INVESTIGATION OF TRANSPORT MODELLING AND SOIL STRUCTURE INFLUENCING EFFECT OF BIODIESEL BY-PRODUCT IN AGRICULTURAL SOILS

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Abstract

Our investigations are parts of a complex research work which have been started by Department of Soil Science and Agricultural Chemistry of Szent István University. This research work focuses on agricultural application of biodiesel by-product as an alternative nutrient and its effects on the cultigens and on the environment (Kovács et al., 2011a, Kovács et al., 2011b, Tolner et al., 2011, Kovács et al., 2012). The safety use of this material requires the accurate knowledge of its behavior thence several experiments were performed.

The first step of our research was the transport modeling of the biodiesel by-product. The basics of models were column tests where the leaching of biodiesel by-product was investigated in presence of nitrate in different agricultural soils. During leaching tests the by-product was substituted by glycerol because of its decisive glycerol content. The second part of our research was the geotechnical investigation of soil parameters. In these experiments the soil structure modifying effect of glycerol was determined.

According to results of transport modeling the leaching of glycerol mainly depends on the soil type and on the presence of nitrate. The amount of washed-out glycerol is significantly high from sandy soils but it decreases by adding of nitrate. The soil structure influencing effect of glycerol was proven by geotechnical investigations. Changes of soil mechanical parameters were observed in cases where the soils were treated with glycerol.

Keywords: biodiesel by-product, leaching test, transport modeling, consolidometer test, shearing test

Összefoglalás

A bioüzemanyagok, mint megújuló energiaforrások egyre nagyobb teret hódítanak a világban, amit az is igazol, hogy a 2000 és 2007 közötti időszakban a világ bioüzemanyag termelése a háromszorosára nőtt (Coyle, 2007). Az üzemanyagok előállítása során azonban jelentős mennyiségben keletkeznek melléktermékek, melynek felhasználásáról, elhelyezéséről gondoskodni kell, ugyanis az üzemanyag előállítás növekvő trendjének következtében, ezek mennyisége is növekedni fog.

A biodízel előállítása során nagy mennyiségű melléktermék keletkezik, magas glicerin tartalommal. Ez a magas glicerin tartalmú melléktermék ugyanakkor növényi részekkel való szennyezettsége miatt a kozmetikai ipar számára nem felhasználható (Wilkie, 2008). Viszont épp emiatt a növényi tartalom miatt képzelhető el ennek alkalmazása a mezőgazdaságban, alternatív tápanyag-forrásként. A glicerin számos baktérium faj számára hasznosítható szénforrás, segítségével intenzifikálható a mikrobiális tevékenység a talajban, melynek következtében nő a humusztartalom és javul a talajszerkezet.

Vizsgálatink célja, hogy megismerjük a biodízel melléktermék transzportfolyamatát a talaj háromfázisú zónájában, valamint a talaj szerkezet módosító hatását.

Önmagában a glicerin migrációja a talajban főként az adott talajtípus hidrogeológia paramétereitől függ, mivel terjedése uralkodóan advektív transzporttal zajlik. Kísérleteink során viszont azt tapasztaltuk, hogy nitrát hozzáadásával a kimosódás intenzitása csökkenthető, ezáltal fokozható a gyökérzónában történő hasznosulása és csökkenthető a

talajvíz terhelése. A talajba jutatott glicerin azon túl, hogy terhelést jelenthet a felszíni vízadókra a gyors kimosódásával, a talaj szerkezetében is változásokat okozhat. A talajok geotechnikai vizsgálatait ezen változások megfigyelésére végeztük el, melyek során eltéréseket tapasztaltunk a glicerinnel kezelt és kezeletlen talajok fajlagos összenyomódása, kohéziója és belső súrlódási szöge között.

Introduction

Industry of biofuels is a part of renewable energy sources which gains ground by leaps and bounds. Between 2000 and 2007 global biofuel production tripled from 4.8 billion gallons to 16 billion gallons. The biodiesel production was about 3 billion gallons in 2007 and more than 50 % of this quantity was produced by EU (Coyle, 2007). By prognosis this process will increase which raises issue of by-product utilization.

During biodiesel production a huge amount of useable by-products are produced with high glycerol content. Outputs of biodiesel production largely depend on oil type and quality. Approximately for 100 liters of vegetable oil 25 liters of methanol and 0.8 kg KOH catalyzer are used to produce 75 liters of biodiesel and 25 liters of crude glycerol (Wilkie, 2008). In general the glycerol used by cosmetic and chemical industry but biodiesel by-product is contaminated by vegetal parts. But this „vegetal contamination" makes it perfect for use by-product like fertilizer on fields.

The glycerol is an easily available and adequate carbon source for micro-organisms (Lee et al., 2001; Tickell, 2003). It could intensify microbial activity of soils which can helps to increase availability of vegetal nutrients. Furthermore the microbes enrich organic nutrient content and organic part of soils which increase the humus content and result good texture.

The application of biodiesel by-product as a fertilizer in the agriculture could be an alternative way to utilize the huge amount waste of biofuel industry (Kovács et al., 2011b, Tolner et al., 2011). Before utilization the probable effect of by-product on environment must be ascertain. Our first research works were the mobilization investigations of glycerol in column tests which were simulated in a transport modeling program. The spread of glycerol was investigated alone and in presence of nitrate in two types of soil. The second work was the investigation of soil structure modifying effect of glycerol by oedometer and shearing machine.

Materials and Methods

The transport calculations were accomplished by VS2DT (Variably Saturated 2-D Flow and Transport Model) which module is integrated in software package of WHI UnSat Suite Plus. This module is a suitable tool to model transport of chemicals in unsaturated zone of soil. In porous media the components of chemical mass flow are advection, diffusion and dispersion. Furthermore the amount of chemicals in water phase are depend on adsorption and chemical, radioactive decay (Kovács, 2004). In this experiment the decreasing of glycerol amount were measured which were taken as a basis to compute the decay constant of glycerol. That was applied in transport calculations to simulate the microbial degradation.

The basic of models were the column tests. Two different soil types were applied in the experiment. Primary, one groups of columns were filled up with 1 kg of loamy sand soil while the other group with 1 kg of loam soil. The columns were treated with different concentration of glycerol and nitrate base solutions. (The concentration of glycerol and nitrate base solution was 8000 μg/ml and 2000 μg/ml, respectively.) The first solution only included glycerol while second solution included nitrate near glycerol. After treatment of soil columns with base solutions 3 days long resting period was left for microbes to degrade the nutrients. After the third day 100 cm^3 distilled water was filled in the columns to investigate the wash-out of the chemicals. The biodegradation of glycerol is only possible in aerobic conditions therefore after 15 minutes 100 cm^3 solution was exhausted from the columns. This procedure was repeated in every 18th hours until the end of experiment which was on the 11th days. The glycerol content of the exhausted solutions was analyzed by CARL ZEISS F1 refractometer and the nitrate content was determined by Parnass-Wagner distillation apparatus. The main parameters of soils are shown in Table 1.

Table 1. Initial parameters of modeling

Parameters of soils	**Loamy Sand soil**	**Loam soil**
Horizontal hydraulic conductivity (*m/day*)	2	0.25
Specific storage (*1/m*)	0.1	0.1
Porosity (*v/v*)	0.41	0.45
Residual moisture content (*v/v*)	0.07	0.11
Bulk density (g/cm^3)	1.6	1.6
Longitudinal dispersivity (*m*)	0.5	0.5

In the agriculture the good condition of soil structure is a decisive moment from point of view of plant develop. Oedometer tests and shearing tests were performed to determine the soil structure modifying effect of glycerol. The oedometer test gives information about compressibility of soil. In the shearing tests the internal friction (φ) and the cohesion (τ) are determined. The soils could be classified into two groups, the cohesive and the cohesiveless soils. In the cohesive soils (loam, clay) there are internal binding forces between grains about the high effective surface of particles so the value of cohesion (τ) is higher than 0 (at normal stress (σ) of 0) while in the cohesiveless soils (gravel, sand) these forces do not work, the cohesion is 0 (at normal stress (σ) of 0). The cohesive soils are characterized by low internal friction contrary to the cohesiveless soils.

During geotechnical investigations the used soil types were different in contrast with the column test ones. There was not a significant difference between geotechnical parameters of the soil types used in column test so the effect of glycerol could not be sensible after treatment and investigation. One of them was a sandy soil from seashore with low effective surface of grains which means lower cohesive reactions but it is an optimal material to observe the effect of glycerol on the internal friction. The second one was a clayey soil from a Hungarian agricultural field close to Cegléd. The high effective surface of grains could give a high surface reaction so the investigation of cohesive force changes is more significant than in case of sandy soil.

As we can see on the Figure 1 the grain size distributions of investigated soils are totally different. The clayey soil is a well graded material but the soil from the seashore includes same grain size particles. More than 85% of the grains are in interval of 0.1 to 0.08 mm.

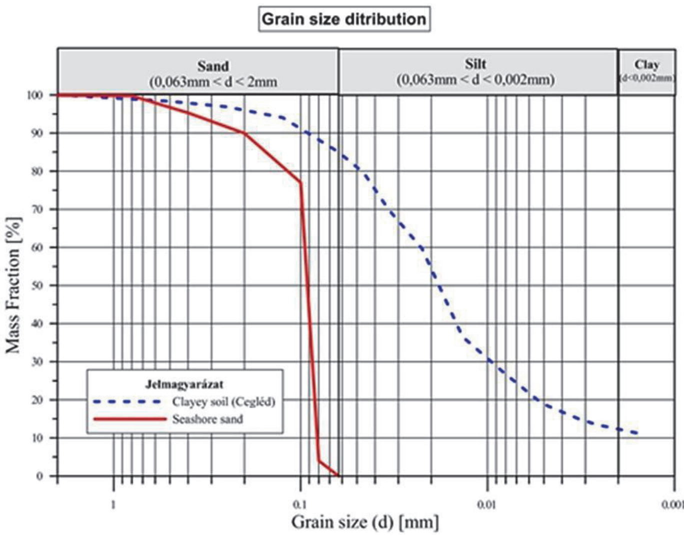

Figure 1. Grain size distributions of investigated soils

Two traditional soil mechanical methods were chosen to investigate the soil structure changing effect of glycerol. Before geotechnical investigations the soils were treated with the same glycerol base solution (8000 µg/ml) which was applied in column tests.

Oedometric measurements were selected to describe the compaction behavior. During this method the investigated material is filled into a rigid cylinder than it is pressed with a predefined normal stress from the axial direction. The normal stress is following a step by step increasing function and after the measurement we can calculate a specific compression value. These values could show the compressibility of the soil.

Other geotechnical parameter is the shear resistance which could characterize the effect of glycerol on soil structure. A torsion shear machine was used to investigate the changes of the cohesion and the internal friction. Torsional shearing (Figure 2) is a special shear method because it was developed to measure not only the maximum shear strength of different kind of soils but the residual shear strength as well. This machine consists of a standing upper part with two force gauges where the resistance forces are measured and a rotating bottom part where we can control the velocity of the displacements. An axial displacement sensor measures the changes of the sample height during all the test periods.

The oedometric and shearing tests were performed with two soil conditions. The first measurements were standard measurements with given moisture contents which was 10 % (m/m) and 14 % (m/m) in the sandy and the clayey soil, respectively. After that the soils were treated with the same glycerol base solution which was used during column tests to investigate the changes of geotechnical parameters.

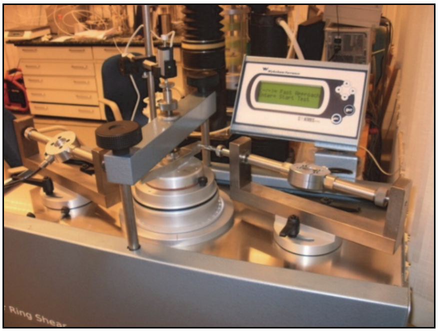


Figure 2. Shearing apparatus

Results

The different characteristics of leaching processes in the two soil type are shown on Figure 3 and Figure 4. On the figures Line 1 shows the concentration distribution of glycerol after filling up of glycerol base solution. Line 2 is the concentration distribution after 3 days long resting period which is an equilibrium concentration distribution. The concentration of glycerol increased in the lower layers which were caused by flow of base solution. But this process is significantly slower in loam soil than in loamy sand one. The difference between Line 2 and Line 3 were caused by filling up of distilled water. The concentration decrease in loamy sand soil is experienced along the whole cross-section while in loam soil it is only observable to the middle of column. The Line 4 shows the concentration decreases after exhausting.

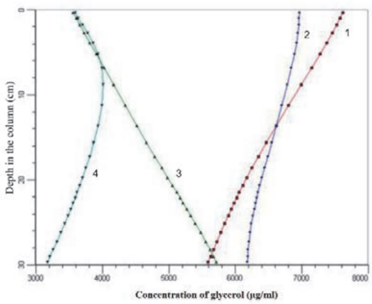

Figure 3. Concentration change of glycerol in loamy sand soil after first filling and exhausting of distilled water (the meanings of lines are explained in the text)

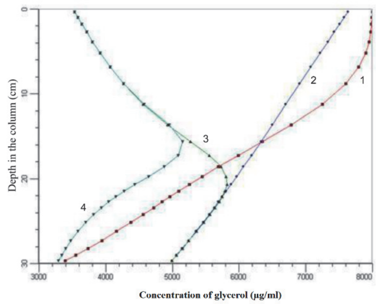

Figure 4. Concentration change of glycerol in loam soil after first filling and exhausting of distilled water (the meanings of lines are explained in the text)

Figures 5, 6 show the wash-out concentrations of glycerol from loamy sand and loam soils in lack of nitrate. The Figures 7, 8 show the leached glycerol concentrations in presence of nitrate. The figures (Figures 5, 6, 7, 8) present simultaneously the measured concentrations from labor experiments and calculated concentrations. To compare the results of measurements and calculations correlation was calculated. The values of correlation coefficients were higher than 0.85 in three cases (Figures 5, 6, 7) which mean high similarity. The effect of nitrate in loam soil was not calculated perfectly, the value of correlation coefficient was 0.71.

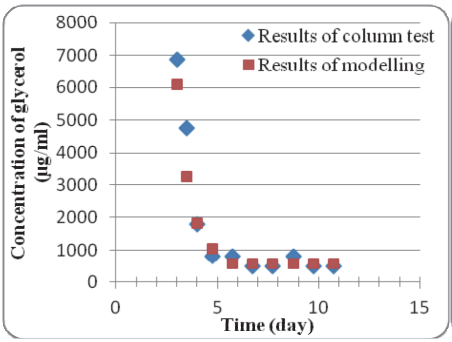

Figure 5. Concentration change of glycerol in lack of nitrate in loamy sand soil

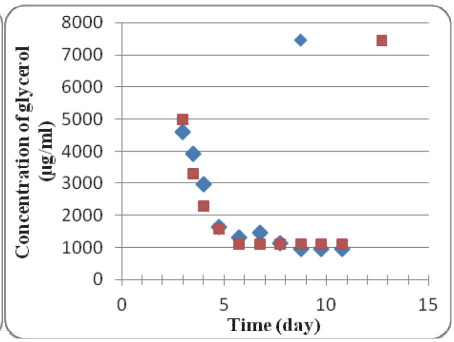

Figure 6. Concentration change of glycerol in lack of nitrate in loam soil

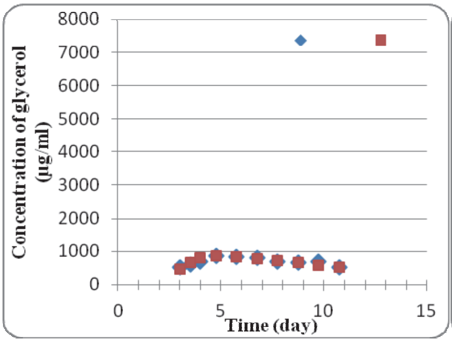

Figure 7. Concentration change of glycerol in case of added nitrate in loamy sand soil

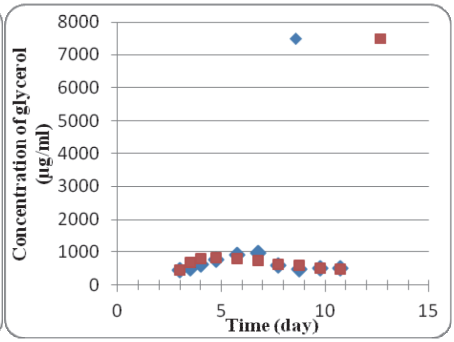

Figure 8. Concentration change of glycerol in case of added nitrate in loam soil

Figure 9 shows the different soils with different compaction characteristics. We found that the glycerol helps the consolidation of soils in both type of soils but the changes are not significant.

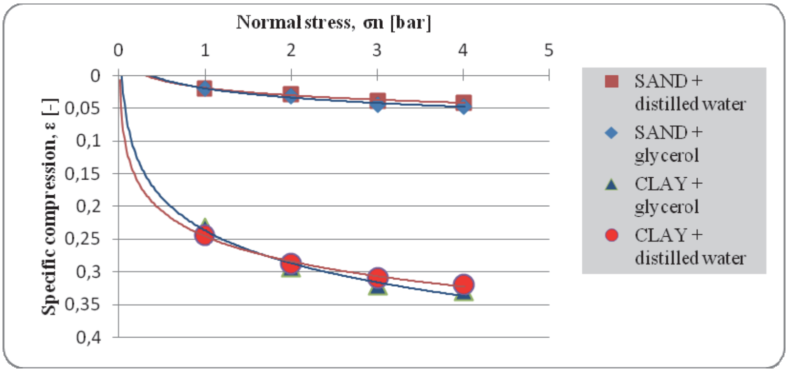

Figure 9. Results of oedometric measurements

In case of shearing measurements the changes are different. In the aspect of clayey soil we can see that only the cohesion of the soil was changed but the internal friction was the same. At zero normal stress (σ) the cohesion increased from 9.3 kPa to 23.4 kPa (Figure 10).

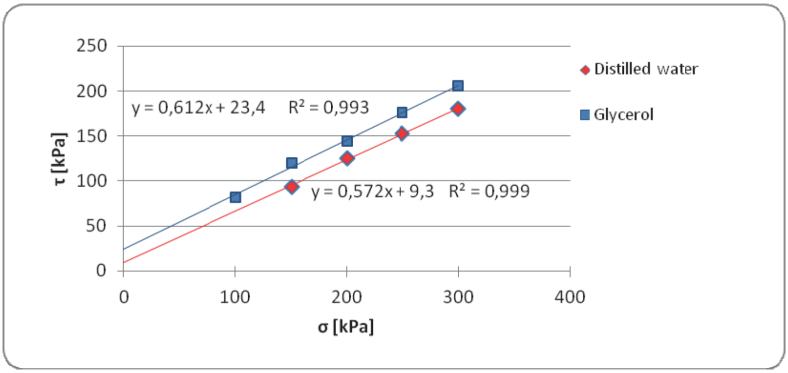

Figure 10. Results of shearing measurements (Clayey soil (Cegléd))

In case of seashore sand sample a small difference was observed. Differences between angular coefficients of lines (Figure 11) show decreasing of internal friction (φ) after glycerol treatment meanwhile the cohesion of the soil was not changed. (Figure 11).

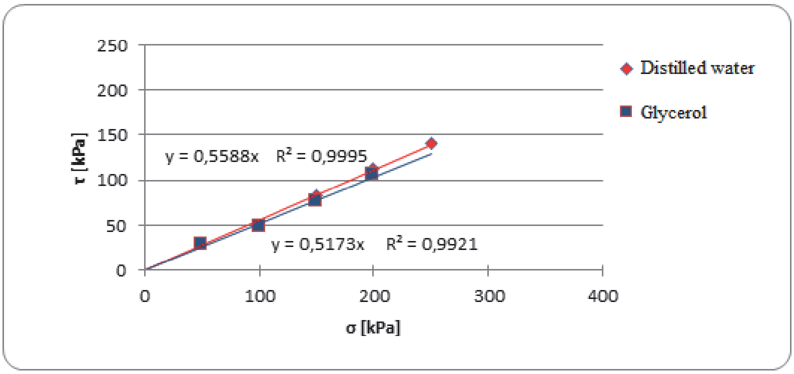

Figure 11. Results of shearing measurements (Seashore sand)

Discussion

The glycerol is a water soluble chemical so its adsorption is not significant on surface of inorganic and organic colloids in soils, therefore the migration of glycerol decisively advective transport. That means the wash-out of glycerol significantly depends on the hydrogeological parameters of soils which mainly determined by soil type. The intensity of leaching in sandy soils is higher than in loamy ones. But the nitrate can decrease the amount of leachable glycerol content of treated soils. The added nitrate as nitrogen source can intensify the microbial activity in the soil which increases the degradation of glycerol. The intensified biodegradation can cause lower leached glycerol concentrations.

Differences were experienced in geotechnical parameters of soils after treatment of glycerol. The specific compression increased which means the glycerol helps the consolidation in both type of soils. During shearing test of clayey soil the internal friction was not changed but the cohesion increased. It is easy to explain it because the high effective surface of the clayey soil we had a high reaction surface where the glycerol solution could build up stronger bond between grains. The sandy soil was cohesiveless before and after treatment of glycerol but the internal friction was decreased because the glycerol worked as a lubricant between the grains of soil.

Acknowledgement

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Figure Captions

Figure 1. Grain size distributions of investigated soils

Figure 2. Shearing apparatus

Figure 3. Concentration change of glycerol in loamy sand soil after first filling and exhausting of distilled water

Figure 4. Concentration change of glycerol in loam soil after first filling and exhausting of distilled water

Figure 5. Concentration change of glycerol in lack of nitrate in loamy sand soil

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