Remediation of sandy soils contaminated with hydrocarbons and halogenated hydrocarbons by soil vapour extraction

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ABSTRACT

This paper presents the study of the remediation of sandy soils containing six of the most common contaminants (benzene, toluene, ethylbenzene, xylene, trichloroethylene and perchloroethylene) using soil vapour extraction (SVE). The influence of soil water content on the process efficiency was evaluated considering the soil type and the contaminant. For artificially contaminated soils with negligible clay contents and natural organic matter it was concluded that: (i) all the remediation processes presented efficiencies above 92%; (ii) an increase of the soil water content led to a more time-consuming remediation; (iii) longer remediation periods were observed for contaminants with lower vapour pressures and lower water solubilities due to mass transfer limitations. Based on these results an easy and relatively fast procedure was developed for the prediction of the remediation times of real soils; 83% of the remediation times were predicted with relative deviations below 14%.

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1. Introduction

Human activities lead to the introduction of large amounts of a wide variety of contaminants in the soil. This situation becomes more harmful to public health if the contaminant manages to percolate through the soil and subsequently reaches the groundwater. The most widely found contaminants in soils are volatile halogenated organic compounds, including trichloroethylene (TCE) and perchloroethylene (PCE), and petroleum hydrocarbons, including benzene, toluene, ethylbenzene and xylene (BTEX) (USEPA, 2010).

The choice of the appropriate remediation technique depends on the type of contaminants present in the soil, their location, the physical and chemical properties of the soil, and the operational conditions. In the last thirty years, in the USA, soil vapour extraction (SVE) was the most frequently used technology, being applied in about 23% of all remediation projects (USEPA, 2010). SVE is an efficient technology for the remediation of soils contaminated with volatile or semi-volatile organic compounds located in the unsaturated zone of the soil; it involves the application of a vacuum to the soil, creating an airflow through the soil matrix that transports the contaminants to extraction wells (Suthersan, 1999) and air treatment units before their release in the atmosphere. Several works studied the application of SVE to soils contaminated with BTEX, TCE and PCE. Switzer and Kosson (2007) evaluated the performance of SVE for the extraction of TCE from a landfill in the Savannah River Site, Lee et al. (2001) and Al-Maamari et al. (2009) performed similar tests to remediate petroleum hydrocarbon-contaminated sites in Korea and Oman, respectively. In all these cases the clean-up goals were reached, confirming the high efficiency of this technology.

However, SVE is affected by several factors that cause direct repercussions on the remediation time and the process efficiency. These factors can be grouped into: operational conditions (such as soil temperature and airflow rate), contaminant properties (such as vapour pressure and solubility), and soil properties (such as water and natural organic matter content).

The soil temperature influences the partition of the contaminant through the soil phases and therefore determines its availability for extraction by SVE. In some cases a 20 °C temperature increase can triple the vapour pressure of the contaminant which leads to an increase in its mobility (Poppendieck et al., 1999). There are several soil remediation technologies that use temperature as a key factor in the extraction of contaminants from the soil: heated SVE (Lucci

et al., 2007), thermally enhanced SVE (Park et al., 2005; Harmon et al., 2001), and soil heating using radio-frequency (Price et al., 1999; Roland et al., 2007) or microwave radiation (Kawala and Atamanczuk, 1998).

The airflow rate influences the mass transfer of the dispersed contaminant to the gas phase, desorption of the contaminant from the soil, and its dissolution from the aqueous phase. In a previous study, SVE experiments were performed in sandy soils with different water contents (0–4%), contaminated with benzene, toluene, ethylbenzene, xylene, trichloroethylene and perchloroethylene (250 mg kg^{-1}). When different airflow rates were used it was concluded that for airflow rates below 1.9 cm^3 s^{-1} equilibrium in the contaminant mass transfer was reached and slow diffusion effects were not observed. This led to a more efficient remediation process compared to those performed with higher airflow rates (19 cm^3 s^{-1}) (Albergaria et al., 2008).

Contaminants with high water solubilities tend to dissolve in the aqueous phase, decreasing their availability and consequently lowering the efficiency of the soil vapour extraction.

Soil water content (SWC) has multiple effects on SVE: it reduces the air-filled pores of the soil, it acts as a barrier between the pollutant and the soil matrix (influencing the contaminants' adsorption on the soil), and it dissolves the contaminant. In soils with high SWC the soil porosity decreases, rendering the movement of the air into soil difficult and consequently, affecting the efficiency of the process (Yoon et al., 2008; Poulsen et al., 1999). Experiments performed in soils contaminated with cyclohexane (250 mg kg^{-1}) showed that an increase of the SWC from 0 to 6% led to longer remediation times (from 1.8 to 4.9 h) (Alvim-Ferraz et al., 2006a, 2006b). On the other hand, a positive impact on SVE occurs due to the competition between soil water and the contaminants for adsorption sites (Tekrony and Ahlert, 2001). This competition can cause desorption of the contaminant from the soil, increasing the contaminants' mobility and consequently increasing the SVE efficiency.

The estimation of the remediation time is also extremely important to identify the most efficient remediation technology for a specific contaminated site. These estimations can be obtained through mathematical models based on differential equations (Sleep and Sykes, 1989; Baehr et al., 1989), analytical methods based on batch flush models (Falta et al., 1989), or mathematical models based on laboratorial simulations (Kaleris, 2002). Continuous research in this area is required to improve the accuracy of the estimation of the remediation time.

This work reports the study of an SVE process performed in sandy soils with different SWCs containing six of the most common soil contaminants: benzene, toluene, ethylbenzene, xylene, trichloroethylene and perchloroethylene. The inclusion of several contaminants allows the evaluation of the influence of SWC on different levels. The main objectives of the present study were: (i) evaluation of the influence of SWC on the remediation time and efficiency; (ii) evaluation of the influence of contaminant properties, such as vapour pressure and water solubility, on the remediation time; and (iii) development of a new and simple methodology to predict remediation times.

2. Experimental

2.1. Reagents

The used benzene, perchloroethylene (Riedel-de Haën), toluene, xylene, ethylbenzene (Merck), and trichloroethylene (Fluka) standards were of analytical grade quality and were used without further purification. All other substances were of analytical grade quality.

2.2. Apparatus

An Ai Cambridge GC95 gas chromatograph equipped with a Chrompack Hayesep Q 80–100 mesh (3 m × ¼″ × 4 mm) column and a flame ionisation detector (FID) were used for the quantification of the contaminants in the gas emissions using the external standard calibration method. The injector and the detector were set at 230 °C and the oven was maintained at 200 °C throughout the analysis. The flame gases of the detector were air (4.5 cm^3 s^{-1}) and hydrogen (0.50 cm^3 s^{-1}). The carrier gas was nitrogen used at a flow-rate of 0.50 cm^3 s^{-1}. Chromatographic data were recorded using Barspec Data System software. Using these experimental conditions the retention times of the contaminants were: 25 min for benzene and trichloroethylene, 51 min for toluene and perchloroethylene, 99 min for ethylbenzene and 101 min for xylene.

For quantification purposes, the external standard calibration method was used. For each contaminant, seven standards were prepared within the desired range (0.7–53 g m^{-3} for benzene and trichloroethylene, 0.7–32 g m^{-3} for toluene and perchloroethylene and 0.7–17 g m^{-3} for ethylbenzene and xylene) and analysed in triplicate. The obtained calibration curves showed correlation coefficients between 0.9914 and 0.9996. The relative standard deviations of the results of the triplicate analysis were below 4.7% which indicates that the method has an adequate precision.

2.3. Soil preparation and characterization

The sandy soil was collected at a 3-m depth at different locations on a beach near Porto (Portugal). The main components of this soil are silica and shell debris. The soil only contains negligible amounts of clay and natural organic matter. The soil was stored in plastic, non-contaminated vessels to guarantee the maintenance of its physicochemical properties. The preparation of the soils with different water contents involved five steps: a) washing until clear water was obtained; b) drying, first at room temperature during 5 days and then at 110 °C for 24 h, in order to obtain a soil with negligible water content; c) sieving through a 2-mm sieve to obtain a fraction of the soil with uniform physical properties; d) addition of different amounts of water to the sand in order to induce 2, 3 and 4% water contents; and e) homogenization by mechanical mixing. The prepared soils were stored in stoppered vessels and identified as P_0, P_2, P_3 and P_4, the subscript indicating the water content (%). The real sandy soils studied in this work were collected at different depths (from 20 cm to 1 m) from a different beach located in the same region. These sand samples were sieved through the 2-mm

Table 1
Characteristics of prepared (P_0, P_2, P_3 and P_4) and real sandy soils ($R_{0.5}$, $R_{0.6}$, $R_{0.8}$, $R_{1.0}$, $R_{1.2}$, and $R_{2.4}$) (particle size < 2 mm).

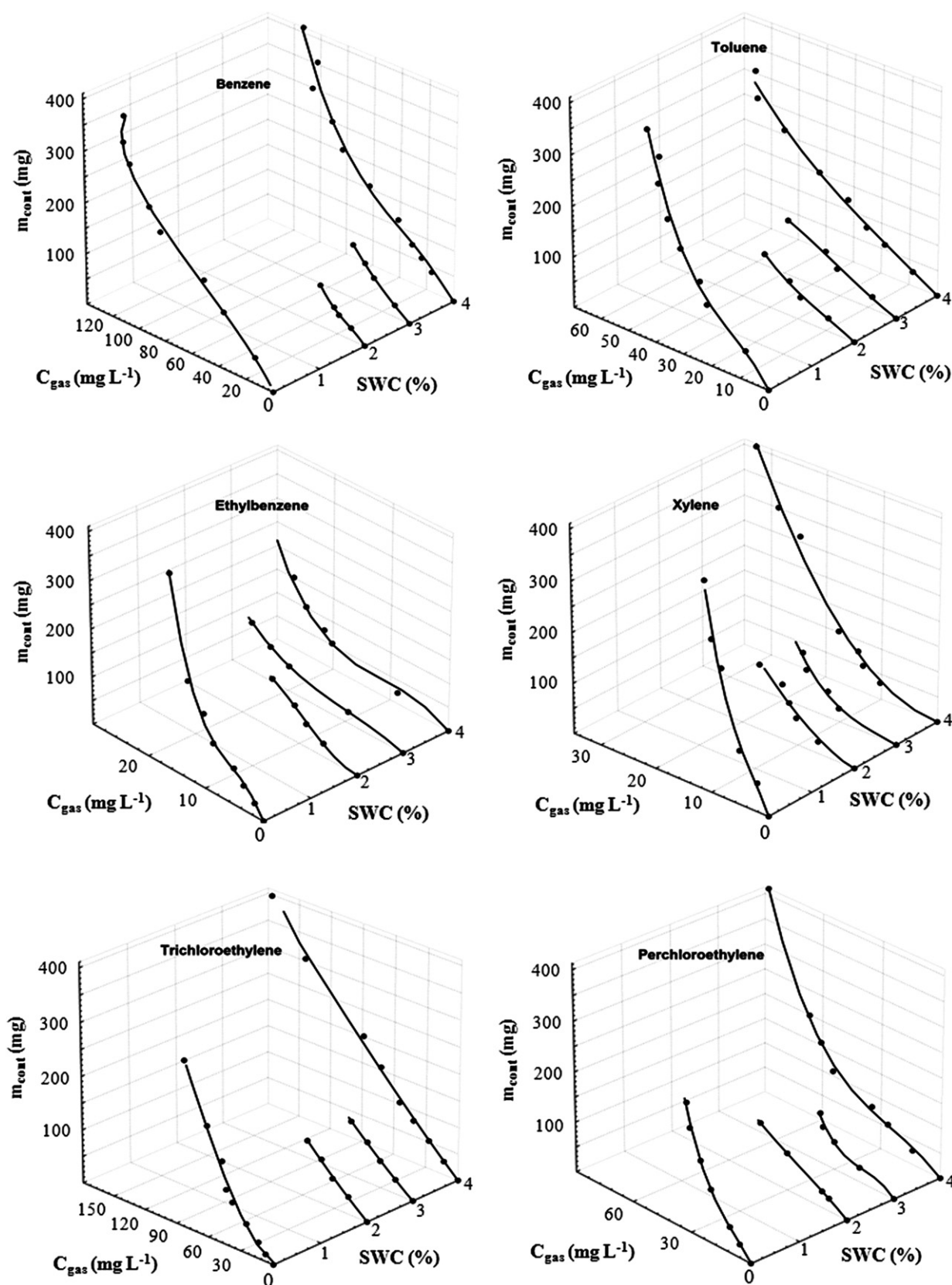| Soil	Apparent density (g mL^{-1})	Particle density (g mL^{-1})	Porosity (%)	pH	Water content (%)	Natural organic matter content (%)
P_0	1.5	2.5	42	8.8	0.0	<0.02
P_2	1.3	2.5	49	8.8	2.0	<0.02
P_3	1.3	2.5	50	8.8	3.0	<0.02
P_4	1.2	2.5	51	8.8	4.0	<0.02
$R_{0.5}$	1.4	2.4	44	8.1	0.5	<0.02
$R_{0.6}$	1.4	2.4	44	8.1	0.6	<0.02
$R_{0.8}$	1.4	2.4	45	8.1	0.8	<0.02
$R_{1.0}$	1.4	2.4	45	8.1	1.0	<0.02
$R_{1.2}$	1.4	2.4	46	8.1	1.2	<0.02
$R_{2.4}$	1.3	2.4	47	8.1	2.4	<0.02

Fig. 1. Relation between the contaminants' concentration in the gas phase of the soil (C_{gas}) and the amount of contaminant in the soil matrix (m_{cont}) at equilibrium conditions (296 K) in the prepared soils (P_0, P_2, P_3 and P_4) and the respective trend lines.
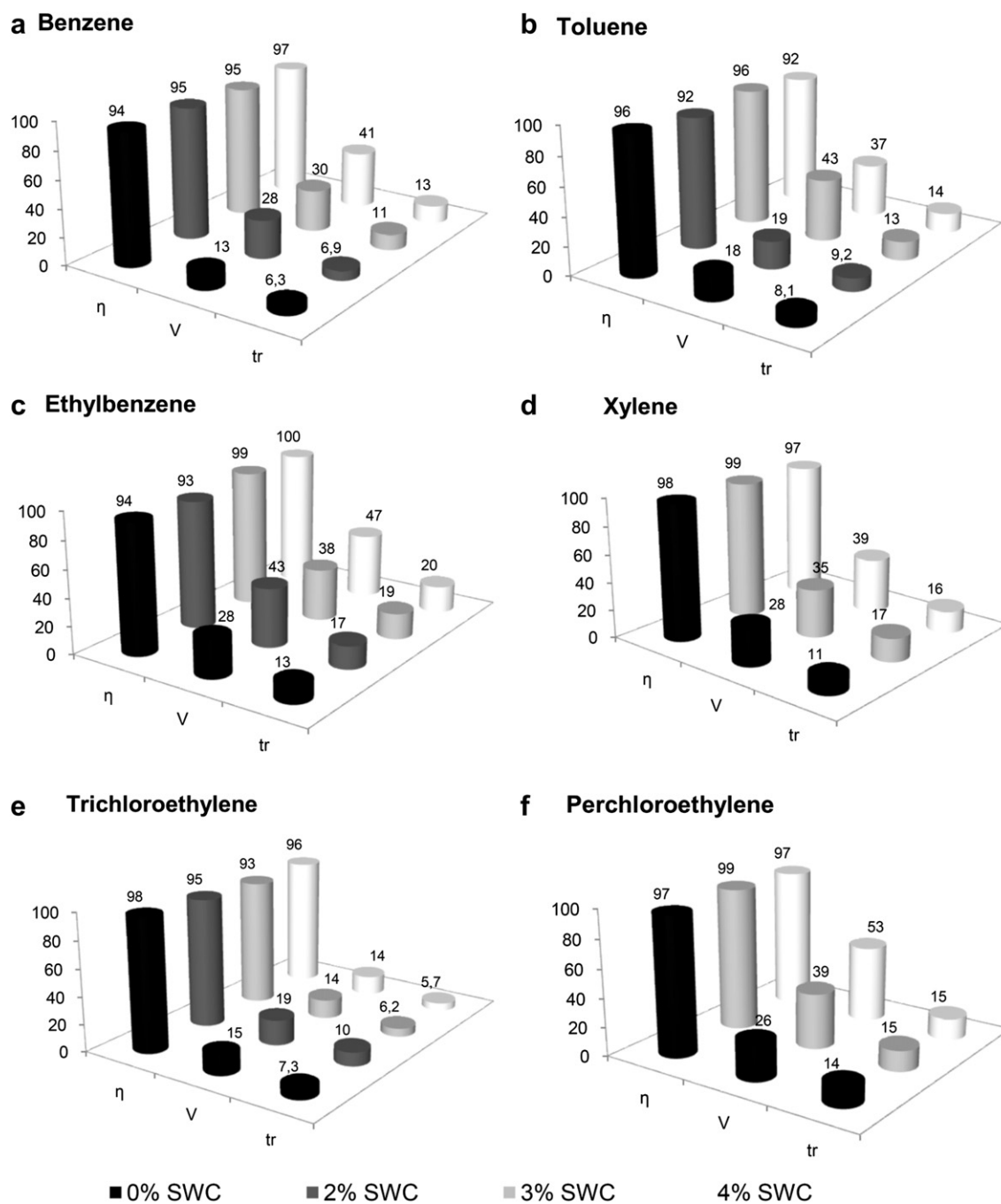
Fig. 2. Efficiency (η, %), volume of air used at STP (V, L) and remediation time (t_r, h) for SVE of the prepared soils (P$_0$, P$_2$, P$_3$ and P$_4$) (airflow rate: 0.64 ± 0.15 cm^3 s^{-1}).

sieve, stored in stoppered vessels and identified as R$_{0.5}$, R$_{0.6}$, R$_{0.8}$, R$_{1.0}$, R$_{1.2}$ and R$_{2.4}$, the subscript indicating the water content (%).

International standard methodologies were used for the characterization of the prepared and real soils and included the determination of apparent density, particle density, porosity, pH, and the water and natural organic matter contents (Albergaria, 2010).

2.4. Equilibrium isotherms

The equilibrium isotherms used in this work relate the concentration of the contaminant in the gas phase (C_{gas}) with the mass of contaminant in the soil matrix. This tool was used to calculate the amount of contaminant remaining in the soil matrix after the SVE.

The equilibrium isotherms of all the studied soils were determined using a stainless steel column ($h = 37$ cm and i.d. $= 10$ cm) and prepared using the following procedure: a) introduction of the
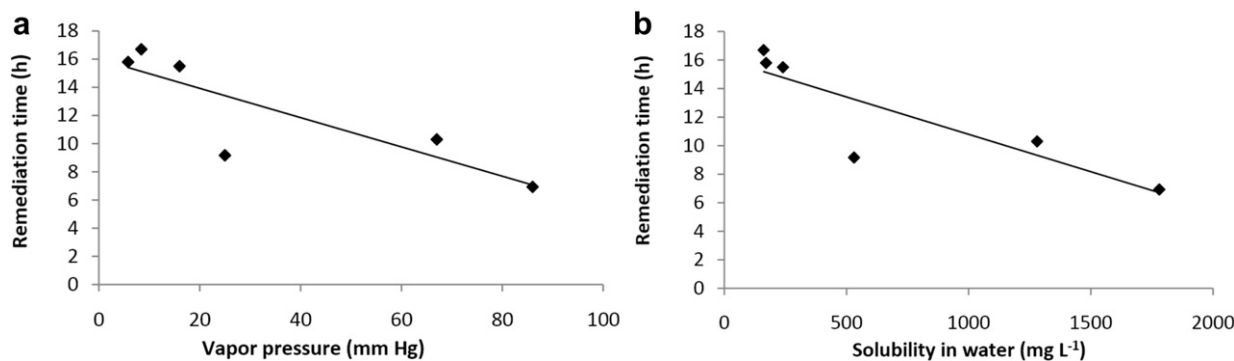
Fig. 3. Relation between the remediation time of the SVE and the (a) vapour pressure and (b) water solubility of the contaminants.

soil into the column (4.0 kg); b) contamination of the soil by adding 0.025–0.400 g of contaminant; c) equilibrium settling (48 h); and d) determination of the concentration of the contaminant in the gas phase of the soil at different heights of the soil column (Alvim-Ferraz et al., 2006a, 2006b).

2.5. Soil vapour extraction

The SVE experiments were applied to the remediation of prepared and real soils. The soil columns were prepared as described in Section 2.4 using 1.0 g of contaminant. After the equilibrium was reached the vacuum pump was turned on and the airflow rates were adjusted using a rotameter (airflows between 0.50 and 4.9 cm^3 s^{-1}, measured at STP, were evaluated). The air passed through the column, percolating through the soil matrix, and then through a sampling system where the contaminated emissions were collected and afterwards monitored by gas chromatography (Alvim-Ferraz et al., 2006a). To avoid any atmospheric contamination, the contaminants in the emissions were adsorbed on activated carbon before reaching the atmosphere. The remediation process was considered finished when C_{gas} was below 1.0 g m^{-3}. The time required to reach this point was considered the remediation time (t_r).

3. Results and discussion

3.1. Soil characteristics

The characteristics of the prepared and real soils are shown in Table 1. In all cases the natural organic matter content was below the limit of detection (0.02%) and the clay content was negligible; the relatively high pH values can be explained by the presence of shell debris. The real soils R$_{0.5}$, R$_{0.6}$, R$_{0.8}$, R$_{1.0}$, R$_{1.2}$, and R$_{2.4}$ have water contents within the range covered by the prepared soils.

3.2. Equilibrium isotherms

Fig. 1 presents the equilibrium isotherms including the respective trend lines at 296 K for all contaminants in the prepared soils (P$_0$, P$_2$, P$_3$ and P$_4$) under equilibrium conditions. These equilibrium isotherms were used to calculate the remaining amount of contaminant in the soil after SVE and the process efficiency. From Fig. 1 can be also concluded that in sandy soils, where adsorption phenomena are not significant, the concentration of the contaminant in the gas phase of the soil is highly influenced by its vapour pressure. The increase of the SWC reduces the monolayer capacity and consequently the adsorption capacity of the soil due to the decrease of the contact between the gas phase and the solid matrix,

leading to an increase of the concentration of the contaminant in the gas phase (Albergaria et al., 2010).

3.3. Soil vapour extraction

3.3.1. Influence of soil water content

As described in Section 2.5, the SVE experiments were monitored by gas chromatography until C_{gas} reached 1.0 g m^{-3}. After reaching t_r the column was left isothermically to reach a new equilibrium. The amount of contaminant remaining in the soil matrix was calculated using the equilibrium isotherms presented in Fig. 1.

For each experiment the volume of air passed through the soil column was calculated, as well as the process efficiency (η), using Eqs. (1) and (2), where Q is the airflow rate, t is the time, m_{cont} is the amount of contaminant spiked to the soil and m_{rem} is the amount of contaminant remaining in the soil matrix after SVE.

$$V = \int Q \, dt \tag{1}$$

$$\eta = \frac{(m_{cont} - m_{rem})}{m_{tot}} \times 100 \tag{2}$$

To evaluate the influence of SWC (Fig. 2) on the remediation process experiments were performed using an airflow rate of 0.64 ± 0.15 cm^3 s^{-1} (at STP). The choice of this flow-rate was based on a previous study (Albergaria et al., 2008).

The results showed that all the extraction efficiencies for the prepared soils were higher than 92%. Similar results were obtained by Qin et al. (2010) in experiments performed with chlorobenzene, where 96% of the contaminant was removed from two silty soils (0.4% of organic matter content), with SWC of 1 and 4%, after 72 h. This can be explained by the extremely low natural organic matter content in the soil, reducing the strong bonding between the soil and the contaminants, which in turn increases their availability for extraction. Under these conditions no significant influence of SWC on the process efficiency was observed. Qin et al. (2010) obtained a less efficient extraction (82%) when a soil with significant higher SWC (13%) was tested. The analysis of the remediation time and the used air volume indicated that SWC has a negative impact on SVE, leading to longer remediation times and higher volumes of pumped air. The different behaviour of trichloroethylene could be explained by small variations of the airflow rate which overlapped the influence of SWC.

3.3.2. Influence of contaminant properties

The influences of the contaminants' vapour pressures and water solubilities (Table 2) on the remediation time were also evaluated for all soils using an airflow rate of 0.64 ± 0.15 cm^3 s^{-1} (at STP). Fig. 3 shows, as an example, the results obtained with the P$_2$ soil.
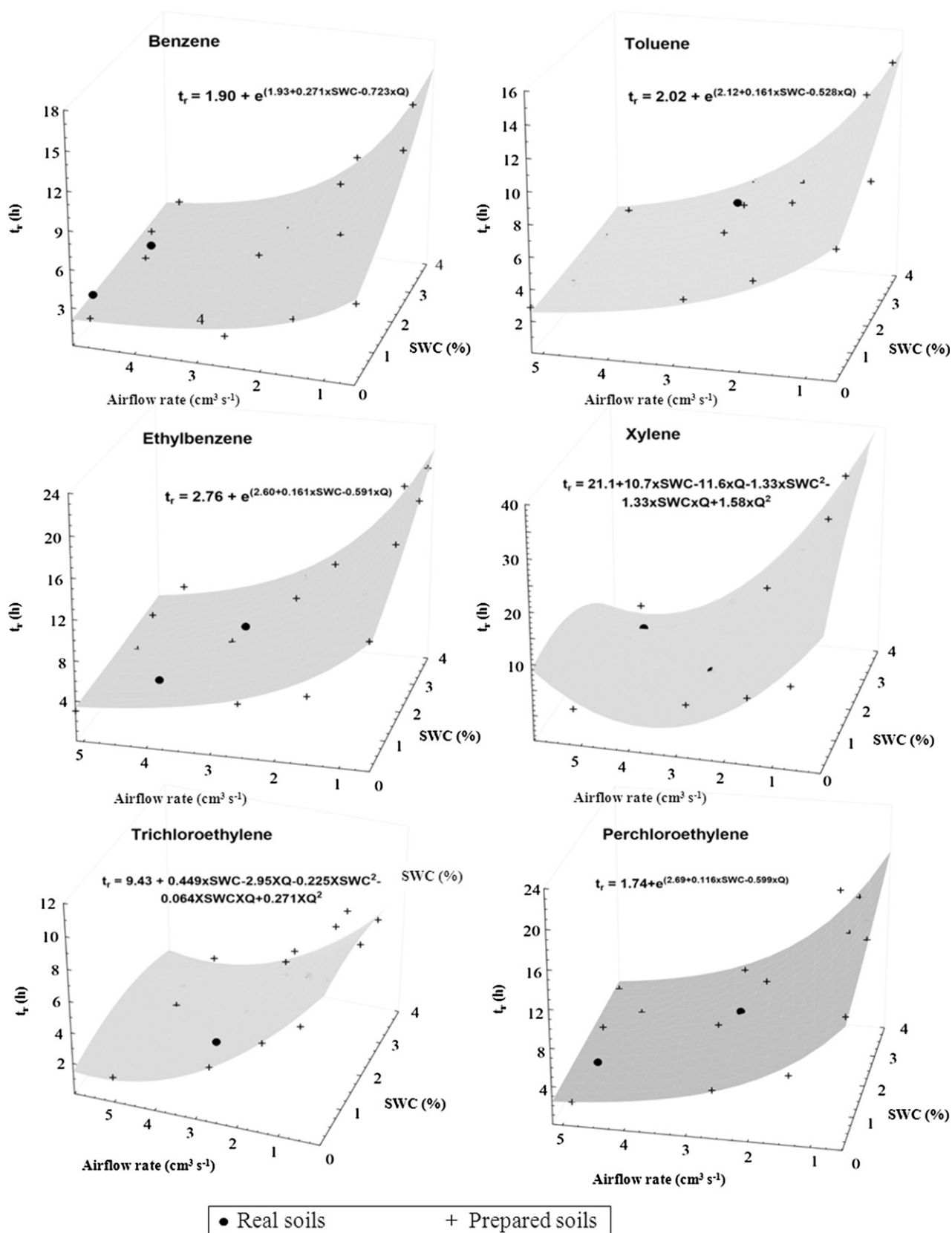
Fig. 4. Comparison of the remediation times obtained in SVE of real soils with the predicted times by the mathematical fitting of experimental results (weight of soil: 4.00 kg; airflow rate: 0.78 cm^3 s^{-1} STP).

For all the experimented soils, the results showed that contaminants with higher vapour pressures allow faster remediation processes because, in these cases, high amounts of contaminant were in the gas phase where they have increased mobility and are, therefore, more easily extracted from the soil. Contaminants with lower vapour pressures have a low tendency to vaporize and tend to form non-aqueous liquid phases which results in mass transfer limitations to the gas phase and consequently in longer remediation periods. This also occurs due to the decrease of the interfacial area between the two phases. Fig. 3 also shows that the remediation time was inversely proportional to the water solubility of the contaminant. This was unexpected because contaminants with high solubilities tend to dissolve in water and create mass transfer limitations to the gas phase, which hinders the extraction process and increases the remediation time. However, the influence of the vapour pressure of these contaminants, which were the highest among the studied compounds, exceeded the negative influence of the contaminant's solubility, leading to shorter remediation times. This indicates that the vapour pressure has a more important role in SVE than the contaminants' water solubility.

3.3.3. Prediction of the remediation time

Through mathematical adjustments of the obtained results for the prepared soils the remediation times of real soils could be predicted. Fig. 4 shows the surfaces obtained using the adjustments for the six contaminants (correlation coefficients > 0.9817). The equations indicated in Fig. 4 were used to predict the remediation time of soils with SWCs and airflow rates within the studied range: 83% of the remediation times for real soils were predicted with relative deviations below 14%, corresponding to a maximum deviation of 32 min with regard to the actual remediation time. The results demonstrate that this simple procedure can provide important information about the time needed to achieve the predefined clean-up goals of a remediation, representing a valuable tool to professionals.

4. Conclusions

For sandy soils with negligible amounts of clay and natural organic matter, contaminated with benzene, toluene, ethylbenzene, xylene, trichloroethylene and perchloroethylene, it was concluded that:

(i) All the remediation processes presented efficiencies above 92%, and were not influenced by the used contaminant. This can be explained by the type of soil studied in this work in which there is no strong bonding between the contaminant and the soil particles.
(ii) An increase of the soil water content led to a more time-consuming remediation because of the negative impact of SWC on the air movement. Benzene was the contaminant that presented the highest relative increment on the remediation time.
(iii) SVE experiments applied to soils containing the contaminants with the highest vapour pressures (benzene and trichloroethylene) were the fastest while the slowest were obtained for soils containing the contaminants with lower vapour pressures (xylene and ethylbenzene).
(iv) More soluble contaminants tend to dissolve in water and consequently present mass transfer limitations to the gas phase, hindering the extraction process. However, and in this case, these contaminants were also the ones that presented higher vapour pressures what overlapped the influence of the contaminant's solubility in water turning the remediation faster.

Using a simple mathematical adjustment of the experimental results an easy and relatively fast procedure was developed for the prediction of the remediation times of real soils; 83% of the remediation times were predicted with relative deviations below 14%.

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