the groundwater 2 weeks (A) and 4 weeks (B) after an extreme rainfall event with infiltration height of 100 mm in 24 h.

The components of mechanical dispersion tensor D_{ij} may be expressed as follows:

$$D_{ij} = \begin{bmatrix} \alpha_L \frac{u_x^2}{|\bar{u}|} + \alpha_T \frac{u_y^2}{|\bar{u}|} & (\alpha_L - \alpha_T) \frac{u_x u_y}{|\bar{u}|} \\ (\alpha_L - \alpha_T) \frac{u_x u_y}{|\bar{u}|} & \alpha_L \frac{u_y^2}{|\bar{u}|} + \alpha_T \frac{u_x^2}{|\bar{u}|} \end{bmatrix} \quad (4)$$

In Eq. (4) α_L and α_T represent longitudinal and transverse dispersivity coefficients, respectively. Adsorption is supposed to take place without considering any interaction between cadmium ions and other adsorbed species. Under isothermal conditions ($T = 20^\circ\text{C}$), the second term on the left hand side of Eq. (4) reads

$$\frac{\rho_b}{n} \frac{\partial \omega}{\partial t} = k_c a [c_{\text{Cd}} - c_{\text{Cd}}^*(\omega, c_i)] \quad (5)$$

In Eq. (5) $c_{\text{Cd}}^*(\omega, c_i)$ derives from the corresponding adsorption isotherm and c_i represents the concentrations of dissolved ionic species.

The initial liquid and solid cadmium concentrations are assumed to be zero throughout the entire flow domain and the boundary conditions are reported in Eq. (6):

$$\begin{aligned} \text{Inflow boundary: } & \frac{\partial c_{\text{Cd}}}{\partial x} = 0, & x = 0, & 0 < y < H \quad \forall t > 0 \\ \text{Outflow boundary: } & \frac{\partial c_{\text{Cd}}}{\partial t} + u_x \frac{\partial c_{\text{Cd}}}{\partial x} = 0, & x = \lambda, & 0 < y < H \quad \forall t > 0 \\ \text{Impermeable bed: } & \frac{\partial c_{\text{Cd}}}{\partial y} = 0, & 0 < x < \lambda, & y = 0 \quad \forall t > 0 \\ \text{Soil surface: } & \frac{\partial c_{\text{Cd}}}{\partial y} = 0, & 0 < x < \lambda, & y = H \quad \forall t > 0 \end{aligned} \quad (6)$$

The numerical integration of Eqs. (3)–(5) with the boundary conditions (Eq. (6)) has been carried out by means of a first order finite difference implicit scheme with a dedicated Fortran code and by

using the SEEPTM code for the determination of the groundwater flow field in each computational mesh.

3.3. Numerical results

Fig. 4 reports the iso-concentration lines of cadmium in the aquifer at different time intervals after the rainfall event. The concentration of the contaminated plume reaching the river may attain concentration levels higher than 0.020 mg/l and largely above the 0.005 mg/l quality limit prescribed by 2000/60/CE EU Directive for surface waters.

After the introduction of the PAB (Fig. 5) the contaminated plume is adsorbed by the activated carbon and the cadmium concentration level reaching the river is around zero for the first 3 months. Then, the barrier starts to saturate, but the out-flowing cadmium level remains below the quality limit of 0.005 mg/l for more than 7 months.

The cadmium profile near the barrier is better described in Fig. 6. The highest value in cadmium concentration is reached after 1 month and the PAB is able to completely clean the inflow groundwater. After 3 months, the cadmium concentration starts to increase due to PAB progressive saturation, meanwhile the inflow concentration diminishes as well. Hence, the PAB ensures good long-term efficiency capturing almost all the leached cadmium and preserving the river for at least 7 months. Finally, Fig. 7 reports the simulated cadmium concentration distribution on the activated carbon of the PAB as a function of time. The presence of a peak of cadmium concentration at the centre of the PAB for long times is related to the progressive cadmium desorption due to the corresponding incoming clean groundwater through the barrier (Fig. 7). As a consequence, the PAB is able to self-clean. Furthermore, it is

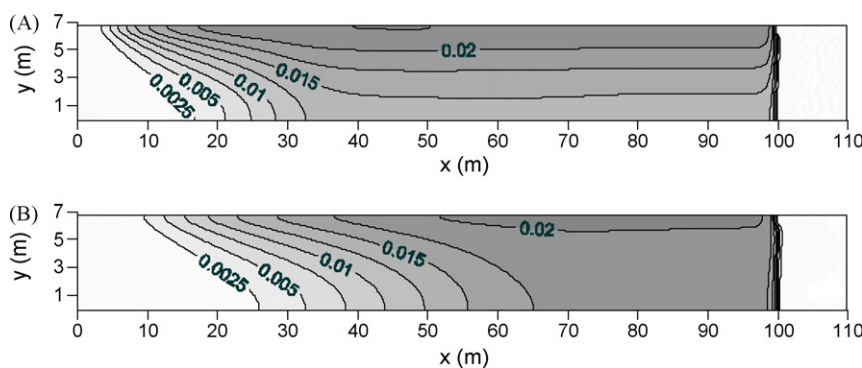


Fig. 5. Simulated Cd^{2+} concentration (mg/l) distribution in the groundwater 2 weeks (A) and 4 weeks (B) after an extreme rainfall event with infiltration height of 100 mm in 24 h in presence of PAB.

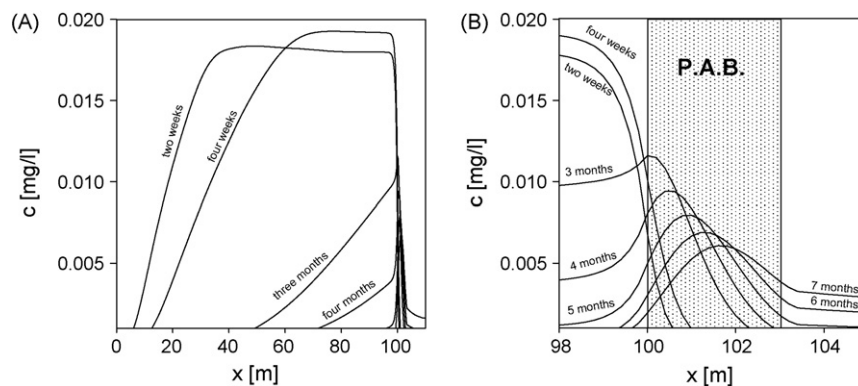


Fig. 6. Simulated Cd^{2+} concentration (mg/l) in the groundwater over a distance of 2 m behind the polluted soil at various stages after an extreme rainfall event with infiltration height of 100 mm in 24 h in presence of PAB: (A) overall cadmium concentration profile; (B) cadmium concentration profile near the PAB.

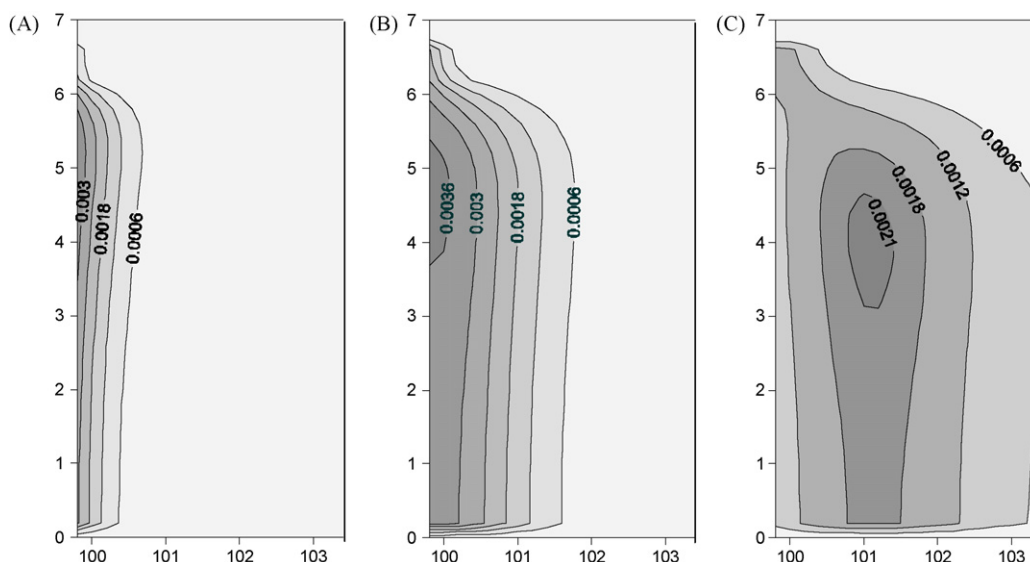


Fig. 7. Simulated distribution of adsorbed Cd^{2+} (mg/g) within the PAB at various stages after an extreme rainfall event with infiltration height of 100 mm in 24 h: (A) 1 month; (B) 3 months; (C) 6 months.

worth noticing that the maximum adsorption cadmium concentration is less than $4.0 \mu\text{g/g}$, which is far from the equilibrium value of around $30 \mu\text{g/g}$.

4. Conclusions

This paper analyses the possible use of an activated carbon permeable adsorbing barrier, PAB, to remove cadmium from a contaminated shallow aquifer. Laboratory tests have been carried out to characterize the equilibrium and kinetic adsorption properties of the activated carbon towards cadmium-containing aqueous solutions. A 2D numerical model is used to describe pollutant transport within groundwater and the pollutant adsorption on the PAB. The model is applied to a given case study: a PAB is used to protect a river from an inflowing groundwater contaminated by the mobilization of $\text{Cd}(\text{II})$ from a polluted topsoil associated to an extreme rainfall event. Numerical results show that the PAB ensures long-term efficiency preventing river pollution for as long as 7 months.

The reversibility of the adsorption process implies that $\text{Cd}(\text{II})$ ions are progressively released from the barrier when clean groundwater flows through it. However, simulations results show how, with a properly designed barrier, the out-flowing $\text{Cd}(\text{II})$ concentration can be always kept below critical limit values.

As the PAB reduces the concentration of inflowing pollutants and which are then gradually released over time the same pollutant in long times, it is not a removal technology but a way to properly “dampen” pollutants concentration peaks and to keep them below hazardous values. In this sense, although the overall pollutant emission is not reduced, the PAB results to be a reliable way to assure the compliance with environmental safety indications and to reduce pollution hazards.

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