Restoration of Biological Function of Degraded Soil via Chemical Method

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Abstract—The studies concerned an effect of six variants of ion exchange substrate (nutrient carriers with a different potential impact on pH of soil solution) on vegetation of orchard grass during two different periods (42 and 84 days). In the pot experiment plants were grown on sand (model of degraded soil) and six mixtures of sand and 2% (v/v) additions of particular variants of ion exchange substrate (with pH ranged from 5.5 to 8.0). The study results showed that the addition of the substrate at pH=6.5 caused the highest increase in plant yield after shorter vegetation period whereas the addition of the substrate at pH=5.5 increased dry stem and root biomass of orchard grass after longer vegetation period. Thus, the ion exchange substrate at pH=6.5 can be recommended for restoration of exhausted soils when shorter vegetation period is planned; the ion exchange substrate at pH=5.5 can be used for the same purpose when longer periods of vegetative growth are considered.

Keywords—ion exchanger, ion exchange substrate, soil restoration

I. INTRODUCTION

INCREASING threats of a global nature towards the existence of human civilization called remedial actions. One of the most important was Brundtland's report that defined the basic paradigms of sustainable development which pointed to the need for a systemic approach to global threats. Tasks facing the population were detailed in *Millennium Development Goals for 2015* where it was considered the most important task of ensuring the sustainable development of modern civilization.

To better understand problem of sustainability one has to take into account its multidimensionality [1] referring to global [2]-[5], environmental [6]-[8] economical [1], [9]-[12] and even philosophical aspects [13]-[18].

These are pillars of pathways of development of the present world. The fact that resources are less and less available makes it all the more serious. A lot has been said and written in the recent years about climate change, and much less about the fact that the main source of anthropogenic carbon dioxide emission to the atmosphere, i.e. burning fossil fuels is associated with the depletion of fossil fuel resources. The consequences of energy shortage could be much more severe to the world than the greenhouse effect.

Current estimates say that, at the present level of consumption, there is enough oil for about 40-50 years, natural

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gas for 60-70 years and coal for about 140-150 years. This shows that two of those main primary energy resources necessary to uphold human civilization will be exhausted within a single generation. Even if we assume a large error in the estimates, one must accept that a major crisis in access to conventional energy sources will occur within a short time, measured in decades. This means that one of the cardinal rules of sustainable development, namely intergenerational justice, is at stake. The present generation seems to live at the expense of future generations.

All the above clearly points out that the development of modern civilization is highly unsustainable. In reference to the term "humanity ecological foot print", which sets the smallest necessary area of Earth surface for the human population to survive it has been proven that our planet's capacity to sustain our population has been exceeded in approximately 1986 [19]-[20].

Under the influence of human activity soil degradation is progressing rapidly. Nowadays, every year 0.5%-0.7% of soils disappear and degraded lands occupy about two billions ha in the world [21]. According to postulates of sustainable development these territories should recover their utilizable and natural values and hence require the kind of biological reclamation. Biological restoration of such lands often involves formation of the top soil layer containing humic compounds because humus advantageously influences physical, chemical and biological properties of soil [22]-[24]. Due to its relatively high capacity and buffering properties humus, together with inorganic colloids, retains nutrient ions and adjusts pH of the soil solution. In addition, humic compounds significantly influence creation of specific soil structure (crumbs) by initiating clotting process and playing the role of an adhesive. Humic substances also increase the content of nutrients in soil. During slow microbiological decomposition they release additional amounts of macro- and micronutrients. Some of humic compounds accelerate division of microbe cells and influence the nitrogen fixation and nitrification process. By forming chelates with cations, humus blocks their bonding with PO_4^{3-} ions and prevents precipitation insoluble tricalcium phosphates [25].

Such different influence of humus on soil is indubitably caused by its various properties. To find or prepare the substances of identical or even similar influence on a soil environment seems to be a very difficult task. Our studies are directed to replace humus on the first stage of soil reclamation by addition of ion exchange substrates. In fact, they are mixtures of cation and anion exchangers saturated with macro- and micronutrient ions in proper ratios [26]. These materials

can play role of a rich source of nutrients for plants cultivated during biological restoration of soils. Moreover, they are able to retain nutrient ions introduced into soil with conventional fertilizers and hence, prevent, to some extent, nutrient leaching from ground of weak sorption properties. Ion exchange substrates (trade name Biona®) are produced in limited amounts at the experimental plant of the Institute of Physical Organic Chemistry of the Belarus National Academy of Sciences (BNAS) and differ from each other in characteristics such as nutrient content and exchanger composition [26].

In the paper we present study results concerning influence of different variants of ion exchange substrate (as nutrient carriers with potentially different effect on the pH of the soil solution) on the plant vegetation process. It was decided to observed plant growth during two different periods (42 and 84 days) because intensification of plant development and amount of obtained organic matter (as material for humus formation) seem to be of importance in effectiveness of biological soil restoration.

II. MATERIALS AND METHODS

A. Characteristics of Sand and Ion Exchangers

In the study sand, ion exchange resins of the KU-2 (strong acid cation exchanger) and EDE-10P (polifunctional anion exchanger with weakly dissociating groups) types were used. The sand was used as a model of degraded soil. It came from sand mine in Golab near Pulawy (Poland). The pH value of its water extract was 5.77. Chemical analysis indicated that sand was very poor in macronutrients (Table I).

TABLE I
AMOUNTS OF AVAILABLE MACRONUTRIENTS IN SAND [MG PER 100G]

N^a	P^b	K^c	Mg^d	Ca^e	S^f
0.198 ($N-NH_4$)	0.48	<1.99	1.00	4.41	0.53 ($S-SO_4$)
<0.128 ($N-NO_3$)					

[a] - N determined in 1% K_2SO_4 extract, [b] - P determined in 0,04 M $(CH_3CHOHCOO)_2Ca$ extract, [c] - K determined in 0.04 M $(CH_3CHOHCOO)_2Ca$ extract, [d] - Mg determined in 0.0125M $CaCl_2$ extract, [e] - Ca determined in 0.03M CH_3COOH extract, [f] - S determined in 0.5M $CH_3COOH+0.25M$ CH_3COONH_4 extract

Both ion exchangers were produced in Russia. The total ion exchange capacity of resins was 11 mmol/g for anion exchanger and 5 mmol/g for cation exchanger, respectively. The specific mass of air-dry anion exchanger was 0.52 kg per 1 dm^3 while for air-dry cation exchanger it took value of 0.79 kg per 1 dm^3.

B. Preparation of Ion Exchange Substrate Variants

Preparation of ion exchange substrates is based on providing the mixtures of cation and anion exchangers with the ionic composition that assures the availability of biogenic elements to the same degree as in hydroponic nutrient solution [26]. In fact, there are three methods for preparing the ion exchange substrates: a dynamic, static and a method of monoionic forms [27]-[28]. The process of obtaining the substrate by a method of monoionic forms proceeds in two stages. In the first instance an individual monoionic forms

containing biogenic ions are prepared. Based on a cation exchanger, calcium, potassium and magnesium forms are prepared whereas on the basis of anion exchanger - nitrate(V), sulphate(VI) and phosphate(V) forms are prepared. Micronutrient ions can be introduced into one of the forms containing a given macronutrient. Preparing monoionic forms on the basis of cation exchanger is performed by saturation of ion exchange portion with a solution of relevant salt or relevant hydroxide. On the other hand, preparing monoionic forms based on anion exchanger occurs by means of relevant acids. After the preparation monoionic forms are subject to analyses for content of biogenic ions. The results of the analyses and the quantitative proportions found between macronutrient ions in a substrate sample obtained by dynamic method allow to determine weighted amounts of individual forms in order to obtain a unit mass of a complete substrate. To prepare monoionic forms and thus ion exchange substrate, basically any cation and anion exchanger can be used. The application of anion exchangers with weakly dissociating functional groups for the preparation of monoionic forms or also the complete substrate should take into account their influence on pH of the soil solution after the introduction into the ground. The influence depends on anion content in anion exchanger and also on the current salts concentration dissolved in soil solution. The lower the anion contents in monoionic forms and the higher salt concentrations in soil solution are, the higher pH of the solution contacting with anion exchanger being the part of the substrate. Taking into consideration the high changeability of salt concentration in soil solution in time, one should select the monoionic forms prepared on the basis of polifunctional anion exchanger in such a way that eventual pH changes of soil solution being in the contact with the substrate, will correspond to physiological requirements of the plants.

In the study substrate variants were prepared using the method of monoionic forms. Anion exchanger was used for preparing six variants of nitrate, phosphate and sulphate forms differing in the pH of solutions equilibrated with them. Three monoionic forms: calcium, magnesium and potassium forms were prepared on the basis of cation exchanger.

The preparing monoionic forms on the basis of the cation exchanger consisted in saturation of resin portions with relevant ions in water solutions containing: KOH, CaO and MgO, respectively. During preparation of monoionic forms on anion exchanger basis, resin portions were placed in solution of relevant potassium salt. Then particular acids (HNO_3, H_3PO_4, H_2SO_4) were added into reaction zones. The amounts of acids ensured fixed pH value of solution contacting with particular resin portion. In such way, 18 variants of monoionic forms were obtained enabling six variants of ion exchange substrates to be prepared (Table II). The variants differed in pH values of solutions equilibrated with particular monoionic forms and hence would have potentially different effect on the pH of the soil solution.

In order to determine ratios between the monoionic forms in particular variants of ion exchange substrate, small samples of cation and anion exchanger (3g) have been saturated with

nutrient solution (salt concentration about 1.65g/dm^3) in dynamic conditions until equilibrium state was achieved. Ratios between ions found in resins in equilibrium state and contents of nutrients in monoionic forms were used to calculate amounts of individual forms that were mixed to prepare mass unit of particular substrate variant.

TABLE II
CONTENTS OF MACRONUTRIENT IONS IN DIFFERENT VARIANTS OF ION EXCHANGE SUBSTRATE [MMOL PER 100G]

Substrate[a]	NO$_3^-$	H$_2$PO$_4^-$	SO$_4^{2-}$	Ca^{2+}	Mg^{2+}	K$^+$
At 5.5	64.99	23.64	216.62	367.72	65.96	18.84
At 6.0	64.58	23.49	215.26	365.38	65.60	18.71
At 6.5	63.60	23.12	212.02	359.96	64.60	18.45
At 7.0	62.37	22.67	207.88	352.88	63.28	18.09
At 7.5	60.12	21.86	200.42	340.18	61.04	17.46
At 8.0	48.12	14.50	160.42	272.32	48.90	13.97

[a] - Contents of ions were determined in 2M HCl extract

C. Pot Experiment

The prepared substrate variants were evaluated in a plant experiment. For the need of the pot test seven series of media were prepared: the control series (sand) and six test series - the mixtures of sand and 2% (v/v) additions of particular variants of ion exchange substrate (Table III). Then, 50 seeds of orchard grass (*Dactylis glomerata* L.) - var. Amba was sown to each pot of experimental series. After 5 days since the moment of seed sowing the number of plants was standardized to 28. The experiment was carried out in a phytotron with 13/11 hours light/dark regime. Daytime air temperature (between 7 a.m. and 8 p.m.) was 25°C. The night-time air temperature (between 8 p.m. and 7 a.m.) was 16°C. During the experiment plants were watered with distilled water. The vegetative growth period lasted 42 days in the first part of the experiment. The aboveground shoots of plants were cut down and roots were separated from nine pots of the each series. In five pots of the each series stems were also cut but roots were not separated, thus plants grew during successive 42 days under identical conditions as described above. The wet and dry (dried at 105°C) biomass of shoots and roots was measured after six and twelve weeks of vegetative growth. The results obtained were used for calculation of mean values of variables characterizing plant growth in the experimental series (arithmetical mean values). The significance of differences between mean values was assessed by t-Student test or v Aspin-Welch's test at confidence coefficient p=0.95 [29]-[31].

TABLE III
MEDIA SERIES IN POT EXPERIMENT

Series[a]	S	S+5.5	S+6.0	S+6.5	S+7.0	S+7.5	S+8.0
Sand amount [cm^3, g]	300 531.12	294 520.50	294 520.50	294 520.50	294 520.50	294 520.50	294 520.50
Fertilizer amount [cm^3, g]	-	6 4.33	6 4.39	6 4.30	6 4.26	6 4.30	6 4.02
Number of pots	14	14	14	14	14	14	14

[a]S - the control series (sand); S+5.5 - the mixture of sand and addition of the substrate containing monoionic forms equilibrated with solution at pH=5.5; S+6.0 - the mixture of sand and addition of the substrate containing monoionic forms equilibrated with solution at pH=6.0; S+6.5 - the mixture of

sand and addition of the substrate containing monoionic forms equilibrated with solution at pH=6.5; S+7.0 - the mixture of sand and addition of the substrate containing monoionic forms equilibrated with solution at pH=7.0; S+7.5 - the mixture of sand and addition of the substrate containing monoionic forms equilibrated with solution at pH=7.5; S+8.0 - the mixture of sand and addition of the substrate containing monoionic forms equilibrated with solution at pH=8.0

III. RESULTS AND DISCUSSION

The study results obtained after six weeks of vegetative growth are presented in Table IV. The addition of all variants of ion exchange substrate to sand affected the vegetation cycle of orchard grass advantageously increasing values of vegetative parameters significantly. Specifically, wet stem biomass obtained on sand with fertilizer additions was greater than that in the control series almost or over twenty times (the exception was series S+8.0, wherein wet stem biomass was eight times as great as that in the control S). As a rule, dry stem biomass of plants growing on sand enriched with additions of substrate variants exceeded that on sand alone by more than 1000% (with the exception of series S+8.0, wherein considered variable was higher by 400% as opposed to the series S). Wet root biomass obtained in series: S+5.5; S+6.0; S+6.5; S+7.0; S+7.5 and S+8.0 was greater than that obtained in the control series by six, six and half, seven and half, more than seven, almost seven and more than three and half times, respectively. Dry root biomass in fertilized series was in most cases almost or more than six times higher than that obtained on sand only medium (this trend was not observed for series S+8.0, wherein considered variable exceeded that obtained in series S three and half times).

Among all media series supplemented with addition of ion exchange substrate the lowest values of vegetative variables were observed in series S+8.0 (Table IV). Thus, wet and dry stem and root biomass of orchard grass growing on sand enriched with addition of the substrate at 8.0 was significantly lower than those obtained on other fertilized media. Wet and dry stem and root biomass in series: S+5.5; S+6.0; S+6.5; S+7.0; S+7.5 exceeded in most cases those in series with addition of the substrate at pH=8.0 by 150% and more than 50%, respectively. Such results can be explained by abundance of substrate variant at pH=8. In fact, the substrate at pH=8 contained less macronutrients than other variants of ion exchange substrate (Table II).

The addition of the substrate at pH=6.5 to sand caused the highest increases in values of vegetative parameters (Table IV). Wet and dry stem and root biomass of orchard grass growing on sand supplemented with substrate at pH=6.5 were significantly higher than those obtained in series: S+5.5, S+6.0 and S+8.0. At the same time values of these variables did not differ significantly as opposed to values obtained in series S+7.0 (and in series S+7.5 regarding wet and dry root biomass).

TABLE IV
MEAN VALUES OF VEGETATIVE PARAMETERS IN SERIES OF POT EXPERIMENT AFTER SIX WEEKS OF VEGETATIVE GROWTH [G PER POT]

Series	Wet stem biomass	Dry stem biomass	Wet root biomass	Dry root biomass
S	0.298 ± 0.021[f]	0.074 ± 0.008[f]	0.899 ± 0.120[f]	0.122 ± 0.020[f]
S+5.5	5.869 ± 0.290[af]	0.918 ± 0.081[af]	5.477 ± 0.371[af]	0.687 ± 0.042[af]
S+6.0	5.381 ± 0.310[abf]	0.867 ± 0.059[bf]	5.768 ± 0.507[bf]	0.700 ± 0.064[bf]
S+6.5	6.313 ± 0.551[abcf]	1.000 ± 0.093[bcf]	6.790 ± 0.619[abcf]	0.864 ± 0.070[abcf]
S+7.0	5.998 ± 0.482[bdf]	0.926 ± 0.011[df]	6.562 ± 0.558[abdf]	0.820 ± 0.091[abdf]
S+7.5	6.050 ± 0.334[bef]	0.964 ± 0.005[bef]	6.138 ± 0.440[acef]	0.781 ± 0.075[abcef]
S+8.0	2.383 ± 0.249[abcdef]	0.382 ± 0.04[abcdef]	3.389 ± 0.446[abcdef]	0.443 ± 0.059[abcdef]

Names of series are the same as under Table III; ± - a standard deviation;
[a] - significant differences between series S+5.5 and other series;
[b] - significant differences between series S+6.0 and other series;
[c] - significant differences between series S+6.5 and other series;
[d] - significant differences between series S+7.0 and other series;
[e] - significant differences between series S+7.5 and series S+8.0;
[f] - significant differences between series S and other series; the results followed by the same letters are statistically different

The study results obtained after twelve weeks of vegetative growth are presented in Table V. The additions of substrate variants in successive 42 days of vegetative growth affected plant development advantageously increasing values of vegetative parameters. Wet stem biomass of orchard grass growing on sand enriched with fertilizer additions exceeded that obtained in the control by more than 1000% (with the exception of series S+8.0 wherein wet stem biomass was higher by 550% than that in S series). Dry stem biomass in fertilized series was 7-9 times greater than that obtained on sand alone (the exception was series S+8.0 wherein the analyzed parameter exceeded by 270% that obtained in the control series). Wet root biomass of orchard grass on sand supplemented with fertilizer additions was almost or more than four times higher than that attributed to sand alone (this tendency was not observed for series S+8.0 wherein wet root biomass was almost three times as great as that on sand-only control). Dry root biomass of plants growing in series: S+5.5; S+6.0; S+6.5; S+7.0; S+7.5 was grater than that in control series by almost six, five and half, over five and almost five times, respectively. Regarding series S+8.0, dry root biomass was higher by 226% as opposed to the control.

TABLE V
MEAN VALUES OF VEGETATIVE PARAMETERS IN SERIES OF POT EXPERIMENT AFTER TWELVE WEEKS OF VEGETATIVE GROWTH [G PER POT]

Series	Wet stem biomass	Dry stem biomass	Wet root biomass	Dry root biomass
S	0.496 ±0.035[f]	0.133± 0.010[f]	1.682± 0.146[f]	0.192± 0.013[f]
S+5.5	7.332± 0.523[af]	1.246± 0.086[af]	7.574± 0.193[af]	1.114± 0.059[af]
S+6.0	6.468± 0.154[abf]	1.07± 0.044[abf]	7.872± 0.776[bf]	1.066± 0.088[bf]
S+6.5	7.376± 0.455[bcf]	1.11± 0.070[acf]	7.618± 0.247[cf]	1.018± 0.068[acf]
S+7.0	7.312± 0.871[bdf]	1.122± 0.121[df]	6.266± 0.656[abcdf]	0.968± 0.084[adf]
S+7.5	6.382± 0.571[acef]	0.936± 0.935[abcdef]	6.997± 0.521[acef]	0.935± 0.104[aef]
S+8.0	3.188± 0.204[abcdef]	0.492± 0.034[abcdef]	4.726± 0.261[abcdef]	0.626± 0.038[abcdef]

Explanations are the same as under Table IV

Similarly to the case of vegetative period of six weeks, among all media series supplemented with addition of ion exchange substrate, the lowest values of vegetative variables were observed in series S+8.0. Wet and dry stem and root biomass of orchard grass growing on sand enriched with substrate at pH=8.0 were significantly lower than those obtained in other fertilized series. Wet and dry stem and root biomass in series: S+5.5; S+6.0; S+6.5; S+7.0; S+7.5, exceeded in most cases those in series S+8.0 by 100% and more than 50%, respectively.

Analysis of vegetative variables attributed to fertilized series showed that wet stem and root biomass of orchard grass growing on sand enriched with the substrate at pH=5.5 did not differ significantly from those obtained in series: S+6.5; S+7.0 and S+6.0; S+6.5, respectively. At the same time, series S+5.5 was characterized by the greatest dry stem and root biomass of plants. These vegetative variables were significantly higher than those obtained in almost all series where sand was supplemented with other substrate variants.

The increase in yield of orchard grass observed for series S+5.5; S+6.0; S+6.5; S+7.0; S+7.5 (after six weeks of vegetative growth) was higher than that in the previous studies using the same amounts of substrates prepared as mixtures of monoionic forms. Soldatov et al. [32] showed that the 2% addition of Biona-111(mono) caused a two-fold increase in wet stem biomass and one and half-fold increase in dry stem biomass of D. glomerata L. Chomczyńska and Pawłowski [33] found for orchard grass 7-fold increase in wet stem biomass, 5.5-fold increase in dry stem biomass and 4-fold increase in dry root biomass after application of Mp substrate (the mixture of monoionic forms prepared of spent ion exchangers) to sand. The differences in increases of plant biomass observed in the present experiment and those in previous studies could result from different amounts of macronutrients in ion exchange substrates, varied fertility of control media (contents of nutrients in sand) as well as from different experimental conditions (e.g. air temperature).

IV. CONCLUSIONS

The results obtained allowed the following conclusions to be formulated:

- The ion exchange substrates prepared on the basis of monoionic forms equilibrated with solutions at pH in the range 5.5÷8.0 were efficient fertilizers significantly increasing plant biomass after 42 days as well as 84 days of vegetative growth.
- Regarding that there were rather small differences between plant biomass for series: S+5.5; S+6.0; S+6.5; S+7.0; S+7.5 (however some of them were statistically significant), it can be supposed that eventual pH changes of soil solution being in the contact with the substrate

variants were similar and lay in the range of the plant tolerance.

- Among tested substrate variants, the ion exchange substrate at pH=8.0 caused the lowest increase in values of vegetative variables of orchard grass that could result from its richness in nutrients and its impact on pH of soil solution.
- The addition of ion exchange substrate at pH=6.5 to sand was associated with the highest yield of *Dactylis glomerata* L. after shorter vegetation period lasting six weeks.
- The substrate containing monoionic forms equilibrated with solutions at pH=5.5 caused the highest increases in dry stem and root biomass of orchard grass (variables characterizing fertilizer efficiency the best and important from restoration point of view) after longer vegetation period lasting 12 weeks.
- The ion exchange substrate at pH=6.5 can be recommended for biological restoration of exhausted, nutrient-poor soils when shorter vegetation period is planned; the ion exchange substrate at pH=5.5 can be used for the same purpose when longer periods of vegetative growth are considered.
- The study results confirm that ion exchange substrates can replace humic compounds in their function of delivering nutrient ions to plants

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