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Application of Surfactants in Soil Remediation

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ABSTRACT

This paper will discuss the behavior and the toxicity of the surfactants in the soil - water phase system and its associated application effect, which could provide conditions for further study the impact of surfactants on microbial degradation of HOCs.

Keywords: surfactant, soil remediation, HOCs.

INTRODUCTION

The migration of hydrophobic organic compounds (HOCs) in the soil / water phase system is a significant migration process, which could affect the removal and biodegradation of organic pollutants in soil. Such substances that have low water solubility are susceptible to adsorb the soil particles, while HOCs in the adsorbed state are generally difficult to microbes, which will impact on the degradation rates and processes of organic matter in soil[1,2]. Numerous studies show that, the slow release to the aqueous phase of HOCs limits its microbial degradation process, and this phenomenon is known as limited bioavailability[3].

Surfactant can improve the HOCs distribution of water in the soil / aqueous phase system to provide the conditions for the subsequent removal of biodegration or other methods[4,5,6]. Meanwhile, compared to the large amount of organic solvent system, surfactants are more attractive in the environment remediation applications with their low toxicity, biodegradability and economical use-cost[3,7].

Characteristics of the surfactants

Typically, surfactants means the substances that are composed of both the hydrophilic, polar head end (hydrophilic group) and the lipophilic, non-polar hydrocarbon tail (hydrophobic group).Surfactants can significantly reduce the interfacial tension[8].

According to the charged state of the hydrophilic group, Surfactants can be classified into anionic surfactant, cationic surfactants, non-ionic surfactant and zwitterionic surfactants; according to the synthesis method, surfactants can also be classified into Chemical surfactants and biosurfactants.

Hydrophobic groups of the surfactant make surfactants molecules tends to be accumulated at the interface in the water; when it reaches a certain concentration, micelles will form in solution, and there will be a hydrophobic microenvironment formed in the non-polar interior of a micelle. The surfactant concentration during the formation of micelles is called Critical micelle concentration (CMC)[1,3,8]. When it reaches this concentration, surfactant molecules can rapidly aggregate to form colloidal ordered aggregations with 20 to 200 molecules or ions[9]. In the presence of a surfactants, by being attracted to the hydrophobic microenvironment of micelle, the apparent solubility of HOCs are significantly improved, which is the solubilization of HOCs.

Surfactant molecules aggregating in the solid phase cause a reduction in the surface tension of the internal, which may increase the contact between the aqueous phase and the solid phase.

The formation of Semi-micelle often significantly increased adsorption of surfactants, and may cause an increase in adsorption of HOCs[10]. However, when the adsorption layer of surfactants forms on the NAPL- water interface, the Capillary force that constraint the DNAPLs in the soil pores will lower; thereby, mobility of contaminants will increase ,which is called mobilization of surfactants[1].

Interaction of surfactants and soil

Surfactant of low concentration in soil - water system could exist in the aqueous phase in the form of monomer molecules, while surfactant can also exist in the aqueous phase in the form of micelles when the concentration is higher than CMC[1]. In the meantime, the CMC of surfactant in the aqueous phase will chang with the difference of structure of surfactants, temperature of the solution and type of electrolyte and organic compounds.

With the increase of the hydrophobicity of surfactants, the CMC will decrease. The CMC of anionic and cationic surfactants in the pore water may be lower than that in pure water, while the CMC of non-ionic surfactants in the pore water does not significantly reduce. Studies have shown that, due to differences in pH, organic matter content and mechanical composition of soil samples the adsorption of surfactants by different soil is also differences. Adsorption capacity of surfactants by soil depends mainly on soil organic matter content, increasing with the increasing of organic matter content. However, under the similar soil organic matter content, adsorption capacity is mainly affected by soil particle size, the smaller size of particles more beneficial to adsorption[11] .

Some studies have shown: in the soil system when the solubilization occurs the concentration of the surfactants is considered to be effective CMC (CMCeff), which is much larger than the CMC in pure water; and Experiments show that the rise of surfactants' CMC is caused by the adsorption of surfactants[12]. The interaction of surfactants and organic matter may reduce soil hydraulic conductivity. Surfactant may change or even destroy the electrical double-layer structure in the surface layer of clay particles, causing swelling, dispersed, or flocculation of clay particles; Ultimately, surfactants bring about changes in soil structure and porosity, which will affect the stability of soil aggregates[8].

Biodegradability of the surfactant will reduce because of the adsorption on the soil, although there is the evidence that the surfactant adsorbed on the soil can be degraded largely. Surfactants may be present toxic effects on soil microbes. Surfactant may damage cell membranes through interaction with the liquid component in the cell membrane or may react with functional proteins of cells. In general, the toxicity of the cationic surfactants is generally greater than the non-ionic surfactants anions or the nonionic surfactants. At a pH of 7 or higher, the toxicity of the cationic surfactant is greater than others, while anionic surfactants exhibit greater toxicity at low PH values. the toxicity of nonionic surfactants is generally smaller than others. Some studies show that, anionic surfactants do not pose danger to humans, animals and plants or the environment; or although there is toxicity, anionic surfactants do not constitute a long-term potential hazard, and have no three-induced effects[13].

Application and effect of surfactants

Shao[2] compared the effects of desorption behavior of 2-nitro-biphenyl on artificially contaminated soil with five different kinds of additives, and found that: the addition of HP-β-CD is most beneficial to the desorption, HP-γ-CD coming second; Triton X-100 and Tween 80 could show the promoting effect only when the amount of the surfactants for using is large enough.

Mao[14] found the order of the removal rate of PAHs in soil by different surfactants used alone is SDBS>APG>TX100. The mixed surfactant(APG:SDBS, 9:l) can offer a higher removal rate of PAHs in soil, the removal rate from (63.3 ± 2.0)% increasing to (75.6 ± 2.0)%; but the mixture of APG, Txl00 has no benefit to the removal rate.

The research of Huang[15] shows that: the order of PCBs desorption capability of surfactants is Tween 80>SDBS>HTAB. And they found that: surfactants in the aqueous phase promote PCBs desorption, while the others adsorbed on soil particles restrain the desorption; the desorption is closely related to micelle concentration.

Liu[16] found that both the rhamnolipid (RL 306mg/L)and POE 6 (302mg/L) all can offer the elution rates above 60% to artificially PCBs contaminated soil samples, but for aging soil samples with PCBs pollution, the elution rates of two kinds of surfactants are less than 20%. The mixture of RL and POE 6 (mass concentration, 0.434:1) have lower CMC than the other mix-proportion.; when the concentration of surfactants for aging soil sample elution is 1505mg/L, the RL-POE 6 mixture have a higher elution rate than RL and POE 6 (Respectively, 38.5%, 32.4%, 28.9%).

The experiments with artificial PAH contaminated soil, aging five months, Zheng[6] found that, under a small proportion of soil/water have a higher rate of solubilization. [12] Ricardo D. Villa, et al. found that: when the concentration is 3 times of CMCeff, TX-100 can remove 36% DDT and 49% diesel in the frist flushing, while 60% DDT and 87% diesel can be removed under 12 times of CMCeff . In addition continuous flushing may increase pollutant removal rate.

At supra-CMC SDHS (i.e., 70 mM), Mathurasa[17] found that, the desorbed TBT was not degraded because high concentrations of TBT and SDHS posed synergistic toxic effects to the bacteria. Consequently, the presence of anionic surfactant at sub-CMCs will be beneficial for the cleanup of TBT contaminated sites.

CONCLUSION

(1) The HOCs desorption of surfactants on the aging contaminated is much lower than that on artificially contaminated soil samples, the difference of elution rate up to 40%. (2) Due to the presence of the adsorption of surfactants on soil, the CMC in soil solution is generally higher than in the pure water. Thereby, we should consider the impact of the adsorption to the concentration of surfactants when choosing the using concentration, which typically causes an increasing in usage amount of the surfactants. (3) The presence of surfactant micelles at high concentrations, as well as the formation of microemulsion, could have the two opposite impact on porosity of the soil, water conductivity. If surfactants resulting in a smaller soil porosity and a higher soil solution viscosity, the difficulty of the subsequent remediation of soil , especially in-situ remediation, will be increased. (4) Low concentrations of surfactants does not constitute a toxic impact on the microbes, but at the concentration up to a certain value, surfactants may produce adverse effect on the microbial degradation, or even lead to the stagnation of pollutants degradation.

According to above, new type of surfactants and mixing formulas and the introduction of other auxiliary methods should be found to get better desorption results at relatively low concentrations without obvious adverse effects on the subsequent remediation, the soil and the microbes.

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