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Enhanced flushing of polychlorinated biphenyls contaminated sands using surfactant foam: Effect of partition coefficient and sweep efficiency

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Abstract

Foam flushing is an *in situ* soil remediation technology based on the traditional surfactant flushing method. The contribution of mobility control to contaminant removal by foam is helpful for improving this technology. Foam flushing of polychlorinated biphenyl (PCB)-contaminated unconsolidated media was performed to evaluate the effect of the partition coefficient (PC) and sweep efficiency (SE) on PCB removal. Column flushing with surfactant solution and foam with different types and concentrations of surfactant was carried out for PCB removal. Two types of quartz sand were investigated to evaluate the Jamin effect on the SE value of the washing agent. The results demonstrate that a small PC value and large SE value are necessary to achieve high PCB removal for foam flushing. Compared with solution flushing, the introduction of foam can effectively control the mobility of the washing agent. Similar to solution flushing, solubilization is a key factor which dominates the removal of PCBs in foam flushing. In addition, the SE value and PCB removal by foam flushing is less affected by particle size. Therefore, foam flushing was proved to be more effective in porous media with low hydraulic conductivity and high porosity. An integrated flushing with water, surfactant solution and foam was performed and the results prove that this technology successfully combines the advantages of solution solubilization and mobility control by foam, and thus further increases the remediation efficiency of PCBs to 94.7% for coarse sand.

Key words: PCBs; foam flushing; partition coefficient; sweep efficiency

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Introduction

Actual and potential PCB contamination usually enters the unsaturated zone as discrete liquid phases, which migrate downward due to gravitational and capillary forces. Because of the low solubility of hydrophobic organic compounds in water, the residual organic phase usually represents a long-term contamination source for soil and groundwater. An effective remediation technique for such situations is the surfactant-solution flushing approach (Martel and Gelinas, 1996; Lee et al., 2002, 2005). However, remediation with surfactants requires a great consumption of surfactant with low removal efficiency. The foam-enhanced flushing technology has been developed to overcome these disadvantages. Foams have been investigated for soil remediation due to the fact that they can improve the contact between the washing agent and the pollutant and reduce the interfacial tension between the contaminant and the aqueous phase (Huang and Chang, 2000; Oliveira et al., 2004). In addition, foams can carry nutrients and oxygen underground to aid further bioremediation (Roy et al., 1992; Brockman et al., 1995).

Injection of surfactant foam has already been used in the field of oil extraction to increase recovery efficiency. In the past ten years, many scientists in the oil recovery industry have focused on the foam flushing of consolidated media and micromodels contaminated by nonaqueous phase liquids (NAPL) such as trichloroethylene and tetrachloroethylene (Kovscek et al., 1995; Jeong et al., 2000, 2002; Tsai et al., 2009). Based on some theories for oil recovery, the capillary effect (Jamin effect) is the primary mechanism which dominates the fluid flow in consolidated media (Vassenden and Holt, 1998; Karin and Idar, 1999). The Jamin effect can be defined as an additional capillary resistance that is generated when immiscible fluids flow through the narrowest restriction of media. When foam flows in porous media, it first flows into the coarse pores. However, the larger value of the apparent viscosity of foam in coarse pores and the piling-up Jamin effect eventually cause the blockage of large pores. Therefore, the foam has the ability to flow uniformly in porous media.

Soil flushing and oil displacement differ in some aspects. First, compared with consolidated media, soil media possess a different pore structure and permeability. This discrepancy is able to lead to different flow behaviors for foam in porous media. Second, compared with oil displacement, the amount of contaminant in soil is much smaller. Therefore, when treatment is performed, the

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detached contaminant can hardly form a NAPL phase before completely dissolving into the surfactant solution. As for foam flushing, results from a few investigations (Apaydin and Kovscek, 2001; Couto et al., 2009) demonstrate the superiority of this technology, compared with solution flushing. At a constant liquid flow rate, an increase in gas-liquid volumetric flow rate ratio may result in increased total contaminant recovery (Huang and Chang, 2000). Further studies (Mulligan and Eftekhar, 2003) indicate that the type and concentration of surfactants and the bubble size may affect the removal of pentachlorophenol in soil flushing. Couto et al. (2009) investigated the remediation of soils contaminated with diesel oil using surfactant solution and foam. High removal efficiencies were obtained with regular foams and aphrons and only small amounts of surfactant. Remediation of soil contaminated by trace pollutants such as PCBs, polycyclic aromatic hydrocarbons and organic-chlorine pesticides with foam flushing has rarely been investigated. Roy and Kongaraa (1995) used a colloidal gas aphron (CGA) to flush naphthalene-contaminated soil. However, the results showed that using a gas-surfactant suspension as a flushing medium may result in pore clogging in the soil and the eventual removal efficiency was not higher than that achieved by solution flushing.

The partition coefficient (PC) value reflects the sorption/desorption and solubilization of contaminants. For PCBs, the PC value is a function of the washing solution composition and the mechanisms of displacement (dissolution). Similar to traditional solution flushing, foam flushing is also influenced by PC values (Martel et al., 2004). The sweep efficiency (SE) is related to the efficiency of an injection pattern and it is defined as the ratio of the volume of contaminant contacted by the washing solution or polymer solution to the volume of contaminant originally in place (Lake, 1989). Compared with surfactant solution, foam was found to hold promise for improving the SE values of washing agents in soil flushing processes. However, the effect of solubilization and foam mobility is determined by the types and concentration of surfactant, particle size, foam texture and flushing manner. Although soil flushing with surfactant foam has been carried out a few times (Roy and Kongaraa, 1995; Huang and Chang, 2000; Couto et al., 2009), the effect of dissolution and mobility on contaminant removal during soil flushing is still unclear. The relationship among PC, SE value and removal efficiency needs to be studied. Besides, whether additional mechanisms such as friction and squeeze, which have been demonstrated to take place in oil displacement, would play an important role in contaminant removal requires further experimental study.

One of the objectives of this study was to assess the efficiency of a foam flushing process in removing PCBs from a contaminated quartz sand column in comparison with the results obtained by a solution flushing process. The role of PC and SE values in PCB removal for solution flushing and foam flushing was investigated. Two types of quartz sand were chosen to evaluate the Jamin effect on the SE value and the PCB removal for the solution and foam flushing, respectively. In this article, PC and SE values were tested first in batch experiments and in a two-dimension (2-D) sand box. Second, column flushing with solution and foam with different types and concentrations of surfactant were carried out to obtain the removal efficiencies of PCBs. Lastly, an integrated solution-foam flushing was performed to evaluate the enhanced removal of PCBs.

1 Method

1.1 Contaminated media

Since a much higher pressure gradient was required for foam flushing for actual soil (Wang and Mulligan, 2004), sand soil was chosen to perform this experiment. The two types of quartz sand used herein were 99 wt.% in purity and manufactured by Chen Guang Co., Ltd. (Beijing, China). Grain sizes of sand ranged from 0.12 to 0.20 mm, and 0.38 to 0.83 mm, respectively. The intrinsic permeability of the sand was 120 and 15 Darcy, for coarse and fine sand, respectively. The sand was soaked in nitric acid (1%, m/m) for 24 hr, and then washed with distilled water several times and dried in the oven overnight (105°C) before use.

Transformer oil containing about 71.8% (m/m) of PCBs Aroclor 1260 was obtained from the Shenyang Hazardous Waste Incineration Base (China), where a disposal service for removed PCB-containing electrical equipment by rotary kiln incineration is provided. The sands were artificially polluted with transformer oil (200 mg/kg) and put aside for more than a month before being experimented. The PCB concentration of the sand was tested to be about 90–110 mg/kg.

1.2 Surfactants and foam generation

A special screening experiment was performed with ten types of surfactant to evaluate the foaminess and the PCB solubilization. Among these surfactants, Triton X-100 (TX-100) and sodium dodecyl sulfate (SDS) were chosen due to their good solubilizing ability and foaminess. Polyethylene glycol lauryl ether (Brij35), which possesses relatively poor solubilization and foaminess, was also used. Surfactants from Sigma Co. (Sigma, USA) with analytical grade purity were used in all experiments. TX-100 has a molecular mass of 646.86 g/mol and a critical micelle concentration (CMC) of 0.18 mmol/L (0.12 g/L) at 25°C. SDS has a molecular mass of 288.4 kg/kmol and CMC of 8.2 mmol/L (2.3 g/L). Brij35 has a molecular mass of 362.5 kg/kmol and CMC of 0.23 mmol/L (0.085 g/L). Distilled water was used to prepare solutions containing different concentrations of surfactant.

Foam was generated when the surfactant solutions and nitrogen passed simultaneously through a T-shape mixer (Hua Kang Co., Ltd., Beijing, China) and then a porous stone (Hua Kang Co., Ltd., China) (Fig. 1). Flow meters (Z68-JSG, Kai Feng Co., Ltd., Shanghai, China) controlled the flow rate of solution and gas, respectively, before injection into the system. In this experiment, the ratio of gas to liquid was intended to be 100:5 (V/V) and the

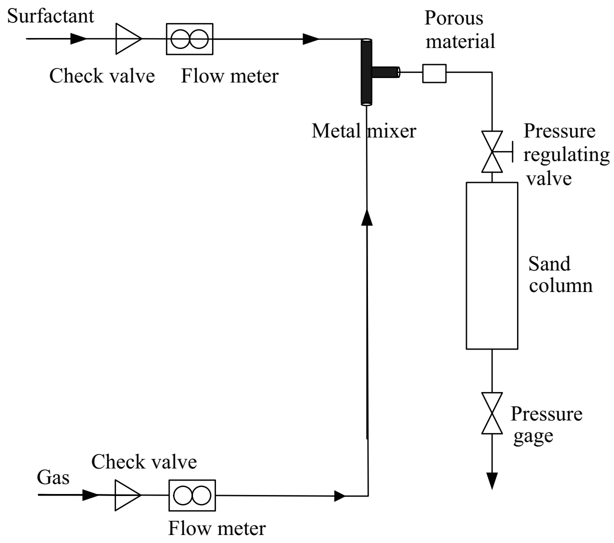

Fig. 1 Schematic of apparatus for foam flushing.

flow rate of surfactant was set at 0.1 mL/sec. The foam stability was characterized by its half-life period, which was determined by the Ross-Miles method (Ross Mile 2152, Long Tuo Co., Ltd., China). The average sizes of bubbles in foam generated with different surfactants at different concentrations were tested to be within the range of 0.89–0.98 mm, which indicated that the porous stone used for foam generation was effective in controlling the bubble size.

1.3 Experimental methods

This research consisted of three stages. Stage 1: The PC values for PCBs under different concentrations of surfactant were tested via batch experiments to characterize the solubilization of the surfactant. In the batch tests, surfactant solutions having concentrations ranging from 0.01 to 20.00 g/L were prepared, and 3.00 g PCB-contaminated sand was added to 30.00 mL of the surfactant solutions. The mixers were then continuously shaken with a water bath shaker (model SB-303, TKS, Taiwan, China) at 25°C for 24 hr. The sample vials were then centrifuged (Sigma 3K30, Germany) at 5000 r/min for 20 min for phase separation. Portions of the resulting aqueous phases were then withdrawn for PCB analyses by gas chromatograph equipped with an electron capture detector (GC/ECD). All the experiments were performed in triplicate and the results varied by less than 10%. The partition coefficients (PC) are expressed as the ratio of liquid PCB mass to the total PCB mass:

$$\mathrm{PC} = \frac{C_l V_l}{C_l V_l + C_s m_s} \quad (1)$$

where, C_s (mg/kg) and C_l (mg/L) are the concentrations of PCBs in sand and surfactant solution, respectively. V_l (L) is the volume of surfactant solution. m_s (kg) is the sand mass. The tested PC values are listed in Table 1.

Stage 2: The sweep efficiencies were measured via two-dimension flushing combined with photo capture by stereomicroscope (SMZ-168-TL, Motic Co., Ltd., Xiamen, China). A 2-D polymethylmethacrylate (PPMA) box of size 7.5 cm × 6 cm × 0.5 cm was first filled with clean sand, then flushed with surfactant solution or foam (thirty pore volume (PV) of surfactant solution), and lastly put in the view field of the stereomicroscope. A motic images advanced 3.2 image acquisition and processing system were installed on the computer. A video camera (Moticam 2005, Motic Co., Ltd., China) was installed on the stereomicroscope. Parameters were acquired via the statistical analysis method. The detailed steps included image acquisition, image binarization (Photoshop 7.0), image digitalization (MapInfo 7.0) and data acquisition and analysis (SPSS 13.0). The SE value has been commonly used in the field of oil displacement to characterize the reduction of mobility of the displacing liquid in porous media. In the process of foam flushing, the sweep efficiency (SE) value was calculated as Eqs. (2)–(5) (Li et al., 2009):

$$\mathrm{SE}_l = \mathrm{SE}_l^a \times \mathrm{SE}_l^a \quad (2)$$

$$\mathrm{SE}_f = \mathrm{SE}_f^a \times \mathrm{SE}_f^a \quad (3)$$

$$\mathrm{SE}_l^a = \frac{A_{ls}}{A_{ps}} \quad (4)$$

or

$$\mathrm{SE}_f^a = \frac{A_{fs}}{A_{ps}} \quad (5)$$

where, $\mathrm{SE}^a{}_l$ (%) and $\mathrm{SE}^a{}_f$ (%) are the plane sweep efficiency of the surfactant solution and foam, respectively; A_{ls} (mm^2), A_{fs} (mm^2), and A_{ps} (mm^2) are the solution area, the foam area and the pore area, respectively. The values of A_{ls}, A_{fs}, and A_{ps} were obtained from the captured photos.

Stage 3: A series of column flushing experiments (Fig. 1) were conducted for the study of the effects of

Table 1 Tested PC values for PCBs via batch experiments

Concentration (g/L)	TX-100		SDS		Brij35	
	Coarse sand	Fine sand	Coarse sand	Fine sand	Coarse sand	Fine sand
0.00	0.050	0.040	0.056	0.048	0.044	0.053
0.01	0.043	0.052	–	–	–	–
0.05	0.049	0.061	–	–	0.07	0.13
0.10	0.077	0.053	0.053	0.052	0.073	0.099
0.50	–	–	0.067	0.28	0.21	0.15
1.00	0.49	0.19	0.042	0.22	0.44	0.37
5.00	0.87	0.76	0.78	0.52	0.70	0.64
10.00	0.93	0.89	0.76	0.55	0.80	0.71
20.00	–	–	0.83	0.64	–	–

SDS: sodium dodecyl sulfate; – means that the PC values under several concentrations were not tested.

porous media, surfactant and flushing manner on PCB removal. PCB-contaminated sand of 900 g was packed in each PPMA column (internal diameter 7.5 cm; sand height 25 cm), which was used in experiments conducted with flushing fluids. A pressure-regulating valve (Kai Feng Co., Ltd., China) was installed between the foam generator system and the sand column to control the inlet pressure of the column. In the column flushing, 30 PV of surfactant solution was consumed. In order to investigate the combined effect of foam solubilization and mobility reduction on contaminant removal, an integrated water-solution-foam flushing experiment was carried out. In this column flushing, 5 PV of water, 10 PV of surfactant solution, 10 PV of foam and 5 PV of water were used to remediate the contaminated sand. Foam exiting the contaminated column was collected and left for 24 hr to collapse, then transferred to smaller vials for analyses of PCB concentration.

1.4 PCB analysis

The effluent of 5 mL was extracted with 10 mL hexane (AccuStandard, USA) three times and the extracts were concentrated to near dryness by rotary evaporation and diluted with a small amount of hexane for further cartridge separation. Prior to extraction, the effluent was spiked with the recovery surrogate standards Aroclor 1260 (1 mL, 10 mg/L) and PCB 209 (1 mL, 1 mg/L) (AccuStandard, USA). PCBs in concentrated hexane extracts were separated using Florisil cartridges with 1 g anhydrous sodium sulfate overlaying the Alumina to remove any remaining small quantities of water. The obtained extract was then reduced via rotary evaporation and concentrated to 1 mL with a gentle purified N_2 stream. Prior to transfer to the GC-ECD, defined quantities of internal standard bromonitrobenzene (BNB) were added.

Quantitative analysis of PCBs was accomplished with an Agilent 7890a GC/ECD (USA). The injector and detector temperatures were set at 225 and 310°C, respectively. N_2 was used as carrier gas with a flow rate of 1 mL/min. The column temperature was programmed as follows: 110°C, 8°C/min to 280°C and 5 min hold at 280°C. Each sample of 1 μL was injected manually in the splitless mode.

Experiments were carried out in duplicate. The variation in PCB concentrations of duplicated samples was less than 10%. Two blank samples were included in each batch of samples. No PCB was detected in blank samples. Aroclor 1260 and PCB 209 standards were added to samples to monitor the procedures of sample extraction, cleanup and analysis. Recoveries of the PCB added to the soil samples were between 60%–120% for Aroclor 1260, and 70%–110% for PCB 209. All the values reported in this article were adjusted to reflect 100% recovery.

2 Results and discussion

2.1 Sweep efficiency value

Figure 2 depicts the pore scale of foam morphology acquired from the observation via stereomicroscope for coarse and fine sand. As shown in Fig. 2, the large bubbles tended to reside in large pores and the small bubbles were more likely to reside in small or dead end pores. This characteristic of foam helped the washing agent to spread among heterogeneous pores. The sweep efficiencies of the foam were calculated based on the detailed parameters obtained from the captured pictures and the calculated data are listed in Table 2. The degrees of foam stability (characterized by half-life period) with different surfactants at different concentrations are also listed in Table 2. When TX-100 foam was introduced, the values of SE increased from 0.85 to 0.98 for coarse sand and from 0.71 to 0.93 for fine sand, due primarily to the Jamin effect. Clearly, the increase of SE values for fine sand was larger than for coarse sand as foam was generated. In addition, the experimental test indicated that the value of sweep efficiencies was also affected by the type and concentration of surfactant. Clearly, surfactants with good stability such as TX-100 and SDS tended to have better foam SE values than Brij35. Furthermore, a positive correlation between SE values and foam stability was observed from Table 2. As the concentration of TX-100 increased from 0 to higher than the CMC value (0.20 g/L) the SE values for coarse sand increased quickly from 0.85 to 0.95 and the further increase of the value became more gradual. The reason was the fact that foam stability, which reached its maxi-

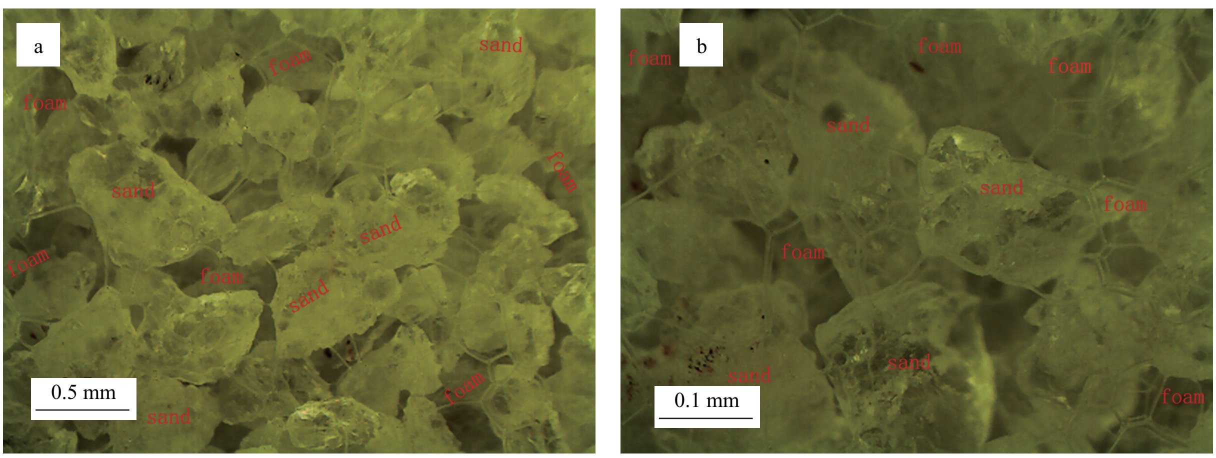

Fig. 2 Image of foam in coarse sand (a) and in fine sand (b). SDS 5.00 g/L.

Table 2 Calculated SE values under different conditions

Surfactant	Sand type	Fluid type	Foam stability (min)	SE value	Pressure gradient (psi/m)
SDS (5.00 g/L)	Coarse sand	Foam	25.2	0.99	21.6
Brij35 (5.00 g/L)	Coarse sand	Foam	5.58	0.89	12.3
TX-100 (0.00 g/L)	Coarse sand	Foam	0.00	0.85	11.0
TX-100 (0.05 g/L)	Coarse sand	Foam	6.74	0.86	10.9
TX-100 (0.20 g/L)	Coarse sand	Foam	15.6	0.95	16.2
TX-100 (1.00 g/L)	Coarse sand	Foam	20.3	0.98	19.2
TX-100 (5.00 g/L)	Coarse sand	Foam	21.6	0.98	19.9
	Coarse sand	Solution	–	0.84	5.91
TX-100 (5.00 g/L)	Fine sand	Foam	–	0.93	12.5
	Fine sand	Solution		0.71	9.32

–: means that no foam was generated under such conditions.

mum value when the surfactant concentration was slightly higher than the CMC, a critical factor in controlling the foam mobility (Wang and Mulligan, 2004; Li et al., 2006). In general, as foam was generated, the non-Newtonian flow manner of the surfactant effectively increased the SE value of the washing agent. Stable foam was favorable for non-Newtonian flow and was thus favorable for enhancing the SE value. However, it is important to observe the sharp increase in the pressure gradient that occurred as the foam grew more stable. This may have been caused by the fact that the generation of foam and increased foam stability led to the increase of flow resistance and the decrease of the hydraulic conductivity of the fluid.

2.2 Solution and foam flushing

Experiments were performed to evaluate the ability of foam to remediate the coarse sand and the fine sand. The PCB concentrations in the effluent and the cumulative removal profiles are presented as a function of pore volum for coarse and fine sands under the surfactant solution or foam flushing, as shown in Fig. 3.

In Fig. 3a, the maximum concentration of PCBs in the effluent was 93.5 and 88.9 mg/L and was observed after 1–2 PV for coarse sand for the Triton X-100 solution (5.00 g/L) and foam, respectively. The PCB concentration in the effluent was negligible after around 20 PV. For coarse sand, the ultimate removals were 82.6% and 85.1%, after flushing with 30 PV of solution and foam, respectively. For fine sand (Fig. 3b), the maximum concentration in the effluent was 67.6 and 66.8 mg/L for solution and foam, respectively, and the ultimate removal values were 61.6% and 80.9%, respectively. These results showed that better results were obtained in the coarse sand than in fine sand for both solution and foam flushing. This was a direct result of the smaller PC values (Table 1) and larger SE values (Table 2) of the solution and foam for coarse sand than for fine sand. Additionally, it was interesting to note that the foam flushing removed not much more PCBs than solution flushing for coarse sand while removing much more pollutant than solution flushing for fine sand. As is shown in Table 2, although the SE value of TX-100 foam was larger than the value of solution for coarse sand, the cumulative PCB removal rate after 30 PV by foam did not achieve a significant increase, comparing with the value with solution. The reason may be that the smaller amount of surfactant in the liquid film between the sand and fluid led to a slight decrease in local solubilization (Kovscek and Bertin, 2003). That is to say, the PCB solubilization for foam may have grown smaller compared with the surfactant solution. Actually, in the field of oil displacement or, when the contamination concentration was sufficiently high, this effect of solubilization decrease was negligible, because displacement was a primary NAPL removal mechanism. For fine sand, the more obviously increased amount of PCB removed by foam compared to that by solution, arising from the higher SE value (0.93) of foam, indicated that foam flushing was more effective in porous media with low hydraulic conductivity and high porosity. The results showed that the Jamin effect played a more positive role in fine sand than in coarse sand. For solution flushing, the SE value only decreased from 84% to 71% as the media changed from coarse sand to fine sand. For foam flushing, the SE value only decreased from 98% to 93% (Table 2). This indicated that the SE value and the

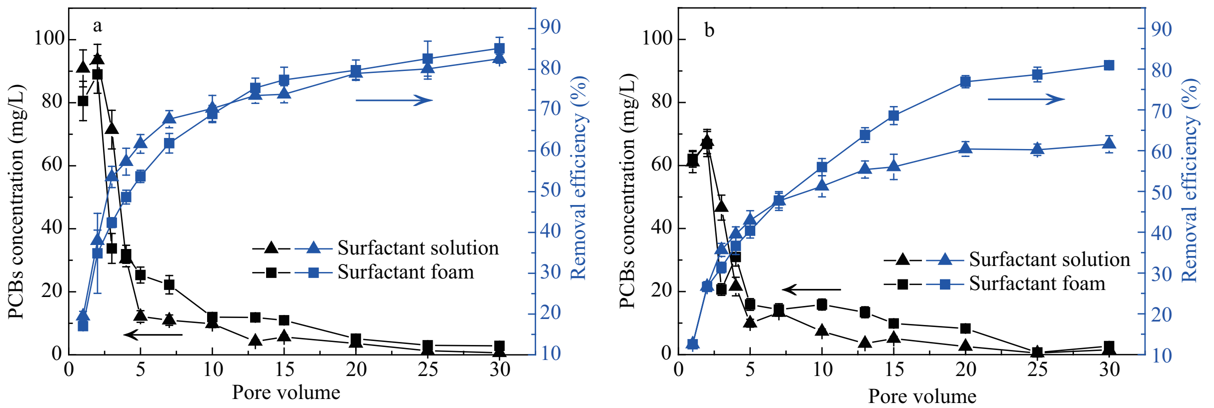

Fig. 3 Effluent concentration and removal of PCBs after flushing contaminated coarse (a) and fine sand (b) with TX-100 (5.00 g/L) solution or foam.

PCB removal by foam flushing was less affected by particle size. Previous studies (Jeong et al., 2000; Rothmel et al., 1998) using foam for the removal of contaminants did not indicate this mechanism of removal. It also could be seen that fine sand needed more PV of washing agent to reach the final removal level. The reason may be that the time required for distribution of foam through the media and the desorption process of the pollutant was longer for media with a low hydraulic conductivity. The foam flushing was proved to possess an advantage over solution flushing, either for coarse sand or for fine sand, due primarily to the large-scale increase of SE values. It can be seen from the images of foam in porous media (Fig. 2) that both the size and the shape of bubbles were changed after foam entered the pores. Foam fracture and transfiguration, distinguished by the degree of change of the bubble size and shape, were two primary behaviors for foam flow in porous media (Li et al., 2006). When foam was present, the Jamin effect arising from transfiguration and fracture could reduce the foam mobility and could make it possible to achieve flow uniformity in pore-scale heterogeneous media, eventually improving the sweep efficiency. Considering the fact that the Jamin effect played a more positive role in fine sand than in coarse sand, a conclusion can be deduced: the existence of the Jamin effect was helpful to the remediation of both pore-scale and small-scale (media with different grain size or permeability) heterogeneous media.

2.3 Effect of surfactant types and concentration

The capability of foam for extracting and mobilizing the contaminants from the soil is a function of many parameters such as surfactant concentration, gas liquid ratio (Mulligan and Eftekhar, 2003; Kovscek and Bertin, 2003). Experiments were thus performed with varying gas-liquid ratios and flow rates to evaluate the effect of PC and SE values on PCB removal for coarse sand by injection of foams of SDS and Brij35. Results obtained by analyzing effluent samples as summarized in Fig. 4a were compared with the results of TX-100. The maximum PCB concentrations in effluents were 75.6 and 61.6 mg/L for SDS and Brij35 foam flushing, respectively. The ultimate removal of PCBs after 30 PV flushing was 75.8% and 65.7% for SDS and Brij35, respectively. According to Table 2, the SE value of SDS foam was higher than the value of TX-100, due to the better foaminess of SDS. However, the maximum PCB concentration in effluent and the removal of PCBs were lower than the values for TX-100 (Fig. 3a). This was probably due to the relatively lower PC values of SDS (Table 1) and the lower surfactant concentration arising from much more surfactant sorption onto sand (Levchenko et al., 2002). For Brij35, the poor foam ability and stability and solubilization led to a low PCB removal efficiency. Results obtained from flushing with different types of surfactant indicated that for foam flushing, surfactants with good foaminess, good solubilization and low adsorption tend to have better remediation efficiency. Compared with solution flushing, the PC values still dominated the PCB removal in foam flushing and the increase of SE value could also effectively improve the contaminant removal.

Further experiments were performed with TX-100, for this surfactant removed more PCBs. The concentration of TX-100 was evaluated (0.05, 0.20, 1.00, 5.00 g/L) and the experiment results are plotted in Fig. 4b. Regarding sorption/desorption processes occurring in the sand throughout the test column, it could be concluded that foam generated with higher concentrations of surfactant had a greater tendency to extract contaminants from the quartz sand. When the concentration increased from 0.05 to 0.20 g/L, PCB removal increased from 0.15 to 0.23, primarily due to the increase of SE values from 0.86 to 0.95 (Table 2), for the solubilization did not show an obvious increase (Table 1). However, the PCB removal was kept at a low level, due primarily to the PC values for this low surfactant concentration. The PCB removal was significantly improved as the concentration further increased to 1.00 g/L and then to 5.00 g/L. Maximum PCB removal for the 5.00 g/L surfactant foam was 70% higher than that for 0.20 g/L surfactant foam. This behavior may have been caused by the observably increased PC values, as shown in Table 1. The test results obtained from this flushing indicated that when the surfactant concentration increased, the PCB removal was first positively affected by the increased SE value and then clearly improved by the increased PC value. Solubilization was still the most important factor which dominated the removal of PCBs, since the contribution of PCB removal caused by

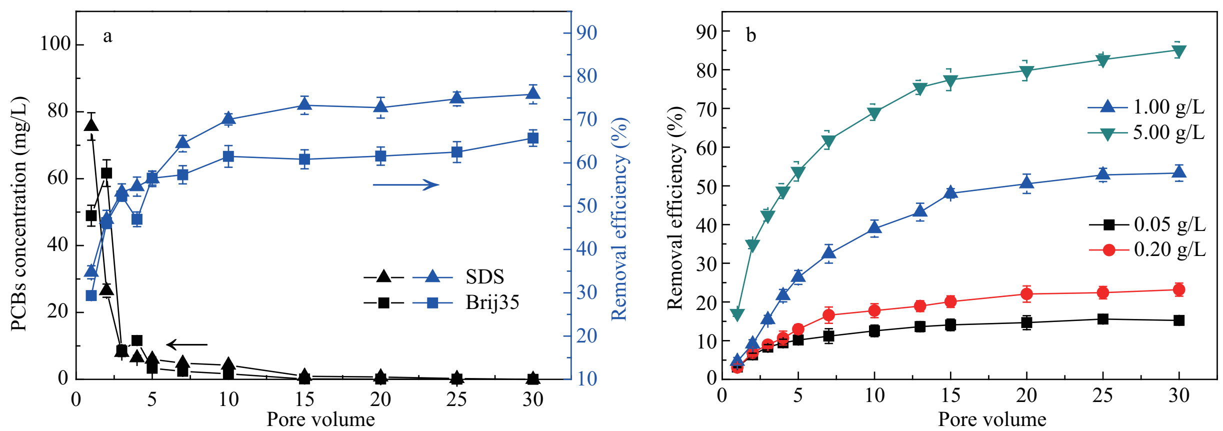

Fig. 4 (a) Effluent concentrations and PCB removal after flushing contaminated coarse sand with SDS and Brij35 (5.00 g/L) foam, (b) PCB removal after flushing contaminated coarse sand with different concentrations of TX-100.

increased solubilization was larger than the value caused by improved SE values. For coarse sand, although the introduction of foam increased the SE value from 0.84 to 0.98, a suitable concentration was more important than a suitable mobility.

2.4 Integrated solution-foam-water flushing

Although foam could effectively enhance the spreading of the washing agent, the slightly reduced solubilization from the introduction of foam may restrict the removal of contaminants, especially for trace level contaminants. An innovative technology which could combine the effects of solubilization and mobility reduction was performed to evaluate the PCB removal. Integrated solution-foam-water flushing was divided into four steps: 5 PV water flushing; 10 PV solution flushing; 10 PV foam flushing; and 5 PV water flushing, as shown in Fig. 5. In the flushing, the concentration of TX-100 was 5.00 g/L. As can be seen from the graph, the cumulative PCB removal after 30 PV reached 94.7% for coarse sand, which was nearly 10% higher than the value for TX-100 foam alone (Fig. 3a). In the first 5 PV of water flushing, the maximum PCB concentration in the effluent was 4.40 mg/L and the PCB removal less than 10%, primarily due to low solubilization and the low flow uniformity of water. When solution flushing was started, the effluent PCB concentration increased sharply to the maximum value of 95.40 mg/L and then decreased gradually to less than 10 mg/L after more than 5 PV of solution flushing. The decreased PCB concentration and the slow removal after 10 PV of solution flushing were caused by the formation of channel flow in the porous media (Roy and Kongaraa, 1995; Jeong et al., 2002). PCBs residing in the fixed flow channels were almost completely removed by TX-100 solution, while the pollutants residing in other areas were hardly contacted by the washing agent. The calculated contribution of PCB removal in this step was 57.5%. The third flushing with 10 PV of foam again raised the effluent PCB concentration to 56.90 mg/L, and the additional removal contribution of foam flushing was 27.1%. The introduction of foam caused the washing agent to spread into the unflushed area

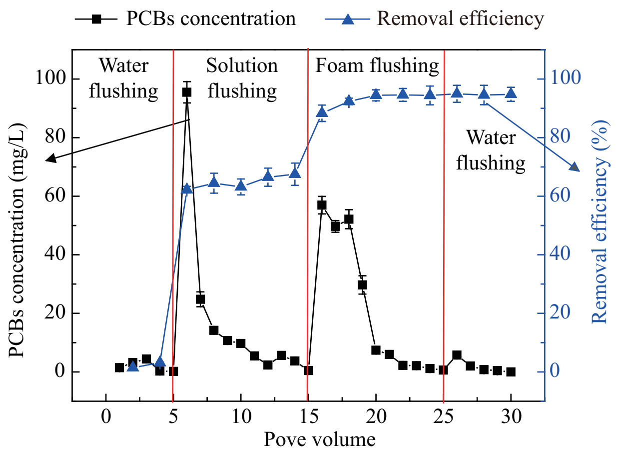

Fig. 5 Effluent concentrations and PCB removal after flushing contaminated coarse sand with 30 PVs of washing agent (water (5 PVs)+ solution (10 PVs)+ foam (10 PVs) +water (5 PVs)).

and carried the trapped PCBs in fine and dead-end pores out of the column. The concentration and the removal contribution for foam flushing were smaller than the values for surfactant flushing. The reason was that after water and solution flushing, the residual PCBs residing in fine or dead-end pores and the proportion of PCBs was less than 35%. The last 5 PV of water flushing was performed to displace the residual surfactant, which could contain some amount of pollutants. In this step, the maximum value in the effluent was 5.77 mg/L and the contribution to PCB removal was less than 1%. From a theoretical point of view, the removal efficiency for single flushing should be smaller than the PC values. However, the combined flushing efficiency removed more than the PC values of PCBs for TX-100 (5.00 g/L). This was probably due to the fact that additional removal mechanisms such as encapsulation of contaminant by bubbles (Wang, 2007) played an important role in the integrated flushing, although the contribution of this mechanism still requires further investigation. In fact, it can be seen from Fig. 5 that the foam not only weakened the channel effect to a low level and effectively improved the flushing efficiency, but also reduced the consumption of surfactant dose by 33.3%. The results indicate that the integrated water-solution-foam flushing successfully took full advantage of the solubilization by the solution and mobility control by the foam and could, therefore, be applied in soil flushing as an innovative and cost-effective technology.

3 Conclusions

For foam flushing, partition coefficient and sweep efficiency are key factors dominating contaminant removal, during which solubilization is still the primary mechanism. Compared with solution flushing, foam slightly reduces the solubilization of washing agent and prolongs the PCB remediation time. Nevertheless, foam can effectively increase the SE value of the washing agent by reducing foam mobility and thus improve the PCB removal for both coarse sand and fine sand. Due to the Jamin effect, both the flow uniformity in single media and the discrepancy between the sands are improved. Therefore, the Jamin effect is helpful to the remediation of both pore-scale and small-scale (media with different grain size or permeability) heterogeneous media.

Surfactant types and concentration were found to affect the foam remediation by affecting the foam solubilization and flow uniformity. Surfactants which have good foaminess, solubilization and low adsorption should be chosen to carry out foam flushing. For flushing of unconsolidated media with fixed grain-size, solubilization is still the most important factor which dominates the removal of PCBs, because the increased removal efficiency resulting from decreased mobility is smaller than the increased value arising from solubilization. The integrated water-solution-foam flushing can combine the effects of solubilization and mobility control and weaken the channel effect. The integrated flushing technology demands a lower amount of surfactant and increases PCB removal to over 94%. In addition to solubilization, an additional removal mechanism such as encapsulation of pollutants by foam may exist and enhance the remediation.

The results obtained from this study serve to evaluate the two primary mechanisms which control the remediation of trace level PCBs from unconsolidated media by surfactant foam. However, there are some limitations and constraints regarding foam flushing. For example, relatively high pressure gradient required tends to destroy the soil structure and requires more energy to accomplish remediation. Furthermore, when performing foam flushing with fine soil (silt and clay), the occurrence of clogging also suspends the remediation. Solutions to these problems need to be investigated in further studies.

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