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Study on the Use of Manganese-Containing Materials as a Micro Fertilizer Based on the Local Mineral Resources and Industrial Wastes in Hydroponic Systems

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***Abstract*—**Hydroponic greenhouses systems (production of the artificial substrate without soil) are becoming popular in the world. Mostly the system is used to grow vegetables and berries. Different countries are taking action to participate in the development of hydroponic technology and solutions such as EU members, Turkey, Australia, New Zealand, Israel, Scandinavian countries, etc. Many vegetables and berries are grown by hydroponics in Europe. As a result of our research, we have obtained material containing manganese and nitrogen. It became possible to produce this fertilizer by means of one-stage thermal processing, using industrial waste containing manganese (ores and sludges) and mineral substance (ammonium nitrate) that exist in Georgia. The received material is usable as a micro-fertilizer with economic efficiency. It became possible to turn practically water-insoluble manganese dioxide substance into the soluble condition from industrial waste in an indirect way. The ability to use the material as a fertilizer is predetermined by its chemical and phase composition, as the amount of the active component of the material in relation to manganese is 30%. At the same time, the active component elements presented non-ballast sustained action compounds. The studies implemented in Poland and in Georgia by us have shown that the manganese-containing micro-fertilizer- $Mn(NO_3)_2$ can provide the plant with nitrate nitrogen, which is a form that can be used for plants, providing the economy and simplicity of the application of fertilizers. Given the fact that the application of the manganese-containing micro-fertilizers significantly increases the productivity and improves the quality of the big number of agricultural products, it is necessary to mention that it is recommended to introduce the manganese containing fertilizers into the following cultures: sugar beet, corn, potato, vegetables, vine grape, fruit, berries, and other cultures. Also, as a result of the study, it was established that the material obtained is the predominant fertilizer for vegetable cultures in the soil. Based on the positive results of the research, we consider it expedient to conduct research in hydroponic systems, which will enable us to provide plants the required amount of manganese; we also introduce nitrogen in solution and regulate the solution of pH, which is one of the main problems in hydroponic production. The findings of our research will be used in hydroponic greenhouse farms to increase the fertility of vegetable crops and, consequently, to get bountiful and high-quality harvests, which will promote the development of hydroponic greenhouses in Georgia as well as abroad.

***Keywords*—**Hydroponics, micro-fertilizers, manganese ore, chemical amelioration.

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I. Introduction

It is well known that particular interest worldwide as well as in Georgia is given to the development of agriculture and the provision of quality agricultural products. The most popular and progressive innovation in this sphere is considered the use of micro-elements as fertilizers to contribute to the scientific and practical solution of the problem to the certain extent. The application of the mentioned approach in relation to the sorts of various cultures of plants becomes determinant in the issues of increase, development, fertility, and quality of products. It is noteworthy that micro-elements predetermine the consumption of the main elements (nitrogen, phosphorus, potassium) by plants at the expense of biochemical processes, and, consequently, it becomes essential to systematically use materials that contain the substitute elements (micro-fertilizers). Plant food in the form of micro-elements gets into the animal organism and as a result of consuming these animals - into human bodies. The dose of micro-elements use by human beings is individual, but in case of manganese, the daily norm is 5-10 mg and it is 2-10-times more compared to other micro-elements which, in turn, results, in the necessity of its accelerated (intensive) use.

It is well-known that the materials containing manganese, boron, copper, cobalt etc. used as fertilizers in agriculture are represented in the products of the worldwide and Europe-wide famous companies (the products of Akzo-Nobel in the form of Rexoline). The micro-fertilizers which represent topdressing and water-soluble materials (mono-fertilizer represented by manganese chelate) take a particular place among those materials. The use of manganese chelate is accompanied by the intensive character of application, adherence to strict specifications and etc., which in turn, limits its efficiency and often the sustainability in time as well. Consequent from the above the quality of the mentioned micro-fertilizers to dissolve and decompose in short period of time causes ecological problems (decomposition into toxic radicals when exposed to the sun, penetration from soil into the underground water etc.). It is also known that the manganese content in the best quality chelate does not exceed 14 weight%, while the remaining amount is just the ballast which decreases the trade value of the material [1].

To solve the mentioned problems we propose to use the manganese containing micro-fertilizers received from the industrial waste and mineral substances, which is characterized by the simplicity of its production technology (the product is received through thermal processing) and the economic efficiency due to small dosage of consumption; besides, it can also be used both for leaf and root fertilizing of plants, which does not characterize functional quality of the similar products available in the market today. The opportunities to implement and potentially establish large-scale production of the above mentioned micro-fertilizer are predetermined by its chemical and phase composition, as the volume of the active component of the material (valuable, i.e. consumable by plants) in relation to manganese is 30% and it is 50 weight% more by its useful elements. At the same time, the active component elements are presented by an amorphous crystal manganese compound of non-ballast, sustained action, which is obtained through single-stage thermal synthesis of new manganese compositions. As a result of the study of binary compositions of various components, we determined that the materials received as a result of manganese oxides participation (thermal processing of corresponding ores); it became possible to turn practically water-insoluble manganese dioxide substance into soluble condition through the indirect way.

The goal of the research is to study the application opportunities of the manganese containing materials received from the industrial waste to increase the productivity of the meliorated soil.

II. Methodology

The production of new type of product (the manganese containing micro-fertilizer) became possible in the conditions of Georgia due to the use of existing raw materials base (the manganese containing ores and sludge, ammonium nitrate, etc.), which in the long run will contribute to production and provision of agricultural workers with efficient, effective, competitive product of high value. As a result of our work, the manganese containing materials with the high composition of useful substances was received. To study the expected behavior of materials and corresponding ores used in the process of receiving the manganese containing micro-fertilizers through the thermal processing the differential-thermal, X-ray phase analysis and other research methods were used.

All materials were studied on the matter of solubility tendency, while manganese containing materials (ore concentrates, sludge, and dioxide) were additionally tested on solubility kinetics, and by the spectral analysis of the solutions, the possibility of the presence of soluble manganese in them was defined. It was determined that as a result of thermal processing of the manganese containing materials the expected phase composition change can define the solubility tendency of materials. For the model system the thermo-dynamic evaluation using Gypsy free energy minimization method and the kinetics of the reactions of one of the leading MnO_2-NH_4NO_3 was defined [2].

The composition of materials used in experimental researches is given in Table I.

In order to determine the materials solubility capacity, a 2% citric acid aqueous solution was taken as test reagent, while the synthesis of materials was realized in electric furnace, in air circulation conditions, in porcelain glazed pots (material synthesis up to 200 ^{0}C) or in corundum pots (high temperature synthesis up to 1000 ^{0}C). The conditions of materials thermal synthesis was determined with consideration of the type and composition of material to be received taking into account the data given in reference literature [1]-[3].

The results of the research presented in Table III show that manganese (IV) oxide solubility in test reagent is very low, which indicates ineffectiveness of purposeful direct using of manganese oxide and manganese oxide containing materials. But, the solubility of the received materials differs from solubility of the initial components while according to solubility index they can be conventionally attributed DM-composition with low solubility and average solubility (MP, MB) materials. It should be mentioned that all three types of compositions are very particular as they contain manganese and also, potassium and magnesium very important for plants.

TABLE I
CHEMICAL COMPOSITION OF MANGANESE CONTAINING MATERIALS

#	Name and symbolic notation	Chemical composition, %						
		SiO_2	Al_2O_3	CaO+ MgO	MnO+ MnO_2	$MnSO_4$	Fe_2O_3	Losses at heating
1	Manganese ore (MR)	9.9	1.5	2.5	68.5	-	1.8	15.8
2	Manganese sulfate slime (MS)	45.9	4.9	0.3	28.5	4.1	0.2	16.6
3	Manganese dioxide (M2)	-	-	-	99.0	-	-	1.0

TABLE II
COMPOSITION OF MONO AND BINARY CHARGES AND SOLUBILITY OF MANGANESE CONTAINING MATERIALS TREATED AT DIFFERENT TEMPERATURES

Charge material index	Charge compositions, mass%				Effect of thermo treatment in materials' test reagent, solubility, %		
	MS	MR	MnO_2	H_3BO_3	750^{0}C	850^{0}C	950^{0}C
MS	100	-	-	-	-	-	-
MR	-	100	-	-	-	-	-
MSB	87.5	-	-	101.4	22.1	18.2	7.9
MRB	-	84.8	-	101.4	38.0	17.3	10.2
M2B	-	-	50.9	101.4	53.7	34.4	11.9

TABLE III
CHARGES OF MANGANESE CONTAINING MATERIALS, CONDITIONS OF THEIR SYNTHESIS AND SOLUBILITY INDICES

#	Material's index	Composition components, weight%		Conditions of synthesis		Solubility losses weight % in test reagent
		Manganese dioxide	Second component	Time, hours	Temp., ^0C	
1	M	100	-	3.0	300±20	1.6
2	MD	43.5	$\frac{CaCO_3 \bullet MgCO_3}{56.5}$	3.0	800±20	23.6
3	MP	57.0	$\frac{K_2CO_3}{45.0}$	3.0	800±20	36.5
4	MB	19.5	$\frac{H_3BO_3}{80.5}$	2.0	800±20	55.1
5	MN	21.5	$\frac{NH_4NO_3}{70.5}$	2.0	185±5	41.4
6	ML	38.5	$\frac{C_2H_2O_4 \bullet 2H_2O}{60.0}$	2.0	185±5	11.5
7	MC	40.0	$\frac{C_6H_8O_7 \bullet H_2O}{61.5}$	2.0	185±5	89.5
8	B	-	$\frac{H_3BO_3}{100}$	2.0	600±10	93.5
9	D	-	$\frac{CaCO_3 \bullet MgCO_3}{100}$	2.0	110±10	11.2

Especially important is the synthesis of manganese borate as of the material having mean solubility (65%) which does not contain any "ballast" and represents micro fertilizer of practically 100% absorption. Very high solubility is fixed for MN (manganese nitrate) material received on the basis of MnO_2 and NH_4NO_3.

Different values of solubility are characteristic to manganese organic compounds, particularly, those indicated with indices ML and MC. Especially low solubility is characteristic to manganese oxalate, manganese citrate is solved better. In both material, Mn concentration is optimum (30-38%) and is in absolute correlation with its "classic" composition presented in manganese sulfate [4].

With participation of MR and MS materials MSB and MRB have been composed, as well as charges of model M2B materials, in which the possibility of manganese borate receipt determined interrelation existing between the ingredients. It was determined that the ($MnO_2 + 2NH_4NO_3 + 3/2O_2 \rightarrow Mn(NO_3)_2 + N_2O + H_2O$; $MnO_2 + 4NH_4NO_3 \rightarrow Mn(NO_3)_2 + 3N_2 + 8H_2O$) reactions sequence of the process of getting MN is expected to be implemented under the temperature interval of 170-200 °C, when for the intensification of the process it becomes desirable to bring ammonium nitrate into melted condition (t > 169,5 °C); while the upper limit of the temperature is defined as ≥ 195 °C – the temperature of $Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$ disintegration.

Given the fact that the application of the manganese containing micro-fertilizers significantly increases the productivity and improves the quality of the big number of agricultural products, it is necessary to mention that it is recommended to introduce the manganese containing fertilizers into the following cultures: sugar beet, corn, potato, veggies, vine grape, fruit, berries and other cultures [3]. It is also worth mentioning that the scheme of the consequent technological operations to obtain the manganese containing micro-fertilizers is already developed.

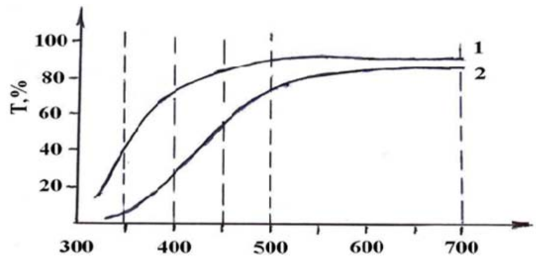

Fig. 1 Spectral curves of extracts obtained with treatment of MSB(1) and MRB(2) materials in 2% CA

Based on the above and aiming at the increase of agricultural land fertility it will become possible to implement the theoretical and laboratory research results of the manganese containing fertilizers production on the basis of the industrial wastes in Georgia conducted by us, which in turn will support improving the effectiveness of melioration processes in agriculture, increase the productivity of the processes and correspondingly receiving rich and quality harvests [5]. At the same time, model M2B is characterized with higher solubility than MRB and MSB materials differing with complicated composition and manganese content which is proved with respective spectral researches.

The effect of granulometry (δ) of synthesized materials on solubility (OG) in reagent has been determined and the kinetics of solubility process has been studied for MRB and MSB compositions. The particular effect of materials grain sizes for 0 ≤ δ ≤ 2 mm case has been detected. The further growth of grain sizes has less effect on solubility index of researched materials [6].

The results of changes of weight losses (OG) received with tests are studied for 2-24 hours (τ, h) interval and it has been stated that MSB material solubility in water is less effective than in 2% CA but in both cases solubility decrease is fixed in the whole interval of reagent action (Fig. 1). It appeared that model M2B composition and initial material showed similarity to MR (ore) solubility and stability of losses is achieved after 4-8 hours. In general, with the tendency to solubility materials can be presented in series Mr→MRB→MSB→M2B.

The received results should be directly depended on the change of materials phase composition at thermal treatment which is proved with carried out differential-thermal and X-ray phase researches [7].

Our plant research has been implemented of wetland soils based on the Colchis (Poti, Georgia) Agricultural-Ecological Experimental Station to explore the use of manganese-containing micronutrient produced from industrial waste for raising the fertility for chemical amelioration of wetland soils.

Fig. 2 An experiment of a Lettuce

III. Conclusion

As a result of the study, it was established that the material obtained is the predominant fertilizer for vegetable cultures in the soil. Based on the positive results of the research, we consider it expedient to conduct research in hydroponic systems, which will enable us to provide plants for the required amount of manganese; we also introduce nitrogen in solution and regulate the solution of pH, which is one of the main problems in hydroponic production.

The findings of our research will be used in hydroponic greenhouse farms to increase the fertility of vegetable crops and, consequently, to get bountiful and high-quality harvests, which will promote the development of hydroponic greenhouses in Georgia as well as abroad.

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