

Using Chemically Treated Organic Recycling Materials to Enhance Freshwater Purification

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Abstract

The greatest source of phosphorus pollution in the freshwater ecosystem is erosion from agricultural areas and point sources. Although this pollution is typically moderated by precipitation and sedimentation, biological and physicochemical methods can be used. The aim of our study was to construct an alternative prototype solution incorporating a filter bed made of suitable recycled phytogenic materials (hemp and harl flax) mixed with chemical compounds ($\text{Ca}(\text{OH})_2$, FeCl_3 , and $\text{Al}_2(\text{SO}_4)_3$) based on the results of laboratory and field experiments. An 80-90% reduction was noted for deposits with $\text{Ca}(\text{OH})_2$ and $\text{Al}_2(\text{SO}_4)_3$ compounds, and 42% for FeCl_3 during laboratory studies. The field studies did not provide such a high reduction of phosphates – only 2% for the $\text{Ca}(\text{OH})_2$ deposit and 49% for the FeCl_3 deposit. This could be attributed to variable physical parameters (pH, temperature and dissolved oxygen) and high negative correlation ($r = -0.6296$; $p = 0.003$) with nitrate reduction for the $\text{Ca}(\text{OH})_2$ deposit. However, greater reduction was noted when the phosphate concentration exceeded $1 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ in field experiments.

Keywords: phosphorus pollution, organic recycling materials, freshwater purification, dephosphorization

Introduction

The development of civilization and its accompanying anthropopressure have increased the accumulation of biogenic elements in aquatic ecosystems, which has

accelerated the eutrophication of water bodies all over the world [1-3], and by doing so increased the production of tides of toxic cyanobacteria [4-5]. There is, therefore, a need to integrate ecohydrology with engineering solutions on the catchment scale to slow the rate of eutrophication [6], with the potential to permanently decrease the content of bioavailable phosphorus in water supplies

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[7-11]. The use of phosphate retention media is one method employed to remove phosphorus pollution. Different materials and chemical compounds can be used for this purpose, for example natural materials (snail shells, tree bark, limestone), industrial by-products (fly ash, acid mine drainage residuals) and manufactured materials (including Fe, Al, and Ca salts) [12-16]. Binding phosphorus in the sediments of lakes and reservoirs is a common and easy technique to prevent algal blooms, but this solution has a high cost of use and needs large quantities of compounds [17-18]. Moreover, for the development to be sustainable, the solution requires the use of mineral fertilizers [19], which could be also made from the materials used to remove phosphorus pollution from water.

The aim of this study was to evaluate the efficiency of a new type of deposit intended for the removal of phosphorus pollution from streams and for drainage ditches to prevent algal blooms occurring in reservoirs. A prototype device was made to prepare the deposit, consisting of waste materials – harl made from hemp (*Cannabis sativa*) and flax (*Linum sp.*) – plus calcium, aluminium, and iron compounds. The produced deposits were tested at laboratory and field scales. To examine the effectiveness of the biodegraded fibrous deposits at removing phosphorus compounds from the water, the conducted study evaluates the efficiency of the chemical deposits at improving the quality of the tested water.

Materials and Methods

Technological Preparation of the Filter Bed

A prototype was constructed for the physical and chemical processing of natural fibrous raw materials (mainly agricultural waste) into biodegradable fibrous deposits. In the first processing stage, the prototype device was designed and constructed by defibrating/milling the fibrous material into a particular fraction of about 3 mm (Figs 1-2.). This stage was necessary because milling the fibrous materials involves significantly disturbing the fibrous structure. The obtained dust product forms a water-absorbent wall on the surface of the substrate, which is less absorbent than the fibrous form. In the fibrous form, appropriate defibrating/milling increases the degree of potential water absorption by up to four times, resulting in the loss of vital hydrophysical properties. This method allows for the level of defibration to be changed based on the nature of the fibrous material and its intended use. The fibrous substrate can be obtained from various materials within the unified fraction, while the dust fractions from the process are stored separately for further processing in other applications (e.g., in agrotechnics).

The present interdisciplinary study resulted in the design of an innovative method of defibrating and a new model laboratory device that can be used for experimental purposes. In this innovative method, raw material is defibrated at a low speed, which gradually increases

to maximum speed as the mass of fibrous molecules decreases. This approach ensures minimal dust in the defibrated mass, which ensures no negative impact on its desired properties. The apparatus that can be used for the preparation of the filter bed has been registered with the Polish Patent Office under No. P.401776. It needs to be stated that the process of wet defibration followed by desiccation is not a competitive option in the pulp and paper industry because of its particularly high energy consumption, which makes the process a few times more expensive.

The second preparation stage was the impregnation of defibrated fibrous material with calcium, aluminium, and iron compounds in their colloidal form. These compounds are inexpensive, easily available, and readily form insoluble compounds with phosphorus.

The use of a colloidal form of metal compounds in preparing the deposit is a modern method that has been made possible by the use of an appropriate fibrous structure. This structure allows for the formation and monitoring of hydrophysical properties that determine the permeability of the deposit and the effective “confinement” of the colloidal form of the metal compounds within it. A prototype chemical device was used to ensure the even mixing of fibrous material with appropriate phosphorus-binding chemical compounds (Fig. 3).

After the impregnation process, the prepared deposit was used in laboratory and field experiments.

Laboratory Experiment

All laboratory experiments were conducted in 2.2 m pipes (0.12 m diameter) connected to 200 L barrels with a pollution mixture. Artificial sewage was made using POLIDAP ammonium phosphate fertilizer containing 18% nitrogen (N) as ammonium and 46% phosphorus (P) as P_2O_5 (Fig. 4). The deposits in the pipes were prepared according to the following steps using the devices given in Figs 1 and 3. First, 10 kg of the fibrous substrate was passed through a 4 mm mesh sieve, and 20 L of Ca



Fig. 1. Device for fragmentation of the fibrous raw materials to the appropriate fractions.

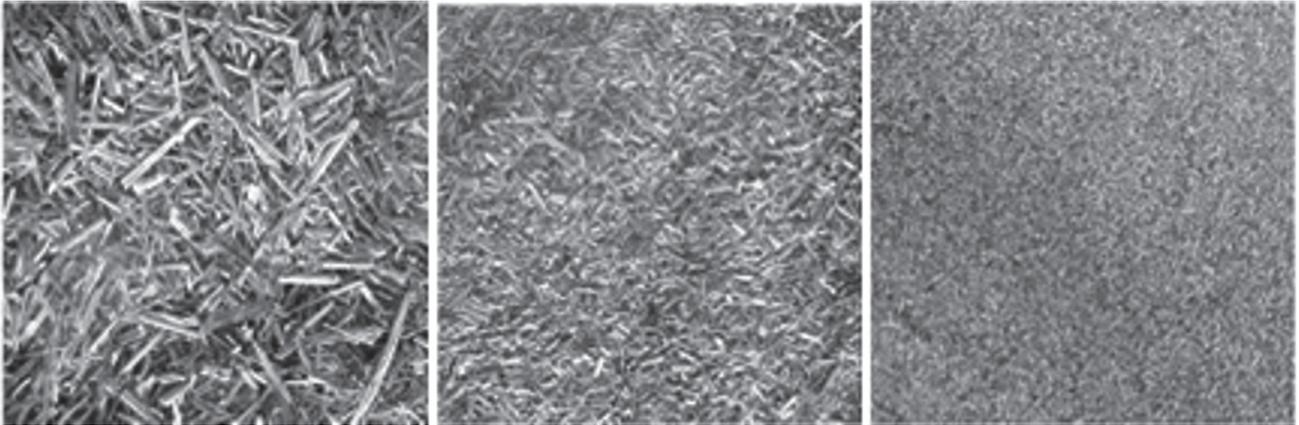


Fig. 2. Fractions of fibrous raw materials.



Fig. 3. Tanks for the preparation of chemical solutions used to impregnate raw fibrous materials (left); impregnation process of fibrous raw materials in the reactor (middle); impregnation process of fibrous raw materials in the reactor (right).

(OH)₂, FeCl₃, or Al₂(SO₄)₃ was prepared at the required concentration. The solution and the fibrous substrate were then introduced to the reaction vessel and mixed for two hours.

Experimental reactors were built for the laboratory tests (Fig. 4). They consisted of fibrous deposits with chemical compounds that form insoluble salts with phosphorus: one based on Ca(OH)₂ (two different phosphate inflows with concentrations of 5.87 mg PO₄³⁻ L⁻¹ and 12.20 mg PO₄³⁻ L⁻¹), the second on FeCl₃ (three different concentrations: 1%, 5%, and 10% of FeCl₃), and the third on Al₂(SO₄)₃ (three different concentrations: 6.8%, 13.6%,

and 27.2% of Al₂(SO₄)₃). The experiments continued for 40-46 days (Table 1). Water samples were taken manually (typically twice a week).

Field Experiment

Initial field trials were conducted in Tresta Rządowa (Tomaszów province; 51°46'N, 20°00'E), at the Department of Applied Ecology field station located 500 m from the northeastern shore of Sulejów Reservoir. A 20 kg deposit of fibrous substrate with Ca(OH)₂ was put into each of 10 jute bags and placed at the bottom of the 20 m-long outflow from the fishpond at 2 m intervals (Fig. 5). The experiment continued for 98 days. Water samples were taken manually before and after the treatment zone. Samples were taken twice a week until day 69, and then once a week until the end of the experiment (Table 1). No specific permission was required because these locations/activities and field studies did not involve endangered or protected species.

The second field experiment was carried out in the city of Łódź (central Poland) on the Sokolówka River (51°48'N, 19°27'E). A 10 kg of deposit with FeCl₃ was put into each of 10 jute bags and placed at the bottom of the 50 m section of the river at 5 m intervals (Fig. 6). Samples were taken once a week and the experiment was conducted for 51 days (Table 1). No specific permission

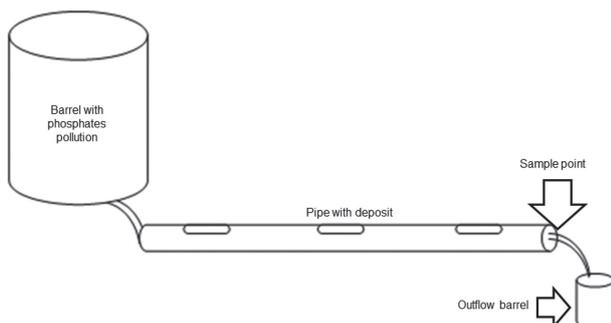


Fig. 4. Laboratory experiment scheme for all tested deposits.



Fig. 5. Tresta field experiment with $\text{Ca}(\text{OH})_2$ deposit at the outflow from a fish pond. Sample points: 1 – outflow from fish pond, 2 – at the end of the deposit zone.

was required for these locations/activities and field studies did not involve endangered or protected species.

Physico-Chemical Analysis

YSI Professional Plus was used to measure the physical parameters of the water *in situ*: pH, temperature, and dissolved oxygen (DO). The concentrations of selected ions (phosphates and nitrates) were analyzed using a Dionex ion chromatograph with a cation column (CG18, IonPac CS18, CSRS-ULTRA II) and an anion column (AG22, IonPac AS22, ASRS ULTRA II). The systems were operated in isocratic elution at 30°C at a flow rate of 1 mL min⁻¹. Combined standards were used for ion identification (Dionex Corporation).

Results

Laboratory Experiment

The highest average pH (9.35) was measured in deposits with $\text{Ca}(\text{OH})_2$ in the laboratory, followed by



Fig. 6. The Sokolowka field experiment with the FeCl_3 deposit placed in the urban river.

pH = 7.5 for the FeCl_3 field experiment. In the other experiments, pH ranged from 6.3 to 6.5 (Table 2). The temperature remained steady between 19.5 and 21.0°C in all laboratory experiments but was 11.9°C during the FeCl_3 field experiment (Table 2). The DO level was found to be similar in the laboratory tests, with 5.75 mg L⁻¹ for $\text{Ca}(\text{OH})_2$ and 5.91 mg L⁻¹ for $\text{Al}_2(\text{SO}_4)_3$, while the FeCl_3 deposits were found to be 1.27 mg L⁻¹ in the laboratory and 7.68 mg L⁻¹ in the field (Table 2).

Table 1. Characteristics of the analyzed deposits and duration of experiments with the frequency of sampling.

Study site		Deposit material	Chemical compound	Flow velocity [L s ⁻¹]	Experiment duration [days]	Sample collection frequency
Laboratory	Hemp		25% $\text{Ca}(\text{OH})_2$	0.00037	46	Once a week
			25% $\text{Ca}(\text{OH})_2$	0.00055	42	Twice a week
			1% FeCl_3		40	
			5% FeCl_3			
			10% FeCl_3			
	Flax		6.8% $\text{Al}_2(\text{SO}_4)_3$	0.00040	42	
			13.6% $\text{Al}_2(\text{SO}_4)_3$			
27.2% $\text{Al}_2(\text{SO}_4)_3$						
Field	Fish pond outflow		25% $\text{Ca}(\text{OH})_2$	n.a.	98	Twice a week (until 69 day) Once a week (after 69 day)
	Small urban river		25% FeCl_3	n.a.	51	Once a week

Table 2. Average physical parameters measured in the laboratory (inside the deposit) and field tests (inside the purification zone).

Average of measurement parameters (\pm SD)	Laboratory experiments			Field experiments	
	Ca(OH) ₂	FeCl ₃	Al ₂ SO ₄	Ca(OH) ₂	FeCl ₃
pH	9.35 \pm 1.01	6.30 \pm 0.98	6.50 \pm 1.15	6.5 \pm 0.42	7.5 \pm 0.34
Temperature [°C]	19.5 \pm 0.5	21.0 \pm 0.4	20.0 \pm 0.25	n.a.	11.9 \pm 3.77
DO [mg L ⁻¹]	5.75 \pm 0.80	1.27 \pm 0.21	5.91 \pm 0.30	n.a.	7.68 \pm 1.44

n.a. - not analyzed

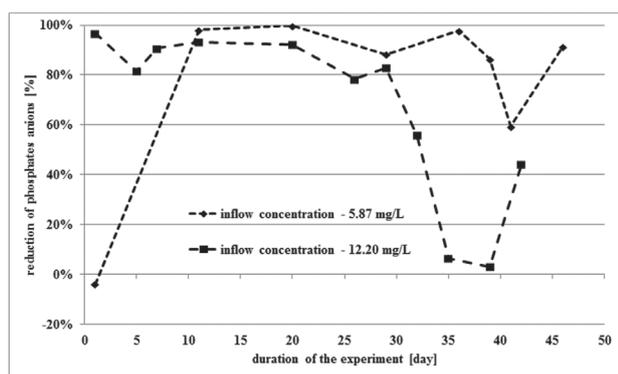


Fig. 7. The percentage reduction of phosphate ion concentration PO₄³⁻(mg L⁻¹) for the Ca (OH)₂ deposit.

The chemical deposit based on calcium hydroxide was found to work more efficiently with the lower inflow of phosphates. The average reduction at an inflow of 5.87 mg L⁻¹ was 90%, compared to 71% for the higher inflow of 12.20 mg L⁻¹ (Table 3). Both deposits demonstrated a decrease in efficiency around the 40th day of the experiment (Fig. 7).

In order to estimate the ability of iron(III) chloride to reduce phosphate levels, three different concentrations were used. The highest efficiency was noted for the 5% FeCl₃ deposit (the medium tested concentration). The deposit with a 10% concentration demonstrated an average reduction of about 22%, while no reduction was reported for the deposit treated with 1% FeCl₃ (Table 3). All analysed deposits with FeCl₃ released phosphates on the

Table 3. Reduction in phosphate content by the different deposits observed under laboratory and field conditions with statistical analysis.

Study site	Raw material	Chemical compound	Reduction of phosphates	Before deposit		After deposit		Anova Kruskal-Wallis results	
				Average inflow concentration [mg PO ₄ ³⁻ L ⁻¹]	Standard deviation	Average inflow concentration [mg PO ₄ ³⁻ L ⁻¹]	Standard deviation	H	p
Laboratory	Hemp flax	25% Ca(OH) ₂	90%	5.87	9.47	0.59	0.75	13.9839	0.0002
		25% Ca(OH) ₂	71%	12.20	5.97	3.58	3.61	11.8847	0.0006
		1% FeCl ₃	-4%	12.20	5.97	12.71	4.56	0.0269	0.8696
		5% FeCl ₃	42%	12.20	5.97	7.06	4.02	6.0636	0.0138
		10% FeCl ₃	22%	12.20	5.97	9.46	3.86	1.9932	0.1580
	Harl flax	6.8% Al ₂ (SO ₄) ₃	83%	0.85	0.11	0.15	0.17	77.1199	0.0000
		13.6% Al ₂ (SO ₄) ₃	56%	0.85	0.11	0.38	1.11	53.5617	0.0000
27.2% Al ₂ (SO ₄) ₃		81%	0.85	0.11	0.16	0.21	71.1730	0.0000	
Field	Fish pond outflow	25% Ca(OH) ₂	2%	0.19	0.26	0.19	0.18	0.0885	0.7666
	Small urban river	25% FeCl ₃	49%	0.42	0.51	0.21	0.24	1.1797	0.2774

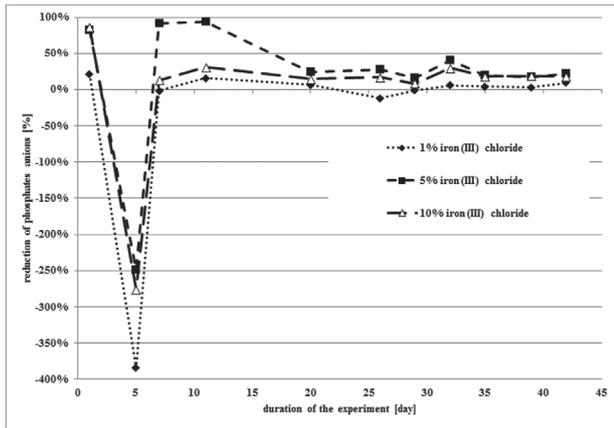


Fig. 8. The percentage of the reduction of phosphate ion concentration PO_4^{3-} ($mg L^{-1}$) for deposits with $FeCl_3$.

5th day of the experiment, and demonstrated the greatest efficiency on the 11th day of the experiment (Fig. 8).

Three concentrations of aluminum were also examined. The highest reduction (83%) was noted for the lowest concentration, of 6.8% $Al_2(SO_4)_3$ (Table 3). A similar reduction (81%) was obtained for 27.2% $Al_2(SO_4)_3$, while 13.6% $Al_2(SO_4)_3$ was only found to have 56% efficiency (Table 3). A day-to-day plot of the efficiency of treatment (Fig. 9) indicates that the deposit with lowest concentration had the most stable results throughout the whole experiment, with efficiency falling below 80% only after the day 38. A similar fall was reported for 27.2% $Al_2(SO_4)_3$. For both the highest and lowest concentrations, the starting efficiency was low – even below 0% for 13.6% $Al_2(SO_4)_3$ (Fig. 9).

Field Trials

The Tresta field experiment was conducted first. The average reduction of phosphate ions was 2%, with a 0.16 $mg L^{-1}$ average inflow rate (Table 3). In addition, a 30% mean reduction of nitrate concentration was observed across the purification zone, from 12.18 $mg L^{-1}$ at the inflow to 8.53 $mg L^{-1}$ at the outflow. A day-by-day analysis (Fig. 10) indicates that the reduction of nitrates was high, while phosphate reduction was low or even not observed.

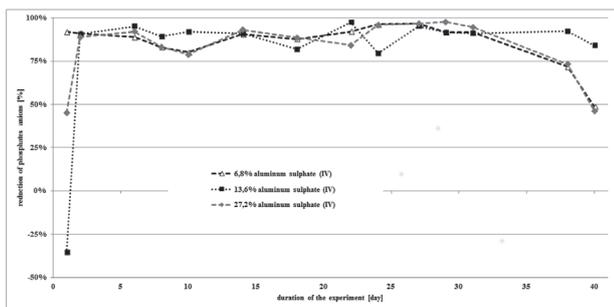


Fig. 9. The percentage reduction of phosphate ion concentration PO_4^{3-} ($mg L^{-1}$) for the deposit of Al_2SO_4 .

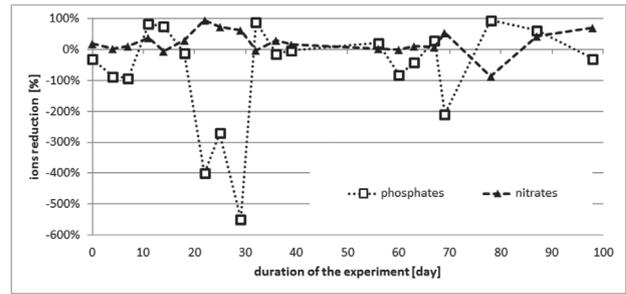


Fig. 10. The changing levels of phosphate and nitrate ions before and after filtration in the Tresta field experiment.

Statistical analysis revealed a strong negative correlation ($r = -0.6296$; $p = 0.003$) between the reduction of both ions (Fig. 11). In addition, strong reduction (86%) was noted on day 11, when a high level of phosphates was measured ($1.24 mg PO_4^{3-} L^{-1}$, Fig. 10).

The second set of field experiments was conducted in the Sokolowka, an urban river in Łódź. Jute bags with an $FeCl_3$ deposit were placed across a one-meter width of the river bed. Samples were taken before and after the treatment zone. However, due to the flow being more varied, this experiment was only continued for 58 days (shorter than the Tresta trials).

In this case, a 49% reduction of phosphates was noted (from $0.41mg L^{-1}$ to $0.21mg L^{-1}$) (Table 3). Nitrate

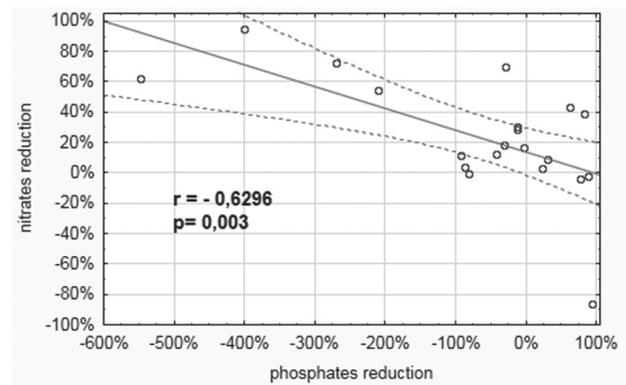


Fig. 11. Spearman correlation between phosphate and nitrate reduction in the Tresta field experiment.

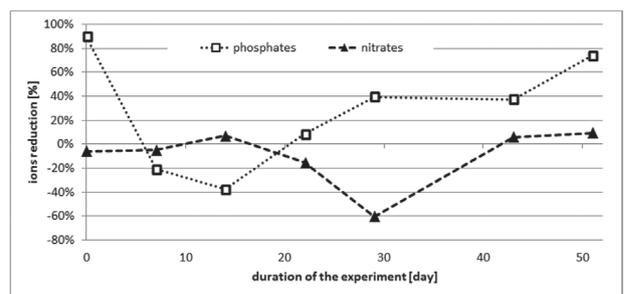


Fig. 12. The changing levels of phosphate and nitrate ions in the Sokolowka River before and after filtration.

reduction was not observed (10.77 mg L^{-1} before the zone and 11.18 mg L^{-1} after). Only a few days with reduction (Fig. 12). High reduction of phosphates (90%) was noted on the first day of the experiment, when high inflow occurred ($1.4 \text{ mg PO}_4^{3-} \text{ L}^{-1}$) (Fig. 12).

Discussion

Most of the P loading in the Baltic Sea in 2000 originated from point sources (56% of the total load), with municipalities being the major contributor. Of the remaining 44%, the majority (around 80%) originated from agricultural activities [20]. Despite extensive work to decrease nutrient loading in the Baltic, fulfilling the goals of current legislation and international agreements (e.g., the EU Marine Strategy Framework Directive, the Urban Wastewater Treatment Directive, the Nitrates Directive, and the Water Framework Directive) without further reductions in nutrient discharge seems to be impossible [20]. Therefore, the suite of P-remediation measures must therefore be expanded to include new methods that employ P-sorbing materials. These P-sorbents fall into three groups according to their origin: natural materials, industrial by-products, and manufactured materials [21]. The materials may also be classified according to their chemical composition as follows: those containing metals (mostly Fe and Al), those containing soluble divalent earth metals (Ca, Mg), and mixtures of the two [12]. Several studies have shown that some materials are capable of removing P from household wastewater or agricultural runoff, but more studies are needed to optimize the design of filter beds intended for field conditions [12].

Many successful attempts have been made to reclaim reservoirs suffering increased eutrophication, either by limiting the supply of sources of nutrients (especially phosphorus) or by removing them. One such example is that of Lake Constance on the border of Germany, Austria, and Switzerland, where in 1980-2007 control of phosphorus input decreased its concentration to background levels, and with it the chlorophyll concentration and phytoplankton population [22]. However, it should be noted that reclamation based only on reducing the supply of phosphorus is a long process, often due to the load that has already been bound by phytoplankton and bottom sediments within the water body. Therefore, to effectively recover water reservoirs as quickly as possible, it is necessary to apply methods aimed at removing the accumulated stock. So far, the methods used to remove excess phosphorus from surface waters can be divided into two groups: chemical (sediment precipitation) and phytoremediation (accumulation in plant biomass).

Compounds based on salt are the best known methods for removing phosphate pollutants from surface water. They rely on the direct application of selected iron(II) sulphate or chloride, for example, in the processing of pulp, clay (mostly sulphate), or calcium carbonate. The precipitation of phosphorus from deep water is

based on the application of a substance which, during sedimentation, coagulates suspended solids into lumps on which phosphorus absorbance takes place. However, the use of this method is limited to the purification of water bodies such as ponds and lakes, as these methods involve expensive reactants and increase the salinity of treated wastewater, and result in the accelerated corrosion of equipment and the production of a large amount of sludge [23].

PIX, PAX, Phoslock, and Sinobent are widely known substances used for treating surface water contaminated with harmful phosphorus compounds. Their biggest drawbacks, however, are the high cost of their use and the need for large quantities to be used in natural ecosystems [18, 24-25]. The purpose of the study was to design an apparatus for the removal of phosphorus compounds from contaminated freshwater in the most efficient manner possible, at the lowest possible consumable cost and with the least technical requirements. To fulfil these requirements, the proposed solution incorporates fibre deposits of waste materials. It requires little technical skill to produce and can be constructed cheaply where the natural fibrous waste that is used as the raw material is plentiful. From the ecological point of view, it is also important that the fibrous deposit may be used both in water courses and in lakes and ponds. Hence the use of fibrous, biodegradable chemical deposits to block excessive quantities of phosphates from fields and restrict their flow into surface water would reduce eutrophication and improve the ecological status of water as required by the Water Framework Directive [26].

In order to understand the functions of the bodies of water there is a need to understand the processes occurring both in sediments and in the water column and the interaction between them during the retention and release of phosphorus [27]. The deposits presented in this article, composed of defibrated biodegradable waste material (hemp and harl flax) mixed with chemical compounds (contents of calcium, iron, or aluminum ions) bound phosphates from water column could be used as fertilizer after saturation with P [28].

The use of various calcium materials and compounds for phosphate precipitation is a common method, mainly because of their low cost and ease of handling [10, 28]. The deposit of calcium presented in this study allowed between 71% and 90% reduction of phosphate concentration (Table 3), which corresponds with the range obtained in other studies (75-98%) [29-31]. The lower efficiency observed during the second laboratory experiment with the higher phosphate inflow (Table 3 and Fig. 7) may be caused by the low Ca/P ratio [30]. The field experiment at the outflow of a fish pond did not provide such a great reduction of phosphates as noted in the laboratory (Table 3). Only 2% of phosphate reduction observed in the field study (Table 3) might be caused by the different pH levels present between field and laboratory experiments. Other studies have shown that the pH has a significant impact on the efficiency of phosphate absorption by Ca ions [10, 30]. Correlation analyses indicate that the phosphate reduction

had a high negative correlation ($r = -0.6296$) with nitrate reduction (Fig. 11), suggesting that the low level of phosphate reduction observed in the field experiment could also be caused by the influence of calcium ions on denitrification [32].

Iron compounds could also be used for phosphate absorption from a water column [33]. Iron chloride deposits demonstrated the lowest phosphorus removal efficiency in the laboratory study (Table 3). The best 43% PO_4^{3-} reduction was noted for the deposit with 5% FeCl_3 . Although this reduction was half what could be achieved, it could be much worse with a low Fe/P ratio – even below 10% [34-35]. The low DO level (Table 2) could be another factor that affects the low reduction in laboratory studies [34-36]. The efficiency measured during the field experiment was found to be similar (49%) to the lab results for 5% FeCl_3 (Table 3), despite the use of a higher FeCl_3 concentration. This might be due to the higher variability of parameters, such as pH, DO, and temperature, affecting phosphate absorption by iron ions [34-35] in the field experiment (Table 2). Aluminum sulphate was the last compound to be mixed with deposit material. A high phosphorus removal rate of about 90% was observed (Table 3), which corresponds with results ranging from 80 to 99% noted in other studies [37-39]. The lower P reduction demonstrated by the 13.6% Al_2SO_4 deposit was caused by the released phosphates in the first days of the experiment (Fig. 9). The reasons for this loss are unclear and further investigation is needed to shed light on them. The optimum pH and Al/P ratio might also have contributed to this high reduction of phosphate content [39].

Two factors might influence the obtained results. While P appears in inorganic and organic forms under field conditions, laboratory experiments mostly use inorganic P. Secondly, sufficient contact time between the filter material and the flow solution is likewise a crucial point in developing P filters [12].

The removal efficiency of phosphates provided by Fe, Ca, and Al depends mainly on the physical parameters (pH, DO, and temperature) and also the Fe/P, Ca/P, or Al/P ratios [30, 34-35, 37]. The ratio of the mentioned ions to phosphorus could be easily changed and controlled in streams and drainage ditches by applying tested deposits. The achieved level of phosphate reduction, combined with the low cost of producing the deposit using the new device (about \$80 per ton of deposit) and the use of waste materials, makes the technology widely applicable and complementary to other methods for reducing phosphate pollution and preventing cyanobacterial blooms in reservoirs [40-43]. Another feature that is extremely important from the point of view of sustainable development is that the chemical deposits are formed only from natural, biodegradable fibrous raw materials. Hence, after a filter has degraded, it can then be used as fertilizer itself, which is an excellent source of phosphorus and organic compounds to increase the humification of the soil.

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