

EFFECTS OF SURFACTANTS ON THE AGGREGATE STABILITY OF SOILS

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In spite of surfactants being widely used and their toxic effects on living organisms has been well known we have only little information about how they influence the different properties of soils. However, surfactants may cause changes in the physical, chemical and microbiological parameters of soils. They can modify the structure of soils through the aggregate stability, as well as the fertility indirectly. In our study we investigated the effects of cetylpyridinium chloride (a cationic surfactant) on aggregate stability of eight different soil horizons. Aggregate stability measurements were performed based on the wet sieving method immediately following various pre-treatment procedures. There were compared the SAS values (percentages of the stable aggregates) of soils pre-treated with distilled water or surfactant solutions of various concentrations. It was found that the aggregate stability of soils increases to the highest level in case of the soil samples treated with moderate amounts of surfactant which form nearly monomolecular adsorptive layer on soil surfaces.

Keywords: soil pollution, surfactant, aggregate stability, wet sieving method

Introduction

Surfactants are one of the most common organic pollutants in the subsurface environment. They originate mainly from detergents used by households and industry. The amount of surfactants in the soil system is increasing due to wastewater irrigation and land application of sewage sludge. Moreover, they are indispensable components of agrochemicals because they are used during pesticide formulations [1-3]. Surfactants are also frequently used in remediation technologies to remove NAPL (nonaqueous-phase liquids, such as fuels, chlorinated solvents) from the subsurface [4, 5]. It is possible to control water infiltration into the soil during irrigation using surfactant treatments of soils [6].

Surfactants are organic molecules composed of strongly hydrophilic and hydrophobic groups or moieties. This is often referred to as amphiphilic because of its dual nature. The hydrophobic portion of the surfactant molecule is typically a long alkyl chain (lengths of C10 to C20). The hydrophilic group often includes anions or cations, has an electrical charge, or is polarized, and can form hydrogen bonds [7].

Surfactants may contaminate the soils in relatively high concentrations [8-10]. Depending on the extent of accumulation or adsorption of surfactants on gas- and solid-liquid interfaces, surfactants may affect the physical properties of soils, including hydraulic conductivity [11, 12], water retention [3] or stability of soil aggregates [13].

Although the potential effects of surfactants on soil-water interactions have been discussed in the literature [14-16], little information is available regarding the changes in aggregate stability caused by surfactant adsorption. The soil aggregate stability may change, if the adsorbed surfactants modify the soil hydrophobicity, destroying the cementing agents of aggregates or exchange the cations. The altered soil aggregate stability enables changes in soil porosity and pore size distribution and thereby affects the fluid retention and fluid conductivity of soils [17].

The aim of this study was to improve our understanding the effects of surfactant adsorption on the soil aggregate stability. Aggregate stability measurements were performed using the traditional wet sieving method involving different Hungarian soils pre-treated with a cationic surfactant (cetylpyridinium chloride).

Materials and methods

In our investigation a cationic surfactant, cetylpyridinium chloride (CPC) was used in three different concentrations. CPC has a positive charged pyridine end and it is a widely used cationic quaternary compound of several household products, for example anti-static additives and emulsifiers.

Properties of the investigated eight soil samples from six different soil types are shown in *Table 1*.

Table 1: The origin and properties of the studied soil samples

Sample number	WRB soil classification & name of the closest city	Symbol and depth of genetic horizons (cm)	Clay + Fe-oxihydrates % (<0.002 mm)	Silt % (0.002-0.05 mm)	Sand % (>0.05 mm)	Humus (%)	CaCO ₃ (%)	CEC (mgeq/100 g)
1	Vertic Stagnic Solonetz (Clayic) <i>Karcag</i>	B 5–30	51.09	45.90	0.88	2.00	0.13	40.85
2	Hortic Terric Cambisol (Dystric. Siltic) <i>Keszthely</i>	A 0–30	21.09	33.13	44.28	1.45	0.05	11.84
3	Hortic Terric Cambisol (Dystric. Siltic) <i>Keszthely</i>	B 30–50	22.90	33.87	42.29	0.93	0.00	12.38
4	Cutanic Luvisol (Siltic) <i>Várvolgy</i>	A 0–20	15.27	29.35	54.05	1.33	0.00	10.36
5	Cutanic Luvisol (Siltic) <i>Várvolgy</i>	B 20–50	22.30	26.56	50.49	0.65	0.00	12.78
7	Vertic Gleyic Luvisol (Manganiferic. Siltic) <i>Magyarszombatfa</i>	B 20–50	38.96	25.93	34.61	0.49	0.00	16.78
9	Vermic Calcic Chernozem (Anthric. Siltic) <i>Kápolnásnyék</i>	A 0–30	27.60	51.68	7.50	3.70	9.52	30.25
12	Gleyic Vertisol (Clayic) <i>Kisújszállás</i>	A 0–30	53.88	41.19	1.05	3.89	0.00	35.69



Figure 1: Wet sieving apparatus for aggregate stability measurement

Equipment used during the aggregate stability measurements was constructed by the Federal Agency for Water Management, Institute for Land & Water Management Research (from Petzenkirchen, Austria) (Fig. 1). It works according to the principle of wet sieving method [18]. However, in this case not the soil but the water surrounding the soil sample is moved, thus water percolates through the soil during the shaking.

The aggregate stability measurements were done according to the wet sieving method, mentioned below.

To separate the fractions between 1 and 2 mm, air dried soil samples were sieved for the pre-treatments. It is not allowed to pulp or destroy the samples during drying nor or sieving, only to crumble them gently.

After sieving we placed the different sized soil particles into a measuring pot and four grams of them in three repetitions were weighted with an analytical scale. We had to be very careful not to disturb the soil particles.

The soil samples were thereafter pre-treated with distilled water or solutions or there remained in dry untreated condition (see below).

Then the samples were taken in the six small sieves of the equipment. The mesh of the sieves was 0.25 mm in diameter. 80 ml distilled water was poured into the iron cups which were fixed to the upper side of the measuring equipment. After that the cups and the soil samples were taken into the apparatus.

As we wetted the soil samples with some distilled water, the floating soil particles sank down to the bottom of the iron cup. After five minutes of wet sieving the soil samples were dried at 105 °C for 48 hours (drying 1). The weights of the dried samples were measured.

To determine the amount of the residual aggregates of the investigated soil samples after wet sieving, the aggregates were destroyed using Sodium hexametaphosphate. Thus the aggregates were separated from the sand particles larger than 0.25 mm and from the organic and inorganic debris. After disaggregating the samples we repeated the wet sieving and the drying stages. Finally, the weight of soil samples were measured again (drying 2) and the percentage of the stable aggregates (SAS) was calculated according to the Eq 1.

$$SAS = \frac{m_1 - m_2}{m_0 - m_2} \cdot 100 \quad (1)$$

where:

- m_1 – weight of the soil sample after the first drying (g),
- m_2 – weight of the soil sample after the second drying (g),
- m_0 – weight of the originally used dry soil sample (g).

The aggregate stability measurements were performed after applying various pre-treatment methods. First the soil aggregate stability was measured according to the

standard method. It means that the soil aggregates were taken in dry condition on the small sieves of wet sieving apparatus, without any previous soaking in distilled water or surfactant solution. Secondly the aggregate stability measurements were performed with soil samples which were previously soaked in distilled water or surfactant solution for two days. Based on the results of our preliminary experiments, there were used surfactant solutions of three different concentrations (Table 2). The applied surfactant concentration values were determined based on the soil sample with the highest adsorption capacity (sample 12, Gleyic Vertisol) (Table 1). At the sample 12 the effect of wetting procedure was also investigated. It was compared the aggregate stability of with distilled water gradually and normally wetted soils.

Table 2: The different concentration of surfactant solutions

Concentration of surfactant solutions (g/ 1000 ml)		
K. 1	K. 2	K. 3
30.9700	3.0970	0.3097

Results

Fig. 2 shows the results of our preliminary experiments with sample 12. The aggregate stability of this highly clayey soil sample was relatively high at all pre-treatments. Comparing the standard method with soaking in distilled water is visible that two days soaking destroys some aggregates. The effect of carefully wetting was moderate.

If we compare the percentages of stable aggregates between distilled water and surfactant treated samples (after two days soaking) it is ascertainable that the surfactant adsorption increases the aggregate stability. The highest stability was observed in case of applying surfactant solution in medium concentration. This was the concentration at which the solution covers the surface of the soil particles approximately in monomolecular layer. Our results showed that the aggregates were less stable both in case of the applied minimum (K3) and the maximum concentration (K1).

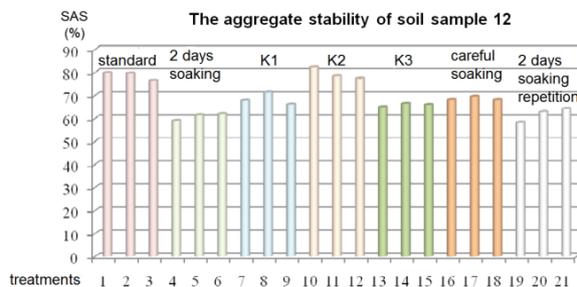


Figure 2: The aggregate stability of soil sample 12

As the results of the standard measurement demonstrate in Fig. 3, the sample 1 (Vertic Stagnic Solonetz) (which tends to be strongly dispersed because of its high sodium content) was the less stable and the sample 4 (Cutanic Luvisol) was found to have the most stable aggregates. That might be caused by the combined

effect of clay minerals, humus materials and Fe-oxihydrates as cementing agents.

The effectiveness of the surfactant treatment at different soils was evaluated according the rate of stable aggregates of surfactant treated and non-treated (two days in distilled water soaked) soils. Fig. 4 shows the effects of the different pre-treatment methods on soil aggregate stability at the different soil samples. It is visible how the surfactant solutions in various concentrations change the resistance of soil particles against water. Fig. 4 does not contain the results of the sample 1 because the change of this sample's aggregate stability was extreme and not comparable with the other samples in that case (Fig. 5).

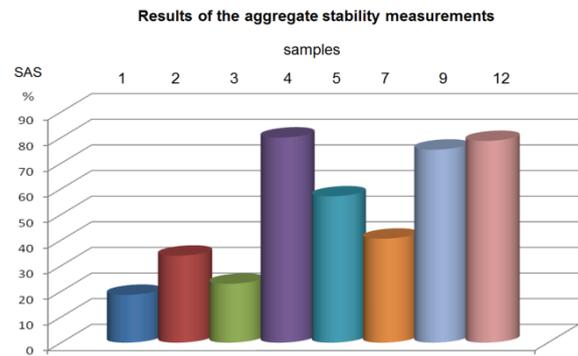


Figure 3: The results of the aggregate stability measurements according to the standard

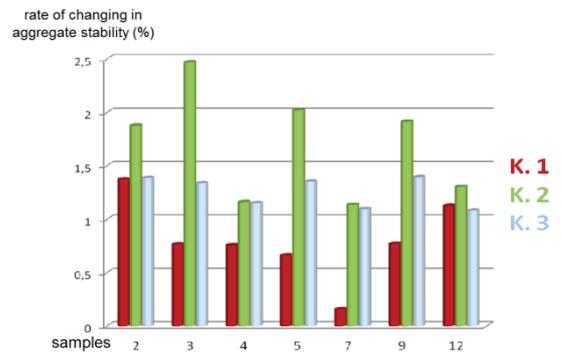


Figure 4: Increasing in aggregate stability in case of different concentration of surfactant solutions

The sample 2 has favorable aggregate stability states, both after using the standard method as well as after 2 days of soaking because of the relative high organic matter and clay content of the soils. Different rate of effects of surfactants on the soil sample's aggregate stability was observed in case of all three surfactant concentrations.

According to our results sample 3 has the same stability both after the standard method and also with soaking. A decrease of aggregate stability was observed at high surfactant concentration (K1), which was caused by the multilayer adsorption of surfactants on the surfaces of soil particles. In that case the surfactant might create a partly hydrophilic layer on the surfaces which may lead to the dispersion of the particles. The highest aggregate stability values were measured in case of medium surfactant concentration. At this concentration the soil

surfaces are covered with surfactant molecules in approximately monomolecular layer and therefore the soil show hydrophobic characteristics. Using the K3 concentration the soils weren't able to adsorb enough surfactant molecules, the surfaces remained partly hydrophilic.

Similarly to sample 3, the CPC had the same stability effects on sample 4-9. The big amount of adsorbed surfactant at K1 concentration caused the highest decreasing of stability rate at sample 7. The pre-treatment with K3 surfactant solute enhanced the stability moderately and the surfactant adsorption from K2 solute caused stable aggregates.

The aggregate stability value of sample 1 (Vertic Stagnic Solonetz) was nearly 100% (Fig. 5). This was the only soil whose aggregate stability was the highest in case of maximum surfactant solution concentration. This might be explained with the large surface area, increasing the efficiency of the surfactant and the high amount of exchangeable sodium ions. However, almost all of the aggregates were disaggregated by the two days soaking in distilled water.

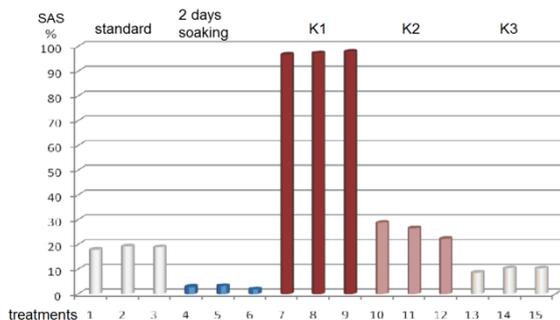


Figure 5: Aggregate stability values of soil sample 1

Discussion

In each case the highest aggregate stability was observed if cetylpyridinium chloride being applied in medium concentration. This CPC concentration value means those surfactant amounts, which could form approximately a monolayer hydrophobic coating on solid surfaces protecting the soil aggregates against the destructive effect of dipole water molecules. Decrease in the aggregate stability of soils was experienced in case of the wet sieving being performed with both the lower and higher concentrations of surfactant solutions, because of the partial hydrophilisation of the soil aggregates.

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