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Spectroscopic analysis of sewage sludge and wood ash from biomass used for land remediation

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The present study aims to determine the possibility of using soil improvers (mixtures of active sludge and wood ash in different proportions) for possible remediation of metal contaminated soils from the mining area near Chelopech village, Bulgaria.

Analyzes of the soil improvers show that the prepared mixtures do not meet the requirements of the Fertilizers Regulation 2003/2003, so they are classified as soil improvers. The chemical analysis shows high calcium content (13.56 wt. %) in sample M1, 8.52% in M2 and 8.43% in M3, which make them suitable for treatment of acidic soils and immobilization of heavy metals in contaminated soils. Of the trace elements found (B, Cu, Fe, Mo, Mn and Zn) in the enhancers, only Fe has favorable concentration. The infrared spectroscopy proved rich contents of acids, proteins, carbohydrates, lipids and their byproducts, which are very important for soils and plants. The thermal investigations proved this prediction and the available functional groups that are defined by IR. The obtained results from FT-IR measurements show that samples M1 and M2 are more suitable for soil improvers because of the established process of mineralization.

Keywords: IR, DTA, soil, mining, remediation.

INTRODUCTION

Land damage resulting from mining activities, especially polluting farmlands, is an actual hot topic and damaged land should be properly reused through land remediation to meet human demand [1, 2]. The remediation of these sites is a complex activity aiming at the restoration of the damaged lands with a view to their future rational use, as well as the creation of balanced ecological systems [3, 4]. A successful technique for reducing heavy metals in the soil and remediation of damaged terrains is the application of soil improvers by adding nutrients [5, 6], which can affect the isolation of heavy metals by promoting the normal metabolism of plants [1, 7–11].

The use of sewage sludge from waste water treatment plants (WWTP) for the remediation of damaged terrain is a well-known opportunity in the world practice because they are source of humus and nutrients – nitrogen, phosphorus, potassium, sulfur and trace elements – iron, manganese, zinc, copper, etc. [12, 13]. To improve the properties of activated sludge and its effect on polluted soils, many authors explore the possibility of mixing with other soil improvers such as coal ash, organic fertilizer, etc. [14–17]. A good alternative to achieve stabilization of the activated sludge is to mix it with wood ash [18, 19], which is characterized by hygroscopicity and high calcium content. The hygroscopicity of the wood ash allows the formation of granules of the two materials with the necessary mechanical strength. The high calcium content contributes to the neutralization of the soil, whose pH is in the acidic region [20–24].

The purpose of this study is to determine the possibility of using a mixture of active sludge and wood ash in different proportions on metal contaminated soils from mining area. For characterization of the soil improvers, spectroscopic analysis was performed to determine the main organic components contained in the mixtures, chemical analysis was applied to determine the content of macro- and microelements and thermal analysis was conducted to determine the thermal stability of the functional groups in the mixtures.

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EXPERIMENTAL

Materials

Materials: Active sludge from sewage treatment plant – Blagoevgrad and wood ash from Svilosa AD, Svishtov were used.

To achieve the objectives of the present study three mixtures were prepared with different contents of sewage sludge (SS) and wood ash (WA): mixture 1 (M1) has a material ratio of 50:50; mixture 2 (M2) and mixture 3 (M3) respectively – 60:40 and 70:30, in favor of SS. An attempt was made to create a 40:60 mixture in favor of WA. This proved impossible due to the insufficient amount of moisture in the components and the inability to stick together.

Methods

To perform the chemical analysis and determine the qualitative and quantitative composition of the sludge, the High Dispersion ICP-OES Prodigy apparatus of Teledyne Leeman Labs, USA, was used.

Infrared spectroscopy, by identifying characteristic vibrations of the functional groups, was performed by FT-IR Spectrometer, Varian 660-IR, Austria, 2009; KBr pellets.

The thermal analysis was done with STA PT 1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis), manufactured by LINSEIS Messgeräte GmbH, Germany. The analysis is carried out in a dynamic heating mode in the temperature range of 20–1000 °C with a heating rate of 10 °C.min^{-1}. The specimen type is a powder with a particle size of 0.5 mm. The gas environment is static air gas. All analyzes were carried out at the Central Research Laboratory (CRL) at the University of Chemical Technology and metallurgy, Sofia.

RESULTS AND DISCUSSION

The chemical analysis shows high calcium content of 13.56 wt.% for M1, 8.52 for M2 and 8.43 for M3 in the mixtures and presence of Mg. The presence of these elements is of particular importance for the efficiency of soil improvers. Their content in these amounts helps to neutralize the pH of contaminated soils, which is in the range of 4.0–5.0. These changes in pH value help to immobilize heavy metals in contaminated soils.

The chemical analysis also shows that soil improvers meet the requirements for minimum trace elements in Regulation (EC) No 2003/2003 of the European Parliament and of the Council from 13 October 2003 relating to fertilizers on the basis of the fertilizer by weight of B, Cu, Fe, Mo and Zn. The requirements for the production of compost from active sludge set the following boundary values: Cd – 3 mg/kg DW, Cu – 500 mg/kg DW, Ni – 100 mg/kg DW, Pb – 200 mg/kg DW, Zn – 1500 mg/kg DW, Hg – 3 mg/kg DW, Cr – 150 mg/kg DW, As – 0 mg/kg DW. The results of the chemical analyses of the three mixtures are presented in Table 1.

Table 1. Results of the ICP-OES test on samples wood ash (WA) and sewage sludge (SS) and the soil improvers M1, M2, M3

	Value				
	Wood ash	Sewage sludge	M1	M2	M3
Total Amounts of Mineral Elements (dry subst.), mg.kg^{-1}					
K	520	636	893	587	684
Na	265	165	331	217	225
Ca	14500	2728	13560	8527	8433
Mg	129	1443	1715	1049	1271
P	717	1400	923.2	830	1148
Total Metals (dry subst.), mg.kg^{-1}					
Al	7450	1944	6306	4065	4163
As	11	50	49	30	28
Be	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<0.2	<0.2	<0.2	<0.2	<0.2
Cd	4.47	<0.2	0.15	0.06	0.12
Cr	21.9	10.0	18.32	12.15	12.77
Cu	179	47.4	39.85	29.52	35.48
Fe	6798	3382	5933	4080	4426
Hg	<0.2	<0.2	<0.2	<0.2	<0.2
Ni	<0.2	<0.2	<0.2	<0.2	<0.2
Pb	77	10	4.23	3.38	5.23
Sb	<0.2	<0.2	<0.2	<0.2	<0.2
Sn	<0.2	<0.2	<0.2	<0.2	<0.2
Zn	270	180	62.46	56.21	78.23

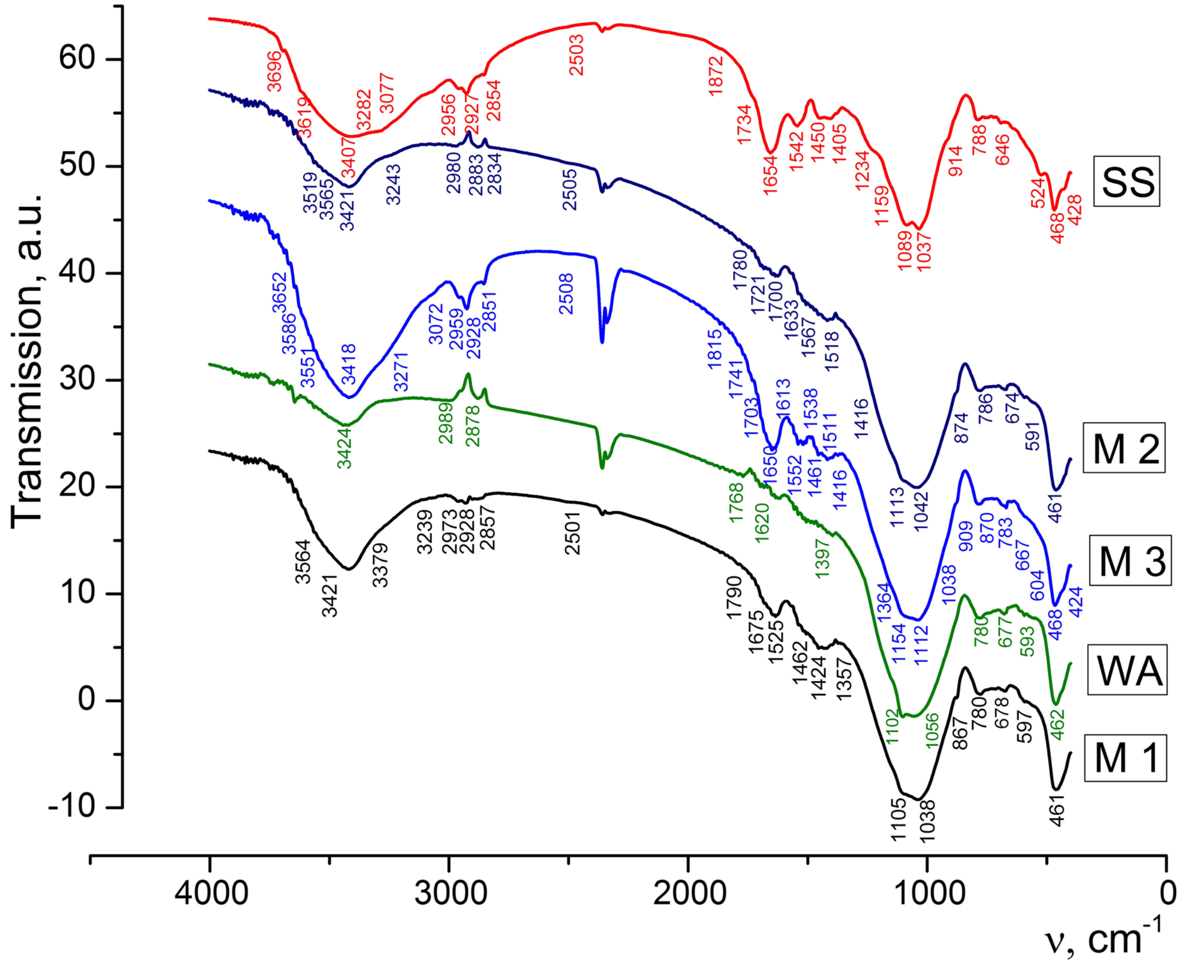

Fig. 1. FTIR Spectrum of WA, SS and the mixtures M1, M2 and M3.

Considering that the IR spectra reflect the chemical composition, preliminary studies of a particular mixture are necessary to select the criteria indicating the decomposition processes of the organic matter. In order to fully characterize soil improvers, they are subjected to infrared spectroscopy by identifying the characteristic vibrations of the functional groups. The results are shown in Figure 1. The peaks in the IR spectra fall within the ranges of acids, proteins, carbohydrates, lipids and their products and prove their high content in the mixtures we have made. The results of IR analysis of WA, SS and the three mixtures are presented in Table 2.

The components $Ca(OH)_2$ and $Mg(OH)_2$ are available in the raw SS and the mixture M3, which are characterized in the range 3619–3750 cm^{-1}. $Ca(OH)_2$ reduces the mobility of metals and phytostability and also reduces absorption of metals from plants.

The absorption bands in the 3407–3424 cm^{-1} range are typical for bonded and unbounded hydroxyl groups and H_2O molecules. Other hydroxyl groups are in the range 2501–2508 cm^{-1}. These bonds are characteristic for amino acids. This is important for plant productivity and also plays essential role in all plant growth processes. Roots have the ability to take up organic N in the form of amino acids. They are contained in all mixtures.

The presence of a band at 1872 cm^{-1} in raw SS and 1815 cm^{-1} bond in mixture M3 is a sign for presence of alkenes and lactam. Both of them contaminate soils -alkenes with hydrocarbons, which are part of petroleum oil and lactam is resistant culturable bacteria. The other characteristic band (1234 cm^{-1} and 914 cm^{-1}) for SS is for sulfones and phosphate esters, which are toxic for plants and damage the soil. Due to the presence of high percentage of precipitate in the M3 mixture, this peak also appears there (1154 cm^{-1} and 909 cm^{-1}). Acid chlorides (914 cm^{-1}) are available only in raw SS.

The main absorbance in the FT-IR spectra of SS and the three mixtures (Fig. 1) in the region 1080–

Table 2. Infrared spectroscopy of soil improvers WA, SS, M1, M2 and M3

No	Band/ cm^{-1}					Bond	Compounds
1	WA	SS	M1	M2	M3	–	
2	–	3696 3619	–	–	3750 3698 3652	ν (Ca–O) ν (Mg–O)	$Ca(OH)_2$, $Mg(OH)_2$
3	–	–	3564	3565 3519	3586 3551	ν_s (O–H)	Internally bonded Hydroxyl groups [28]
4	3424	3407	3421 3379	3421	3418	ν_s (O–H) ν (N–H)	Absorbed water [28] Amino groups
5	–	3282	3239	3243	3271	ν_{as} (N–H)	$R–NH_2$ – Amine group in Aromatic primary amine
6	–	3077	–	–	3072	ν_{as} (C–H) ν_s (C–H) ν_{as} (N–H)	$–CH_3$ and $–CH_2$ – Aliphatic methylene group in Hemicellulose, Aldehyde, Ketone, Carboxylic acids, Esters, Alkanes[28–37]
7	2989	2956 2927	2973 2928	2980	2959 2928		
8	–	2854	2857	2883	–		
9	–	–	–	2834	2851		
10	–	2503	2501	2505	2508	ν_s (O–H) ν (N–H)	Hydroxyl groups very broad Amino acid(NH_3^+)
11	–	1872	–	=	1815	ν (C=C) ν (C=O) ν (R–NH=O)	Alkenes Anhydrides Laktam
12	–	–	1790	1780	–	R–C–Cl	Acid chlorides (carbonyls)
13	–	1734	–	1721	–	R–CO–SH	Thioester
14	=	–	–	1700	1714 1703	ν_s (C=O)	Carbonyl group in Hemicellulose, Aldehyde, Ketone, Carboxylic acids, Esters, Acide halides [13–20]
15	–	1654	1675	1633	1650 1613	ν_s (C–O) ν_s (C=O) ν_s (C=C) δ_{as} (O–H)	Aromatic ring modes, Alkenes, Amides I, Carboxylates [24,31] Absorbed water
16	–	1542	–			ν_s(N–H)	Amides I
17	–		1525	1567 1518	1552 1538 1511	ν_s (C=O) δ_{as} (O–H)	Aromatic skeletal vibtarion of Lignin and Lingo Cellulose, Alcohols [34]
18	–	1450	1462 1424	1416	1461 1416	ν_{as} (C–O) ν_{as} (COO^-) ν_{as} (C=C) δ_{as} ($C–H_2$)	Carbonate ($CaCO_3$) Carboxylic acides; Lignin aromatic skeletal vibration [34,35]
19	=	1405	–	–	–	ν_{as} (N–O) ν_{as} (N–H)	NO_3^- group in Nitrate Amines I [28, 33, 36]
20	–	1367	1357	–	1364	ν_s (C–N)	Aromatic primary and secondary amines
21	–	1234	–	–	–	$(OR)_3P=O$ ν_{as} (R–S=O)	Phosphate esters Sulfones
22		–	–	–	1154	ν_s (R–S=O) (P=O) (C–O)	Sulfones Phosphine oxides Carbonyl compounds: acids
23	1102	–	1105	1113	1112	ν_s (C–O–C) δ_{as} (C–H) ν_{as} (Si–O–Si) ν_{as} (P=O) ν_{as} (S=O)	Secondary aliphatic alcohol, Organic Silicon in Oxy compounds [37] Lignocelluloses [29,31] PO_4^{3-} in β–$Ca_3(PO_4)_2$ SO_4^{2-} in Sulphates
24	1056	1089 1037	1038	1042	1038	ν_{as} (Si–O–Si) ν_{as} (P=O) ν_s(C–O)	Organic Silicon in Oxy compands, PO_4^{3-} in β–$Ca_3(PO_4)_2$ Symmetric stretching (cellulose; hemicellulose; methoxy groups of lignin [29, 31]

Table 2. (continued)

25	–	914	–	–	909	ν_s (S–O) ν_s (P–O)	Sulfonate Phosphate esters
26	–	–	867	874	870	δ_s (C–O out–of plane bending mode)	Carbonate
27	780	788	780	786	783	δ_s C–H out of plane (N–H)	Aromatic compounds, R–NH_2 in Primary amines
28	677	646	678	674	667	δ_s C–H δ_s and L(O–H) ν_s (S=O)	Alkynes, Alcohols SO_4^{2-} in Sulphates [37]
29	593	524	597	591	604		
30	462	468	461	461	468	δ_{as}(O–Si–O) ν_s (S=O)	Quartz SiO_2[37] SO_4^{2-} in Sulphates [37]
31	–	428	–	–	424	δ_s(O–P–O)	PO_4^{3-} in Phospates

1030 cm^{-1} is assigned to C–O stretching of polysaccharides or polysaccharide-like substances, Si–O of silicate impurities, and clay minerals, possibly in a complex with humic acids and cellulose; hemicellulose; and methoxy groups of lignin [24].

Absorption bands in the region 1500–1600 cm^{-1} could be assigned to the aromatic rings of lignin. Lignin, a major component of cell walls of vascular plants, is considered as a first line defense against successful penetration of invasive pathogens. Lignification renders the cell wall more resistant to mechanical pressure applied during penetration by fungal appressoria as well as more water resistant and thus less accessible to cell wall-degrading enzymes [25]. Additional bands of hemicellulose are available in mixtures M2 and M3 in ranges 1700–1714cm^{-1} and 1511–1567 cm^{-1}.

Carbonate ($CaCO_3$) with 1316–1462 cm^{-1} and 867–874 cm^{-1} bands is present in all mixtures. Its presence reduces the phytotoxicity in soils.

Comparison of the IR spectra of WA (Table 2) showed a similarity of the absorption bands in the 1102 cm^{-1} and 1056 cm^{-1} region. These bands are available for the mixtures as well. The absorption bands in the 950–1200 cm^{-1} region correspond to the C–O, C–C groups and deformation vibrations of ring structures of CH_2OH origin [24]. The most intensive broad absorption band appears in the characteristic carbohydrate region with maxima at 1058 and 1033 cm^{-1} assigned to vibrations of C-3-H–O-3-H and C-6-H2– O-6-H of cellulose groups [24].

Three broad bands at 1542, 1654, 1405 cm^{-1} are of protein origin (Amide II and Amide I, respectively) but the Amide I band disappears in a recast in mixtures SS spectra. In the spectra of SS the absorption bands at 2834–3077cm^{-1} are attributed to aliphatic methylene groups and assigned to fats and lipids. These bands are in all mixtures. Lipids are an important fraction of SS that could influence the water retention capacity of amended soils, their structural stability and the biodegradation–humification balance in soils [24].

As much as 20% of soil humus occurs in the form of lipids. Lipids of the following types are known to be present: paraffin hydrocarbons, phospholipids, fats, waxes, fatty acids, and terpenoids. It is thus possible to deduce from the wavelength of the carbonyl absorption band whether (for example) the environment of this grouping is a carboxylic acid or ester. Similar considerations apply to other groupings [26].

The spectra 1102–1113 cm^{-1} is also characteristic for PO_4^{3-} in β-$Ca_3(PO_4)_2$ which reduce the mobility of the metals from the roots to the plants.

The bands at 424–468 cm^{-1} and 590–677 cm^{-1} in the raw materials and mixtures proved the content of sulfate groups. They occupy the center of the S cycle, with a significant portion of the cycle being in soils. Soil as a medium for plant growth and development receives SO_4^{2-} from a variety of sources, part of which is used by plants, incorporated in microbial biomass retained in soils by chemical or physicochemical reactions, and yet a fourth portion is lost from the soil system by leaching [27].

For full characterization, the three soil improvers were subjected to thermochemical analysis. The analysis provides information on their behavior when heated at different temperatures and physical processes initiated by increasing the temperature, accompanied by heat release and absorption. The results are presented in Table 3.

At the “first stage” the temperature range mass loss varied between 0.1–3.3% (mixtures M1, M2, M3). From room temperature (RT) to 525 K some oxygen-containing functional groups like carboxyl and hydroxyl groups (2501–2508 cm^{-1}) [38] were

Table 3. Effects of thermal treatment of soil improvers M1, M2, M3

Mixture	Effect number	Effect	Temperature, K			Mass loss
			Inflection point	Beginning, T_{onset}	End, T_{offset}	%
M_1	1	Endo	316.6 396.6 456.5 505.2	312.8	525.2	–0.1
	2	Exo	552.5 592.6 646.3 694.9 762.4	525.2	789.7	–6.0
	3	Exo	809.7 922.1 940.6 984.5 1033.2 1094.4 1132.9 1166.6 1206.7	789.7	1226.5	–13.3
						Total: –19.5 %
M_2	1	Endo	331.6 394.1 435.2 451.5 503.8	298.0	521.9	–2.6
	2	Exo	598.6 669.9 711.0	521.9	765.8	–5.3
	3	Exo Endo	785.9 828.3 923.3 951.9 985.8 1034.4 1093.1 1131.7 1171.6 1232.8	765.8	1195.9	–14.9
						Total: –22.5 %
M_3	1	Endo	330.4 399.1 455.2	304.2	493.2	–3.3
	2	Exo	507.6 561.3 593.9 666.1 709.7 758.6	493.2	787.6	–8.5
	3	Exo Endo	811.0 860.9 919.6 985.8 1004.3 1029.4 1139.2 1200.4 1230.2	787.6	1175.6	–12.2
						Total: –24.5 %

decomposed and organic materials began to undergo some thermal decomposition, losing chemically bound moisture (dehydration of crystal water and adsorbed water 3379–3424 cm^{-1}). Between 423–473 K (organic materials) and in the range 1357–1367 cm^{-1} (aromatic primary and secondary amines (-C-N-) the bands indicate undergoing of some thermal decomposition. The effects are endothermic due to the absorption of heat from the released moisture.

Second stage – the 521–789 K range corresponds to decomposition of crystal and release of structural H_2O molecules (3519–3586 cm^{-1}). Hemicelluloses are degraded at 473 K to 523 K, cellulose at 513 K to 623K, and lignin at 553K to 773K (2854–3077 cm^{-1}; 1511–1567 cm^{-1}; 1416–1462 cm^{-1}; 1101–1113 cm^{-1}, respectively). For humic acids, exothermic reactions below 673K have been attributed to the thermal degradation of aliphatic and carbohydrate compounds, and higher temperature exotherms to oxidation of aromatic rings [39]. The temperature range between 693–785 K is associated with dehydrolization of $Ca(OH)_2$ (3619–3750 cm^{-1}). Resulting from the burning of volatile components, proteins, carbohydrates and lipids all of the peaks are exothermic. These chemical conversions occur concurrently with rapid changes in mass loss during the partial combustion process, which has to be taken into account when quantifying the chemical changes. Reported mass losses are from 5.3 to 8.5% from different mixtures.

Decomposition of the mixtures continues during the third stage of the thermal process in the range of 765–1226 K. The weight loss is the greatest (13–16%) and is due to the "burning" of macromolecules of the organic component. Sulphur remains as a sulphate (1102–1113 cm^{-1}) until approximately 758–786 K at which temperature it starts to transform to an insoluble sulphide. At these temperatures the decomposition of inorganic components, mainly calcite, occurs. Above 953–963 K an exothermic reaction process is running indicating decarbonization of $CaCO_3$ (867–870 cm^{-1}). An endothermic effect is detected too mainly due to thermal decomposition of carbonates

CONCLUSIONS

From the performed analyzes we can conclude that the produced mixtures do not meet the requirements of the Fertilizers Regulation 2003/2003, and they are classified as soil improvers. The concentrations of Ca and Mg in the produced soil improvers make them suitable for treatment of acidic soils. From the trace elements found in the enhancers, only Fe has a favorable concentration. The ICP-OES analysis demonstrated the presence of As and Pb is in the range of 0.002–0.04% (As) and 0.003–0.005% (Pb). Infrared spectroscopy proves the rich content of (amino) acids, proteins, carbohydrates, lipids and their byproducts, which are very important for soils and plants. The thermal analyses reveal that weight losses due to the burning of macromolecules and the organic component are in the range 13–16%. The obtained results from FT-IR measurements show that samples M1 and M2 are more suitable for soil improvers because of established process of mineralization.

REFERENCES

1. E. Zheleva-Bogdanova, Rehabilitation of damaged terrains, PSSE, Sofia, 2010.
2. E. Zheleva, P. Bozhinova, N. Dinev, Remediation of contaminated soils and overcoming the ecological damages from "OCC" JSC – Kardzhali, Ambroziq NT Ltd, Sofia 2012.
3. A. Atanasov, Ecological Problems and Recultivation of Land Degraded by the Mining Industry,Publish. House "St. Ivan Rilski ", Sofia, 2007.
4. B. Zaharinov, Y. Naydenov, Recultivation and methods for soil research, NBU, Sofia, 2014.
5. B. Wang, Z. Xie, J. Chen, *J. Env. Sci.*, **20**, 1109, (2008).
6. A. Singh, M. Agrawal, *Eco. Eng.,* **36,** 1733 (2010).
7. G. C. Chen, Z. L. He, *J. Trace Elem. Med. Bio.*, **20**, 127 (2006).
8. J. M. Novak, W.J. Busscher, D.L. Laird, M. Ahmedna, D.W. Watts, M. A. S. Niandou, *Soil Sci.,* **174**, 105 (2009).
9. L. Beesley, O. Inneh, *Envir. Pollution*, **186**, 195 (2014).
10. S. Kabas, A. Faz, J. Acosta, *J. Geochemic. Explor.* **123**, 69 (2012).
11. A. Mahar, P. Wang, R. Li, *Pedosphere,* **25**(4): 555 (2015).
12. M. Banov, S. Marinova, A. Tasev, (First conf. of the BAV, Sofia, 2016), *The sludge from the WWTP: problems and solutions*, Sofia, 2016, p.62
13. Ciarán J. Lynn, Ravindra K. Dhir, Gurmel S. Ghataora, *Leaching assessment, Resources, Conservation & Recycling* **136,** 306 (2018).
14. L. Wang, Y. Zhang, J. Lian, J. Chao, Y. Gao, F. Yang, L. Zhang, *Bioresour. Technol.* **136**, 281 (2013).
15. L. Wang, Z. Zheng, Y. Zhang, J. Chao, Y. Gao, X. Luo, J. Zhang, *J. Hazard. Mater.* 244 (2013).
16. J.W.C. Wong, *Envir. Int.*, **29**, 895 (2003).
17. H. Zhang, S. Lina, *J. Env. Sci.,* **20**, 710 (2008).
18. R. Rehmana, M. Rizwanb, M. Farooq Qayyuma, S. Alib, M. Zia-ur-Rehmanc, M. Zafar-ul-Hyea, F. Hafeezd, *J. Env. Manag.,***223,** 607 (2018).
19. J. Pesonen, V. Kuokkanen, *J. Env. Chem. Eng.,* **4**(4), 4817 (2015).
20. J. Xu, X. Dong, Q. Wang, *J. Hazard. Mater.,* **217–218**, 58 (2012).

21. M. Wolters, E. Brannvall, R. Sjoblom, J. Kumpiene, *J. Env. Manag.,* **159**, 27 (2015).
22. A. Merino, B. Omil, M. T. Fonturbel, J. A. Vega, M. A. Balboa, *Appl. Soil Ecology,* **100**, 195 (2016).
23. L. Żołnierz, J. Weber, M. Gilewska, S. Strączyńska, D. Pruchniewicz, *Catena*, (2015).
24. M. Grubea, J.G. Lin, P.H. Leeb, S. Kokorevicha, *Geoderma,* **130**, 324 (2006).
25. N. H. Bhuiyan, G. Selvaraj, Y. Wei, J. King, *Plant Signal Behav.*, **4**(2), 158 (2009).
26. D. Chapman, *J. Am. Oil Chem. Soc.*, **42**(5), 353 (1965).
27. M. AN Tabatabai, *Physicochemical Fate of Sulfate in Soils – JAPCA,* **37**, 34-38 (1987).
28. K. Nakamoto, Infra Red and Raman Spectra of Inorganic and Coordination Compounds, John-Wiley & Sons, Hoboken, 2009.
29. B. C. Keri, G H. Patrick, U. Minori, M. N. Jeffrey, S. Ro Kyoung, *Bioresource Technol.*,**107**,419 (2012).
30. M. Keiluweit, P.S. Nico, M.G. Johnson, M. Kleber, *Environ. Sci. Technol.*, **44**(4), 1247 (2010)
31. A. Ouatmane, M.R. Provenzano, M. Hafidi, N. Senesi, *Compost Sci. Util.*; **8**, 124 (2000).
32. K.H. Tan, Humic Matter in Soil and the Environment – Principles and Controversies. Marcel Dekker, New York Basel, 2003.
33. M.R. Derrik, D. Stulik, J.M. Landry, Infrared Spectroscopy in Conservation Science, Scientific Tools for Conservation, Los Angeles1999.
34. M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, Georg Thieme Verlag Stuttgart, New York, (1987).
35. D.C. Lee, D. Chapman, *Bioscience Rep.*, **6**(3), 235 (1986).
36. G. Davis, Compost Maturity and Nitrogen Release Characteristics in Central Coast Vegetable Production – Integrated waste management board, Integrated Waste Management Board, Sacramento, (2002).
37. J. Coates, Interpretation of Infrared Spectra, A Practical Approach – Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), John Wiley & Sons Ltd, Chichester, 2000.
38. L. Liqing, Y. Xiaolong, L. Hailong, L. Zheng, M. Weiwu, L. Xin, *Jour. of Chem. Eng. of Japan*, **47**(1), 21 (2014).
39. J. Leifeld, *Org.Geochem.*, **38**, 112–127 (2007).