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Mariola CHOMCZYŃSKA[1], Vladimir SOLDATOV[1] and Henryk WASĄG[1]

EFFECT OF DIFFERENT VARIANTS OF THE ION EXCHANGE SUBSTRATE ON VEGETATION OF *Dactylis glomerata* L ON THE DEGRADED SOIL

WPŁYW RÓŻNYCH WARIANTÓW SUBSTRATU JONITOWEGO WPROWADZONYCH DO ZDEGRADOWANEJ GLEBY NA PRZEBIEG WEGETACJI *Dactylis glomerata* L

Abstract: Ion exchange substrates are the mixtures of cation and anion exchangers saturated with nutrient ions in the proper ratios. After introducing into degraded soil, the substrates may act as a source of macro- and micronutrients initiating plant growth that is necessary for biological restoration. In order to determine an effect of different variants of ion exchange substrate (with a different potential impact on pH of soil solution) on plant vegetation, a pot experiment with orchard grass (*Dactylis glomerata* L) as the test species was carried out. For the need of the study seven series of media were prepared: the control series (sand as a model of degraded soil) and six test series - the mixtures of sand and 2% (v/v) additions of particular variants of ion exchange substrate (each variant contained monoionic forms differing in the content of NO_3^-, $H_2PO_4^-$, SO_4^{2-} thereby, differing in the pH of solutions equilibrated with them). The study results showed that additions of the substrate at pH = 5.5; pH = 6.0; pH = 6.5; pH = 7.0 and pH = 7.5 to sand significantly increased plant yield. The 2% addition of the substrate at pH = 6.5 caused the highest increase in wet and dry stem and root biomass, however mean values of the vegetation parameters obtained in the series with the substrate at pH = 6.5 were not significantly higher than parameters obtained in the series with the substrates at pH = 7.0 and 7.5. In the light of study results, it can be said that particular variants of substrate at pH in the range of 5.5÷7.5 are effective fertilizers intensifying plant growth during relatively short period.

Keywords: ion exchange substrate, soil restoration, cation exchangers, anion exchangers

Degraded areas constitute a significant problem in environmental engineering. These territories are characterized by different devastation degree and require technical and biological reclamation. Biological reclamation involves intensive cultivation of humus--productive plant mixtures. Initialization of cultivation of the mixtures mentioned requires the application of agrotechnical procedures such as i.a. mineral fertilization or introduction into recultivated soil enriched materials of organic, organic-mineral and mineral character [1]. Mineral fertilization which is recommended in biological reclamation can be realized by addition to ground synthetic ion exchangers saturated with biogenic ions. These materials can play a role of a rich source of macro- and micronutrients for plants. Moreover, they are able, to some extent, to prevent nutrient leaching from ground of weak sorption properties, which is of importance in the protection of waters from eutrophication.

The research conducted until now has proved the possibility of applying, prepared on the basis of ion exchange resins, the so-called ion exchange substrates as fertilizer add-ons [2]. In fact, they are the mixtures of cation and anion exchangers saturated in relevant proportions with macro- and micronutrient ions [3]. Owing to high exchange capacity of ionites the nutrient contents in substrates can be tenfold higher than in the best natural soils. Preparation of ion exchange substrate is based on providing the mixture of cation and anion

[1] Faculty of Environmental Engineering, Lublin University of Technology, ul. Nadbystrzycka 40B, 20-618 Lublin, tel. 81 538 44 04, email: m.chomczynska@wis.pol.lublin.pl

exchangers with the ionic composition that assures the availability of biogenic elements to the same degree as in hydroponic nutrient solution [4, 5]. In fact, there are three basic methods for preparing the ion exchange substrate: a dynamic, static and a method of monoionic forms [5]. In the dynamic method the preparation of ion exchange substrate consists in passing the selected nutrient solution through a mixture of cation and anion exchangers placed in a column by the time an ion exchange equilibrium is achieved. The equilibrium state is set at the moment when the concentrations of biogenic ions in the effluent from the column are the same as in the solution that enters the column. Obtaining ion exchange substrate by a static method is connected with the saturation of resins with biogenic ions originating from the mixtures of reagents dissolved in water. Depending on whether the cation and anion exchangers are saturated together (salt variant of the method) or separately (acid-base variant of the method) the mixtures can contain only salts, only acids or only hydroxides. The preparation of substrate by static methods must be preceded by obtaining the sample of substrate in dynamic conditions. In the sample, ion contents of biogenic elements are determined and subsequently the quantitative proportions between them are calculated. These ratios are necessary to ensure appropriate proportions between ions in the substrate prepared in static conditions. As far as the static method is concerned, in order for the prepared substrate to have a proper ionic composition, the quantitative proportions between contained ions must correspond to the proportions that occurred in the substrate sample obtained in dynamic conditions, that is a sample remaining in the state of equilibrium with nutrient solution. 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 element 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 are 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 biogenic ions content. 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 utilization 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 polyfunctional anion exchanger in such a way that eventual pH changes of soil solution being in the contact with the substrate, correspond to physiological requirements of the plants. In the light of the above-mentioned information it can be expected that various variants of ion exchange substrates are able to modify the reaction of soil solution. Thus, the aim of the presented research was to verify the influence of consequent variants of ion exchange substrate, potentially differently affecting the pH of the soil solution, on the plant vegetation process.

Materials and methods

In the study sand, ion exchange resins of the KU-2 (strong acid cation exchanger) and EDE -10P (polifunctional anion exchanger) types were used. The sand was used as a model of degraded soil. It came from sand mine in Golab near Pulawy. The pH value of its water extract was 5.77.

The total ion exchange capacity of resins was 5 mval g^{-1} for cation exchanger and 11 mval g^{-1} for anion exchanger, respectively. Three monoionic forms: calcium, magnesium and potassium forms were prepared on the basis of cation exchanger. Anion exchanger was used for preparing six variants of nitrate, phosphate and sulphate forms differing in the pH of solutions equilibrated with them.

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. The variants differed in pH values of solutions equilibrated with particular monoionic forms.

In order to determine ratios between the monoionic forms in particular variants of ion exchange substrate, small amounts of cation and anion exchanger (3 g) have been saturated with nutrient solution (salt concentration about 1.65 g dm^{-3}) in dynamic conditions until equilibrium state was achieved. Ratios, between ions found in ion exchangers in equilibrium state, were used to calculate amounts of monoionic forms used for preparation of mass unit of particular substrate variant.

Table 1

Media series in vegetative experiment

Series	S	S+5.5	S+6.0	S+6.5	S+7.0	S+7.5	S+8.0
Sand amount [cm^3]	300	294	294	294	294	294	294
Fertilizer amount [cm^3]	-	6	6	6	6	6	6
Number of pots	9	9	9	9	9	9	9

Explanations: 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

The substrate variants were evaluated in a vegetation 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 1). 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 13/12 h light/dark. 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. When the experiment was terminated, the aboveground shoots of plants were cut down and roots were separated. The wet and dry (dried at 105°C) biomass of shoots and roots was measured. The results obtained were used for calculation of mean values of variables characterizing plant growth in 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 [6-8].

Results and discussion

The study results are presented in Table 2. 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 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 in the control series by six, six and half, seven and half, over seven, almost seven and over three and half times, respectively. As a rule, dry stem biomass of plants growing on sand enriched with additions of substrate variants exceeded that on sand alone by over 1000% (with the exception of series S+8.0, wherein considered variable was higher by 400% as opposed to the series S).

Table 2

Mean values of vegetative parameters in series of pot experiment [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}

Explanations: 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; ± - a standard deviation; a - significant differences between series S+5.5 and the rest of series; b - significant differences between series S+6.0 and the rest of series; c - significant differences between series S+6.5 and the rest of series; d - significant differences between series S+7.0 and the rest of series; e - significant differences between series S+7.5 and series S+8.0; f - significant differences between series S and the rest of series; the results followed by the same letters are statistically different

Wet root biomass obtained on sand with fertiliser additions was greater than that obtained in the control series almost or over twenty times (again the exception was series S+8.0, wherein wet root biomass was eight times as great as that in the control S). Dry root biomass in fertilized series was in most cases almost or over 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 2). 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 over 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 3).

The addition of substrate at pH = 6.5 to sand caused the highest increases in values of vegetative parameters (Table 2). 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 3

Content of ions in different variants of ion-exchange substrate [mval per 100 g]

Substrate	NO_3^-	$H_2PO_4^-$	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+
At 5.5	64.99	23.64	108.31	183.86	32.98	18.84
At 6.0	64.58	23.49	107.63	182.69	32.80	18.71
At 6.5	63.60	23.12	106.01	179.98	32.30	18.45
At 7.0	62.37	22.67	103.94	176.44	31.64	18.09
At 7.5	60.12	21.86	100.21	170.09	30.52	17.46
At 8.0	48.12	14.50	80.21	136.16	24.45	13.97

Summary and 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÷7.5 significantly increased plant biomass after introducing into sand.

Among tested substrate variants, ion exchange substrate at pH = 8.0 caused the lowest increase in biomass of orchard grass; the addition of ion exchange substrate at pH = 6.5 to sand was associated with the highest yield of *Dactylis glomerata* L.

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 said that particular variants of substrate at pH in the range of 5.5÷7.5 are effective fertilizers intensifying plant growth during the observed six weeks of vegetation period.

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WPŁYW RÓŻNYCH WARIANTÓW SUBSTRATU JONITOWEGO WPROWADZONYCH DO ZDEGRADOWANEJ GLEBY NA PRZEBIEG WEGETACJI *Dactylis glomerata* L

Wydział Inżynierii Środowiska, Politechnika Lubelska

Abstrakt: Substraty jonitowe są mieszaninami kationitów i anionitów nasyconych w stosownych proporcjach jonami pierwiastków odżywczych. Materiały te po wprowadzeniu do gleby zdegradowanej mogą pełnić rolę bogatego źródła makro- i mikroelementów, inicjującego rozwój pokrywy roślinnej niezbędnej w czasie biologicznej rekultywacji. Aby określić wpływ różnych wariantów substratu (o potencjalnie różnym oddziaływaniu na pH roztworu glebowego) na przebieg wegetacji roślin, przeprowadzono doświadczenie wazonowe z kupkówką pospolitą (*Dactylis glomerata* L) jako gatunkiem testowym. Na potrzeby tego eksperymentu przygotowano siedem serii podłoży: jedną serię kontrolną (piasek jako model gleby zdegradowanej) oraz sześć serii testowych będących mieszaninami piasku i 2% (objętościowo) dodatków poszczególnych wariantów substratu jonitowego (każdy wariant zawierał formy monojonowe różniące się zawartością anionów: NO_3^-, $H_2PO_4^-$, SO_4^{2-} i tym samym różniące się wartościami pH roztworów pozostających z nimi w równowadze jonowymiennej). Rezultaty przeprowadzonego eksperymentu wykazały, że dodatki substratu o pH = 5,5; pH = 6,0; pH = 6,5; pH = 7,0 i pH = 7,5 po wprowadzeniu do piasku znacznie zwiększyły plon roślin. Dodatek substratu o pH = 6,5 spowodował największe przyrosty świeżej i suchej biomasy pędów oraz korzeni kupkówki, aczkolwiek średnie wartości parametrów wegetacyjnych uzyskane w serii z tym substratem nie były istotnie większe od wartości parametrów uzyskanych w serii z dodatkiem substratu o pH = 7,0 i 7,5. W świetle otrzymanych wyników należy stwierdzić, iż poszczególne warianty substratu o pH w zakresie 5,5÷7,5 są skutecznymi dodatkami nawozowymi intensyfikującymi rozwój roślin w stosunkowo krótkim okresie czasu.

Słowa kluczowe: substraty jonitowe, rekultywacja gleb, kationit, anionit