^{1}H NMR relaxometry and FT-IR spectroscopy used for characterization of organo-mineral fertilizers based on biosolids

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ABSTRACT

Biosolids from stabilized sludge presents a high fertilization potential due to its rich content of nutrients and organic matter. Three formulas of organo-mineral fertilizers based on biosolids were manufactured having at least 2 % N, 2 % P_2O_5, and 2 % K_2O. The content of N, P and K in the final formula was measured using specific reactants combined with VIS-nearIR spectroscopy. Additionally, all three formulas were characterized by advanced ^{1}H NMR relaxometry and FT-IR spectroscopy. Four dynamical components were identified in the T_2-distribution [1] showing that the rigid component is into a percentage larger than 90 %. In order to evaluate the release properties of organo-mineral fertilizers kinetic measurements of electric conductivity and pH were performed, by placing 0.25 g of formulas (V1, V2 and V3) in 200 ml of distillate water or acid solution. It was found that V3 present the smallest release velocity, but release the largest amount of fertilizers. Two release mechanisms were observed.

INTRODUCTION

Today, a matter of great importance is reducing the impact of sewage sludge on the environment. Due to its content in organic matter and nutrients, the stabilized sludge, also called biosolids, has a high potential for fertilization [2]. Biosolids containing organic matter and nutrients are organic solids obtained by digestion and stabilization of raw sewage sludge [3]. If the content of nutrients in biosolids is low this means that for production of high-performance organo-mineral fertilizers it is necessary, in addition to biosolids, to introduce in their manufacturing formula, fertilizers and mineral compounds. This can be done into a thermo-mechanical process by reactive extrusion, which take place in a reactor extruder with co-rotating screws (see Fig. 1). That ensures, a very good mixing at the molecular level [3]. Biosolids used in agriculture resulting from wastewater treatment must have a reduced concentrations of pathogens and toxic chemicals below a certain levels, only then can be safety used as fertilizers without harming the health of plants, soil and groundwater, and thereby, the health of consumers of agricultural or animal products [4].

THE EXPERIMENRAL INSTALATION

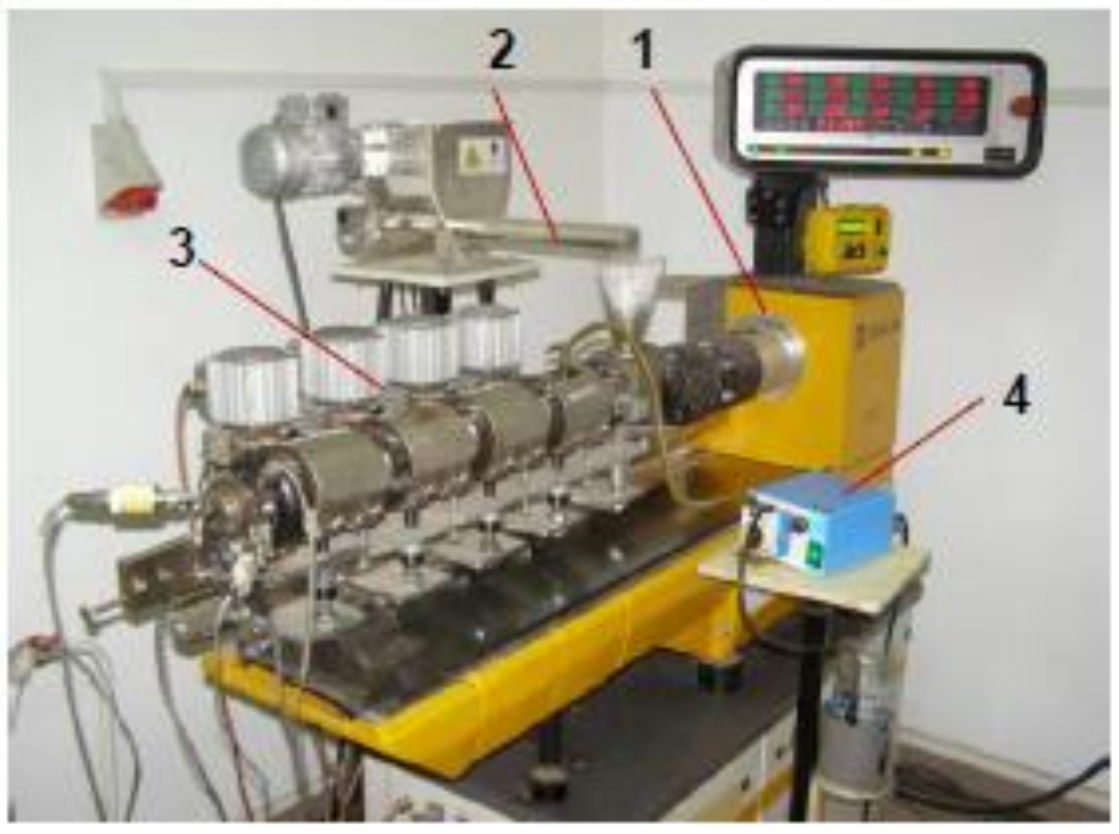

FIGURE 1. The installation for realization of granular organo-mineral fertilizers: 1 – extruder ZK 25x30; 2 – twin screw feeder; 3 – cooling-heating system; 4 – peristaltic pump.

Nitrogen, Phosphorus and Potassium content

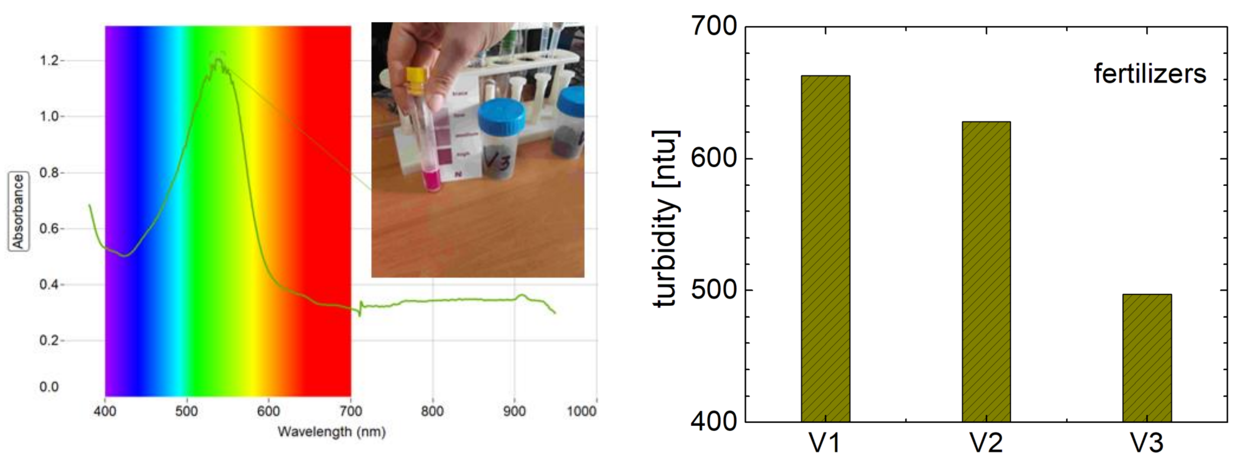

FIGURE 2. VIS-nearIR spectroscopy used for the quantitative assessment of nitrogen and phosphorus content (left) and turbidity measurements for quantitative assessment of potassium (right) content for V1-V3 fertilizers.

RESULTS

Composition of manufactured variant samples

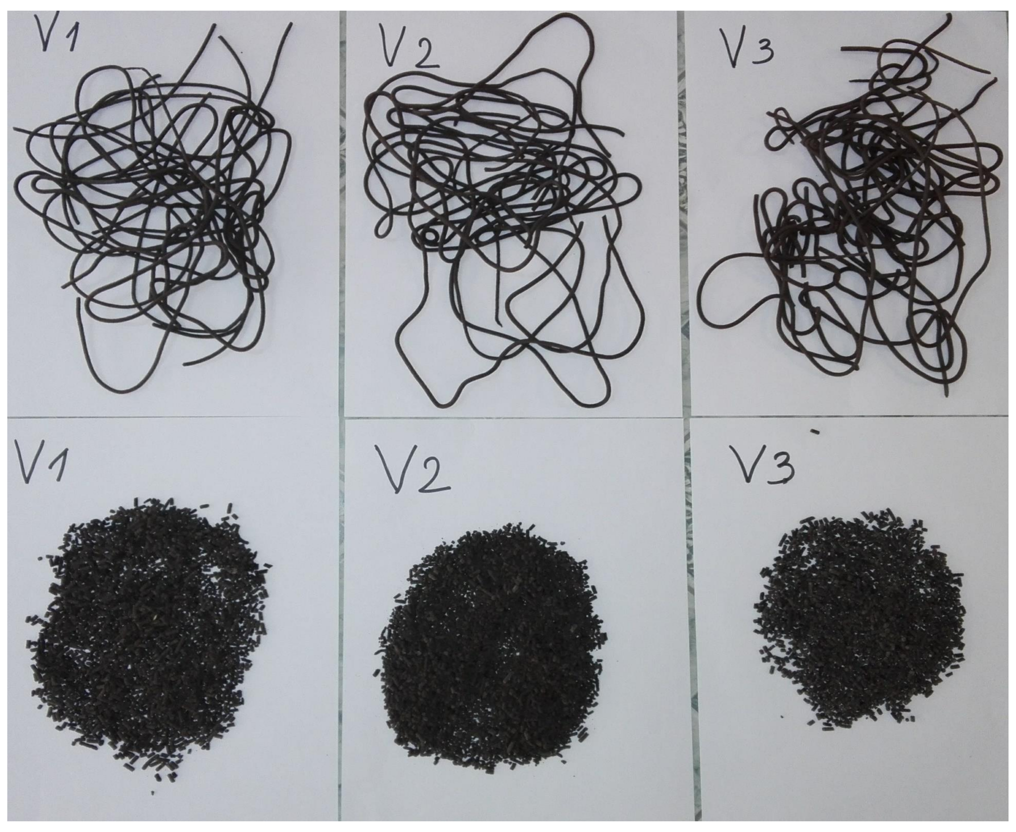

FIGURE 3. Granular organo-mineral fertilizer based on biosolid: (top) before granulation, (bottom) after granulation.

TABLE 1. Composition of manufacturing variant.

Nr crt.	Used substance	Percentages, %		
		Variant I	Variant II	Variant III
1	Dry biosolid, humiditaty 20%	30.00	30.00	30.00
2	Monoammoniumphosphate (MAP)	24.50	0	25.00
3	Mineral fertilizer, NP 20:20	0	24.00	0
4	Potassium nitrate, KNO3	22.20	23.10	23.00
5	Urea	5.30	6.30	6.20
6	Protein hydrolyzate, solution 11 %	4.00	4.00	4.00
7	Starch	7.98	7.47	7.50
8	Magnesium sulphate, MgSO4	3.30	2.82	3.56
9	Zinc sulphate, Zn SO4	0.08	0.07	0.09
10	Copper sulphate, CuSO4	0.05	0.04	0.06
11	Iron sulphate, FeSO4	0.11	0.09	0.11
12	Manganese sulphate, MnSO4	0.22	0.19	0.24
13	Cobalt sulphate, CoSO4	0.03	0.03	0.03
14	Molasses from sugar beet	2.23	1.89	0.00
15	Orthophosphoric acid, H2PO4	0.00	0.00	0.21

^{1}H NMR relaxometry and DQ measurements

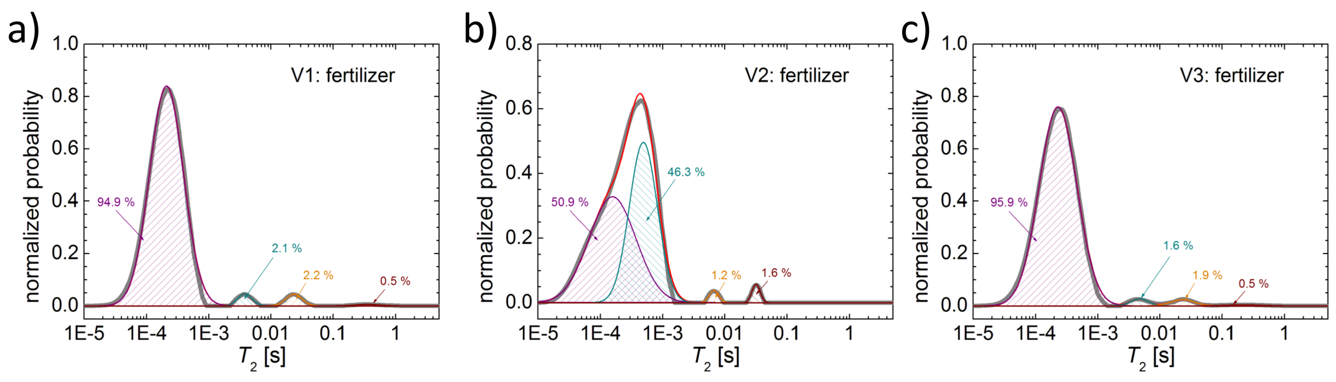

FIGURE 4. ^{1}H NMR T_2 distributions and deconvolution of measured fertilizers (a) V1; (b) V2, and (c) V3.

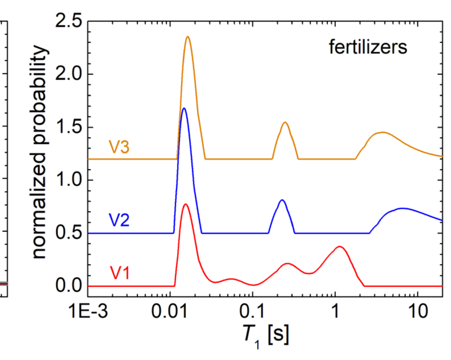

FIGURE 5. ^{1}H NMR T_1 distributions of measured fertilizers V1, V2, and V3.

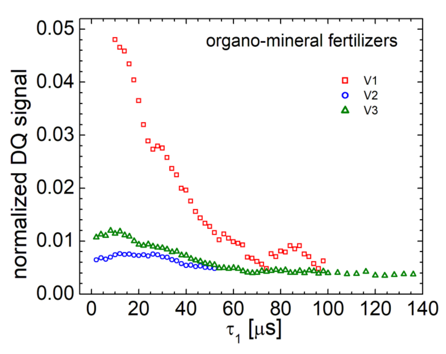

FIGURE 6. ^{1}H NMR DQ build-up curve of measured fertilizers V1, V2, and V3.

FT-IR spectroscopy

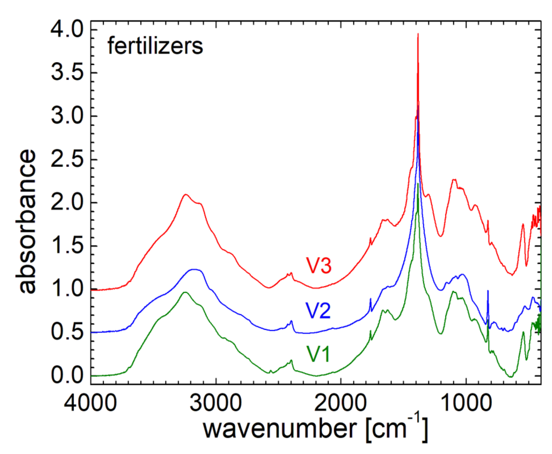

FIGURE 7. FT-IR spectra of fertilizers V1, V2, and V3.

pH, electric conductivity and TDS

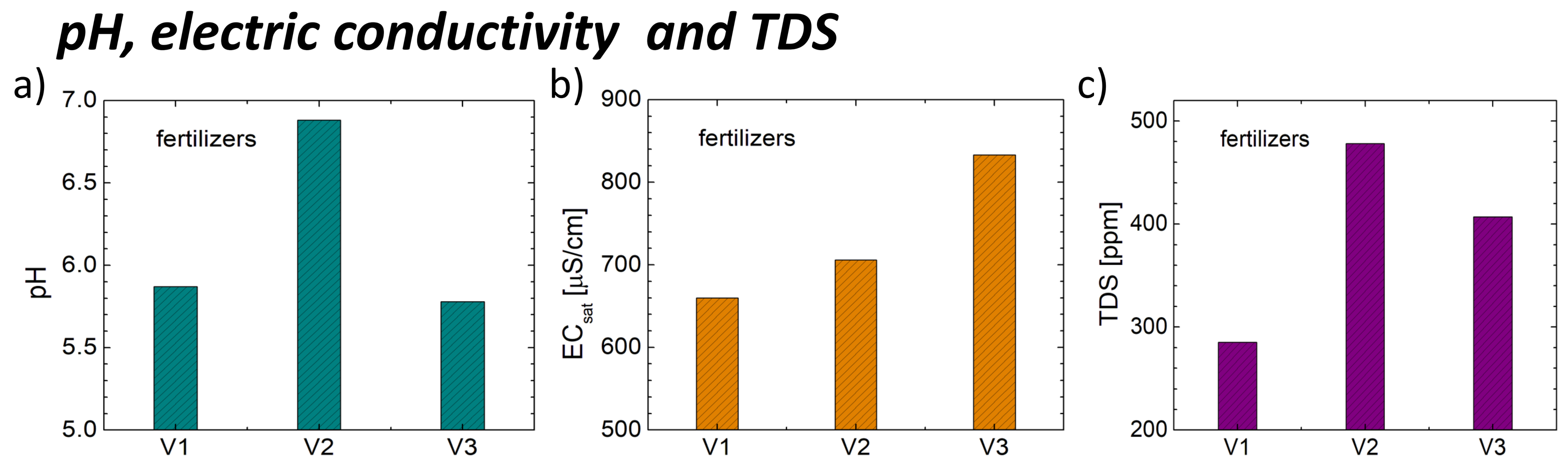

FIGURE 8. a) pH; b) Electric conductivity (EC) and c) Totally dissolved solids (TDS) measured for granular organo-mineral fertilizers.

The solubility kinetics of organo-mineral-fertilizers

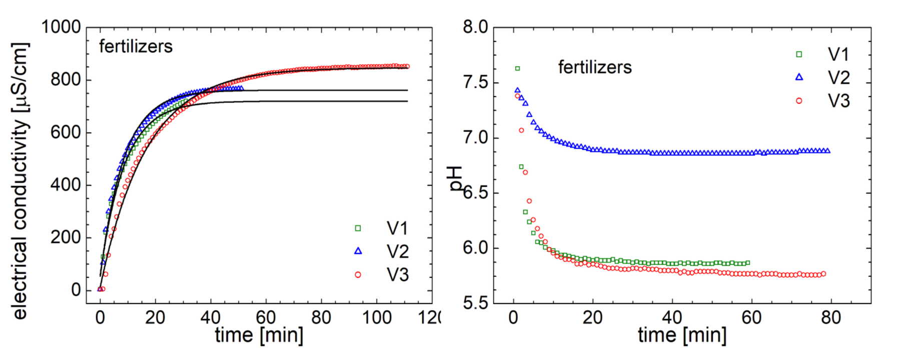

FIGURE 9. a) Electrical conductivity build-up curves and b) pH decay curves measured for V1 – V3 organo-mineral fertilizers during dissolution in distilled water.

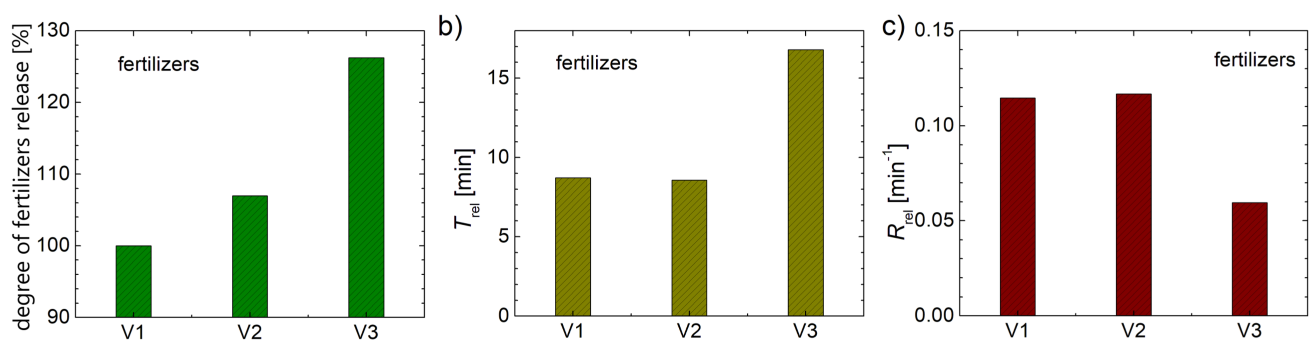

FIGURE 10. a) The degree of fertilizers release; b) the specific release time and c) the velocity of release determined from electric conductivity build-up curves.

CONCLUSIONS

New methods for characterizing biomaterials such as biosolids obtained by extrusion and used as organo-mineral fertilizers were proposed and devloped. In this stady 3 types of biosolids used as fertilizers were measured by advanced ^{1}H NMR methods (T_1, T_2 distributions and DQ curves) and by FT-IR spectroscopy, pH, electrical conductivity and totally dissolved solids. The nitrogen, phosphorus and potassium content for 3 versions of organo-mineral fertilizers were evaluated qualitatively and quantitatively by VIS-nearIR spectroscopy and turbidity. The measurement of the degree of release of fertilizers was made by dynamically recording the time variation of electrical conductivity in solutions with a neutral pH of 200 ml of distilled water and 0.25 g fertilizer. The experimental data were approximated with a function whose parameters allow us in addition, the extraction of a specific release time which characterizes the release rate for V1, V2 and V3 organo-mineral fertilizers based on biosolids .

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