Surfactant Combinations for Enhanced Removal of Contaminants

By

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Introduction

The paper gives an overview of results obtained in recent years working on selection of surface-active additive combinations for different purposes [1,2]. This included surfactant combinations for the hydraulic in-situ remediation of soils [3-8], for the stimulation of biodegradation [9,10], several surfactant formulations with high extraction efficiency for different contaminants [7,8,11], special additives for the enhanced washing of tar contaminated soils [8,12] as well as the development of a two-step bioreactor process for removal of contaminants with low bioavailability [10,13-15].

The article is intended to provide a basis for discussion of problems associated with surfactant application and possibly for future cooperation.

One of the main restricting factors in the remediation of soils is the low aqueous solubility of several organic compounds, which leads to resistance to mobilization by conventional pump and treat measures and to low bioavailability. The application of surfactants to resolve these problems has been a focus of research in recent years. However, usefulness of surfactant addition has been conversely discussed in literature. Promising results obtained with model contaminations in the laboratory often failed under real world conditions.

Surface-active additives have the potential to improve the efficiency of soil clean-up by physico-chemical and biological processes if their functional properties are adjusted to the special demands of the remediation technology and the soil/contaminant system. However, how to find tailor-made solutions by applying the different utilizable wetting, dispersing, emulsifying and solubilizing properties, is not understood properly so far.

In-situ pump and treat

A key problem of surfactant application for enhanced removal of contaminants by in-situ pump and treat measures is the reduction of soil permeability or clogging of contaminated zones. One strategy to overcome these problems is the adoption of combined polymer surfactant systems to increase the viscosity of the displacing fluid [16,17]. Our approach in relation to mineral oil contaminations was to avoid the formation of viscous emulsions. In small scale column tests a surfactant combination can be selected readily, which fulfil the requirements, i.e., maintenance of permeability, low surfactant losses, and low residual levels of oil. The selection is based on testing non-ionic surfactant pairs which combine an efficient emulsifier with a polar compound intended to adjust the permeability. Optimum surfactant composition very much depends on the actual contamination, i.e. in model experiments it was distinctly different for weathered and unaltered diesel oil.

The selection principle could be also adopted to tar polluted soils by using surfactants with good solubilizing properties for PAH instead of an emulsifier. Fig. 1 demonstrates that the removal rate of PAH could be enhanced by orders of magnitude by improving the permeability of the soil adding 30% of the polar compound (B) to the surfactant with good solubilizing properties (A).

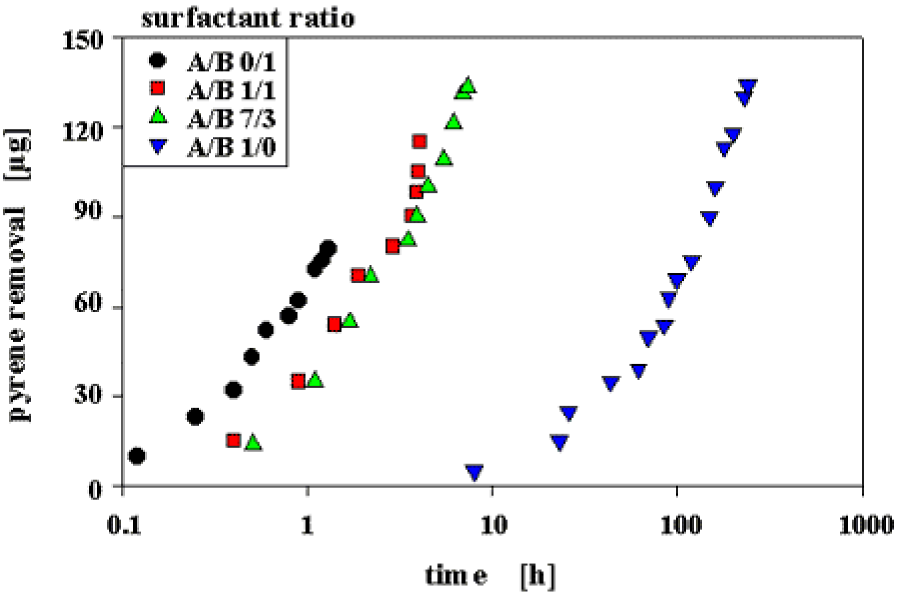

Fig. 1 Optimization of surfactant composition in column experiments with a heavily tar polluted soil

Ex-situ soil washing

For application in ex-situ soil washing processes different surfactant combinations with high extraction efficiency for mineral oils, PAH and PCB have been developed. They have been used in a soil washing process developed by HGN Hydrogeologie GmbH [18], in a purification process for reuse of oil-binding materials [19] and were also successfully tested for deinking of paper. The washing procedure mentioned resembles the BioGenesis Soil Washing Process in that the soil-water mixture is agitated in a washer without separating the soil-fines. Therefore contaminant removal relies very much on the extraction efficiency of the surfactant. On the other hand a search for additives effective in clean-up of tar contaminated soils by soil washing revealed that addition of surfactants may cause a substantial increase in recontamination of particles by tar components during soil processing. In this case addition of low amounts of a selected dispersant (< 0.02 wt% of soil) enhanced the performance of the washing process substantially [12].

Bioremediation

Bioremediation, often a very economical option for soil decontamination, has restricted applicability for soils contaminated with pollutants having low bioavailability and/or low biodegradability, such as PAH or PCB.

Different attempts have been made to overcome these problems by developing bioreactor processes and/or by adding surfactants. However, transfer rates are so low, that with soil samples of PAH-contaminated sites degradation rates of only 50% could be observed after 3 month, even under efficiently stirred conditions [20].

To develop remedial alternatives different options for a combined physicochemical and biological treatment process have been evaluated [10,13,14]. These included a washing pre-treatment (attrition in the presence of different additives and fractionation by size) with subsequent biological treatment of the soil, a preextraction with surfactant solutions as well as biodegradation in presence of different additives. Special designed surfactant combinations, which stimulate biodegradation without preferential degradation of surfactants [9], show substantial enhancement of biodegradation if their composition and concentration is selected properly. For example, treating a sandy soil of a former gaswork site with an initial PAH concentration of 1086 mg/kg in a slurry degradation test 10 days the PAH load reduced to 500 mg/kg. A sample previously washed in laboratory attrition cell after separation of the fraction < 50 µm (470 mg/kg PAH) resulted in a value of 146 mg/kg after the slurry degradation test. By adding 0.5% of the special surfactant combination T 10/2 to the original soil sample during the slurry test PAH content was reduced to 365 mg/kg, whereas addition of only 0.01% of the polymeric dispersant Z2 resulted in a residual concentration of 250 mg/kg. However, even under improved conditions biodegradation was to slow to obtain low enough residual values in reasonable times. Therefore a new two stage bioreactor system was developed (Fig. 2). This system consists of a reactor for simultaneous biological and wet processing and of a filled column reactor. In the first stage contaminant material is under continuous agitation, thus adhering particles, contaminant layers and biolayers are continuously removed and suspended. Stirring is adjusted so that soil fines are suspended fully but sand grains underlie mutual attrition. The reactor may be additionally aerated. The slurry of suspended soil fines and particles of low density is continuously transferred to a trickling filter, a column filled with a material of high sorption capacity, which filters off fine particles and bind contaminants. After passing the column the suspension is recirculated.

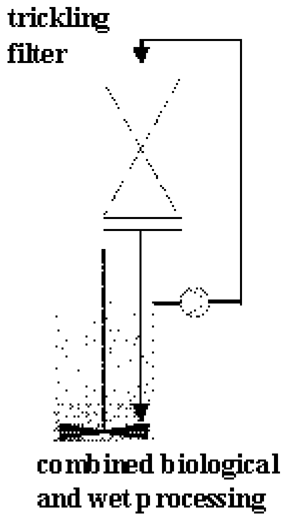

Fig. 2 Scheme of the two stage bioreactor process

The treatment is designed as batch process. After removal of the contaminants the soil is separated and the liquid phase is reused in the next step. The system does not require replacement of the column filling but cycles of back-washing to maintain permeability. The performance of the system is illustrated in Fig. 3. Already without any additives a reduction of more than 60% was achieved in three days, addition of a small amount of biosurfactant had no positive effect. Adding 0.5% T15S the residual PAH load reduced to 400 mg/kg. If 0.1% Z18 (additive intended to stimulate biofilm formation) was added the concentration in soil reduced to 160 mg/kg. Further examples are given in [10].

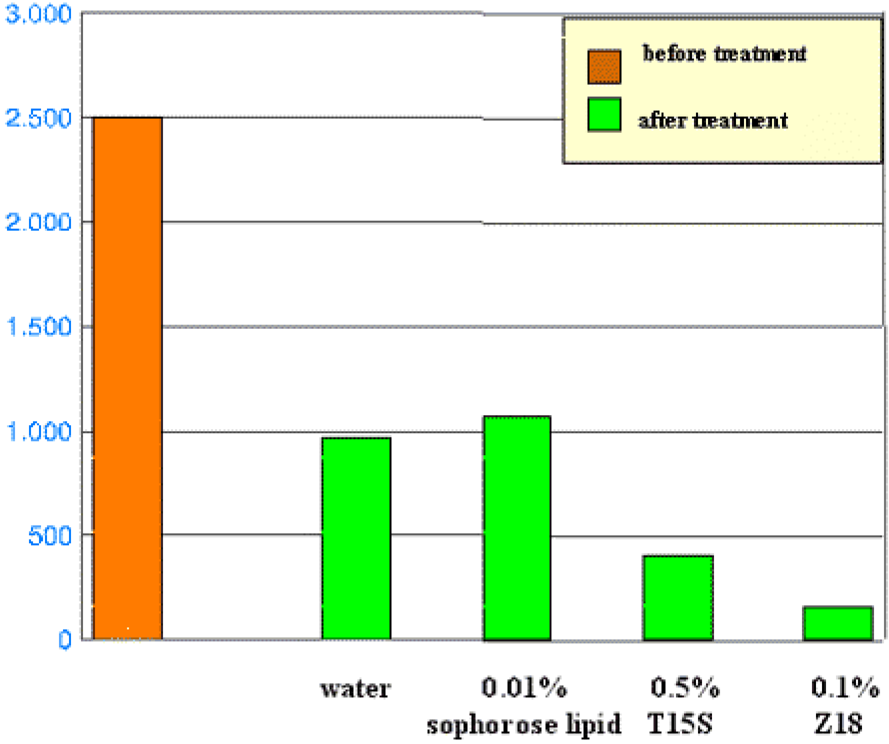

Fig. 3 PAH-removal from a sandy gaswork soil in two-stage bioreactor influence of additives / 3 days of treatment

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