UDC: 628.3
DOI: 10.2298/IJGI1303183D

# POSSIBILITIES OF REDUCING RISKS OF ENVIRONMENT CONTAMINATION FROM SEWAGE SLUDGE

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Received 26 August 2013; reviewed 08 September 2013; accepted 01 October 2013

**Abstract:**The paper deals with the examination of samples of sewage sludge mixed with charcoal. The aqueous extracts were prepared from the experimental samples of the sewage sludge mixing with charcoal. The extracts were monitored by the selective physicochemical parameters. The ecotoxicological properties of charcoal with the addition of sewage sludge were evaluated based on the ecotoxicological tests performed in this experiment. Our investigation obtained results and it is considered to improve the properties of sewage sludge in its future recovery and minimize the negative impacts on the environment, which are to a large extent, sewage sludge unsuitable for further use.

**Keywords:** sewage sludge, charcoal, nutrients, ecotoxicological tests

## Introduction

Wastewater treatment is an important human invention that facilitates the support and development of human civilization. The actual biological wastewater treatment, like most other technologies, is not waste-free technology, because produces a significant amount of waste, sewage sludge. It can therefore be concluded that technological processes for wastewater treatment in one hand bring the desired effect, namely treated wastewater, and on the other hand, unwanted product - sewage sludge. Simply we can say that the pollution, which was covered in water, the treatment of wastewater transferred to the birth of sewage sludge, in waste production (Demko, 2003).

According to data Slovak Hydrometeorological Institute (2011) in Slovakia are discharged more than 612 million tons of waste water per year from point sources into surface waters. Approximately 92% of this amount is accounted for waste water purified, have the largest share slops and urban waste water. These waters are normally cleaned by mechanical and biological means.

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In 2011, the total sludge production was 58 718 tonnes of dry matter in the Slovak Republic. According to the Ministry of Environment of the Slovak Republic and the Water Research Institute was used to 50 469 tonnes (85.95%) in the soil processes of the total sludge solids, temporarily into storage 5943 tons (10.12%) and the dump was saved 2 306 tons of sludge solids (3.9%). Sludge was applied directly to agricultural land at least, in the amount of 358 tons, a decrease 61% compared to 2010

The reasons of small sludge addition into land is especially exceeding limits of selected hazardous substances. The sludge is treated according to the criteria, the common denominator is the protection of the environment and in principle subject to the legislation under the Water Act, Waste Act and the Act on the application of sewage sludge and bottom sediments in the soil.

Although sewage sludge is a rich source of organic matter, nutrients (especially nitrogen and phosphorus) and trace elements, it can greatly improve the physicochemical and biological properties of soil. The basic condition use of stabilized and hygienic sewage sludge in agriculture is the avoid contamination soil, respectively groundwater. From this perspective, it is important, management supported by the legislation. Sludge usage on soils in the EU countries is different. Some Member States (Belgium - Wallonia, Denmark, Spain, France, Ireland, the United Kingdom and Hungary) to 50% and more produce of the sludge to give land. On the other hand, Finland, Sweden, Italy and Slovenia apply less than 17% of the sludge on land, while Greece, Holland, Belgium - Flanders, Slovakia and the Czech Republic distribute sludge on agricultural land directly have little or no. Between states are differences in overall approach, some state showed a decreasing trend. Also certain states or its regions laws prohibit or severely restrict sludge-spreading on agricultural land, which is a stringent limit values for heavy metals and sometimes organic components.

Charcoal is a lightweight, porous material with high calorific value and it excels in high purity (low volatile matter). It is produced by dry distillation of wood, respectively wood heating with reduced air. Quantity fixed carbon is dependent on many factors, but in the dry condition can be up to 95% C.

Charcoal composition depends on the raw material from which it is produced, but usually contains only a negligible amount of phosphorus and sulphur compared to coal and further containing only 1-3% of non-combustible materials (ash). Quality charcoal can be determined only by laboratory analysis or simply judged according to certain indicators. Good charcoal is black, which should not makes a mark, in tap should ring clear sound and the combustion would not burn flame and produce smoke. Other indicators are the density of charcoal, brittleness and calorific value (Kmošek, 2009).

Attempts to use and evaluate long-term sewage sludge are developed environmentaly as well economically impact. Unfortunately they are not largely positive and in this context, increasing the importance of harmless disposal of sewage sludge resulting from their the most natural ways i.e. return nutrients to agricultural land. Different ways of composting using sewage sludge after mixing and dilution of the original composition of other suitable components. This line can produce a mixture of sewage sludge and with charcoal which due to their specific capabilities particularly adsorption can form a useful component in the further use of sewage sludge.

Possibilities of using charcoal together with sewage sludge deal works Ladomerský (2012) and Hroncová (2013).

## Methods and materials

Charcoal was obtained from the pyrolysis of wood at 600 - 700 ° C in a retort by the research project (no. APVV-0353-11): "Design and implementation of pilot retort with reduced emissions to produce biochar for marginal zone and verification applications." The first batch contained beech wood and corn waste. The retort was dealt after the pyrolysis and pyrolyzed samples of both compounds were used for laboratory purposes.

Sample of wood charcoal was modified by crushing and sieving the fraction with a grain size below 2 mm.

Sludge was withdrawn from WWTP Banská Štiavnica of drainage lines - centrifuge. It was the aerobically stabilized sludge with solids 22.6%.

Mixtures were prepared from charcoal and sewage sludge. Total of 9 samples were prepared in a weight ratio of 1+9 to 9+1 (sample 1 = 9 parts charcoal + 1 part sludge, sample 2 = 8 parts charcoal + 2 parts sludge etc.). In the same way were analyzed and sewage sludge and charcoal. Designation of samples for ecotoxicological tests is other than physicochemical tests and is referred in the Table 1.

Table 1. Designation of samples for ecotoxicological tests

| Number of sample | weight ratio | |
|---|---|---|
| | Charcoal* | Sludge* |
| 1 | 8 | 2 |
| 2 | 6 | 4 |
| 3 | 4 | 6 |
| 4 | 2 | 8 |

*The legend: numbers indicate the weight ratios, eg. sample No. 1 is composed of 80 g charcoal and 20 g of sludge

Simulation of natural mixing and homogenization of solid substances in each test sample was prepared such that each sample was added to 100 g of sample 100 ml of water.Extracts were prepared as follows:

Samples were allowed to stand for 10 days (stir every day), and then to identify the solids, was added to the calculated amount of water leaching, followed by shaking in a shaker-type ROTABIT for 24 h at 150 revs / min. The solids were separated from the liquid gradually using separation processes - sedimentation, centrifugation and filtration.

The volume of water added to the extract was calculated according to the formula:

$$L = \left(10 - \frac{\%\,vlh}{100}\right) . m_{vz} . w_{vz}$$

Where: L is the volume of demineralized water are added to the sample (ml);
$\%_{vlh}$ is the quantity humidity of samples (%);
$m_{vz}$ is the total sample mass (g);
$w_{vz}$ the dry mater quantity of samples.

Evaluating the degree of environmental pollution, physical and chemical analyses plays an important role because the sample may be established with high accuracy even for very small quantities of contaminants. However, on the basis of the concentrations of the individual substances, is impossible to reliably determination their toxic effects. It often can not be determined in advance and toxic substances in the mixture will exhibit synergistic or antagonistic effects. Therefore, because these substances increasingly using biological methods to determine toxicity to evaluate the impact on biotic component of the environment. (Pavlíková, 2008).

In prepared extracts were determined selected indicators: pH, ammonium salts, nitrates, phosphates, chlorides and sulphate. Also dry samples were determined:

before leaching, total analyses of charcoal and dewatered sludge were done, too. Tests of ecotoxicological properties were done namely test of acute toxicity on Daphnia and the test of growth inhibition of the root length cultivated plants. Results were evaluated by program STATISTICA 7.

## Results and Discussion

The sewage sludge and charcoal were made the total analysis. Selected physicochemical parameters determined in prepared extracts: nitrogen in the form of ammonium salts and nitrates, phosphorus as phosphates, chlorides, sulphates and reaction liquor. Table 2 - 3 shows the values of determined parameters for the total analyses of the original substances.

Table 2. Total analyses charcoal

| dry matter | C | N | S | Al | B | Ca | Fe | K | Mg |
|---|---|---|---|---|---|---|---|---|---|
| % | % | % | % | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 |
| 98,17 | 80,9 | 0,065 | 0,185 | 123,1 | 12,7 | 5541 | 113 | 4451 | 1059 |
| Mn | Na | P | Zn | Cu | Cd | Pb | Ni | Cr | |
| mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | mg.kg -1 | |
| 136,5 | 92,7 | 477 | 77,5 | 7,36 | 1,42 | 1,93 | 25,9 | 1,47 | |

Table 3. Total analyses sewage sludge

| dry matter | C | N | S | Al | B | Ca | Fe | K | Mg |
|---|---|---|---|---|---|---|---|---|---|
| % | % | % | % | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 |
| 22,64 | 15,1 | 5,36 | - | - | - | 15 580 | - | 3 900 | 4 290 |
| Hg | As | P | Zn | Cu | Cd | Pb | Ni | Cr | |
| mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | mg.kg-1 | |
| 2,9 | 11 | 2 997 | 3 500 | 240 | 35 | 120 | 13 | 18 | |

Charcoal contained 0.065 % N and dewatered sludge 5.36 % of N. Due to ratio of the carbon, which was 80.9 % in sludge in charcoal and around 15 % in sludge, it is appropriate to mix these two commodities in the ratio of 2 parts charcoal + 1 part of sewage sludge, in order to achieve the optimal ratio for composting C/N = 30/1. The addition of charcoal to sludge causes the enrichment land carbon – a basic building component of plant and animal organisms. Comparing of the presence of other elements are problematic especially heavy metals. These are in mixed with charcoal adsorption probably bound, which describes a similar experiment HuanliangLu et al (Huanliang et al, 2012).

Determination of dry mixtures prepared shows a continuous decline in high aquosity of dewatered sludge. The results are in Figure 1.

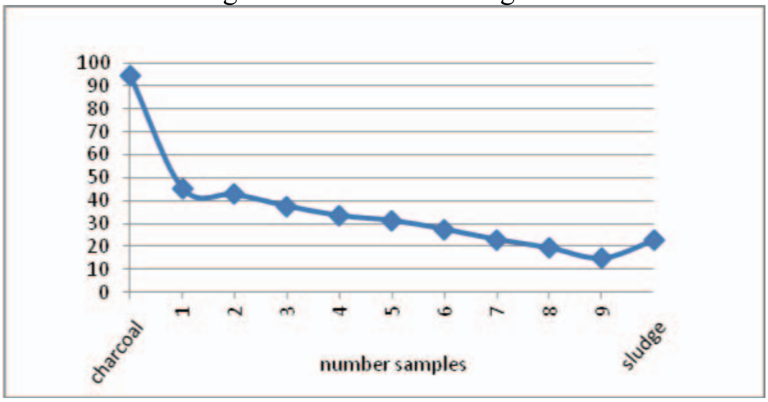


Figure1. The determination of dry mixtures before leaching

The prepared extracts were determined these parameters: nitrogen as ammonia, nitrogen as nitrate - acceptable forms of nitrogen for plants receive. The nitrogen is the most important element for crop production, amino acids and deployment fetuses, but too high concentration causing watery fetuses that are more easily putrefaction. Other parameters which were monitored are phosphates. Phosphorus is responsible for energy metabolism of plants at earlier growth stages of growth, but too high concentration causing so-called incineration plants. Both of these elements are necessary for plants in the gradual release of and access to the root system. Chlorides and sulphates were observed in the sense land of acidification after addition of mixtures of charcoal-sludge. Similarly was monitoring the parameter pH. The results are summarized in Table 4.

The measured results showed that the prepared mixtures are different concentrations of monitored parameters in the leachate. Charcoal works on blending sludge adsorption, slow release of nutrients into the liquor. This was most evident in mixtures a larger quantity coal and parameters of ammonium nitrogen and phosphates. In mixtures with a greater proportion of sludge was shown a significant effect of sewage sludge. Chlorides and sulphates are similarly gradual easing trend in the leachates depending on the amount of each commodity. A positive effect was manifested in the case of pH, where the addition of charcoal slurry before to incorporation to land has a positive influence. All three measured pH are almost borders optimal pH for the soil, which is 6.5 to 7.5.

Table 4. Determination of selected parameters in leachate samples

| number sample | N-NH4+ | N-NO3- | PO43- | Cl- | SO42- | pH |
|---|---|---|---|---|---|---|
| | [mg.dm-3] | [mg.dm-3] | [mg.dm-3] | [mg.dm-3] | [mg.dm-3] | [mg.dm-3] |
| charcoal | 1.130± 0.123 | 0.812± 0.278 | 2.118± 0.082 | 3.393± 0.136 | 11.319± 0.026 | 7.49 |
| samp.1 | 1.053± 0.066 | 1.104± 0.191 | 1.769± 0.116 | 5.182± 0.202 | - | - |
| samp.2 | 0.459± 0.012 | 4.582± 1.120 | 1.404± 0.075 | 5.490± 0.330 | - | - |
| samp.3 | 0.173± 0.156 | - | 1.852± 0.332 | 5.621± 0.473 | 12.348± 0.199 | - |
| samp.4 | 0.471± 0.381 | 7.840± 1.567 | 0.938± 0.107 | 6.345± 0.307 | - | - |
| samp.5 | 1.836± 0.253 | - | 3.450± 0.914 | 6.416± 0.121 | - | 7.59 |
| samp.6 | 1.554± 0.094 | 2.109± 1.336 | 3.381± 1.460 | 8.322± 0.204 | 18.330± 0.367 | - |
| samp.7 | 1.994± 0.170 | - | 5.580± 1.059 | - | - | - |
| samp.8 | 4.318± 0.216 | 1.354± 0.522 | 1.674± 0.883 | 8.945± 0.075 | 23.872± 0.207 | - |
| samp.9 | 4.203± 0.305 | 3.776± 0.794 | - | - | - | - |
| sludge | 1.483± 0.255 | 9.367± 0.505 | 2.405± 0.605 | 15.860± 0.248 | 26.585± 0.111 | 7.33 |

For the determination of inhibition of growth root higher cultivated plants were used seeds of white mustard (Sinapis Alba) with a size of 1.5 to 2 mm and 97 % germination. In parallel with this test was determined growth inhibition on reference substance K2Cr2O7, whose IC50 value after 48 hours was 33.1 mg.l-1, based on which we can conclude that the conditions of the test and quality work.

The test was conducted in the original extracts, in which the growth root inhibition recorded. In Petri dishes with inserted filter papers was pipetted 10 ml of each sample. The same was held as control, where instead of extract, was used the same volume, 10 ml of water dilution. Seeds were evenly stacked in the shape of a rectangular network 6 x5 cm. Petri dishes with the samples were placed in an incubator and incubated at 20 ± 1 °C for 48 hours.

Dependence inhibition of root growth of white mustard is shown in Fig. 2 a basic statistical characteristics are shown in Table 5.

Table 5. Basic statistical characteristics (the negative values are the stimulation accelerated growth compared with control)

| Sample | Measurement number | Average IC (%) | Standard deviation IC (%) |
|---|---|---|---|
| 1 | 2 | -1.25 | 11.21 |
| 2 | 2 | 5.52 | 2.67 |
| 3 | 2 | -5.16 | 3.02 |
| 4 | 2 | 3.74 | 0.89 |
| charcoal | 2 | -3.91 | 7.47 |
| sludge | 2 | -7.12 | 2.49 |

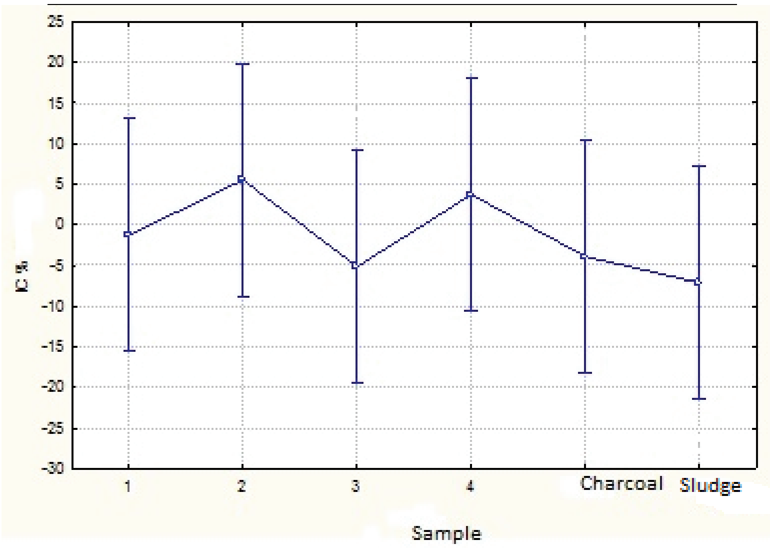


Figure 2. Inhibition of root growth Sinapis alba (IC) in% in each sample

We can conclude that growth inhibition test (IC) root Sinapis alba in the experimental samples was negative for all samples compared to control, according to the results obtained. Inhibition of root growth < 30% or simulation < 75% compared with the control and further testing is not performed (Hybská, 2011).

To determine the acute toxicity test on Daphnia were used microorganism Daphnia magna Straus, with a life expectancy maximum 24 hours.

Microorganism Daphnia magna Straus were obtained acyclical parthenogenesis in terms of healthy animals.

Reference substance $K_2Cr_2O_7$ - standard was also included for the quality control of the work in which the $IC_{50}$ after 48 hours was 1.45 mg.l-1, which satisfy the said requirements, as in the case of control of the work in the test of inhibition of root growth root Sinapis alba. (Hybská, 2011).

The test was performed in four parallel determinations. Is pipetted 5 ml of water extract for each sample in 4 replications in beakers with 25 ml. To each beaker was the 5 individuals. Test took place in a laboratory incubator at 21 ± 2 ° C. The sample was monitored dissolved oxygen and the pH before the test and at the end of the test. Measured data satisfy conditions of the test. During the test there is no change in pH, which at the beginning and end have the same value. All extracts were prepared slightly alkaline (pH 7.33 to 7.59).

The test result is considered as:

– negative if Daphnia immobilization or mortality daphnie ≤ 10% compared to control and further testing is not performed (Hybská, 2011).

The highest immobilization after 48 hours was observed in the sample no. 1 (with the highest proportion of charcoal), where fixed value, as can be seen from Tab. 6, as well as other specified values of inhibition do not show ecotoxicological effects, ie potential environmental risk aqueous extracts from experimental samples of sewage sludge and charcoal, as well as their mixtures on the environment. Due to the negative result set was not necessary to proceed with further testing using basic test selected biotests.

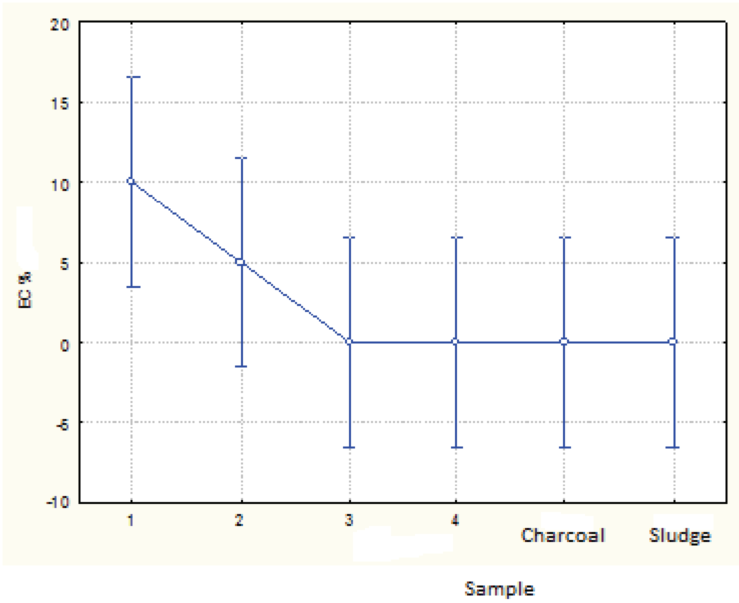


Figure 3. Dependence % immobilization (EC) in % after 48 hours

Table 6. Basic statistical characteristics measured after 48 hours

| Sample | Measurement number | Average EC (%) | Standard deviation EC (%) |
|---|---|---|---|
| 1 | 4 | 10.00 | 5.77 |
| 2 | 4 | 5.00 | 5.00 |
| 3 | 4 | 0 | 0 |
| 4 | 4 | 0 | 0 |
| sludge | 4 | 0 | 0 |
| charcoal | 4 | 0 | 0 |

## Conclusion

People know charcoal from time immemorial. Start of production and use of charcoal may be associated with melting iron ore and processed metals material where charcoal was an important source of heat for melting especially for its higher calorific value than wood.

Sludge as a major a waste product wastewater treatment process consists of a mixture of solids and water. Waste water is treated during the technological process, the number of pollutants in water is significantly reduced, but undesirable constituents are concentrated in sewage sludge. Currently, sewage sludge has not great application. It is not usually used, but it can be deposed on landfills or is combusted. However, sewage sludge is a potential source of macro and micronutrients - especially N, P, C, and small amounts of K, Ca, Mg and other substances. Nutrient content is different depending on the type and composition of wastewater and wastewater treatment plant. Utilization of sewage sludge as a source of nutrients would have a positive benefits of reducing environmental load management.

Existence of charcoal in a mixture of sewage sludge has a positive effect on its properties, due to its application in agriculture. Utilization of sludge in this direction is bound by the rules of all restrictions under applicable law and is necessary to consider the composition of the sludge entering the mixtures with charcoal. It is important to know way of utilization of soil with incorporated a mixture. Based on the results obtained from selected ecotoxicological tests, samples prepared by mixing charcoal and sewage sludge in different proportions, as well as charcoal and sewage sludge do not create potential ecotoxicological risk to the environment. The experiment is continued for determining the mobility of selected heavy metals in the samples analysed in that article for their qualitative composition as well as their contents. After evaluation of the results within the meaning the Act No.220/2004 Coll "The law on the protection and use of agricultural land" another experiment planned. It will be an application of these samples into farmland on experimental plots with additional laboratory testing.

**Acknowledgements**
This work was supported by the Agency for Research and Development under contract no. APVV-0353-11 "Design and implementation of pilot retort with reduced emissions to produce biochar for marginal zone and verification applications."

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