**Synthetic and natural surfactants for environmental applications using SEAR technology: process study by column continuous test**

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**1. Introduction**

Soils and aquifers contamination by Non-Aqueous Phase Liquids (NAPLs) is a serious problem on a global scale, due their strong toxicity [1, 2]. NAPLs are hydrophobic organic pollutants, characterized by a very low solubility and immiscibility in water and a high tendency to accumulate in the soil organic fraction [3]. NAPLs are classified into dense (DNAPLs) and light (LNAPLs) if the density is greater or less than water, respectively [4]. Among the DNAPLs, chlorinated solvents (ethanes, ethenes and chlorinated methanes) are certainly the compounds most widely identified, while LNAPLs are complex petroleum hydrocarbon mixtures [5, 6].

After a spill, NAPLs migrate downward through the vadose zone and remain trapped in the pore space at residual saturation by capillary forces in the form of separate phase droplets or ganglia [7]. Light NAPLs float at the water table, while DNAPLs can penetrate the water table and migrate downward the aquifer [8]. The groundwater flowing in contact with non-aqueous organic liquid phase causes a slow dissolution of pollutants, generating an aqueous plume that moves in the same direction of groundwater, resulting in long-term persistent sources of aquifers contamination [9]. Moreover, particularly in cases of historical contamination by NAPLs, become relevant the processes of molecular diffusion and adsorption of contaminants (present in a separate phase or dissolved in water) in low permeability layers. These layers can act as slow-release secondary sources due to slow back-diffusion and desorption processes which cause the return of contaminants in aqueous phase, triggering the so-called rebound phenomenon [10]. Therefore, the chemical-physical properties of NAPLs, the presence of a trapped and immobile non-aqueous phase, the heterogeneity of the subsoil and the rebound effect make the efficiency of conventional remediation technologies, such as Pump and Treat (P&T) very low [11]. In this regard, during the last years a great attention has been given to the development of innovative technologies that can greatly increase the mobilization of pollutants and, among these, the Surfactant-Enhanced Aquifer Remediation (SEAR) technology, based on *in-situ* soil flushing or *ex-situ* soil washing processes enhanced with surfactants solution, has been proved to be an efficient method for remediation of source areas containing hydrophobic organic compounds, such as NAPLs [12]. Surfactants are able to increase NAPLs mobilization by reducing interfacial tension between immiscible fluids and increasing apparent solubility of poorly soluble compounds by micellation at or above critical micelle concentration (CMC) [14, 15]. Thanks to these properties, SEAR technology may offer several advantages compared with P&T, like the greater efficiency in NAPLs recovery, lower costs, and greater activity on low permeability areas with the possibility of overcoming the rebound effect [16, 17].

The present work is focused on the operative context of contaminated aquifer remediation using SEAR technology. The aim of the research is the evaluation of potential applicability of two selected surfactants as mobilizing agents for adsorbed NAPLs in conditions representative of a real technological approach. In this regard, a continuous column test was carried out in which, under laboratory-controlled condition, a soil flushing process was simulated. In the experimentation toluene for LNAPLs and perchlorethylene (PCE) for DNAPLs were used as reference contaminants. Two sugar-based surfactants, belonging to the families of synthetic alkyl-polyglycosides (APG) and natural rhamnolipids (RL) was investigated, because in a previous study they had shown very low CMC values (7 10-3 %wt and 1.73 10-2 %wt, respectively) and high capacity to reduce the adsorption of NAPLs on a reference adsorbent material.

**2. Methods**

For continuous test, plexiglas (PMMA) columns (13 cm height × 2.6 cm internal diameter) equipped with two sampling points, door IN and OUT, respectively at the entry and the exit of the column, were used. Pine-wood biochar (PWB) was selected as reference sorbent material. It was mixed with silica sand in quantities equal to 4 wt% (equivalents to about 2 g of reactive material). In detail, the first and the last 3 cm of the column were filled only with sand to make the liquid phase front homogeneous in the central reactive zone (7 cm of bed height). A peristaltic pump was used to feed the column upwards at 0.6 mL min−1 as flow rate. Figure 1 illustrates a schematic draw of the experimental configuration. A total of six columns were set up, differentiated by type of used contaminant and flushing solution. Table 1 summarizes the test conditions in terms of contaminant and mobilizing agent used.



7cm reactive zone:

**Sand + 4%wt PWB**

**Figure 1.** Experimental configuration of the fixed-bed column.

**Table 1.** Details of the set-up fixed-bed systems in terms of contaminant and flushing solution used.

|  |  |  |
| --- | --- | --- |
| **Columns** | **Contaminant** | **Flushing solution** |
| **Toluene-APG** | Toluene | APG2 (C=5x CMC), synthetic |
| **Toluene-RL** | Toluene | RL2 (C=5x CMC), natural |
| **Toluene-H2O** | Toluene | Tap water (reference) |
| **PCE-APG** | Perchloroethylene (PCE) | APG2 (C=5x CMC), synthetic |
| **PCE-RL** | Perchloroethylene (PCE) | RL (C=5x CMC), natural |
| **PCE-H2O** | Perchloroethylene (PCE) | Tap water, (reference) |

A tracer test with Br− was first performed to obtain the residence time (HRT), the porosity (ε), and the pores volume for each column. The experimental procedure was carried out in two consecutive steps. In the first *contamination phase*, each column was fed with a synthetic solution of toluene or PCE at concentration of 100 mg L-1 until the exhaustion of bed adsorption capacity when the outlet concentration (Cout) was equal to that of the input (Cin). In *flushing phase* columns feeding was a surfactant solution at concentration five time of CMC or tap water as reference test (details in Table 1). Flushing phase was stopped when the outlet concentration was about 5-6% respect the inlet in previous contamination phase. To monitor the system, samples of influent and effluent were daily collected and analyzed in gas chromatograph with FID detector.

**3. Results and discussion**

The contamination phase was monitored by reporting the concentration at the outlet normalized with the concentration in the inlet (Cout/Cin) as a function of the pore volume of contaminated water passed through the system. Then, the breaktrough curve was obtained (Figure 2a). Whereas, for the flushing phase curve (Figure 2b and 2c), the concentration at the outlet (Cout) is reported against the pore volume. From the area over the breaktrough curve and the area under the flushing curve it was possible calculate adsorbed and mobilized contaminant mass, respectively. Lastly the yield of removal (%R) was calculated for all columns. from the ratio between the amounts of mobilized and adsorbed contaminant.

When flushing is carried out with surfactants, it be possible to see a rapid increase in the outlet concentration, as shown in Figure 2b, due to the increase in the solubility of insoluble compounds and to decrease in interfacial tension between immiscible phases. This behavior demonstrates, therefore, the positive contribution to the mobilization of hydrophobic compounds by surfactants. Instead, as can be seen in Figure 2c, the flushing with tap water led to a continuous slow decrease in the outlet concentration and no maximum point is observed.

|  |  |  |
| --- | --- | --- |
| a) | b) | c) |

**Figure 2.** Breaktrough curve (a) and flushing curves using surfactant (b) or water (c) as mobilizing agent

All obtained results from continuous test, in terms of fluid-dynamic parameters pore volume needed for both process phases, the total amount of adsorbed and mobilized contaminant and yield of removal, are summarized in Table 2.

**Table 2.** Experimental results obtained from each set-up system

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | Contamination Phase | | Flushing Phase | | | |
| **Column** | **HRT (min)** | **ε (%)** | **Pore Volume** | **Adsorbed mg** | **Pore Volume** | **Cout max**  **(mg L-1)** | **Mobilized mg** | **Yield (%)** |
| **Toluene-APG** | 65 | 57.5 | 145 | 296 | 150 | 238 | 204 | 69 |
| **Toluene-RL** | 50 | 43.5 | 117 | 274 | 102 | 316 | 225 | 82 |
| **Toluene-H2O** | 65 | 57.5 | 202 | 305 | 160 | / | 126 | 41 |
| **PCE-APG** | 60 | 50.4 | 339 | 405 | 190 | 325 | 373 | 92 |
| **PCE-RL** | 50 | 42.7 | 293 | 372 | 229 | 323 | 361 | 97 |
| **PCE-H2O** | 50 | 42.7 | 349 | 405 | 458 | / | 218 | 54 |

**4. Conclusions**

This work has been focused on the evaluation of the two investigate surfactants (APG and RL) mobilizing capacity towards NAPLs adsorbed through a continuous column test. Also, in this way it was also possible to carry out a comparative assessment and verify any possible difference in the mobilization capacity of the pollutants according to different origin of surfactant (synthetic and natural). The high capacity of surfactants to facilitate contaminants mobilization has been demonstrated by a significant increase in the effluent concentration of contaminant after a few hours of feeding of flushing solution, compared to a water-only feed where only a slow decrease in the output concentration was observed. Both surfactants investigated have guaranteed good removal yields, with both PCE and toluene. Specifically, the experimental results showed that the biosurfactant RL2 was particularly efficient in the mobilization of both PCE and toluene, compared to the synthetic surfactant APG2. In fact, it has been seen how the columns flushing with the solution of RL2 (5x CMC) has determined a removal of 97% and 82% for PCE and toluene, respectively. While the flushing with APG2 solution (5xCMC) resulted in a removal of 92% and 70% for PCE and toluene, respectively.

The results obtained from continuous test have amply confirmed the validity of the use of surfactants, in particular of the biosurfactant RL2, in soil-flushing processes for the remediation of NAPLs contaminated sites using SEAR technology approach. Moreover, it should be considered that the RL2 biosurfactant, as produced by the secondary metabolism of microorganisms (*Pseudomonas Aeruginosa*), is completely biodegradable, and therefore able to offer a high environmental compatibility and reduce the effect of secondary contamination.

**References**

[1] C. M. Steelman, J. R. Meyer, P. Wanner, B. J. Swanson, O. Conway-White, and B. L. Parker, “The importance of transects for characterizing aged organic contaminant plumes in groundwater,” *J. Contam. Hydrol.*, vol. 235, Nov. 2020, doi: 10.1016/j.jconhyd.2020.103728.

[2] Z. Guo, M. L. Brusseau, and G. E. Fogg, “Determining the long-term operational performance of pump and treat and the possibility of closure for a large TCE plume,” *J. Hazard. Mater.*, vol. 365, pp. 796–803, Mar. 2019, doi: 10.1016/j.jhazmat.2018.11.057.

[3] J. W. Liu *et al.*, “Surfactant-enhanced remediation of oil-contaminated soil and groundwater: A review,” *Sci. Total Environ.*, vol. 756, p. 144142, 2021, doi: 10.1016/j.scitotenv.2020.144142.

[4] L. Huo, G. Liu, X. Yang, Z. Ahmad, and H. Zhong, “Surfactant-enhanced aquifer remediation: Mechanisms, influences, limitations and the countermeasures,” *Chemosphere*, vol. 252. Elsevier Ltd, Aug. 01, 2020, doi: 10.1016/j.chemosphere.2020.126620.

[5] R. García-Cervilla, A. Romero, A. Santos, and D. Lorenzo, “Surfactant-enhanced solubilization of chlorinated organic compounds contained in dnapl from lindane waste: Effect of surfactant type and ph,” *Int. J. Environ. Res. Public Health*, vol. 17, no. 12, pp. 1–14, Jun. 2020, doi: 10.3390/ijerph17124494.

[6] K. Sookhak Lari, J. L. Rayner, and G. B. Davis, “Toward Optimizing LNAPL Remediation,” *Water Resour. Res.*, vol. 55, pp. 87–96, Mar. 2019, doi: 10.1029/2018WR023380.

[7] Y. Fu, C. Qin, S. Gao, C. Lv, C. Zhang, and Y. Yao, “Aquifer flushing using a SDS/1-butanol based in-situ microemulsion: Performance and mechanism for the remediation of nitrobenzene contamination,” *J. Hazard. Mater.*, vol. 424, 2022, doi: 10.1016/j.jhazmat.2021.127409.

[8] M. Le Meur, G. J. V. Cohen, M. Laurent, P. Höhener, and O. Atteia, “Effect of NAPL mixture and alteration on 222Rn partitioning coefficients: Implications for NAPL subsurface contamination quantification,” *Sci. Total Environ.*, vol. 791, Oct. 2021, doi: 10.1016/j.scitotenv.2021.148210.

[9] M. M. Rossi *et al.*, “Combined Strategies to Prompt the Biological Reduction of Chlorinated Aliphatic Hydrocarbons: New Sustainable Options for Bioremediation Application,” *Bioeng. 2021, Vol. 8, Page 109*, vol. 8, no. 8, p. 109, Aug. 2021, doi: 10.3390/BIOENGINEERING8080109.

[10] D. O’Connor *et al.*, “Sustainable in situ remediation of recalcitrant organic pollutants in groundwater with controlled release materials: A review,” *Journal of Controlled Release*, vol. 283. Elsevier B.V., pp. 200–213, Aug. 10, 2018, doi: 10.1016/j.jconrel.2018.06.007.

[11] E. H. Teramoto, M. A. Z. Pede, and H. K. Chang, “Impact of water table fluctuations on the seasonal effectiveness of the pump-and-treat remediation in wet–dry tropical regions,” *Environ. Earth Sci.*, vol. 79, no. 18, Sep. 2020, doi: 10.1007/s12665-020-09182-1.

[12] A. A. Befkadu and Q. Chen, “Surfactant-Enhanced Soil Washing for Removal of Petroleum Hydrocarbons from Contaminated Soils: A Review,” *Pedosphere*, vol. 28, no. 3, pp. 383–410, 2018, doi: 10.1016/S1002-0160(18)60027-X.

[13] T. Gaudin, P. Rotureau, I. Pezron, and G. Fayet, “New QSPR models to predict the critical micelle concentration of sugar-based surfactants,” *Ind. Eng. Chem. Res.*, vol. 55, no. 45, pp. 11716–11726, 2016, doi: 10.1021/acs.iecr.6b02890.

[14] S. T. Malkapuram *et al.*, “A review on recent advances in the application of biosurfactants in wastewater treatment,” *Sustain. Energy Technol. Assessments*, vol. 48, no. August, p. 101576, Dec. 2021, doi: 10.1016/j.seta.2021.101576.

[15] P. Ciampi, C. Esposito, G. Cassiani, G. P. Deidda, P. Rizzetto, and M. P. Papini, “A field-scale remediation of residual light non-aqueous phase liquid (LNAPL): chemical enhancers for pump and treat,” *Environ. Sci. Pollut. Res.*, vol. 28, pp. 35286–35296, 2021, doi: 10.1007/s11356-021-14558-2/Published.

[16] C. Yang *et al.*, “The role of surfactants in colloidal biliquid aphrons and their transport in saturated porous medium,” *Environ. Pollut.*, vol. 265, Oct. 2020, doi: 10.1016/j.envpol.2020.114564.