Study on influencing factors on removal of chlorobenzene from unsaturated zone by soil vapor extraction

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ABSTRACT

This paper deals with the influencing factors on removal of chlorobenzene from unsaturated soils by soil vapor extraction (SVE) method. A series of one-dimensional column experiments were conducted to study the influencing factors for SVE method, the factors included extracted vapor flow rate, soil grain size, extraction mode, soil organic matter content and water content.

The results indicated that: (1) the increase of vapor flow rate led to higher contaminant removal efficiency, but the increment of removal was not significant at higher flow rate levels; (2) soil grain sizes had a great impact on chlorobenzene removal efficiency, the coarser the sand, the higher the removal rate; (3) pulsed vapor extraction and continuous vapor extraction almost had the same contaminant removal effects in the sand column; (4) the higher organic content in the soil could decrease the removal efficiency; (5) water content in the soil had different impact on the contaminant removal efficiency which related with the organic content in the soil.

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1. Introduction

In recent years, with the rapid development of economy, environmental pollution cases due to waste leakage and discharge occurred frequently in China, the volatile organic compounds (VOCs) were the major contaminants which threatened the human health and environment. In situ soil vapor extraction (SVE), which may also be used in association with air sparging (AS), has proven to be an effective means of remediating unsaturated soils that have been contaminated with VOCs. This technique consists in the application of vacuum to the soil matrix, that produces air flow in the soil, which, due to free volatilization, desorption from the soil, and dissolution from the aqueous phase, transports the contaminants to extraction wells. Before reaching the atmosphere, the gas usually needs to be treated, aiming to protect air quality [1–3]. The introduction of air into the subsurface also increases the oxygen concentration of the vadose zone, which stimulates aerobic biodegradation of pollutants [4].

The advantages of SVE systems over other remediation technologies may be attributed to its relative low cost and relative simplicity of installation, system operation and minimal amount of equipment required [5]. In all the in situ methods applied in USA National Super Fund Projects during the 1980s and 1990s, SVE held a large proportion of 26% [6]. Current SVE design methods are heavily based on empirical approaches and limited field experiences rather than a rational design basis because very little is understood regarding the mass transfer mechanisms that occur during the use of SVE. Additionally, only a little is known about the effects of control variables, including vapor flow rate, soil permeability and the soil contents of natural organic matter and water.

The increase of vapor flow rate means the increase of contact areas between the vapor flow and contaminants, which has a positive effect on the removal efficiency [7]. However, there is an optimal vapor flow rate for the contaminant removal, which can be acquired through calculation [8]. SVE is mainly applicable to high permeability soils, especially to the sand with permeability over 10^{-6} cm^2/s. The key factor evaluating the applicability of SVE technology is whether there is enough gas flowing through the contaminated soil. So, soil permeability is the decisive factor, which decides not only SVE applicability, but also SVE designing standards [9]. Humic substances (80% of soil organic matter) represent the major source of the organic carbon content [10]. Because of the similarities in their chemical properties, the contaminants are easily adsorbed in humic substances. Consequently, the sorption of contaminants decreases their mobility and relative volatility, as well as their availability for extraction [11]. Soil water content is one of the parameters that more strongly affects the remediation time and efficiency, due to its influence on contaminant availability and soil permeability, which is the most important factor on the VOC migration into the soil [12].

Although the preliminary experimental results look promising, the relationship between removal efficiency and influencing

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Table 1
Experimental programs.

Test	Flow rate (m³/h)	Soil grain size	Soil type	Dry density (g/cm³)	Porosity (%)	NOM content (%)	Water content (%)	Extraction mode
1	0.1 0.2 0.3	<2 mm	Medium sand	1.63	38	0.1	0.98	Continuous
2	0.2	<0.1 mm 0.25–0.5 mm 1–2 mm	Silt Medium sand Coarse sand	1.24 1.43 1.46	46.4 47.4 48.9	0.4 0.1 0.04	1 0.98 0.95	Continuous
3	0.2	0.1–0.25 mm	Fine sand	1.33	46	0.4	0.98	Continuous Pulsed
4	0.2	<0.1 mm	Silt	1.24	46.4	0.4 1.4 5.4 10.3	1	Continuous
5	0.2	<0.1 mm	Silt	1.24	46.4	0.4 5.4	1 4 8 13	Continuous

factors, especially the vapor extraction mode, water and organic matter content in soils need to be further studied. Therefore, a series of column experiments were conducted in this paper to study the influencing factors for SVE method, the factors included extracted vapor flow rate, soil grain size, extraction mode, soil organic matter content and water content. The major objectives of this study are: (1) to investigate the influence of vapor flow rate and soil grain size on contaminant removal efficiency; (2) to study the contaminant removal effectiveness of pulsed vapor extraction and continuous vapor extraction; and (3) to study the effect of organic matter content and water content in soils on the contaminant removal.

2. Experimental protocols

2.1. Materials

Chlorobenzene, an important raw material in chemical industry and pesticide intermediate, was used as the target contaminant. It is analytically pure and supplied by Beijing chemical plant, China.

2.2. Chromatography

Chlorobenzene is analyzed by gas chromatography (Shimadzu GC2010 equipped with a flame ionization detector), the packed column is HP-5 (30 m × 0.32 mm). The injector and detector are set at 200 and 220 °C, respectively. The column works from 40 to 60 °C at the speed of 2 °C/min. Flame gases are air at 400 cm³/min and hydrogen at 43 cm³/min. Nitrogen is the carrier gas.

2.3. Experimental setup

A plexiglass column with 100 cm in height and 7.3 cm in diameter was used for the experiment, the schematic map of the apparatus is shown in Fig. 1. Seven monitoring ports are located at distances of 11, 24, 37, 50, 63, 76, 89 cm from the bottom of the column, respectively. Three sampling ports are located in the bottom, middle and top of the column, named as port 1, port 2 and port 3. At the bottom of the column, there is a porous plexiglass plate which can sustain the soil at the bottom of the column and distribute the inlet gas uniformly. A dense copper wire net is laid above the plate, which can prevent the sand of small grain size, such as silt, leaking through the plate. After top lid was removed, 4.5 kg test soil with an initial chlorobenzene concentration of 1.1 mg/g was carefully and quickly placed into the column. The top lid was then secured to the column with screws in order to prevent any

VOC leakage to the atmosphere. The air flow rates were measured with a flow meter supplied by Yuyao Instrument Company China, the type of the flow meter is LZB-4. 2.5 g of soil was collected each time in each sampling ports for chemical analysis [13], after ultrasonic extraction, the solvent was analyzed by gas chromatography. The recovery of this experimental method is 87.5%. The amount of chlorobenzene remaining in the soil after remediation, as well as the remediation efficiency, are calculated then.

2.4. Experimental process

In order to determine the effect of influencing variables on the efficiency of SVE system, five series of experiments were designed: (1) the influence of vapor flow rates: three column tests were considered with flow rates of 0.1, 0.2 and 0.3 m³/h, respectively, medium sand was used in this series of experiments; (2) the influence of soil grain sizes: three kinds of sands (silt, medium sand and coarse sand) were selected for testing, the vapor flow rate used in this set of experiments was 0.2 m³/h; (3) the influence of different extraction mode: pulsed vapor extraction and continuous extraction were considered. The pulsed extraction pattern is as follows: the operation period is 12 h, the shutdown periods are 12, 24 and 36 h, respectively; (4) the influence of natural organic matter (NOM) content: the NOM used are already characterized in Ref. [14]. Silt was mixed with different amounts of humic soil with a known NOM content. Four types of soils with NOM content of 0.4, 1.4, 5.4, 10.3% were considered, the vapor flow rate was 0.2 m³/h; (5) the influence of water content: sand columns with water content of 1,
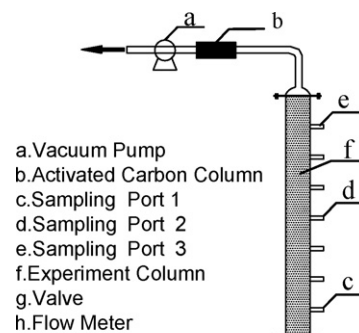

a. Vacuum Pump
b. Activated Carbon Column
c. Sampling Port 1
d. Sampling Port 2
e. Sampling Port 3
f. Experiment Column
g. Valve
h. Flow Meter

Fig. 1. Experimental setup.

4, 8, 13% were used in the experiment, two NOM content (0.4 and 5.4%) were also considered, the soil used in this set of experiments was silt, the vapor flow rate was 0.2 m^3/h.

The experimental programs are listed in Table 1.

The grain size distribution of the sand (<2 mm) is: 4.7% (<0.1 mm), 8.6% (0.1–0.25 mm), 42% (0.25–0.5 mm), 45% (0.5–2 mm).

The measuring procedure for the determination of porosity is: saturating the parallel soil columns with distilled water from the bottom slowly to the top surface of soil in order to displace all the gas in soil column. Then the porosity of the soil column was the ratio of the water volume introduced into the column to the volume of the soil column.

3. Results and discussion

3.1. Influence of vapor flow rate

Figs. 2 and 3 are the results of medium sand column with extraction vapor flow rates of 0.1, 0.2 and 0.3 m^3/h, respectively. Fig. 2 are the sand chlorobenzene content variation curve with time at different sampling ports, it indicated that the chlorobenzene content in the lower port (port 1) decreased dramatically in the early stage of the test, but the content in the middle and the higher ports (ports 2 and 3), instead of decrease, were increased in the early time. This is because that the air flows from the bottom to the top, the vaporized chlorobenzene is also moved upwards, therefore the chlorobenzene content in the upper parts of the sands may increase temporarily. As the time went on, the chlorobenzene contents in all ports were decreased rapidly.

Fig. 3 shows the chlorobenzene removal effect for different vapor flow rates, the Y-axis represents the percentage of chlorobenzene remaining in the sands, which is a ratio of the average measured value in three sampling ports to the initial contaminated value, X-axis is the time. Two stages can be found from the figure, the chlorobenzene remaining percentage in the column is decreased dramatically during the first 24 h of the operation, it reflects the system has a good effect on contaminant removal in this stage, then the chlorobenzene remaining curve declines slightly, in this stage the contaminant removal efficiency in the system is not significant compared with the first stage. It can be found from the figure that the contaminant removal effects are different in different vapor flow rates, the contaminant removal at the flow rate of 0.1 m^3/h during the experiment is about 92%, which is lower than the removal at higher flow rates. In the first stage, the contaminant removal at the rate of 0.3 m^3/h is about 95%, which is larger than the removal at the other two flow rates. This maybe due to the more contact areas formed between contaminant and air flow [7]. Besides, the stronger air flow turbulence in the column may made the contaminant more easily diffuse to the air flow. After 36 h of extraction, the differences in contaminant removal between the flow rates of 0.2 and 0.3 m^3/h is not significant, this indicates that the further increase of vapor flow rate can not significantly improve the contaminant removal, an optimal operation flow rate should be considered.

3.2. Influence of soil grain size

Fig. 4 shows the chlorobenzene remaining percentage in the sands versus time for three different soils (silt, medium sand and coarse sand) at the vapor flow rate of 0.2 m^3/h. It can be found from the figure that 4.2, 1.9, 1.0% of the chlorobenzene still remained within the silt, medium sand and coarse sand respectively after 72 h operation. In medium sand and coarse sand, almost 90% of the chlorobenzene was removed from the system after 24 h, while
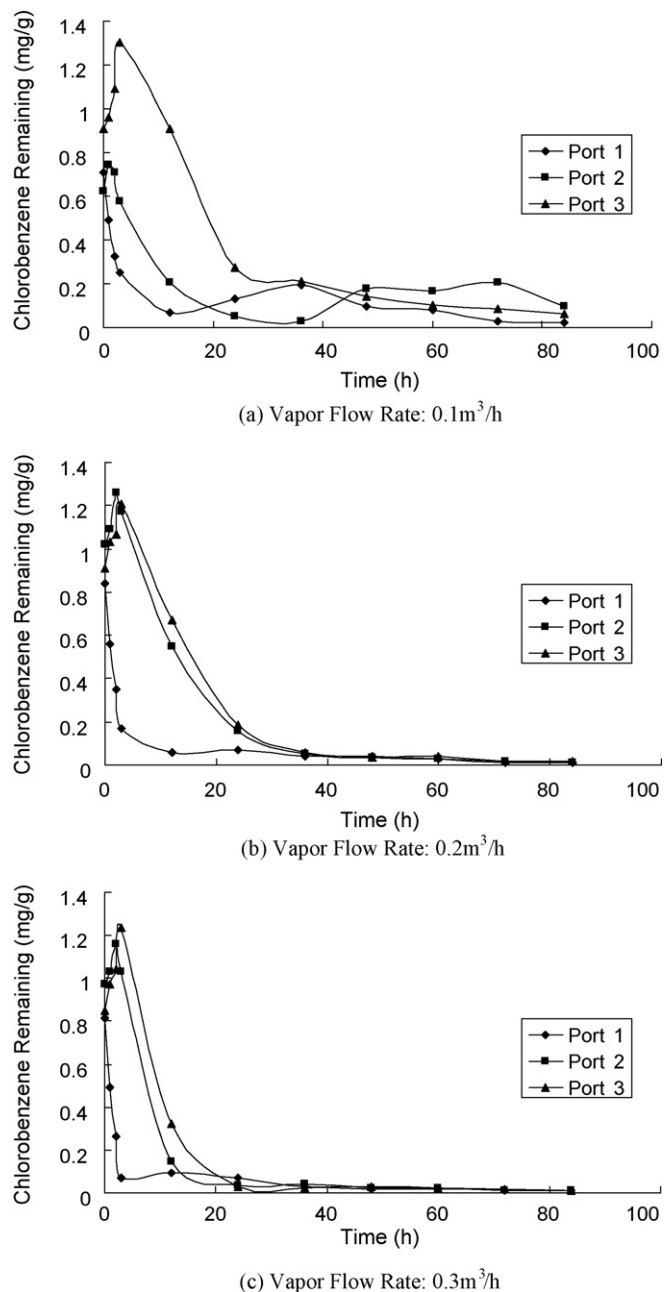

(a) Vapor Flow Rate: 0.1m^3/h

(b) Vapor Flow Rate: 0.2m^3/h

(c) Vapor Flow Rate: 0.3m^3/h

Fig. 2. Chlorobenzene content variation curve in sand with different vapor flow rates. (a) Vapor flow rate: 0.1 m^3/h, (b) vapor flow rate: 0.2 m^3/h, and (c) vapor flow rate: 0.3 m^3/h.

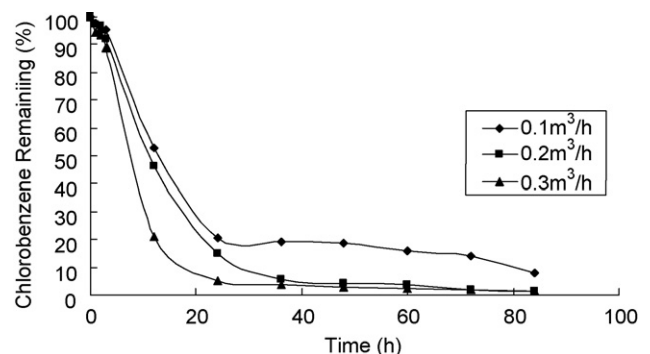**Fig. 3.** Chlorobenzene removal effect for different vapor flow rates.

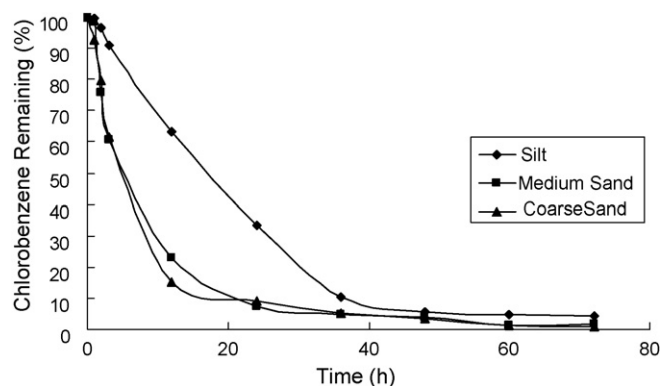**Fig. 4.** Chlorobenzene remaining in different soils.

Fig. 6. Chlorobenzene remaining in soils with different NOM content.

more than 30% of the chlorobenzene within the silt still remained. These differences are caused by various reasons. Firstly the adsorption capacity of the soils to the contaminant is different [15], for silt, it has a large surface area and NOM content which makes the contaminant hard for desorption from the silt compared with that in other two soils. Secondly, the permeabilities of three soils are different, in coarse sand, air flow can easily reach all locations throughout the sand column, which greatly enhance the chlorobenzene volatilization, however, the air flow in silt may be limited to a number of channels due to lower permeability, as a result, the majority of chlorobenzene in soil matrix may not directly contact with the air flow, which means lower volatilization of the contaminants.

3.3. Influence of vapor extraction mode

Fig. 5 shows the chlorobenzene remaining in the soil versus time curves for two different vapor extraction modes used in fine sand at the vapor flow rate of 0.2 m³/h. It can be seen that pulsed extraction mode, though has less operating time, has the same contaminant removal effects compared with continuous extraction. The reasons are as follows: chlorobenzene exists in the soil matrix in different phases, i.e., solid, liquid (aqueous and nonaqueous) and gas [16]. Chlorobenzene in solid phase implies that the chlorobenzene is adsorbed to the soil. At the early stage of the experiment, the contaminants in gas and liquid phases are easily removed by vapor extraction because of the rapid mass transfer from liquid phase to gas phase. As time goes on, most chlorobenzene in gas and liquid phases have been removed, and then the mass transfer from solid phase to gas phase became the main process. The chlorobenzene desorption from soil is relatively slow, furthermore, because of the
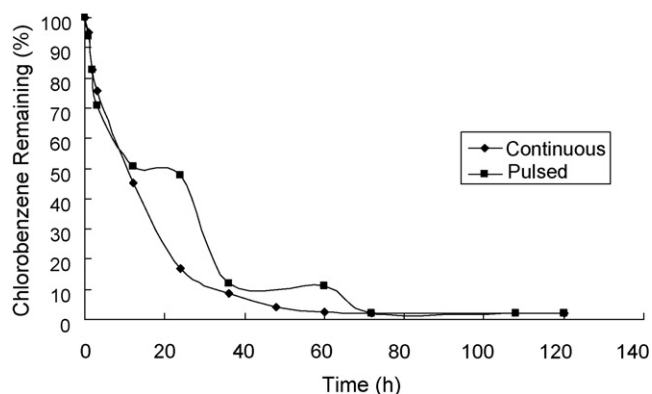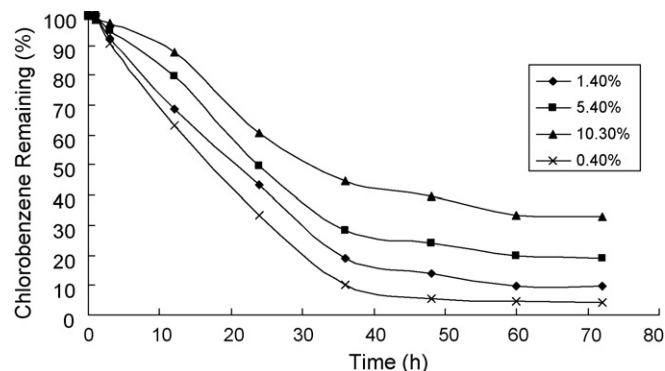
existence of water film covering the solid surface, some of the contaminants have to diffuse to air channel slowly via water film. These lead to a long tailing period in the late stage of the experiment. A period of shutdown can make contaminants redistribution in each phase in soil matrix, which is effective to the contaminant removal [17]. Additionally, it is likely that by means of pulsed extraction, the distributions of the air flow channels can change in the sand column, which allowed contaminants that may previously be far away from the former channel to be located closer to a new channel, which greatly accelerates contaminants removal. Although pulsed extraction did not show any improvement for the final contaminant removal compared with continuous extraction, it is more economic and can increase the removal efficiency of unit energy consumption. Kaleris and Croise also obtained similar results using analytical solutions [18].

3.4. Influence of natural organic matter content

Fig. 6 shows the chlorobenzene remaining percentage in soils with different NOM content, it can be seen that the final chlorobenzene remaining through SVE in soils with 0.4% of NOM content is 4.2%, while for the soil with 10.3% of NOM content, the chlorobenzene remaining is about 33%. The results indicated that the increase of NOM content in soil could strongly decrease the removal efficiency. This is because that the high NOM content soil has the stronger sorption capacity to chlorobenzene which increases the soil sorption amount, the sorption of chlorobenzene in the natural organic matter decreased the availability of the contaminant for extraction. A similar effect was noted for the naphthalene and pyrene removal in the soils with different NOM content using SVE by Sun et al. [19].

3.5. Influence of water content

Fischer et al. [20] studied how water content may affect SVE removal efficiency using toluene as the target pollutant, the results showed that an efficiency of 97% was obtained with a dry soil in 25 h of extraction compared with an efficiency of 72% with a wet soil in 70 h. Similar results were also obtained by Poulsen et al. [21] that increasing the soil water content decreased the soil porosity, influencing negatively the remediation process. However, water may compete the adsorption point in soils with VOC, which means that the presence of water may increase the remediation efficiency [22]. Therefore, the SVE tests are designed by using two kinds of soils (with different NOM content) with four different water contents.

Fig. 7 shows the results of chlorobenzene remaining in soils with different water content, two NOM content soils are considered. From Fig. 7(a) (the soils with 0.4% of NOM content) it can be found that almost 96% of the chlorobenzene has been removed after

Fig. 5. Chlorobenzene remaining in the soils for continuous and pulsed vapor extraction.

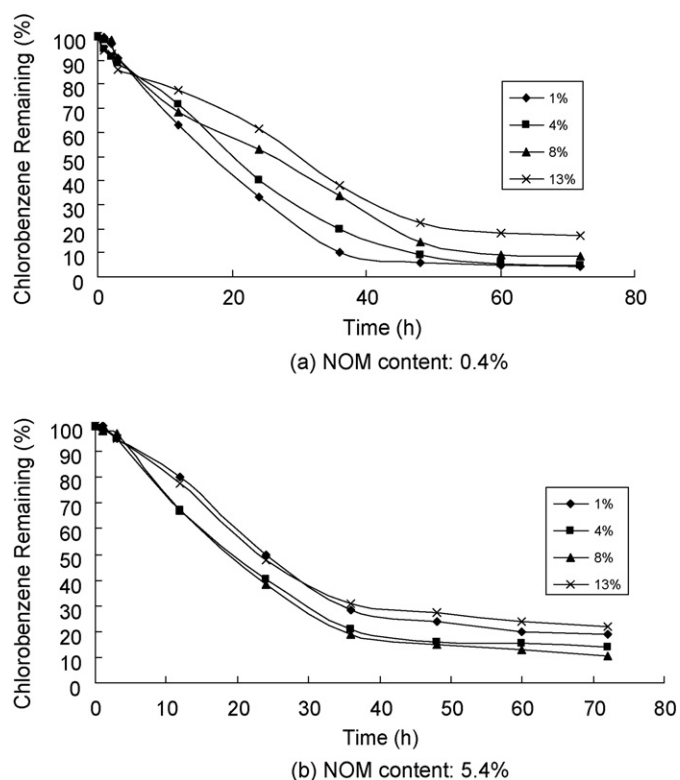**Fig. 7.** Chlorobenzene remaining in soils with different water content. (a) NOM content: 0.4% and (b) NOM content: 5.4%.

72 h in soils with 1 and 4% water content, while only 83.1% of the chlorobenzene in soils with 13% water content has been removed at the same period. That means increase of water content is not good for contaminants removal.

Fig. 7(b) (the soils with 5.4% of NOM content) indicated that increase of water content from 1 to 8% enhanced the contaminant removal efficiency (81.2–89.7%). However, when the water content increased to 13%, the removal efficiency decreased to 78.1%. The different effects of water content on removal efficiency are due to two different mechanisms: the increase of soil water content can decrease the soil porosity and permeability, and then consequently decrease the mobility of contaminant from adsorbed soil phase to air phase; on the other hand, the sorption competition between water and chlorobenzene to the soil can reduce the contaminant adsorption capacity to the soil, which in turn has positive effect on contaminant removal. In this experiment, for the soil with a low NOM content of 0.4%, increase of water content caused a lower contaminant removal efficiency; but for the soil with a relatively high NOM content of 5.4%, the results were different, when soil water content less than 8%, the increase of water content was good for the contaminant removal, but when soil water content increased to 13%, the contaminant removal efficiency became lower.

4. Summaries

In situ soil vapor extraction has shown to be an effective means of remediating VOC-contaminated unsaturated soils. In this study, the column experiments were performed to determine the influences of different factors on contaminant removal efficiency, such as vapor flow rate, soil grain size, vapor extraction mode, natural organic matter content and water content. The following conclusions can be drawn based on the results of this study:

(1) The increase of vapor flow rate can generally accelerate the contaminant removal rate, because large vapor flow increases the interfacial mass transfer area through which contaminant may partition into the vapor phase. But the increment of chlorobenzene removal is not linearly related with the increase of vapor flow, at high flow rate level, the increase of vapor flow is not significant for the increment of contaminant removal.
(2) Soil grain size has great impact on the contaminant removal efficiency. The coarser the sand, the more extensive the channel network formed, which, in turn, led to high removal efficiency.
(3) Pulsed vapor extraction, though has less operating time, has almost the same removal efficiency compared to continuous vapor extraction. This occurred because contaminants redistributed in the intermittent time and the locations of the air channels were changed by means of pulsed extraction, which had positive effect on the contaminants removal.
(4) The increase of natural organic matter content of the soil decreased the remediation efficiency because of the high sorption capacity of the chlorobenzene by organic matter.
(5) Water content had different effects on contaminant removal from the soil, for the soil with 0.4% of NOM content, the increase of water content could decrease the removal efficiency; for the soil with 5.4% of NOM content, the results were different, when soil water content less than 8%, the increase of water content could accelerate the contaminants removal, but when soil water content increased to 13%, it led to lower removal efficiency.

Acknowledgements

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