

Efficiency of foam flushing remediation in heterogeneous soil contaminated by nitrobenzene

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Abstract

The spatial distribution of nitrobenzene in a heterogeneous medium during the foam flushing remediation process was investigated through a two-dimensional simulation device. The remediation efficiency and the mechanisms of action of the surfactant foam remediation process in heterogeneous media were also studied. The experiments showed that during the contamination process, nitrobenzene preferentially enters the low-permeability zones of the medium and is intercepted as a free phase, bypassing the high-permeability zones. In the surfactant foam remediation process, a total removal rate of 95.7% was achieved, with the mobilization effect contributing 69.5%, and the solubilization and volatilization contributing 21.6% and 1.5%, respectively. Mobilization, solubilization, and volatilization are the main mechanisms by which nitrobenzene is eliminated from the soil during the surfactant foam remediation process. Finally, it has also been observed that this process showed a higher removal efficiency in high-permeability media than in low-permeability media due to interface effects.

Key words: foam flushing, heterogeneous soil, nitrobenzene, remediation efficiency

INTRODUCTION

Surfactants, being a type of effective co-solvent, can enhance the solubility of non-aqueous liquids. As such, they have been widely used in recent years in the in-situ flushing of organic-contaminated soils. Surfactant flushing is also one of the methods recommended by the United States Environmental Protection Agency (USEPA) for the in-situ treatment of hydrophobic organic pollutants in soil and groundwater (Yuan *et al.* 2007). However, the efficiency of the solution-based surfactant flushing technology is limited by the low permeability and heterogeneity of the soil to which it is applied. In fact, in heterogeneous soils, a channeling effect is very likely to occur, which means that the eluent will only flow through zones of relatively high permeability, and will hardly spread into the rest of the soil volume. This results in the flushing process having a low efficiency (Mulligan & Wang 2006). In order to resolve this issue, some researchers have proposed an in-situ surfactant foam-enhanced remediation technology (Boonamnuyvitaya *et al.* 2009; Yan *et al.* 2011; Zhang *et al.* 2012; Su *et al.* 2014). Foam is a multi-phase dispersion system with high fluidity, which can distribute more uniformly in a porous medium, thereby effectively avoiding the channeling effect (Géraud *et al.* 2016; Singh & Mohanty 2017). In addition, the flow of the foam in porous media is controlled mainly by the injection pressure rather than by gravity (Mélanie *et al.* 2016). Thanks to this, an unwanted increase in the contaminated area due to the difficulty in controlling the eluent can be avoided. Based on these advantages, the use of foam appears promising for the remediation of organic contaminated soils.

Foam injection has many potential advantages that make it a promising organic pollutant remediation technology: mobility control achieved by an increase in viscosity and shear-thinning behavior, lowering of interfacial tension with the presence of surfactant for enhanced light nonaqueous phase liquid (LNAPL) mobilization and the incorporation in foam of a significant portion of air, thus lowering the amount of liquid surfactant solution required, and promoting the volatilization of LNAPLs (Dariush *et al.* 2016; Mélanie *et al.* 2016). A previous study had allowed the contamination of the sandbox with p-xylene, followed by surfactant and foam injection to assess the remediation efficiency and identify the processes involved (displacement, dissolution, volatilization). Research showed that volatilization would then be responsible for 65% of the total recovery whereas mobilization and dissolution would be responsible for 19% and 16% respectively (Mélanie *et al.* 2016; Dariush *et al.* 2018). Yang *et al.* (2009) investigated the removal efficiency of n-hexadecane from soil and groundwater by surfactants. Their study showed that the mobilization can significantly increase the fluidity of the organic pollutants, and constitutes the main mechanism for pollutant removal. The foam is a gas-liquid mixture, in which the gaseous phase is the main component. During the migration process, the foam ruptures continuously, releasing gas. The volatilization of volatile organic compounds, facilitated by the gas released from the foam, is another mechanism by which organic pollutants are removed during the surfactant foam remediation. Mulligan & Eftekhari (2003) investigated the efficiency of surfactant foam remediation for the removal of pentachlorophenol (PCP) from soil, and calculated the relationship between the pollutant removal efficiency by solubilization and by volatilization during the process. For silt and fine sand, the authors showed that the removal rates of PCP by surfactant foam remediation were 84% and 85%, respectively, with volatilization contributing 57% and 66%, respectively.

Although there are many studies on the mechanism of foam washing organically contaminated soil, research on the efficiency and mechanisms of surfactant foam remediation for the removal of nitrobenzene from heterogeneous soils is, however, very limited. A previous study had allowed the selection of a suitable surfactant for foam production and had shown the conditions needed for the production and injection of foam (Zhao *et al.* 2016; Dariush *et al.* 2017). In the present study, in order to determine the remediation efficiency and identify the mechanisms by which the removal occurs, a two-dimensional indoor simulation device was set up, and the contributions of each mechanism for nitrobenzene removal were discussed in depth. In addition, this study also explored the spatial distribution characteristics of nitrobenzene in a two-dimensional simulation tank after foam flushing, and further clarified the distribution of nitrobenzene in a heterogeneous medium.

METHODS

Materials and equipment

Chemicals and media

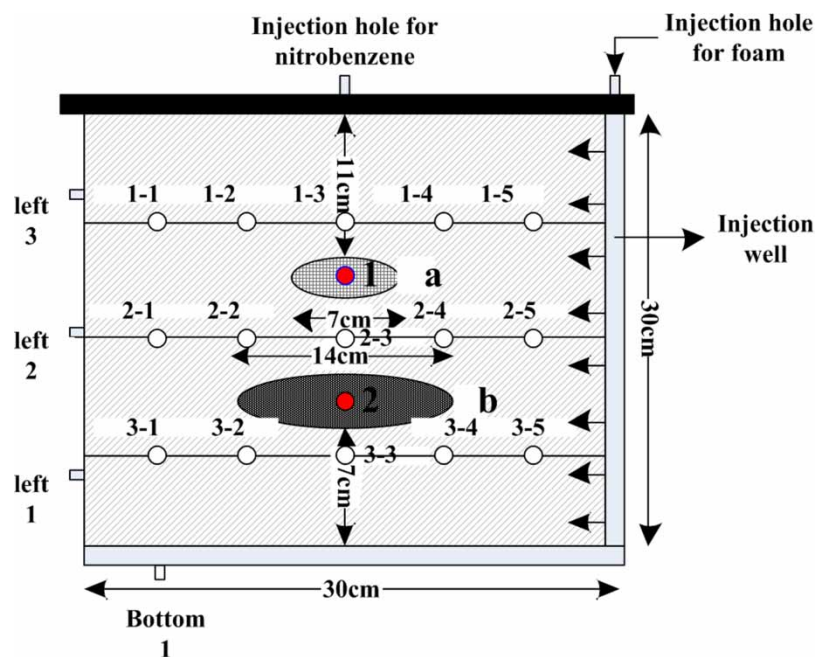
All chemicals used in the experiments were of analytical grade. Sodium dodecyl sulfate (SDS) was selected as the surfactant for the current study. It was purchased, together with nitrobenzene, from Beijing Chemical Pharmaceutical Factory. High-purity nitrogen was purchased from Changchun Juyang Gas Co., Ltd. A peristaltic pump (BT100-2 J) and a gas flow meter (LZB-2WB) were purchased from Longer Precision Pump Co., Ltd. (Baoding), and from Yuyao Huangong Automation Instrument Co., Ltd. (Zhejiang), respectively. The soil for the experiments was collected from a site in Changchun, and sieved to obtain sands with the desired particle size ranges (0.5–1 mm, 1–2 mm, and 0.1–0.25 mm). The concentration of the foaming surfactant was 0.5 wt.%, and the foam quality was set to 91%. The filling properties of the experimental media are shown in Table 1.

Table 1 | Filling properties of the experimental media

Particle size	1–2 mm	0.5–1 mm	0.25–0.5 mm	0.1–0.25 mm
Porosity	0.37	0.38	0.40	0.42
Density (kg/m ³)	1,559.6	1,517.7	1,483.4	1,479.4
Permeability (m ²)	1.115×10^{-10}	7.2×10^{-11}	2.47×10^{-11}	9.87×10^{-12}

Experimental device

The experiments were carried out in a two-dimensional simulation tank, having a length of 30 cm, a width of 2.5 cm, and a height of 30 cm. An injection well was placed on the right side of the simulation tank, and a water distribution partition board was inserted between the injection well and the main body of the tank to ensure uniform foam distribution. Three holes (left 1, left 2, left 3) were made on the left side of the tank and one (lower 1) at the bottom in order to collect foam samples. The concentrations of nitrobenzene in the foam liquid, in the foam gas, and in the foam were analyzed in the samples. Additionally, 15 sampling holes were made at the front of the tank, as shown in Figure 1, and two more (1, 2) were made at the back of the tank to monitor the mass concentration of nitrobenzene in the heterogeneous media (a and b).

**Figure 1** | The experimental device.

Experimental procedure

Filling of the simulation tank

The tank was filled with the medium with a particle size of 0.5–1 mm. It was pressed once every 3 cm to ensure a uniform distribution. A non-homogeneous lens (b), with particle sizes in the range 0.1–0.25 mm, with a length of 14 cm and a height of 4 cm, was placed 7 cm above the tank bottom. A non-homogeneous lens (a) with particle sizes in the range 1–2 mm and a length of 7 cm was placed 16 cm above the bottom. After being filled, the simulation tank was sealed.

Surfactant foam remediation of the nitrobenzene-contaminated soil

After the simulation tank was filled, 38 mL of pure nitrobenzene were injected into the tank through the upper middle injection hole of the tank at a rate of 1 mL/min. The migration of nitrobenzene with time was monitored. After the injection was completed and the migration front of the nitrobenzene stopped expanding, the foam was injected through the injection well at a rate of 19 mL/min using a peristaltic pump. The foam migration process with time was also monitored. During the process, the foam liquid leaking from the bottom sampling holes was collected, and the nitrobenzene concentration and the amount of free-phase nitrobenzene were measured. Meanwhile, the foam gas which was being released was also collected from the 3 sampling holes on the left of the simulation tank. The concentration of nitrobenzene in the foam gas was analyzed by gas chromatography. When the foam reached the left side of the simulation tank, the left 1 and left 3 sampling holes were opened simultaneously, and the foam was collected using an ad hoc sealed bag. The nitrobenzene concentrations in the foam gas and the foam liquid were analyzed after the foam had broken down completely.

The gas chromatography (GC2010, Japan Shimadzu Instrument Co., Ltd.) parameters for the determination of nitrobenzene were as follows: ECD detector, temperature 300 °C; column model HP-35, size 30 m × 250 μm × 0.25 μm; inlet temperature, 250 °C. The temperature program was as follows: the initial temperature, 50 °C, was kept constant for 2 min, then increased to 250 °C at a rate of 20 °C/min, and again kept constant for 5 min. The free-phase nitrobenzene is immiscible with the foaming liquid. Therefore, the volume of the free-phase nitrobenzene was simply read by the naked eye after the liquid mixture was poured into a measuring cylinder. The dissolved phase of nitrobenzene was filtered prior to being submitted to high-performance liquid chromatography (HPLC1260, Agilent Technologies Inc.). The measurement of nitrobenzene in the gas collected before the foam migrated out of the simulation tank was carried out by gas chromatography. Finally, the volume of nitrobenzene in the foam gas collected after the foam migrated out of the simulation tank was calculated based on the saturated vapor pressure of the nitrobenzene and the volume of the gas.

During the foam flushing process, samples of the lens a and lens b media were taken from the center sampling holes (1, 2), while the background medium samples were collected from the 1–3 sampling holes.

After the experiment, the background medium, the high permeability medium, and the low permeability medium were divided into 3 × 3 cm, 1 × 1 cm, and 2 × 1.3 cm cells, respectively. A sample of 5 g of medium was obtained from the center of each cell and placed in 10 mL of methanol. After continuous shaking for 24 h, the concentration of nitrobenzene in the supernatant was determined, and the mass concentration of the nitrobenzene in the medium was calculated.

RESULTS AND DISCUSSION

Migration and distribution features of nitrobenzene in the medium

Due to the heterogeneity of the natural underground environment, especially with the presence of lenses, the migration of Denser Nonaqueous Phase Liquids (DNAPLs) in the aerated zone becomes particularly complex (Liu *et al.* 2011; Shi *et al.* 2012; Cheng *et al.* 2014). After being injected into the simulation tank, the nitrobenzene migrated vertically under gravity. As the migration progressed to lens a, nitrobenzene accumulated on the top of the lens instead of penetrating into it. The saturation increased gradually, leading to diffusion to the left and right sides. Subsequently, the nitrobenzene diffusing to both sides continued to migrate downward driven by gravity towards lens b, into which it was rapidly ‘sucked’ because of the greater capillary force of the fine medium. The nitrobenzene

accumulated in lens b with a gradually increasing degree of saturation. When the injection volume of nitrobenzene reached 35 mL, the nitrobenzene was already covering the entire lens b. The injection was not arrested until the injection volume reached 38 mL. Since the source of nitrobenzene contamination is not a continuous leak, the nitrobenzene will be intercepted and retained in the migration paths during the migration process (Lawrence *et al.* 2004). In heterogeneous media, the capillary force has an important influence on the migration of liquids in both low-permeability and high-permeability media. The equation of the capillary force p_c (Qin 2010) is given as follows:

$$\frac{2\sigma \cos\theta}{R} = p_c \quad (1)$$

where σ is the surface tension of the solution, θ is the contact angle between the solution and the medium, and R is the radius of the capillary channel.

The capillary channel radius in the 0.5–1 mm medium is smaller than that in medium a, which explains the greater capillary force of the former compared to the latter. This caused the nitrobenzene to bypass the high-permeability area a. As for medium b, the capillary channel radius is smaller than that in the 0.5–1 mm medium, resulting in a greater capillary force. Therefore, nitrobenzene preferentially entered the low-permeability medium b. According to the analysis, the mass concentrations of nitrobenzene in lens a and lens b were 0 mg/kg and 150 g/kg, respectively. In the case where there is no free phase in the medium, the maximum mass concentration of nitrobenzene can be calculated as shown in the following paragraph.

The physicochemical properties of nitrobenzene were obtained from a relevant manual: molecular weight $M = 123.06$ g/mol; Henry's constant $H = 2.3 \times 10^{-2}$ atm·L/mol; saturated vapor pressure $P^{\text{vap}} = 1$ mmHg; $1 \text{ gK}_{\text{ow}} = 1.85$. The saturated vapor pressure of nitrobenzene was thus calculated as follows:

$$P^{\text{vap}} = 1 \text{ mmHg} = (1/760) \text{ atm} = 0.0013158 \text{ atm};$$

Therefore, the concentration of nitrobenzene was 1,315.8 ppmV;

$$1 \text{ ppmV nitrobenzene} = 123.06/24.05 = 5.117 \text{ mg/m}^3;$$

$$G = 1315.8 \text{ ppmV} = (1315.8) \cdot (5.117) = 6732.68 \text{ mg/m}^3 = 6.733 \text{ mg/L};$$

Henry's constant was converted to a dimensionless value:

$$H^* = H/RT = 0.023/[(0.082) \cdot (273 + 20)] = 9.57310^{-4};$$

$$K_{\text{oc}} = 0.63 K_{\text{ow}} = 0.63 \cdot (10^{1.85}) = 44.6;$$

$$K_{\text{d}} = f_{\text{oc}} K_{\text{oc}} = (0.02) \cdot (44.6) = 0.892 \text{ L/kg};$$

Finally, the concentration of nitrobenzene in the soil can be calculated as follows:

$$\begin{aligned} \frac{Q_t}{V} &= \left[\frac{\theta_w}{H} + \frac{(\rho_b)K_d}{H} + \theta_a \right] \cdot G \\ &= \left[\frac{(0.4) \cdot (0.5\%)}{9.573 \times 10^{-4}} + \frac{(1.199) \cdot (0.892)}{9.573 \times 10^{-4}} + (0.4) \cdot (1 - 0.5\%) \right] \cdot (6.733) = 6,287 \text{ mg/L} \end{aligned} \quad (2)$$

The concentration of nitrobenzene in soil, i.e. $6,287 \text{ mg/L} \div 1.199 \text{ kg/L} = 5,243.5 \text{ mg/kg}$, was the highest concentration of nitrobenzene pollutant in the absence of free phase. Since the determined content of nitrobenzene in the soil sample was 150,000 mg/kg, which was much larger than the

calculated maximum contaminant content, the main form of nitrobenzene in the low-permeability medium was the free phase.

Efficiency of surfactant foam remediation for the nitrobenzene-contaminated soil

Nitrobenzene distribution in each phase

The nitrobenzene removed by surfactant foam remediation was mainly constituted by three phases: (1) the free phase separated by mobilization, (2) the dissolved phase produced by solubilization, and (3) the volatile phase due to the volatilization effect of the foam gas. Regarding phase (1), the surfactant effectively reduced the interface tension between nitrobenzene and water, as well as the capillary force trapping nitrobenzene in the pores of the medium, leading to an improved fluidity of the pollutant (Liao *et al.* 1999). Regarding phase (2), the surfactant micelle greatly reduced the surface tension of the medium, resulting in the desorption of nitrobenzene from the medium surface. The nitrobenzene then dissolved in the surfactant micelles, and thus the solubility of nitrobenzene in water was enhanced (Taylor *et al.* 2001). Regarding phase (3), the nitrobenzene volatilized with the foam gas and formed a volatile phase. The cumulative curves of nitrobenzene in the gas and liquid phases during the surfactant foam remediation process are shown in Figure 2.

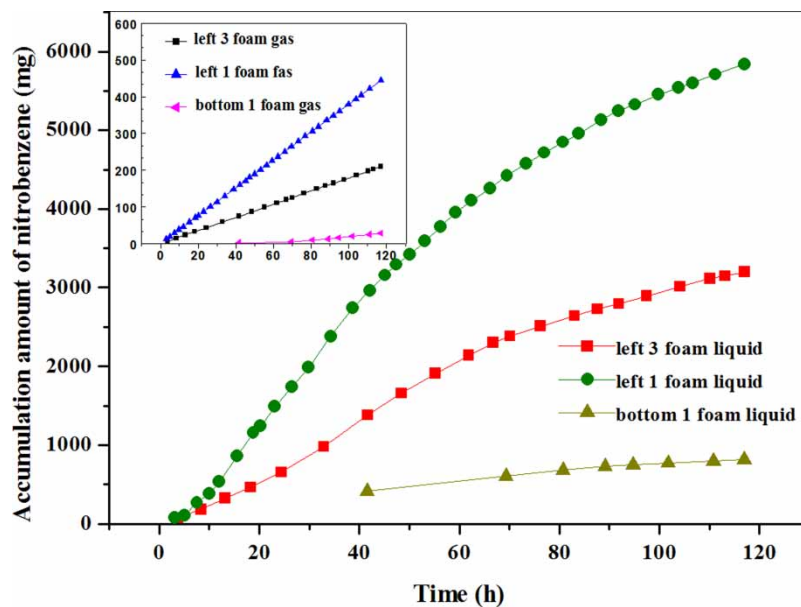


Figure 2 | Cumulative curves of nitrobenzene in the gas and liquid phases.

When the foam came in contact with the nitrobenzene, the interface tension between the nitrobenzene and the medium decreased, and the foam fluid hydraulically substituted, directly or indirectly, the free-phase nitrobenzene droplets trapped in the pores and pore channels of the medium. Nitrobenzene droplets have a large specific surface area. A small portion of them was dissolved in the foam films while the majority migrated with the surrounding foam (Jeong *et al.* 2000). The free-phase nitrobenzene then flew out through the sampling hole on the bottom and through the left 1 sampling hole.

As shown in Figure 2, the cumulative amount of nitrobenzene in the liquid phase (from the left 1 and left 3 sampling holes) suggests that the solubilization effect of the foam on nitrobenzene is also one of the main mechanisms for its removal. The cumulative amount of nitrobenzene in the liquid phase; that is, the total removal of nitrobenzene by solubilization, was 9,855 mg, with the figures for gas phase volatilization and mobilization being 683 mg and 26.4 mL, respectively. The

contribution rates of the solubilization, mobilization and volatilization to the nitrobenzene removal were 21.6%, 69.5%, and 1.5%, respectively. Previous studies have shown that the main mechanism for the removal of p-xylene by foam flushing is volatilization (Mélanie *et al.* 2016), and this study yielded different results, namely that mobilization is the main mechanism for nitrobenzene removal. The main reason is that the p-xylene is more volatile than nitrobenzene, and the solubility of the foam solution to p-xylene is better than that of nitrobenzene. The cumulative growth rate of nitrobenzene in the liquid phase gradually declined, mainly due to the reduced amount of nitrobenzene in the medium during the process. The efficiency of the solubilization during the early stage of the process was guaranteed by the high initial nitrobenzene content in the medium. As the amount of nitrobenzene decreased, less nitrobenzene was collected in the outflowing foam. In contaminated soils containing free-phase nitrobenzene, surfactant foam flushing causes most of the free-phase nitrobenzene to migrate out of the heterogeneous medium. Therefore, it is necessary to consider setting up an extraction well to extract the foam eluent to reduce the risk of groundwater pollution.

Spatial distribution of nitrobenzene in the medium

Figure 3 shows the concentration of nitrobenzene against time in lens a, lens b, and the background medium during the foam flushing process.

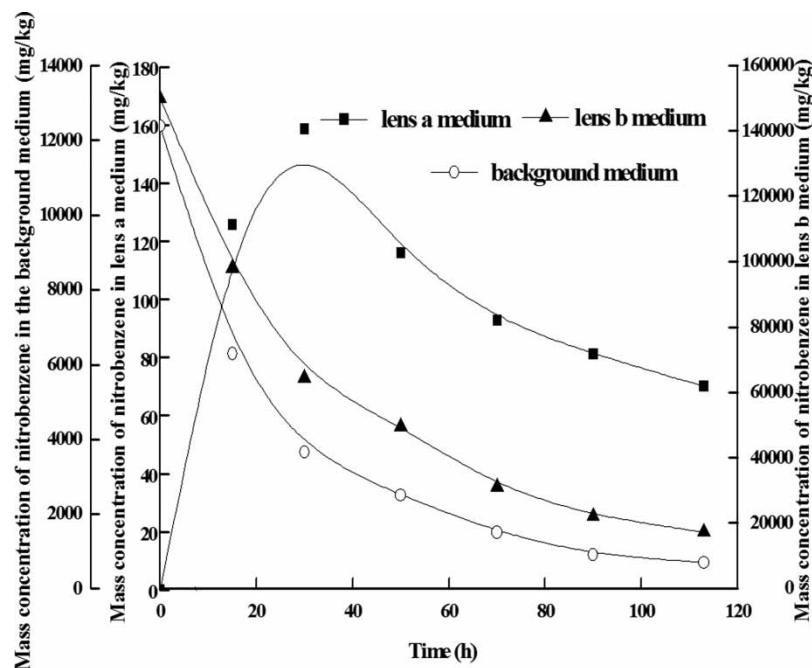


Figure 3 | Mass concentration of nitrobenzene against time in different media.

As shown in Figure 3, at the initial stage of foam flushing, the mass concentration of nitrobenzene in lens b decreased rapidly. In fact, due to the greater capillary suction, the nitrobenzene in the pores and pore channels of medium b was mainly present as a free phase. As the foam liquid entered medium b, the interface tension between the nitrobenzene and the medium decreased, and its mobility was thus enhanced (Pennell *et al.* 1996; Liao *et al.* 1999). The foam migrated in the medium, triggering the solubilization and mobilization effects on the free-phase nitrobenzene. The rate of nitrobenzene mass concentration increased, then decreased, mainly because the amount of nitrobenzene that could be substituted directly (mobilized) decreased, and the residual nitrobenzene in the medium could only be removed by indirect substitution or solubilization (Jeong *et al.* 2000).

The initial concentration of nitrobenzene in lens a was 0 mg/kg. In the previous study about the foam delivery in heterogeneous sediments, it was showed that liquid migrated laterally when it encountered the more permeable sediment, and then bypassed this region (Zhao *et al.* 2016). This was mainly due to the greater capillary suction in the background medium compared to that in lens a. Therefore, at the beginning of the experiment, there was no nitrobenzene in the more permeable medium. However, with the continuous injection of foam, the foam collapsed at the front and form a gas and surfactant solution. The surfactant solution went through successive mixings with nitrobenzene and reduced the interfacial tension between the medium and the nitrobenzene (Mélanie *et al.* 2016). Therefore, the mixed solution entered the more permeable medium and induced increasing nitrobenzene concentration in the more permeable medium. However, since the foam entered lens a preferentially, the mass concentration of nitrobenzene in the medium decreased; it was possible to assess the nitrobenzene mass in the more permeable medium that was mobilized (free phase), dissolved (aqueous phase) or volatilized (gas phase), which in turn led to a decrease in the concentration of nitrobenzene in the more permeable medium.

Since the sampling holes 1–3 were located right above lens a, which was the center of the nitrobenzene contamination pool, the initial mass concentration of the nitrobenzene at this location was 12,389 mg/kg. While the foam was being continuously injected, the mass concentration of nitrobenzene dropped sharply. After injecting the foam for 30 h, the free-phase nitrobenzene in the background medium was completely removed by mobilization and solubilization, and the mass concentration of nitrobenzene decreased to 3,650 mg/kg. Afterwards, solubilization became the main removal mechanism of the nitrobenzene.

After the foam flushing process was completed, the spatial distribution of nitrobenzene in the simulation tank was estimated, as shown in Figure 4. It can be seen that nitrobenzene mainly remained in lens b with high concentration (up to a maximum of 17,277 mg/kg). Some free-phase nitrobenzene remained also in lens b, mainly because of the capillary retention effect at the interface of the lens. In addition, the mass concentration of nitrobenzene in the area above lens b also was greater than 1,000 mg/kg, but lower than the maximum concentration of nitrobenzene (5,243 mg/kg) in the absence of the free phase, indicating the complete removal of free-phase nitrobenzene. Since

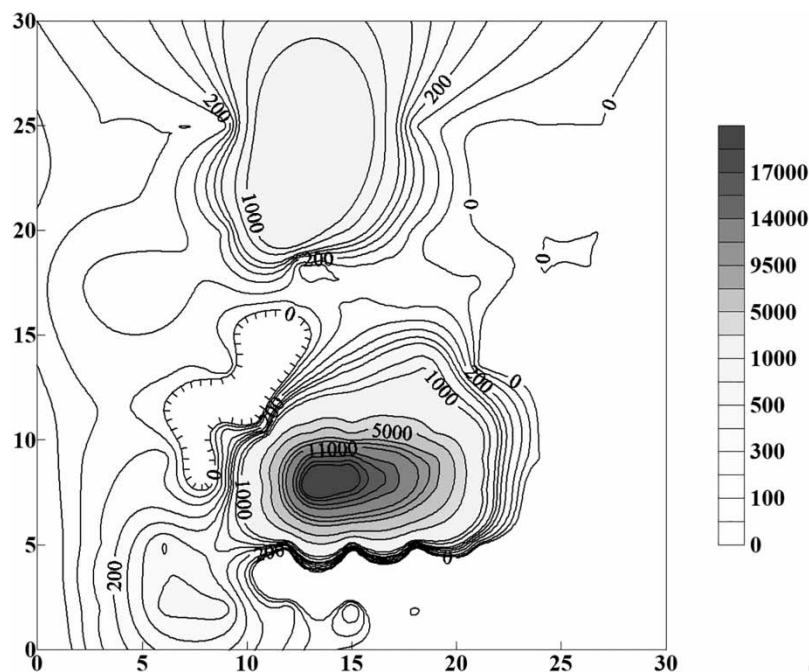


Figure 4 | Spatial distribution of nitrobenzene in the simulation tank after 113 h.

the direction of foam migration was from the right to the left, no nitrobenzene was retained in the medium on the right side of the simulation tank, and nitrobenzene tended to migrate towards the bottom left corner. The integral based on Figure 4 was obtained after 113 h of flushing, by which the total amount of residual nitrobenzene in the simulation tank was evaluated as 1,983 mg, i.e. 4.3% of the initial amount.

CONCLUSIONS

- (1) The main mechanisms of nitrobenzene removal from soil by surfactant foam remediation are the mobilization, solubilization, and volatilization. The formation of free-phase nitrobenzene by mobilization contributed 69.5% to the remediation process. The foam fluid displaced most of the nitrobenzene in the free-phase form out of the gas-bearing zone. The contribution rates of solubilization and volatilization to the nitrobenzene removal were 21.6% and 1.5%, respectively, with 4.3% of the nitrobenzene remaining in the soil.
- (2) Due to interface effects, the surfactant foam remediation performed worse in the low-permeability medium, which exhibited a higher resistance to remediation compared to the background and the high-permeability media. As a consequence, a long period of time is required to achieve the complete removal of nitrobenzene in a low-permeability medium.

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REFERENCES

- Boonamnuayvitaya, V., Jutaporn, P. & Sae-ung, S. 2009 Removal of pyrene by colloidal gas aphrons of a biodegradable surfactant. *Separation and Purification Technology* **68**, 411–416.
- Cheng, Z., Wu, J. C. & Xu, H. X. 2014 Investigation of the migration characteristic of DNAPL in aquifer with lenses and under the action of surfactant flushing. *China Environmental Science* **34**(11), 2888–2896.
- Dariush, N., Hamed, G., Kamran, T. & Jalil, J. 2016 Influence of EDTA and NTA on heavy metal extraction from sandy-loam contaminated soils. *Journal of Environmental Chemical Engineering* **4**, 3512–3518.
- Dariush, N., Jalil, J., Seyed, D. A. & Amir, H. M. 2017 Remediation of heavy metals contaminated silty clay loam soil by column extraction with ethylenediaminetetraacetic acid and nitrilo triacetic acid. *Journal of Environmental Engineering* **143**, 04017026-1–04017026-8.
- Dariush, N., Kamran, T., Mehdi, A., Jalil, J. & Ramin, A. M. 2018 A study of Cr(VI) and NH_4^+ adsorption using greensand (glauconite) as a low-cost adsorbent from aqueous solutions. *Water and Environment Journal* **0**, 1–12.
- Géraud, B., Jones, S. A., Cantat, I., Dollet, B. & Méheust, Y. 2016 The flow of a foam in a twodimensional porous medium. *Water Resources Research* **52**, 773–790.
- Jeong, S. W., Corapcioglu, M. Y. & Roosevelt, S. E. 2000 Micromodel study of surfactant foam remediation of residual trichloroethylene. *Environmental Science & Technology* **34**, 3456–3461.
- Lawrence, D. L., Linda, M. & Abriola, J. R. L. 2004 Influence of hydraulic property correlation on predicted dense nonaqueous phase liquid source zone architecture, mass recovery and contaminant flux. *Water Resources Research* **40**, 1–18.
- Liao, G. Z., Wang, Q. M. & Wang, D. M. 1999 *Principle and Application of Chemical Compound Flooding*. Petroleum Industry Press, Beijing, China, pp. 15–18.
- Liu, Y. L., Cheng, L. R. & Ding, A. Z. 2011 Quick assessment of groundwater risk after NAPL spill and its application in site emergency management. *China Environmental Science* **31**(7), 1219–1224.
- Mélanie, L. G., Richard, M., Thomas, R., René, L. & Lauzon, J. M. 2016 2D sandbox experiments of surfactant foams for mobility control and enhanced LNAPL recovery in layered soils. *Journal of Contaminant Hydrology* **193**, 63–73.
- Mulligan, C. N. & Eftekhari, F. 2003 Remediation with surfactant foam of PCP-contaminated soil. *Engineering Geology* **70**, 269–279.

- Mulligan, C. N. & Wang, S. L. 2006 Remediation of a heavy metal- contaminated soil by a rhamnolipid foam. *Engineering Geology* **85**, 75–81.
- Pennell, K. D., Pope, G. A. & Abriola, L. M. 1996 Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing. *Environmental Science & Technology* **30**, 1328–1335.
- Qin, C. Y. 2010 Study on Remediation of Chlorobenzene Polluted Groundwater and Vadose Zone Using Surfactant-enhanced Air Sparging and Soil Vapor Extraction.
- Shi, X. Q., Jiang, B. L. & Wu, J. C. 2012 Numerical analysis of the effect of leakage rate on dense non-aqueous phase liquid transport in heterogenous porous media. *Advances in Water Science* **23**(3), 376–382.
- Singh, R. & Mohanty, K. K. 2017 Foam flow in a layered, heterogeneous porous medium: a visualization study. *Fuel* **197**, 58–69.
- Su, Y., Zhao, Y. S., Li, L. L. & Qin, C. Y. 2014 Transport characteristics of nanoscale zero-valent iron carried by three different 'vehicles' in porous medium. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* **49**, 1639.
- Taylor, T. P., Pennell, K. D. & Abriola, L. M. 2001 Surfactant enhanced recovery of tetrachloroethylene from a porous medium containing low permeability lenses 1. Experimental studies. *Journal of Contaminant Hydrology* **48**, 325–350.
- Yan, Y. L., Deng, Q. & He, F. 2011 Remediation of DNAPL-contaminated aquifers using density modification method with colloidal liquid aphrons. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **385**, 219–228.
- Yang, J., Chen, J. J. & Lu, Y. 2009 Study on mechanism of surfactant removal of LNAPLs in soil and groundwater. *Environmental Sciences* **30**(7), 2153–2159.
- Yuan, S. H., Shu, Z., Wan, Z. J. & Lu, X. H. 2007 Enhanced desorption of hexachlorobenzene from kaolin by single and mixed surfactants. *Journal of Colloid and Interface Science* **314**, 167–175.
- Zhang, Z. F., Mark, L. Z. & White, D. 2012 Experimental investigation of the effective foam viscosity in unsaturated porous medium. *Vadose Zone Journal* **11**(4), 421–427.
- Zhao, Y. S., Su, Y., Lian, J. R., Wang, H. F. & Qin, C. Y. 2016 Insights on flow behavior of foam in unsaturated porous media during soil flushing. *Water Environment Research* **88**, 2132–2141.