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Original Research

Vermicomposting of Cis-1.4-Polybutadiene Rubber (Br) through Culturing Dense Populations of the Californian Redworm (*Eisenia foetida* Sav.)

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Abstract

One of the biomethods for organic waste utilization is the vermicomposting process, that is run with the use of dense populations of the Californian redworm (*Eisenia foetida*), whose role in the processes of prevention of soil degradation and organic waste recycling is well known. In recent years, shredded material from car tyres has been used more and more frequently for the hardening and filling of road embankments, which poses a hazard to the soil environment.

Our paper attempts to demonstrate opportunities for the use of the red California hybrid (*Eisenia foetida* Sav.) in the bioutilization process of cis-1.4-polybutadiene rubber (BR) vulcanizate, which is a major component of car tyres. The basis for the study was a culture of *Eisenia foetida* on various beddings run over six months, as well as chemical and microscopic analyses using the Quanta 250 scanning electron microscope. The study has shown that the red California hybrid (*Eisenia foetida* Sav.) may be used in the bioutilization process of cis-1.4-polybutadiene rubber (BR) vulcanizate. Following the introduction of the butadiene rubber vulcanizate into the soil with the Californian hybrid, its complete decomposition occurs due to the redworm's trophic activity.

Keywords: earthworm, bioutilization, vermicompost, 1,4-cis polibutadiene rubber

Introduction

One of the biomethods for organic waste utilization is the vermicomposting process. This method is applied to the utilization of organic waste such as straw, sawdust, cardboard packaging, post-farming organic matter, organic matter originating from parks, gardens or greenhouses, and sewage sludge from wastewater treatment plants (Parthasarat et al.). The vermicomposting process is run with the use of dense populations of the Californian redworm (*Eisenia faetida* Sav.), whose role in the processes of soil degradation prevention and organic waste recycling has been demonstrated in several studies [1-5].

Composting in a vermiculture, or processing organic matter with the use of dense populations of the Californian redworm (*Eisenia faetida* Sav.), suggests several benefits to bioremedied substratum, resulting from the preponderance

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of aerobic-over-anaerobic reactions, mineralization of organic matter, loss of odor from decomposing matter, lowering nitrogen and heavy metal content, an increase in the content of available forms of macroelements (P, K, Ca, Mg), as well as improvement of the substratum granulometric structure. These parameters influence economic parameters such as: productivity of potato, spinach, turnip [6], and tomato [7]. Due to the lowering of organic matter content in Poland's soils, observed in recent years, organic remains subject to vermicomposting may provide a valuable supplement to organic soil fertilization, particularly in view of the fact that the parameters of vermicompost properties exceed those of the properties of the substratum obtained as a result of traditional composting [8, 9].

In view of the increasing frequency of the use of shredded or ground material from car tyres, i.e. chips (tyre shreds of 10-50 mm), crumb rubber (1-40 mm) and granulate (1-10 mm) for the hardening and filling of road embankments, these must be utilized. Introduction of these forms of rubber into the soil environment contributes to its contamination, which affects soil flora and fauna [10]. A part from elastomer, the rubber mixture consists of fillers, mainly carbon black, on whose surface are adsorbed certain amounts of polycyclic aromatic hydrocarbons (PAHs), curing agents and plastificators (e.g. paraffin and naphthene oils), which easily contaminate surface waters and soils [11, 20]. Chemical contamination of soil influences, first of all, pedofauna, which accumulate toxic substances within or leave a contaminated area [21, 22]. Crumb rubber bioutilization by means of dense populations of the Californian hybrid has every chance to succeed since redworms demonstrate high tolerance limits to environmental factors, are easily adaptable, and are found in biotopes with heavy anthropogenic modification, for example biotopes containing heavy metals (e.g. strontium and arsenic) [12-15]. Polish attempts at vermicomposting are mostly related to sewage sludge, while research concerns primarily the properties of the vermicompost obtained and condition analysis of redworm biotransferring populations [16]. The objective of the present study is to demonstrate the possibilities for the use of red the California hybrid (*Eisenia faetida* Sav.) in the bioutilization process of cis-1.4-polybutadiene rubber (BR) vulcanizate, a major component of car tyres.

Methods and Materials

The study was conducted in five 5 dm^3 PVC containers over six months. One of these was the control sample; the other four – the study sample. Each bedding contained 2.5 kg of soil taken from the master bed, inoculated with one hundred redworms, fully colored, sexually mature, each with a fully-formed clitelium. The control sample was enriched with 200 g of sawdust; to the study sample was added, apart from the sawdust, 100 g of BR crumb rubber. Each of the samples was filled up, on a monthly basis, with a constant amount of sawdust (200 g). This was significant in view of the necessity to keep the bedding C:N ratio constant at 20:1 (Table 1).

Table 1. Characteristics of substratum before the research.

pH in H_2O	Humidity	C:N	Temperature
6.1±0.5	76%	16±2	19ºC

Table 2. Characteristics of substratum after six months.

pH in H_2O	Humidity	C:N	Temperature
6.9±0.5	84%	21±2	21ºC

Before the commencement of the experiment, ten redworms were selected to be anaesthetized with ethyl acetate, washed, and thermally decomposed at T=500ºC, in inert atmosphere, in a Nabertherm muffle furnace. The material was analyzed in the Quanta 250 scanning electron microscope. The examination was repeated after six months. Before the commencement of the experiment, the properties of the bedding for the redworm culture were also determined, including pH (the potentiometric method) and humidity (the weight method) [23] (Table 2).

Local and spatial chemical analysis was performed with the EDS EDAX Genesis XM 4i microanalyzer (USA), used in the Quanta 250 FEG scanning microscope (FEI Company) with an electron gun with field emission (Schottky emitter) (Figs. 1, 2).

The application of the scanning electron microscope, equipped with the energy-dispersive X-ray detector (EDS), enabled a single-stage-analysis acquisition of data concerning the sample's chemical composition, as well as quantitative data pertaining to concentrations of individual elements in the sample.

In order to investigate the influence of cis-1.4-polybutadiene rubber (BR) on the reproductive processes in the studied population, hatch ratio (R) was used, denoting the total hatch number per total population. It was calculated according to the formula [17]:

$$R = \frac{b}{N}$$

...where:
b – is the number of offspring (colorless specimens)
N – is the average population size (colored and colorless specimens)

After each month, the value of N was calculated according to the formula:

$$N = \frac{N_0 + N_t}{2}$$

...where:
N_0 – is the initial population number
N_t – is the final population number (after time t)

The obtained results are presented in Table 3. The complete developmental cycle of the Californian hybrid covers three main developmental stages (cocoons; colorless immature forms; and colored, sexually mature, forms) that last –

Table 3. Number of cocoons, colorless young forms, and colored adult forms in research test and control test.

Date of measurement	Number of eggs cocoons		Number of colorless stages of young forms		Number of colored adults	
	Research sample	Sample "O"	Research sample	Sample "O"	Research sample	Sample "O"
February	-	-	-	-	100	100
March	13±5	14±5	7±5	27±5	102 ±10	106±10
April	14±5	14±5	11±5	19±5	109±10	136±10
May	17±5	11 ±5	31±5	32±5	128±10	158±10
June	14±5	12±5	34±5	36±5	169±10	181±10
July	19±5	18±5	17±5	20±5	197±10	223±10

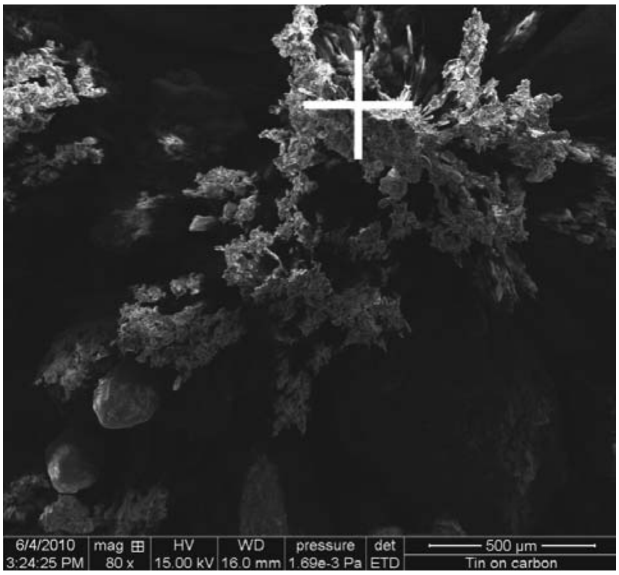

Fig. 1. Local chemical analysis of vermicompost with the use of EDS microanalyzer (Photo M. A. Jóźwiak).

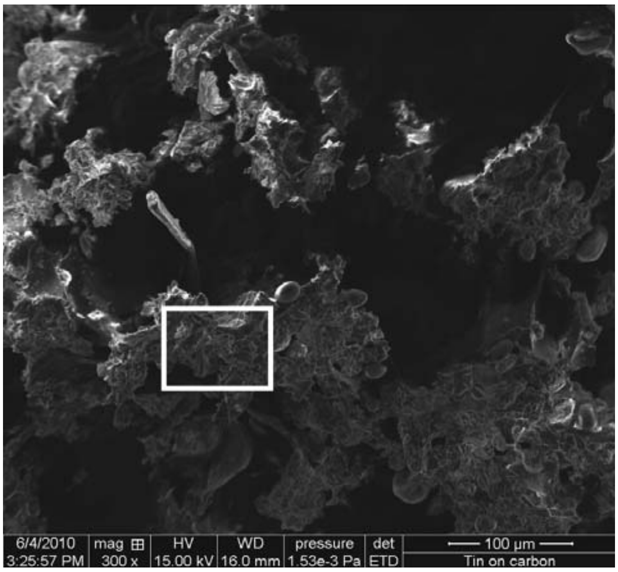

Fig. 2. Spatial chemical analysis of vermicompost with the use of EDS microanalyzer (Photo M. A. Jóźwiak).

jointly – for up to ca. 40 days; hence population numbers estimated on a monthly basis were deemed adequate.

Rubber mixtures were prepared with the conventional method, with the use of a laboratory rolling mill (roller dimensions 100×200 mm, at roller temperature 22-27ºC, front roller velocity Vp=20 revs.×min^{-1}, and friction 1:1.1). Upon preparation, the mixture was stored for 24 hours at room temperature. The composition of the rubber mixture in weight fractions (weight fractions per 100 weight fractions of rubber) was as follows: butadiene rubber (BR) 100, stearic acid (KS) 1, zinc oxide (ZnO) 5, and dicumyl peroxide (DCP) 0.2. Vulcanization of the rubber mixture was carried out in steel moulds placed between electrically-heated shelves of a hydraulic press. In the moulds, pre-weighed portions of the mixture were placed, and covered with teflon foil on two sides (due to mixture adhesion to the metal). Vulcanization temperature amounted to 160ºC, and the pressure on the press shelves – to ca. 15 MPa. Vulcanization times were determined on the basis of reometric curves. The thermal analysis in air atmosphere was performed with the use of a derivatograph, Paulik, Paulik, Erdey system, with Al_2O_3 as the reference substance in the temperature range of 25-800ºC. Weighed samples were 90 mg; heating speed: 7.9ºC×min^{-1}; thermal curve sensitivity as follows: TG=100, DTA=1/5, DTG=1/20.

Derivatographic analysis was performed on three samples.

- Sample 1 (soil with sawdust)
- Sample 2 (soil with sawdust plus peroxide vulcanizate of butadiene rubber in the crumb form)
- Sample 3 (soil with sawdust plus peroxide vulcanizate of butadiene rubber after six months of vermicomposting).

Results and Discussion

The study sample bedding as well as the control sample bedding were obtained from the master bedding, where a Californian hybrid culture is run on the basis of organic matter obtained from a private garden where no plant growth support or pesticides are used. The prepared input bedding was characterized by a slightly acidic reaction and high humidity (Table 1).

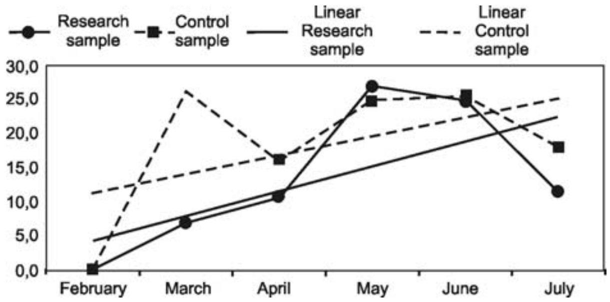

Fig. 3. Birth rate of *Eisenia faetida* in research and control test, together with trend lines.

The obtained culture conditions were highly compatible with the requirements of California hybrid cultures as described by [18, 19].

After six months of redworm culture feeding with butadiene rubber vulcanizate, a component of car tyres, changes to bedding parameters were observed. Acidification decreased, while the C:N ratio increased (Table 2).

We believe that the changes of these parameters were linked to high carbon content in the material added to the culture and redworm trophic activity. However, an increase in bedding humidity and temperature was connected to the culturing conditions. Under these conditions, growth in the California redworm population was recorded over the studied months (Table 3). This growth was recorded at each stage of the development cycle, which shows that the introduction of butadiene rubber vulcanisate into the soil with the California hybrid, thanks to its trophic activity, not only fails to aggravate biotope conditions, but also causes total BR decomposition, which is confirmed by the derivatographic analysis of the studied samples (Fig. 3).

The equation of the trend's linear graph for the control sample shows y = 2.7743x + 8.6733, R^2 = 0.272, and for the study sample y = 3.6514x + 0.6867, R^2 = 0.4214.

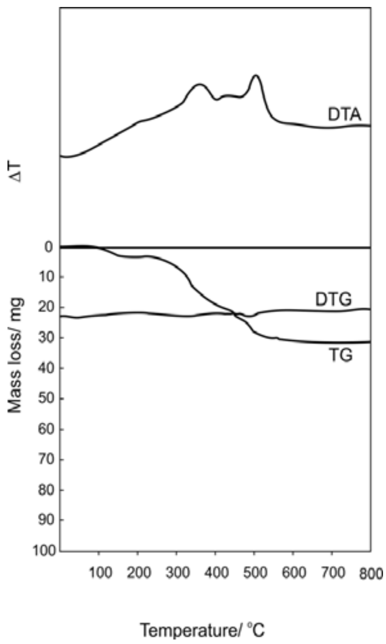

Fig. 4. Thermal curves of sample 1.

Based on the derivatographic analysis, it was found that sample 1 is subject to distinct three-stage decomposition (Fig. 4). The first stage, which occurs at ΔT_1=50-220ºC, is connected to the release of physically and chemically bonded water. This process is accompanied by a 3 mg sample weight loss. The second stage, recorded in the temperature range of ΔT_2=220-440ºC, corresponds to thermal decomposition of cellulose, accompanied by further sample weight loss amounting to 13 mg. The final stage of thermal decomposition, recorded in the TG curve, at ΔT_3=440-750ºC, is linked to decomposition of mineral substances as well as the incineration of organic remains, accompanied

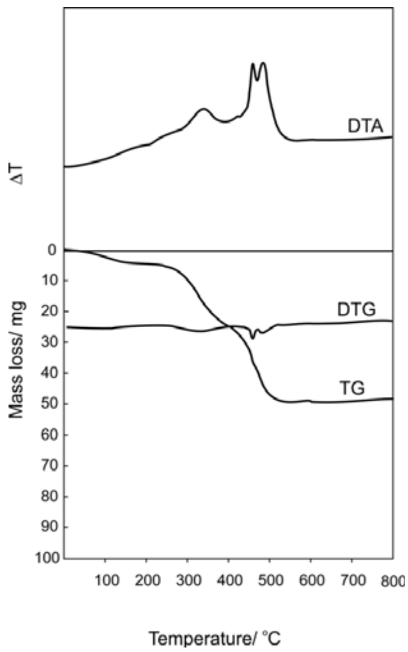

Fig. 5. Thermal curves of sample 2.

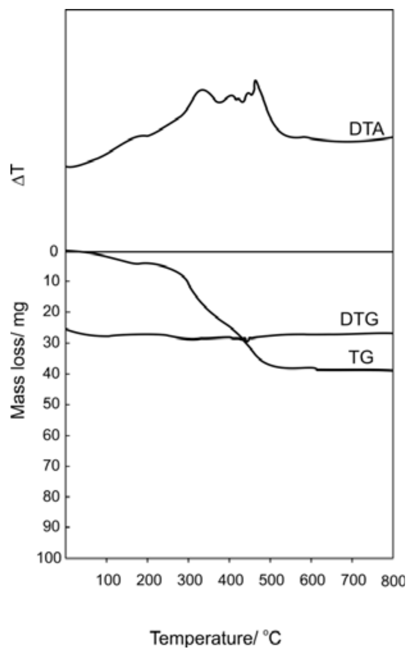

Fig. 6. Thermal curves of sample 3.

by further sample weight loss amounting to 2 mg. Sample 2 is characterized by four-stage decomposition. The first stage, as in the case of the first sample, at ΔT_1=50-22ºC, is connected with water loss; the second stage, as recorded at ΔT_2=220-380ºC, results from thermal decomposition of cellulose; the third, at ΔT_3=380-460ºC, corresponds to thermal decomposition of BR vulcanizate, accompanied by sample weight loss amounting to 10 mg (Fig. 5).

The fourth temperature range, ΔT_4=560-730ºC, as was the case with the first sample, corresponds to decomposition of mineral substances as well as incineration of organic remains in the sample. The derivatographic analysis of the third sample did not show a signal on the TG curve in the range of ΔT=300-460ºC, testifying to the presence of BR vulcanizate in the studied sample (Fig. 5). Based on the performed thermal analysis of Samples 1-3, it may be concluded that six-month-long vermicomposting causes practically complete biological decomposition of crumb rubber, which is confirmed by photographs taken with the use of the stereoscopic microscopy technique (Figs. 7-9).

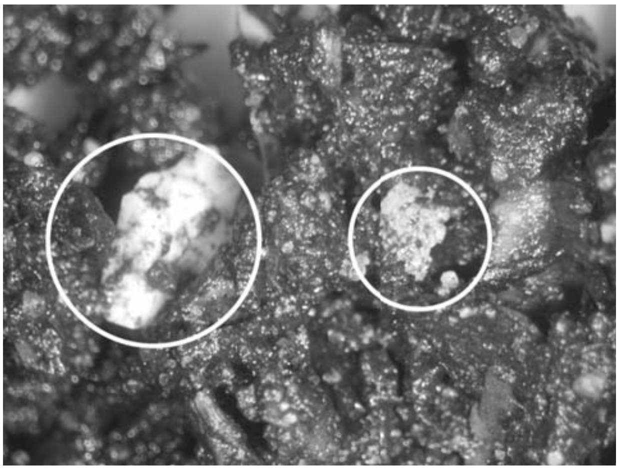

Fig. 7. Ground peroxide vulcanizate of polibutadiene rubber among the particles of vermicompost substratum (Photo. M. A. Jóźwiak).

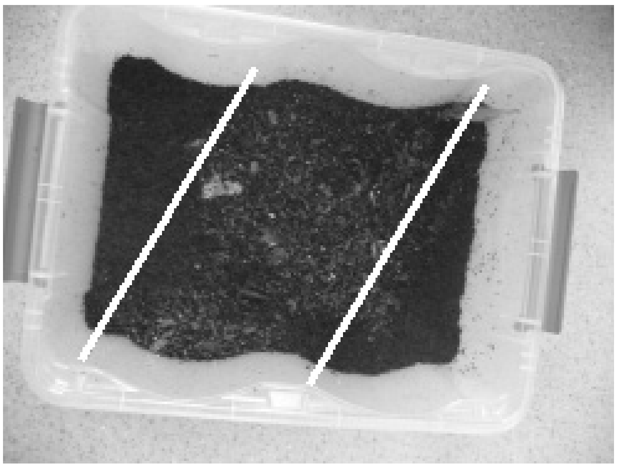

Fig. 8. The result of bioutilization. Visible remains of 1,4-cis polibutadiene rubber in the central part of the sample. On the left and right sides are droppings of *Eisenia faetida* (Photo. M. A. Jóźwiak).

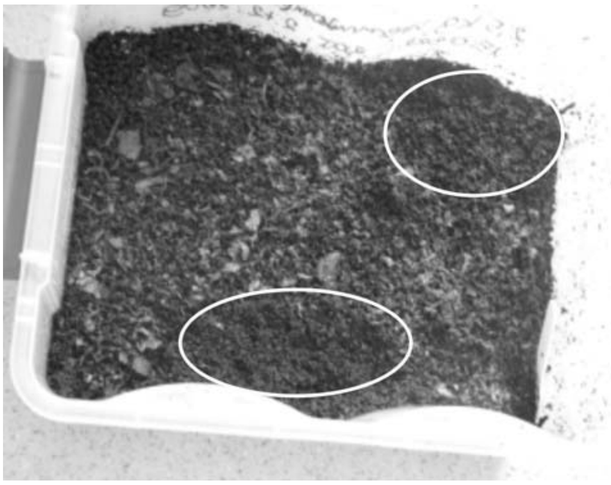

Fig. 9. Control sample with sawdust. Visible remains of sawdust and droppings of *Eisenia faetida* (Photo M. A. Jóźwiak).

A chemical analysis of redworm composition was performed before and after the six-month period of vermicomposting activity (Fig. 10, 11). Based on the obtained results, it was found that carbon content in the redworm body after six months in the studied deposit increased more than twice in comparison to carbon content in the input redworm, with the simultaneous distinct decrease in silicon content, exceeding 60%, in comparison to silicon content in the input redworm. The obtained result may testify to the intensity of occurring biodecomposition processes, despite the high content of the polymer fraction in the studied sample.

Basing on the spatial chemical analyses of input vermicompost and the vermicompost after six months of redworm culture, performed with the application of the EDS microanalyzer, we found no change in carbon percentage content (Figs. 12, 13). It is to be stressed that the percentage content of basic macroelements, such as phosphorus, potassium, calcium or magnesium, also did not decrease.

Conclusions

1. The conducted study has shown that the red California hybrid (*Eisenia foetida* Sav.) may be used in the bioutilization process of cis-1.4-polybutadiene rubber (BR) vulcanizate.
2. The introduction of butadiene rubber vulcanizate into the soil with the Californian hybrid, thanks to the redworm's activity, does not cause environmental contamination.
3. The derivatographic analysis of vermicompost samples containing butadiene rubber vulcanizate points to three decomposition stages, conditioned by the incineration temperature range: release of physically and chemically bonded water; thermal decomposition of cellulose; and decomposition of mineral substances and incineration of organic remains.

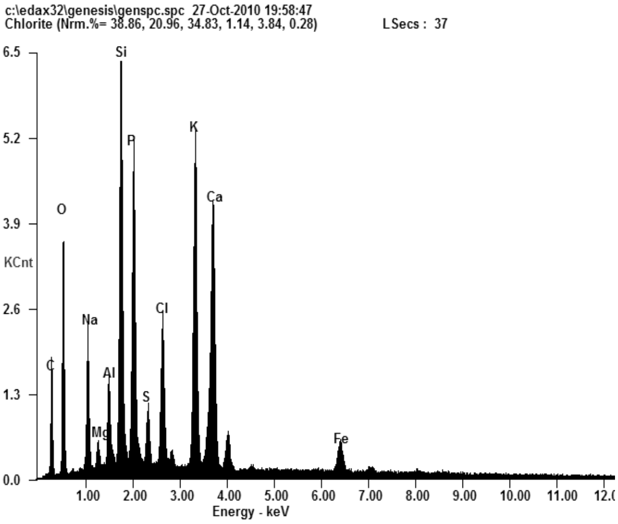

Fig. 10. Chemical analysis of the input redworm, performed with the application of the EDS microanalyzer.

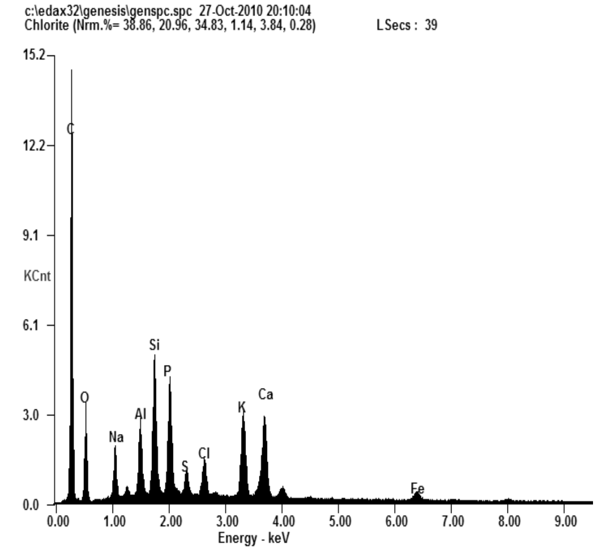

Fig. 11. Chemical analysis of the redworm after six months in the studied deposit, performed with the application of the EDS microanalyzer.

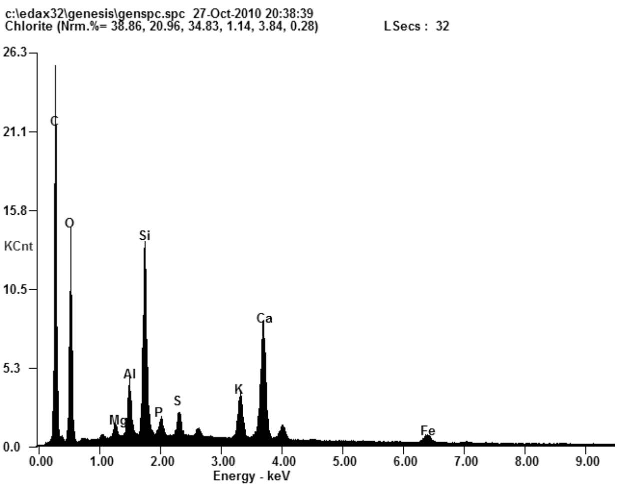

Fig. 12. Chemical analysis of the vermicompost, performed with the application of the EDS microanalyzer.

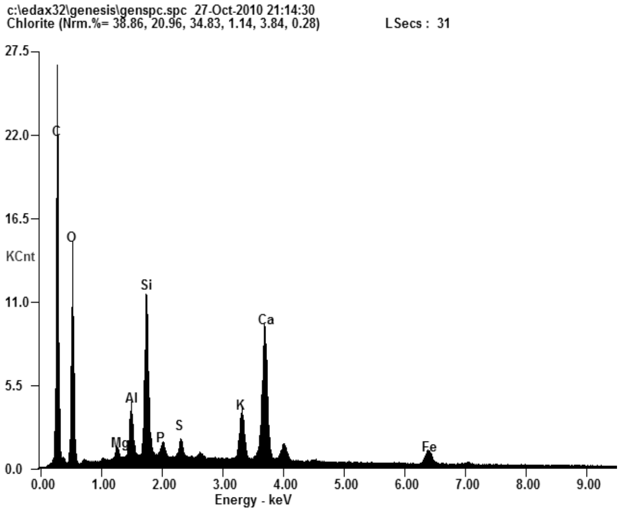

Fig. 13. Chemical analysis of the vermicompost after six months, performed with the application of the EDS microanalyzer.

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