Study of the influence of temperature the venting depollution process of soils contaminated with volatile organic compounds

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Abstract: Venting is one of the most used in situ remediation methods for unsaturated soils contaminated with volatile organic compounds (VOC). The development of mathematical models and their validation by means of experimental results allowed the identification of the main parameters which influence the soil depollution process. The influence of temperature on the venting depollution process of soils polluted with volatile organic compounds was studied in this investigation. It was found that the depollution efficiency is strongly influenced by the vapour pressure of the pollutants. The conclusions, derived from the performed experimental determinations allowed characterization of the depollution process by using an "equilibrium" model. This model considers the existence of equilibrium between the four pollution phases (vapour, aqueous, "solid" and non-aqueous phase organic liquids) at any moment in time. In order to calculate the vapour pressure, a modified equation of the Antoine model was used in the model. Application of the mathematical model indicates that a 10 °C temperature rise leads to a two-fold increase in the vapor pressure of a compound. Comparison of the modeled and experimental curves, as well as the values of the obtained performance criterions, verified that the chosen mathematical model describes the influence of temperature on the depollution process very well.

Keywords: soil depollution, venting, modeling, temperature.

INTRODUCTION

Soil venting, or in situ ventilation, is a technology for removal of volatile organic compounds (VOCs) from polluted soils. The principle of venting consists in sending into the soil a flow of air through a series of dispersion wells installed at the border of the contaminated zone and in pumping into the center of this zone air enriched with polluted gases.

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In soil, volatile organic compounds may be found in four phases: vapour phase, aqueous phase, "solid" phase and non-aqueous phase organic liquids (NAPL). Venting acts directly on the NAPL and on the organic vapors entrapped in the unsaturated zone.\textsuperscript{1}

The aims of this study were to investigate the effect of temperature modification on the depollution process of a soil polluted with volatile organic compounds. This study was realized both by experimentally obtained data and by a mathematical model, which allows a complex explanation of the investigated phenomenon.

The investigations realized in this work show that modification of the temperature of the soil changes the vapor pressure of a compound, the constant of Henry's Law, the adsorption coefficient onto the soil particles and the diffusion coefficient. In their study, Walton \textit{et. al.}\textsuperscript{2} noticed that increasing the temperature of the soil by 15 °C doubled the vapor pressure of trichloroethylene and, thus, doubled its removal rate. The influence of temperature on the constants of Henry's Law is variable, but most compounds partition to a greater extent into the vapor phase at higher temperatures, thus encouraging the depollution process.\textsuperscript{3,4} The value of diffusion coefficients increases with increasing soil temperature.

However, higher temperatures are not always favorable. An example is the situation of soils with a high moisture content. When organics are occluded by water layers, diffusion through the water layer will be slowed when the Henry Law constants lead to lower aqueous concentrations.\textsuperscript{5}

**EXPERIMENTAL**

The studied soil, originating from the Côte Saint André (Isère) Agriculture High School, France, had an organic matter content of 2.2 % a soil porosity of 52.2 % and a humidity of 12 %. Its granulometric composition showed a soil rich in sand and silt (43.2 % – sand; 39.8 % – silt ; 17.0 % – clay). As pollutants, two volatile organic compounds were used. They represent two different classes of hydrocarbons: heptane, which represents the alkanes class, and toluene, which represents that of aromatic hydrocarbons.

The filling of the cylindrical containers and the achievement of pollution were performed by a well-defined method, which offers a homogeneous permeability and porosity of the soil, as well as a homogeneous pollution. The obtained content of pollution of the soil was 6 g /kg soil.

The ageing time of the organic compound in the soil was 11 days, a period considered sufficient for establishing equilibria between the four phases of pollution in the soil. Subsequently, the containers were coupled to the venting with N\textsubscript{2} depollution circuit.

The experimental installation used for venting depollution of the artificially polluted containers is presented in Fig. 1.\textsuperscript{6}

In order to realize depollution gas circulation through the soil column (7), the lower part of the container is connected to a nitrogen cylinder (1) and a reducer (a). This system induces nitrogen flux circulation, giving rise to a slight overpressure in the column. The obtained overpressure was measured in a parallel study by means of pressure detectors fixed in three tapped holes, which are located on the lateral surface of the containers.

Another advantage of this system is the possibility of easy control of the nitrogen flow which passes through the soil column and the possibility of keeping constant the flux humidity. With the view of measuring the value of this flow, a Platon flow meter (6) was fixed at the inlet of the container and at the outlet, a soap bubble flow meter was used. A low value of the depollution flow of 100 ml min\textsuperscript{-1} was chosen to ensure equilibria between the four phases of the pollution in the soil.
On passing through the soil, the nitrogen flux is enriched with pollutant vapour. The composition of this gaseous mixture is analyzed at the outlet of the soil column by means of chromatography (c). From time to time, a gaseous sample was drawn by means of valve and an integrated drawing pump (8). The supply information of the katharometer was sent to a computer (10), which allows the analysis results to be processed in real time. For this purpose, the program EZ-Crom was used.

As the amount of pollutant in the soil column was small, the depollution gases are sent directly to the exhaust hood without any preliminary treatment.

RESULTS AND DISCUSSION

The experimental results obtained by using the installation described in the experimental section were processed and the resulting depollution curves were similar to that presented in Fig. 2. During the treatment, the variation in time of the ratio between the value of the pollutant concentration \( c \) in the depollution flux and the value of the saturation concentration of the pure compound \( c_{\text{sat}} \) at the working temperature was followed. This parameter allowed an easy detection of the influence of temperature on the depollution process.

The mathematical model used was an "equilibrium" model, which considered the existence of an equilibrium between the four pollution phases at any moment in time. The other simplifying assumptions were:
– ideal behavior of the soil vapor phase and aqueous phase;
– constant values of the temperature, of the humidity and of the porosity of the soil during the depollution process;
– the absence of biodegradation of the organic pollutant.

Under steady-state conditions, the distribution of the pollutant in the four existing phases in the soil may be expressed by the following system of equations:

\[
V^s_i c^i = z^i \left[ \left( \frac{p^i_v}{\varepsilon_g V^s} \right) / \frac{RT}{M_w} + n_0 + \frac{p^i}{K^s_i \rho^i V^s / (\alpha^s_i M_w)} \right]
\]

where:
- \( V^s_i \) – considered soil element volume, cm\(^3\);
- \( c^i \) – apparent global molar concentration of compound in the soil, mol cm\(^{-3}\);
- \( z^i \) – molar fraction of compound i in the non-aqueous phase organic liquids (NAPL);
- \( p^i_v \) – vapour pressure of compound i, atm;
- \( \varepsilon_g \) – soil porosity, %;
- \( R \) – gas constant, atm cm\(^3\) (mol K\(^{-1}\));
- \( T \) – absolute temperature, K;
- \( \alpha^i \) – activity coefficient of compound i in water (mol water) (mole compound\(^{-1}\));
- \( K^s_i \) – repartition coefficient between the liquid aqueous phase and the soil;
- \( N \) – number of organic pollutants.

Concerning the dynamic behavior of the soil column, as a result of a hydrodynamic investigation it was shown that it can be assimilated with a succession of two continuous stirred tank reactors. The equations that characterize the reactor balance of the according to this system are:

\[
\begin{align*}
V_1 \frac{dc_1^i}{dt} \bigg|_{t} &= -F y_1^i(t) \\
V_2 \frac{dc_2^i}{dt} \bigg|_{t} &= -F [y_1^i(t) - y_2^i(t)]
\end{align*}
\]
where: $V_1$, $V_2$ – reactors volume, cm$^3$; $F$ – nitrogen molar flow that passes through the column, mol s$^{-1}$; $c_{1i}(t), c_{2i}(t)$ – concentration variation of the pollutant $i$ in the two reactors, g cm$^{-3}$; $y_{1i}(t), y_{2i}(t)$ – variation in time of the molar fraction of pollutant $i$ in the gaseous phase at the outlet of the two reactors.

In a four-phase system, the contaminant volatility will be governed by the VOC’s vapor pressure and mole fraction within the immiscible fluid. The vapor pressure of all compounds increases substantially with increasing temperature, while the solubility in a solvent phase is much less affected by temperature. This suggests that the soil temperature should be taken into account when evaluating VOC recovery for contaminants located near the soil surface (seasonal variations in the soil temperature quickly decrease with depth).

To calculate the vapour pressure, a modified equation of the Antoine model was used in the model:

$$p_v^i = A + B(T + C) + D \ln(T) + E T^F$$

where: $A, B, C, D, E, F$ – constants typical of each compound and which depend of the pressure unit.

The value of saturation concentration was obtained starting from the ideal gas law, thus:

$$c_{\text{sat}} = p_v^i / (RT)$$

The variation of the saturation concentration of the two studied pollutants as a function of temperature is presented in Fig. 3. From the Design Institute for Physical Property Data Base (DIPPR) it was found that the used model is valid for the following temperature ranges: for heptane from $-43.15$ to $267.01$ °C and for tolu-
ene from –94.47 to 318.64 °C. In this study, the temperature range between 0 and 35 °C was focused on.

The shape of the curves calculated based on the Antoine Law shows the variation of the vapour pressure of the two compounds with temperature. In can be seen that heptane is more volatile than toluene and therefore, it can be supposed that it is easier to extract from a polluted soil. This phenomenon is amplified with increasing temperature.

The testing the mathematical model, performance criterions: standard deviation and correlation coefficient were utilized.

By representing on the same axes system the experimental values and the results obtained on the basis of the mathematical model, Fig. 4 is obtained.

The study of the experimental data curve highlights the existence of 4 characteristic zones:

– 1\textsuperscript{st} zone – the depollution curve has an ascending tendency which corresponds to an insertion process due to mass accumulation in the installation at the beginning of the depollution. It characterizes vapour phase extraction;

– 2\textsuperscript{nd} zone – a plateau around the value 1, which corresponds to vapour and liquid phase extraction, and is characterized by the maxim organic compound concentration in the extraction flux;

– 3\textsuperscript{rd} zone – a decreasing zone, corresponding to the extraction of pollutant dissolved in aqueous soil solution;

– 4\textsuperscript{th} zone – a constant around the value 0, corresponding to the extraction of pollutant adsorbed on the soil particles.

In constant, only the last 3 zones can be distinguished on the depollution curve obtained on the basis of the mathematical model. The same type of depollution curve was established by Anderson et al.\textsuperscript{10}

For the situation described above, the following values of the performance cri-
terion were obtained: $\alpha = 0.1013$; $R = 0.9743$. These values indicate a good agreement of the model with the experimental results.

The influence of temperature on the depollution process was studied by 5 experimental sets, the temperature varying between 19.5 and 32 °C. The pollutant used for the first 3 sets was the toluene and for the last two heptane, the alkane being more volatile than toluene. The experimental depollution curves and those obtained on the basis of mathematical model are presented in Fig. 5.

The values of performance criterions for the 5 experimental sets compared with the corresponding data sets obtained by applying the mathematical model are presented in Table I. In this Table are given the values of the depollution efficiency ($\eta$), which show the efficiency of the extraction process.

TABLE I. The values of performance criterions and depollution efficiency for the 5 experimental sets

<table>
<thead>
<tr>
<th>No. pilot</th>
<th>Pollutant</th>
<th>$p_v$/Pa</th>
<th>$t$/°C</th>
<th>$\eta$</th>
<th>$\alpha$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>2836.7</td>
<td>19.5</td>
<td>0.9615</td>
<td>0.1013</td>
<td>0.9743</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>3793.1</td>
<td>25</td>
<td>0.9706</td>
<td>0.0781</td>
<td>0.9845</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>4766.4</td>
<td>29.5</td>
<td>0.9759</td>
<td>0.1276</td>
<td>0.9561</td>
</tr>
<tr>
<td>4</td>
<td>Heptane</td>
<td>5862.9</td>
<td>25</td>
<td>0.9801</td>
<td>0.0416</td>
<td>0.9944</td>
</tr>
<tr>
<td>5</td>
<td>Heptane</td>
<td>8258.2</td>
<td>32</td>
<td>0.9890</td>
<td>0.0606</td>
<td>0.9855</td>
</tr>
</tbody>
</table>

It can be seen that with increasing temperature the saturation concentration increases, which reduces the depollution time. This influence is also confirmed by the good correlation between experimental and the modeled curves for the 4 studied temperatures.

By analyzing the obtained curves, it can be seen that the temperature affects each of the 4 characteristic zones described previously. Thus, the time for the mass accumulation in the first zone is shorter with increasing temperature. Assuming that the mass accumu-
lation in the installation is constant, the higher the temperature is, the higher is $c_{\text{sat}}$, which leads to a shorter accumulation time.

The value of $c_{\text{sat}}$ also influences the length of the $c/c_{\text{sat}} = 1$ plateau. If the quantity of pollutant is the same for all experiments, the higher $c_{\text{sat}}$ is, the shorter is the time for the extraction of the same mass of pollutant.

Also, it can be observed that the depollution efficiency increases with increasing depollution temperature. By comparing the experimental values curves and those established on the basis of the model, the last zone which corresponds to the extraction of pollutant adsorbed on the soil particles (around the value 0), it can be seen that with increasing temperature its length is diminished. This confirms that the adsorption process is dependent on the temperature.

By comparing the results of the depollution process for the soil polluted with toluene and those for the soil polluted with heptane, the rates of depollution can be observed. Thus, the second zone of depollution is shorter in the case of heptane than for toluene. This is in agreement with the vapour pressure of heptane being 1.5 times greater than that of toluene. Thus, the quantity of heptane carried with the depollution gaseous flux is greater than the quantity of toluene.

CONCLUSIONS

The increasing use of the venting depollution technique, for soils polluted with volatile organic compounds has generated assiduous research for the determination of those parameters (physical, chemical and technological) which influence this depollution method.

The presented work constitutes a laboratory study realized in order to establish the influence of temperature on the venting depollution process of soils artificially polluted with toluene and heptane. To evaluate the depollution, an "equilibrium" mathematical model was used. The predictions of the model were verified by comparing them with the results of experimental determinations. The influence of temperature on the vapour pressure of the pollutants was described by using a modified equation of the Antoine model.

Both the experimental and modeled results revealed that with increasing temperature, the rate of the depollution process increases because of the increase in the volatility of the pollutants. Also, it was notice that the adsorption process of the pollutants on the soil particles is dependent on the temperature, but an exactly correlation was not found.

The conclusions generated as a result of the application of the mathematical model were validated by calculating the performance criterions of the model. The obtained values show a good correlation between the mathematical model and the experimental values, thus certifying the chosen equations.

This study was carried out using only thermodynamic laws, mainly the Antoine laws. It can thus be extended to all volatile organic compounds, the only constraints being related to the availability of the coefficients of the Antoine law for the chosen products and respecting the applications conditions of this law.
ИЗВОД

ИСПИТИВАЊЕ УТИЦАЈА ТЕМПЕРАТУРЕ НА ПРОЦЕС ПРЕЧИШЋАВАЊА ЗЕМЉИШТА ЗАГАЂЕНОГ ИСПАРЉИВИМ ОРГАНСКИМ ЈЕДИЊЕЊИМА МЕТОДОМ ПРОДУВАЊА ВАЗДУХОМ

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Продувавање ваздухом је једна од највише коришћених in situ метода за ремедијацију земљишта загађеног испарљивим органским једињењима (VOC).

Постављањем математичког модела и његовим потврђивањем експерименталним резултатима идентификовани су главни параметри који утичу на процес пречишћавања земљишта. У раду је испитиван утицај temperatura на процес пречишћавања земљишта продувавањем ваздухом од загађених испарљивих органских једињењима. Закључци изведени на основу експеримената омогућили су карактеризацију процеса пречишћавања преко "равнотежног" модела. Овај модел разматра постојање равнотеже између четири фазе (газовита, водена, "чврста" и неводена фаза органске течности) загађивача у сваком тренутку. За израчунавање напона паре је коришћен модификована једначина Antoine-овог модела. Математички модел је индицирао удвоштевљивање напона паре при порасту temperature за 10 °C. Упоређивање експерименталних кривих и кривих по моделу, као и добијени критеријуми понашања, потврдили су да изабрани математички модел врло добро описује утицај temperature на процес пречишћавања.

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