Utilisation of secondary raw materials for production of artificial soils substrate

M Dlabaja
ECOCOAL s.r.o., Mrštíkova 885/4, 70900 Ostrava – Mariánské Hory, Czech Republic

Abstract. A large number of secondary raw materials arise from industrial production. It is necessary to find a way for the use of these materials not utilisable for the primary production, for example, to adjust physically-mechanical and chemical properties in order to manufacture the artificial soil substrate for reclamation of those areas which are affected by industrial activities. Then the whole cycle is finally closed. My focus is on the adaptation and utilisation of secondary raw materials. This raw material arises from the treatment of industrial water during cellulose production. The raw material is adapted and utilised by using by-energy products and excavation of soils. We created a special production process for this purpose. We included semi-mobile technological production line that allows for qualitative entry change with the use of physically-mechanical processes, in order to create a certificated reclamation mixture according to specific formulas.

1. Introduction
Humankind is forced to find quick and maximum economical solutions for satisfying its needs due to explosive population growth. When we project this towards industrial activity, we are confronted with the emergence of a large number of secondary products which are not utilisable for primary production. These products have been neglected, sometimes because of stereotyping habits, but more because of the pressure on the efficiency of primary production.
ECOCOAL Ltd. works in the field of research, development, planning, production and implementation of technologies for environmental protection. Its aim is to identify these products and, in case of inability, their re-use within the industrial process, and to analyse their physically-mechanical and chemical properties. The view is the adaptation and utilisation in the manufacture of artificial soil, which applies to the redevelopment of areas affected by the industrial activity. Consequently, the whole cycle is closed. It is possible to find the area in fields like mining and quarrying, paper industry, power engineering, processing, wastewater treatment, and the heavy and chemical industry.
We started using artificial soil for reclamation purposes in 2000. The term reclamation had been used commonly. Terms and rules, according to Act No. 22/1997 Coll., are also applied in our case. “Fly ash and mixtures with fly ash for embankment and backfill”, or “The granulation product for technical reclamation of waste dumps,” according to Act No. 156/1998 Coll. “The substrate for upper or lower layers of the land reclamation”. Both legislations, with the exception of the granulation product, which is used only for waste dumps, are not compatible enough with the physical-mechanical and agrochemical parameters for their products. For this reason, we use the term artificial soil substrate for a more specific description of our products. The products are
manufactured on the basis of formulas which secure their qualitative suitability for particular sorts of reclamations and their measures in a wide range of monitored parameters [1, 2].

2. Materials and methods
We will talk about the paper industry that uses wood as a primary raw material, where cellulose is separated from residual cellulose and non-cellulose rests by a process called leach. These rests are also used, for example, for the production of alcohol. However, this process is accompanied with the emergence of secondary non-utilisable products from the primary production of wastewater treatment. After draining and CaO stabilising, the sludge rises (Figure 1). The sludge is completely unsuitable for further processing in terms of the physical-mechanical properties because of long unbranched chains of D-glucose supplemented between microfibrils and, e.g. xyloglucans, pectins and lignins. From an agrochemical aspect, the sludge is at a high value due to the favourable concentrations for orientation $P_{\text{total}} > 5\,000$ mg/kg, $K > 2\,000$ mg/kg, $N_{\text{total}} > 30\,000$ mg/kg, $Mg > 4\,000$ mg/kg, $Ca > 60\,000$ mg/kg, and non-problematic chemical structure through homogenous entries resulting from the wood processing (more significant results we are getting from usable nutrients, according to Mehlich III acceptable nutrients of artificial soil substrate). Another utilisable advantage is an ability to accelerate microbial disintegration under appropriate conditions, and it has a favourable pH from 10 to 13, which is able to melt dissoluble compounds during gradual changes. Among other selected properties that can be noted: the content of $H_2O\ \text{max.} \ 85\%$, specific gravity from 900 to 1200 kg.m$^{-3}$, content of extraneous matter particles max. 1.0 %, activity of density 226 Ra Max 1000 Bq.kg$^{-1}$, ash from absolute dry matter 5 – 15 %.

The above-mentioned facts encourage investing energy into searching for ways to utilise the sludge. It was necessary to create a production process, including formulas, in order to find the continuous and economical way of physically-mechanical processing near the use of mentioned agrochemical properties. It was also important to create the conditions that support the natural processes running in the soils. The humification in our case-leach celluloid and non-celluloid rests in the form of thickened primary and secondary sludge. However, it is not only about technological equipment. It is also about the suitable raw materials allowing this process. First of all, it is necessary to find the entry material. We must identify its adsorbing, hygroscopic qualities, porosity and a soil microflora that occurred naturally.

Suitable secondary raw materials from manufacturing the products for wastewater treatment from cellulose production
Let us start with the suitable materials with required qualitative parameters according to the type and the sort of raw materials in the range, see Qualitative properties below. These materials meet selected energetic byproducts (hereinafter referred to as EBP) and selected excavation of soil (hereinafter referred to as soil).

Selected EBP appears from coal burning in grate boilers with air inlet from the bottom part on the moving grid with an included crushing degree (Figure 2). Coarse-grained slag with hollow and thin-walled formations appears. The formations allow the adsorbent excess humidity and, due to the bigger surface, even the growth of microorganisms. The positive influence is visible from the results of grains sizes and apparent density. This influence is greatly needed for reducing soils and leads to an increase in the soil air in order to begin the natural soil processes. Final properties depend on the level of reclamation for which the product is intended.
The chemical properties are monitored in the range according to the regulation 294/2005 App. 10 as per App. 12 according to the technical directions, according to Act No. 22/1997 and Act No. 156/1998 Coll. on fertilizers and executive regulations. We have chosen physically-mechanical properties in the range of the acts above, for example, apparent density 900 – 1100 kg.m\(^{-3}\), permeability \(1 \times 10^{-6}\) to \(1 \times 10^{-4}\) m.s\(^{-1}\), compacting PS 950 – 1200 kg.m\(^{-3}\), pH 7.3 – 7.7, load-bearing ratio CBR 35 – 45 %, grain size analysis.

Sources of selected excavation of soil (hereinafter referred to as soil) are mainly line and areal constructions that show homogenous properties. Due to the uneconomical soil use, the constructions are mostly former agriculture lands instead of unused industrial areas (Figure 3). The soils consist predominantly of clays, sands, grit, and stones that need to be sorted according to qualitative properties so as to be usable for further processing. They are in our case, vast reserves of clay soils formed mainly from clay material (mixed strata clay materials grading fraction under 2 μm). The clay material comprises more than 65 % and further mica admixtures and silica ash. We use the term soil from an engineering-geological rock qualification because there are essential mechanical properties of rocks. Their load-bearing ratio CBR, apparent density, and permeability are important too. The permeability ranges from \(10^{-9}\) to \(10^{-7}\) m.s\(^{-1}\), etc. The chemical aspect of indicators is monitored in the range of the regulation 294/2005 Coll. App. 10.

The technological production line was projected as a semi-mobile production line in order to process sludge with long unbranched chains (Figure 4). The chains form fibres at 25 % of the dry solids, using suitable loose materials EBP soils with a continual dosage of solid, loose and liquid fractions and intensifiers (e.g. bio-algens), with the possibility of specifying the density of entry raw materials on strain-gauge (tensometric) scales. The first degree of processing runs on a safe surface with double independent packing. The second degree consists of a separator. It is a hopper of 3 m\(^3\) capacity and two contra-rotating cylinders with separator profiles powered by hydro motors. The separator is equipped with a vibrating machine and nozzles with industrial water for wetting the materials. Next, there are conveyor belts for the transport of material between individual processing degrees. The third degree is a homogeniser for industrial wastes, type EHN1200, of an oval shape, placed in a vertical position selected to continual homogenization of processed material. The material is adjusted in a separator first. It is possible to change the slant in the range of 80° on the vertical axis in order to change the speed of passage of the material. The conveyor feeder belt transports the material to lorries, and/or to the material maturing lots (Figure 5).
3. Results and discussion

We monitored the qualitative properties of resulting artificial soil substrate in ranges (shown in qualitative properties below, Figure 6). The simplified structure of a soil is created by mineral parts (ca. 51%), organic residua (ca. 3 – 9%), pores filled with water and air (40%), and microorganisms (less than 1%). We reached similar rates in our artificial soil with the volume of organic residua as result of the addition of up to 25% of sludge from the processing of the homogenous wastewaters and excavated soils (clay soils). Further, the ash from the grate boilers helped to create the desirable pores containing air and water. Thus the conditions are created for natural soil microorganisms from the genus of *Pseudomonas*, *Achromobacter*, *Bacillus*, actinomycetes, microscopic fungi from the genus of *Mucor*, *Penicillium*, *Trichoderma*, *Aspergillus*, *Fusarium* etc. [3, 4, 5, 6]. Due to the higher contents of the organic matter, the presence of nitrifying and sulphur-oxidising bacteria was detected. The direct contact of the soil with its microflora allows, thanks to its rich contents of various microorganisms, along with time, to obtain the properties of a natural soil [7, 8, 9, 10]. For this spontaneous process, it is desirable under natural conditions specific to the area cleaned.

**Physical-mechanical properties:** the apparent density max. after PS 100% – 950 to 1400 kg.m\(^{-3}\), grading – total siftings through 16mm mesh (80 – 100%), 8mm (60 – 95%), 4mm (40 – 80%), 2mm (30 – 70%), 1mm (20 – 60%), 0.063 (5 – 30%), apparent density of solid particles, humidity 5 – 35%, apparent wet density, permeability – coefficient of filtration 1.10\(^{-6}\) to 1.10\(^{-4}\) m.s\(^{-1}\), shear strength – box shear test 15° to 45°, soil consistency 10 to 50kPa, ashes in the absolute dry matter 5 – 20%, mass activity 226 Ra max. 1000 Bq.kg\(^{-1}\).

**Biological properties:** carbonate Ca and Mg in the 6:8:1 ratio, organic matter 10 – 25%, soil reaction, sulphur, adsorption capacity according to Mehlich, establishing the amount of acceptable/usable nutrients according to Mehlich III acceptable nutrients – phosphorus 400 mg/kg, organic nitrogen, related ration of C:N – 15:24:1, cations of magnesium 80 – 130 mg/kg, potassium – 200 – 300 mg/kg, clay-like materials, establishing the pH from 6.6 – 7.7, establishing the contents of carbonates 2 – 3%, ecotoxicity, phytotoxicity.
Figure 6. Natural conditions specific to the given area.

Chemical properties: analyses while observing the ranges as per Decree No. 294/2005 Coll. are in Annex 12 – the contents of noxious substances in a solid matrix, the ecotoxicity and the chemical elements in the aqueous liquor. Here it is necessary to remark that the total contents of elements in the solid phase of these artificial soils established by a complete chemical analysis indicate the potential pollution inaccurately. Geochemists and physical chemists knowledge of mobility and redistribution of trace elements and of their fixation to a solid phase, toxicologists and physiologists on the differing toxic effects of these elements on living organisms, lead to the necessity of analytical discerning, e.g. speciation of various forms of incident and of ways of fixation in the solid phase created by physical or chemical fixations.

Nevertheless, this conclusion could also be applied to the entry of raw materials that are, out of the broad spectrum of potentially suitable materials, limited by current requirements/specifications without any sound basis [11]. Our current results show that if the resulting artificial soil substrate is balanced in terms of agrochemical properties, the circulation of non-metallic nutrients is extracted by moist acids and transported to the shoots (aboveground parts) of plants [12]. We are tackling this theme within our other research activities [13, 14].

Our existing results show the Cd, Hg, Pb (see Table 1) in the dry matter, at a specific pH we monitored, are used as markers that are objectively measuring quantities and defining the quality of the resulting product [15]. This goes above the usual scope and frequency of the obligatory analyses, the aim being to ensure sufficient quality of the final product.

|       | V1  | V2  | V3  | V4  | V5  | V6  | V7  | V8  | V9  | V10 | V11 | V12 |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Cd    | 1.21| 0.83| 0.77| 1.14| 1.26| 0.94| 0.93| 1.12| 1.11| 0.67| 1.41| 0.86|
| Hg    | 0.23| 0.34| 0.07| 0.09| 0.09| 0.10| 0.21| 0.38| 0.08| 0.07| 0.06| 0.10|
| Pb    | 18.67| 14.47| 13.97| 20.87| 22.67| 15.56| 13.74| 18.87| 19.86| 16.44| 20.32| 11.21|
| pH    | 7.2 | 6.8 | 7.1 | 6.9 | 6.7 | 7.5 | 6.6 | 7.1 | 7.5 | 6.8 | 7.2 | 7.5 |

4. Conclusion
Finding a method of processing and utilisation of sludge from a wood-mass-based pulp-production at a wastewater treatment plant was highly desirable due to its high-value agrochemical properties. Our process follows closely with the needs of our society and within the legal framework of the EU and the Czech Republic, where, according to the action environment programme (Decision 1600/2002/ES), it is necessary to return the biologically decomposable secondary raw materials into agriculture surroundings. Our aim was too controlled from the detailed examination of the sludge properties by finding suitable binders and raw materials for its modification/processing. Further, we also had to define the manufacturing process, including the formulas, and to build the equipment for the continual processing.

Within the process of production, based on the specific/concrete ratio formulas, we monitored the physical-mechanical properties standard for the soil derived from the engineering-geological classification of soils and rocks, and, at the same time, the agrochemical properties closer to the definition of other soils. The technique and equipment we used allow for the creation of artificial soil substrate with qualitative properties that allow for revitalising of the landscape affected by industrial
activities while eliminating the unsuitable qualitative properties and unpleasant smell of the input materials.

References
[1] Haider K and Schäffer A 2017 Soil Biochemistry (CRC Press)
[2] Guenet B, Leloup J, Hartmann Ch, Barot S and Abbadie L 2011 Appl. Soil Ecol. 48 243-246
[3] Šimonovičová A, Ferianc P, Vojtková H, Pangallo D, Hanajík P, Kraková L, Feketeová Z, Čerňanský S, Okenicová L, Žemberyová M, Bujdoš M and Pauditšová E 2017 Chemosphere 171 89-96
[4] Šimonovičová A, Peťková K, Jurkovič L, Ferianc P, Vojtková H, Remenár M, Kraková L, Pangallo D, Hiller E and Čerňanský S 2016 Water Air Soil Pollut. 227 art 336
[5] Vojtková H 2015 Biodiversity of Pseudomonas bacterial strains isolated from Ostrava Lagoons, Czech Republic (Albena: STEF92 Technology) pp 291-96
[6] Peťková K, Vojtková H, Jurkovič L, Ferianc P and Remenár M 2014 Isolation and identification of bacteria isolates from arsenic contaminated anthroposols (Albena: STEF92 Technology) pp 399-403
[7] Vojtková H 2016 Solubilization of Pb-minerals by new isolates Pseudomonas bacteria (Albena: STEF92 Technology) pp 755-760
[8] Kolenčík M, Vojtková H, Urík M, Čaplovičová M, Pištora J, Cada M, Babičová A, Feng H, Qian Y and Ramakanth I 2017 Water Air Soil Pollut. 228 (6)
[9] Urík M, Polák F, Bujdoš M, Miglierini M B, Milová-Žiaková B, Farkas B, Goneková Z, Vojtková H and Matuš P 2019 Sci. Total. Environ. 664 683-89
[10] Vojtková H 2014 14th Int. Mul. Sci. Geo. SGEM 2014 (Albena: STEF92 Technology) pp 451-57
[11] Wong P T W and Griffin D M 1976 Soil Biology and Biochemistry 8 215-218
[12] Janasová V and Vojtková H 2018 Phytoremediation of lead using Chenopodium album and growth-promoting effect of Pseudomonas bacteria (Albena: STEF92 Technology) pp 653-658
[13] Molinková V, Babičová A and Dlabaja M 2017 PGPR-bacteria and their capacities to eliminate lead using phytoremediation (Albena: STEF92 Technology) pp 737-742
[14] Bouchal T, Dlabaja M, Zavada J, Nadkanska H and Bouchalova M 2013 The use of waste materials for reclamation produciton and soil backfill (Albena: STEF92 Technology) pp 1079-1084
[15] Sharma R K and Agrawal M 2005 J. Environ. Biol. 26 301-313