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PHYTOSTABILISATION OF TAILING PONDS WITH USE OF WATER ABSORBING GEOCOMPOSITES AND ORGANIC AND MINERAL ADDITIVES

The effectiveness of reclamation activities in a tailing pond has been evaluated by the application of mineral and organic substances and remediation plants with water absorbing geocomposites. The research was conducted on the tailing pond of the former copper mine in Iwiny, Poland, basing on a strict, trifactorial experiment set up with the use of the split-split-plot method with 4 replications. The main experimental factors were the variants of substrate modification, various species (or mixtures) of reclamation plants and the presence of water absorbing geocomposites. The conducted experiments did not demonstrate a significant influence of various types of tailing additives. The usability of individual species of reclamation grass or their mixtures for the reclamation was similar. Water absorbing geocomposites contributed to the improvement of difficult vegetation conditions that occur in tailing ponds.

1. INTRODUCTION

Copper deposits located near Iwiny village, in the North-Sudetic Basin (Poland), in the so-called Old Copper Basin were mined for nearly 40 years, until 1988. Due to the used excavation technology, the mining of the deposit led to numerous adverse changes to the environment. The excavated ore, containing 1–2% of copper, was crushed and ground and then transported to the flotation machinery. As a result, 30 million m³ of tailings were generated and then were stored in open-air tailing ponds. Because of their physical and chemical properties, these ponds are difficult to reclaim [1]. The copper deposits contaminate plants in adjacent areas and ground waters with heavy metals which may pose a direct risk to human health. The sediments are characterised

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by a high pH reaction, very low content of skeletal fraction and organic matter, very high concentration of heavy metals and low biological activity [2]. The improvement of physical and chemical parameters of the sediments, and as a consequence phytoremediation *in situ*, may be achieved by the addition of mineral and organic matter such as marble waste, sewage sludge, marble mud, pumice, sand and others [3–6]. Particularly valuable materials are those that can improve, apart from the physical properties, also the chemical and biological parameters. They are, among others, straw, woodchips, biochar or pig slurry. Desirable features of remediation plants are as follows: tolerance to high content of heavy metals in tailings and the ability to their accumulation, the resistance to stress factors such as salinity, acidity, nutrient deficiencies [7]. Moreover they bring some extra benefits, for instance, fast growth and the high production of biomass [8]. Grasses, particularly those with C4 photosynthesis pathway, are considered to be species useful for reclamation especially during its initial phase because of their high tolerance to adverse conditions as well as the ability to quick production of organic matter [9].

The dominant percentage of <0.06 mm fraction in flotation sediments results in rainfall retention which makes it inaccessible for plants. The adverse water conditions may be improved by applying various types of absorbents (hydrophilic polymers, HPs, hydrogels, agrogels, or superabsorbents – SAPs). They are hydrophilic, loosely cross-linked polymers capable of absorbing large amounts of water, with an actual absorbing capacity of ca. 600 g·g⁻¹ [10, 11]. By reason of the difference in the osmotic potential between the superabsorbent and plant roots, water is easily accessible for plants [12]. Apart from improving the water properties, hydrogels may be used as fertilizer carriers and also contribute to the improvement of physical and chemical properties of soil [10, 13, 14]. They are available in the form of granules, powder or fibres which may be mixed with soil. The disadvantage of this application method is the restriction of the swelling ability of the hydrogel during water absorption. Superabsorbents used as water absorbing geocomposites turn out to be much more efficient and modern method to apply. Geocomposites consist of a skeletal synthetic polymer structure, where the superabsorbent (SAP) is placed. Loose hydrogel placement enables it to swell freely preventing the skeleton from being crushed by the soil which covers the top. An important element of geocomposites is the non-woven geotextile fabric which surrounds and protects the geocomposite and at the same time allowing the water to flow through and the roots to penetrate into the hydrogel [15].

2. MATERIALS AND METHODS

The experiment was carried out in the summer of 2010 in the tailing pond of the former “Konrad” copper mine in Iwiny (51°13'10.5"N 15°39'45.2"E). The main part of the research was conducted as a strict, tri-factorial experiment in the years 2011–2013.

The experiment was designed as split-split-plot method in 4 replications. 96 field plots, each of them of the area of 2 m², were established.

Characteristics of the “Wartowice” tailing pond. “Wartowice” tailing pond, of the area of 232 ha, located near Iwiny village in the south-west of Poland, was filled with flotation waste from the Ore Processing Department “Konrad” in the years 1971–1988. No reclamation has been conducted there since that time. It was only the subject to natural plant succession. On the border areas, only birch, pine and moss did appear but in the central part, which often contained stagnated rainfall, the reed occurred. The particular size distribution is very adverse for the plants growth. The sediment is a dusty-silty formation, with a marginal addition of sandy fraction and completely lack of skeletal fractions. The dominant compounds are CaO, SiO₂, Al₂O₃, MgO, and K₂O [16]. pH of the sediment ranges from 7.5 to 8.0. High concentration of calcium and potassium negatively affects the uptake of phosphorus by plants. Another growth limiting factor is the low nitrogen content (Table 1).

Table 1

Selected properties of the unamended mine tailings

pH water	Total N (g·kg ⁻¹)	P	K	Mg	Total extractable metals (mg·kg ⁻¹)		Texture
		(mg·kg ⁻¹)			Cu	Pb	
8.0	0.41	5.1	298	350	850	300	clay-loam

Description of the experiment. The main experimental factors were the variants of substrate modification. The control treatment was the unmodified sediment. As the second variant, the sediment mixed with willow woodchips (40 mm overburden) was applied, as the third one, the sediment with sandy gravel (40 mm overburden) and as the fourth one, the sediment with the mixture of sandy gravel and woodchips (20 mm each). All the soil additives were dug up manually to the depth of 20 cm, and then mixed with a tiller. Each plot contained 16.7 vol. % of mine tailings additives.

The second experimental factor was various species (or mixtures) of reclamation plants. The plots were sown with: 1) reed canary grass (*Phalaris arundinacea* L., 7 g·m⁻²) with the mixture of grasses³ (16 g·m⁻²), 2) switchgrass (*Panicum virgatum* L., 9 g·m⁻², 3) reed canary grass (*Phalaris arundinacea* L., 2.5 g·m⁻²) with switchgrass (*Panicum virgatum* L., 2.5 g·m⁻², and the mixture of grasses (11 g·m⁻², see footnote).

The third factor was the presence of water absorbing geocomposites developed at Wrocław University of Environmental and Life Sciences (Fig. 1). The blocks of the

³Westerwold ryegrass *Lolium multiflorum* Lam. var. *westerwoldicum* 20%, Common bentgrass *Agrostis capillaris* L. 20%, Perennial ryegrass *Lolium perenne* L. 20%, Red fescue *Festuca rubra* L. 20%, Birds-foot trefoil *Lotus corniculatus* L. 10%, Crownvetch *Coronilla varia* L. 10%.

dimensions $74 \times 5.5 \times 9$ cm were placed at the depth of 22 cm and covered with a layer of the sediment.

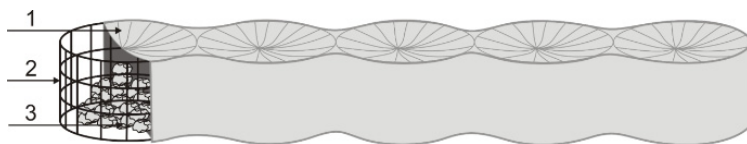


Fig. 1. Construction of water absorbing geocomposite:
1 – nonwoven geotextile, 2 – internal skeleton, 3 – superabsorbent

Before harvest, crops were sampled, from the area of 0.25 m^2 of each plot. Yields of fresh above-ground matter were determined immediately, then the samples were dried up at $105 \text{ }^\circ\text{C}$ for 24 h, and weighted again. Dried plants were milled by using a special plant mill (Retsch SM-1, Haan, Germany). Each sample (0.25 g) was digested with 6 cm^3 of HCl , 2 cm^3 of HNO_3 , and 2 cm^3 of H_2O (aqua regia) in a microwave digestion system (MARS 6 microwave digestion system, CEM Corporation, Matthews, USA) for 30 min and finally diluted to 25 cm^3 with deionized water. The total content of heavy metals was determined by the absorption astrometry method, in the atomic absorption Philips spectrometer AAnalyst 200 (PerkinElmer, Waltham, Massachusetts, USA). Combustion heat was determined with the use of a bomb calorimeter KL-12 (Precyzja-Bit, Bydgoszcz, Poland). Test results were subjected to variance analysis. Statistical calculations were carried out using three-way analysis of variance with the use of the Tukey's test at the confidence level $\alpha = 0.05$.

3. RESULTS AND DISCUSSION

The fresh above-ground matter of reclamation plants was closely correlated only with their species and with the presence of water absorbing geocomposites (Table 2). Significantly the highest crops of fresh weight (on average $0.71 \text{ kg} \cdot \text{m}^{-2}$) were obtained where switchgrass (S) was grown. Both mixtures (RCG + MM and RCG + S + MM) yielded in a similar way (average $0.56 \text{ kg} \cdot \text{m}^{-2}$), which was 26.9% lower than switchgrass.

The tests demonstrated a positive influence of geocomposites on the growth conditions of the reclamation plants. The introduction of superabsorbent to the soil increased fresh weight by 12.2% in comparison with the variant without geocomposites. The effectiveness of superabsorbents which manifests itself in higher crops of fresh weight was proven by Islam et al. [17], and for the remediation of post-mining sediments, also by de Varennes et al. [18].

The differences in the crops of fresh biomass, although not confirmed statistically, were also caused by implementing various additives to the sediment. The highest crop

($0.72 \text{ kg}\cdot\text{m}^{-2}$) was obtained when 100% organic material was added, i.e., woodchips, while the lowest ($0.54 \text{ kg}\cdot\text{m}^{-2}$) when wood shavings and also when only the sandy gravel ($0.57 \text{ kg}\cdot\text{m}^{-2}$) were added. Also the studies by Kordas and Tasz [19] did not demonstrate the influence of additives to tailing sediments on the volume of crops of reclamation plants, either.

Table 2

Fresh above-ground matter of reclamation plants [$\text{kg}\cdot\text{m}^{-2}$] (means for 2011–2013)

Geocomposites	Reclamation plants	Mine tailings amendments					Mean
		None	Crop willow chips	Rock aggregate	Aggregate and wood chips	Mean	
Yes	RCG + MM	0.62	0.75	0.55	0.54	0.62	0.64 A ^{III}
	S	0.70	0.88	0.62	0.73	0.73	
	RCG + S + MM	0.58	0.68	0.48	0.58	0.58	
	Mean	0.63	0.77	0.55	0.62	–	
No	RCG + MM	0.54	0.61	0.54	0.36	0.51	0.57 B ^{III}
	S	0.66	0.76	0.71	0.63	0.69	
	RCG + S + MM	0.50	0.66	0.52	0.39	0.52	
	Mean	0.57	0.68	0.59	0.46	–	
Mean	RCG + MM	0.58	0.68	0.55	0.45	0.57 A ^{II}	–
	S	0.68	0.82	0.67	0.68	0.71 B ^{II}	
	RCG + S + MM	0.54	0.67	0.50	0.49	0.55 A ^{II}	
Mean		0.60	0.72	0.57	0.54	–	

RCG – reed canary grass, MM – meadow mixture, S – switchgrass.

Means followed by the same letters in the columns are significantly different at $\alpha \leq 0.05$. Not marked values do not differ significantly from each other at $\alpha \leq 0.05$. Uppercase letters indicate differences among factors of experiment. The lowercase letters indicate differences among interactions. I – additives for tailings, II – reclamation plants, III – geocomposites.

As in the case of fresh matter similar correlations were also noted for dry matter of reclamation plants (Table 3). Dry matter was significantly correlated with the applied species or their mixtures and with the presence of geocomposites. The highest crops of dry matter were obtained in plots where switchgrass was grown. They were 22.7% higher than the values obtained after sowing reed canary grass with meadowgrass mixture (RCG + MM) and even 28.6% higher than those from the plots sown with the reed canary grass + switchgrass + meadowgrass mixture (RCG + S + MM). The placement of geocomposites in the sediment resulted in a 13.7% increase in the crops, in comparison with the results obtained on sediment without the addition of superabsorbent. The positive effect of geocomposites defined at Wrocław University of Environmental and Life Sciences on the above-ground dry matter of plants was also demonstrated by Lejcuś et al. [20].

The effect of substrate additives on the yield of reclamation plants dry matter was not shown but the outcome indicates that the willow woodchips provided the most optimal conditions.

Table 3

Dry above-ground matter of reclamation plants [$\text{kg DM}\cdot\text{m}^{-2}$] (means for 2011–2013)

Geocomposites	Reclamation plants	Mine tailings amendments					Mean
		None	Crop willow chips	Rock aggregate	Aggregate and wood chips	Mean	
Yes	RCG + MM	0.23	0.29	0.22	0.20	0.24	0.25 A ^{III}
	S	0.24	0.32	0.25	0.28	0.27	
	RCG + S + MM	0.23	0.26	0.19	0.23	0.23	
	Mean	0.23	0.29	0.22	0.24	–	
No	RCG + MM	0.20	0.24	0.20	0.18	0.21	0.22 B ^{III}
	S	0.26	0.28	0.26	0.24	0.26	
	RCG + S + MM	0.20	0.22	0.20	0.15	0.19	
	Mean	0.22	0.25	0.22	0.19	–	
Mean	RCG + MM	0.22	0.27	0.21	0.19	0.22 A ^{II}	–
	S	0.25	0.30	0.26	0.26	0.27 B ^{II}	
	RCG + S + MM	0.22	0.24	0.20	0.19	0.21 A ^{II}	
Mean		0.23	0.27	0.22	0.21	–	

RCG – reed canary grass, MM – meadow mixture, S – switchgrass.

Means followed by the same letters in the columns are significantly different at $\alpha \leq 0.05$. Not marked values do not differ significantly from each other at $\alpha \leq 0.05$. Uppercase letters indicate differences among factors of experiment. The lowercase letters indicate differences among interactions. I – additives for tailings, II – reclamation plants, III – geocomposites.

One of the most important energetic properties of biomass is its calorific value. It depends on several factors. The most important of which are ash and moisture content. In this study, the results are lower, on average by $2.5 \text{ MJ}\cdot\text{kg}^{-1} \text{ DM}$ than the typical values from grass grown in arable land (Table 4) [21]. The conducted experiment demonstrated a significant influence of tailing additives on the calorific value of reclamation plants. The highest calorific value was noted for biomass from facilities reclaimed by adding sandy gravel and a mixture of sandy gravel with wood shavings. It was higher by 4.5% than the value from substrate without any additives. No significant differences were found in the calorific value between individual species or mixture of reclamation plants, nor depending on the presence of geocomposites. The calorific value of reclamation plants also depended on the interactions between the substrate additive and the species of grass of their mixtures. After the application of woodchips, significantly the lowest calorific value was obtained after sowing a mixture of reed canary grass + switchgrass + meadowgrass mixture (RCG + S + MM).

Considerable fluctuations in the amount of lead uptake by reclamation plants were noticed in the research. The study performed by Sreedhar [22] on the reclamation of tailing ponds of a uranium mine also demonstrated highly varied concentrations of lead and other heavy metals in the above-ground parts of plants. The lead uptake by plants was strongly correlated with the presence of geocomposites in the soil (Table 5). The presence of superabsorbent resulted in a reduction in the lead uptake from tailings by 13.4% in comparison with the variant without geocomposites. The interaction between adding organic and mineral materials to the tailings and the species of cultivated reclamation plants was also shown. The highest amount of lead was accumulated in reed canary grass mixed with switchgrass and meadowgrass mixture on a substrate with the addition of sandy gravel.

Table 4

Calorific value [$\text{MJ} \cdot \text{kg}^{-1} \text{DM}$] (means for 2011–2013)

Geocomposites	Reclamation plants	Mine tailings amendments					Mean
		None	Crop willow chips	Rock aggregate	Aggregate and wood chips	Mean	
Yes	RCG + MM	15.3	15.0	16.1	16.1	15.6	15.6
	S	15.4	15.1	16.1	16.1	15.7	
	RCG + S + MM	15.5	14.2	16.2	16.2	15.5	
	Mean	15.4	14.8	16.1	16.1	–	
No	RCG + MM	15.3	14.9	16.0	16.0	15.6	15.5
	S	15.2	14.8	15.9	15.9	15.5	
	RCG + S + MM	15.4	14.2	16.1	16.2	15.5	
	Mean	15.3	14.6	16.0	16.0	–	
Mean	RCG + MM	15.3 a ^{I/II}	15.0 b ^{I/II}	16.1 d ^{I/II}	16.1 d ^{I/II}	15.6	–
	S	15.3 a ^{I/II}	15.0 b ^{I/II}	16.0 d ^{I/II}	16.0 d ^{I/II}	15.6	
	RCG + S + MM	15.5 a ^{I/II}	14.2 c ^{I/II}	16.2 d ^{I/II}	16.2 d ^{I/II}	15.5	
Mean		15.4 B ^I	14.7 A ^I	16.1 C ^I	16.1 C ^I	–	

RCG – reed canary grass, MM – meadow mixture, S – switchgrass.

Means followed by the same letters in the columns are significantly different at $\alpha \leq 0.05$. Not marked values do not differ significantly from each other at $\alpha \leq 0.05$. Uppercase letters indicate differences among factors of experiment. The lowercase letters indicate differences among interactions. I – additives for tailings, II – reclamation plants, III – geocomposites.

On the other hand, the application of the same plant mixture, but on a substrate with the addition of sandy gravel and wood shavings had a negative influence on lead uptake. Taking into consideration the influence of additives for tailings, some differences were noticed, but they were not confirmed statistically. The implementation of sandy gravel to the tailings resulted in an increase in bioremediation by 46% in relation to the results obtained from unmodified tailings.

Table 5

Pb uptake [$\text{g}\cdot\text{ha}^{-1}$] (means for 2011–2013)

Geocomposites	Reclamation plants	Mine tailings amendments					Mean
		None	Crop willow chips	Rock aggregate	Aggregate and wood chips	Mean	
Yes	RCG + MM	9.1	17.2	16.1	12.7	13.8	12.9 A ^{III}
	S	8.3	13.4	10.5	14.1	11.6	
	RCG + S + MM	15.4	16.8	12.4	8.6	13.3	
	Mean	10.9	15.8	13.0	11.8	–	
No	RCG + MM	13.4	17.1	18.5	8.1	14.3	14.9 B ^{III}
	S	23.0	13.5	9.6	13.1	14.8	
	RCG + S + MM	10.7	14.3	30.9	6.5	15.6	
	Mean	15.7	15.0	19.7	9.2	–	
Mean	RCG + MM	11.3 acd ^{I/II}	17.2 ab ^{I/II}	17.3 ab ^{I/II}	10.4 dc ^{I/II}	14.1	–
	S	15.7 ad ^{I/II}	13.5 acd ^{I/II}	10.1 dc ^{I/II}	13.6 acd ^{I/II}	13.2	
	RCG + S + MM	13.1 acd ^{I/II}	15.6 ad ^{I/II}	21.7 b ^{I/II}	7.6 c ^{I/II}	14.5	
Mean		13.4	15.4	16.4	10.5	–	

RCG – reed canary grass, MM – meadow mixture, S – switchgrass.

Means followed by the same letters in the columns are significantly different at $\alpha \leq 0.05$. Not marked values do not differ significantly from each other at $\alpha \leq 0.05$. Uppercase letters indicate differences among factors of experiment. The lowercase letters indicate differences among interactions. I – additives for tailings, II – reclamation plants, III – geocomposites.

Table 6

Cu uptake [$\text{g}\cdot\text{ha}^{-1}$] (means for 2011–2013)

Geocomposites	Reclamation plants	Mine tailings amendments					Mean
		None	Crop willow chips	Rock aggregate	Aggregate and wood chips	Mean	
Yes	RCG + MM	40.9	53.8	56.0	43.1	48.5	45.8
	S	35.2	49.1	42.2	47.2	43.4	
	RCG + S + MM	44.9	52.2	43.9	40.8	45.5	
	Mean	40.3	51.7	47.4	43.7	–	
No	RCG + MM	52.7	54.2	49.8	41.6	49.6	46.9
	S	50.6	45.4	41.5	52.4	47.5	
	RCG + S + MM	45.9	46.4	50.5	31.4	43.6	
	Mean	49.7	48.7	47.3	41.8	–	
Mean	RCG + MM	46.8	54.0	52.9	42.4	49.0	–
	S	42.9	47.3	41.9	49.8	45.5	
	RCG + S + MM	45.4	49.3	47.2	36.1	44.5	
Mean		45.0	50.2	47.3	42.8	–	

RCG – reed canary grass, MM – meadow mixture, S – switchgrass.

Means followed by the same letters in the columns are significantly different at $\alpha \leq 0.05$. Not marked values do not differ significantly from each other at $\alpha \leq 0.05$. Uppercase letters indicate differences among factors of experiment. The lowercase letters indicate differences among interactions. I – additives for tailings, II – reclamation plants, III – geocomposites.

None of the analysed factors had a significant influence on copper uptake by plants. Neither any interaction was shown (Table 6). However, several differences were noticed, in particular for the first experimental factor, which was the implementation of mineral or organic additives to the tailings. The highest uptake was observed after adding woodchips, while the lowest one occurred after the application of a mixture of sandy gravel and wood shavings. The observed differences between the variants reached 17.3%. Geocomposites as well as the reclamation plants had a significantly lower influence on the copper uptake. The significant effect of various types of organic additives to tailings on the concentration of copper in plants was demonstrated in the study by de Coninck [23]. The uptake of this element was noticeably higher in plants that grew on substrate without any additives. The application of montmorillonite and manure in reclamation may also reduce copper uptake [24]. The similar results were also observed after adding a mixture of sand, phosphogypsum and quarry overburden [25]. Most likely, it results, from the dilution effect. Additionally, implementing organic substances to the soil reduces the accessibility of heavy metals for plants [26, 27].

4. CONCLUSIONS

Water absorbing geocomposites contributed to the improvement of difficult vegetation conditions that occurred in tailing ponds. The crops of fresh matter and dry matter of reclamation plants grown on a substrate containing superabsorbent (SAP) increased, by 12.2% and 13.7%, respectively, while plant lead uptake was decreased. No changes in the calorific value and copper uptake were noticed.

The conducted experiments did not demonstrate a significant influence of various types of substrate additives. However, there is a noticeable trend demonstrating that organic or organic and mineral additives are the most efficient in the reclamation process. Such modifications of the substrate resulted in the highest crops and in the lowest uptake of lead and copper.

The usability of individual species of reclamation grass or their mixtures for the reclamation of tailing ponds was similar. The plants did not manifest visible signs of stress or symptoms caused by the presence of heavy metals. Switchgrass crops were the highest, however, the values of the other analysed parameters remained on a similar level.

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