

# Effect of natural sorbents on the stabilization of trace metals in bottom sediments

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#### ABSTRACT

Bottom sediments were tested in order to determine the possibility of immobilization of heavy metals with the use of natural sorbents, chitosan and bentonite. The content of Cu, Zn, Cd and Pb was determined, and speciation analysis was performed using the sequential Tessier methodology. The use of sorbents clearly changes the speciation forms of all tested heavy metals by comparing the distribution of metals before and after the application of the sorbent for both chitosan and bentonite. The addition of natural sorbents affect the immobilization of metals deposited in bottom sediments of water reservoirs. However, the behavior of metals in the presence of sorbents results from their properties and the nature of the sorbent. The positive effect of sorbents on metal immobilization was not observed in every case. The addition of the tested sorbents in the case of cadmium caused an increase in the content of Cd in the mobile fractions, for Zn, Pb and Cu, stronger binding of metals was found in the stable fractions IV and V. Chitosan stabilized metals more strongly than bentonite, which moved Zn, Pb and Cu to the first mobile fraction.

Keywords: Heavy metals; Natural sorbents; Chitosan

#### 1. Introduction

The intensive economy in the world contributes to the pollution of all components of the environment. A number of studies conducted in recent years have shown the presence of a wide range of pollutants in aquatic sediments. Metals (As, Cd, Cu, Hg, Ni, Pb and Zn) [1–5], as well as organic compounds [6–11] can accumulate in sediments. An important indicator of the pollution of water objects are bottom sediments, in which metals entering the aquatic environment are strongly bound. In lakes, this is mainly due to the specific hydrodynamic properties where there is limited water exchange, which favors the accumulation of pollutants in the sediments. Depending on the factors prevailing at the bottom of the reservoir, metals may be a secondary source of water contamination. The increased content of trace elements in sediments leads to a decrease the quality of surface

waters and may lead to poisoning or contamination of organisms living in ecosystems. Therefore, the development of metal immobilization methods in bottom sediments is one of the priorities for ensuring the quality of surface waters.

Often contaminated sediments are excavated and discharged onto land. A relatively small part of them is reused. Once extracted, contaminated sludge is considered waste and must be treated before being reused or deposited in storage centers [12]. Decontamination treatments are often economically infeasible given the level of contamination and the large volume to be treated. The large volume of contaminated sludge has elevated concentrations of elements in anionic and cationic forms, making their removal more complex. The most appropriate technique for managing contaminated waste is to immobilize the pollutants in the solid phase by chemical stabilization. The aim of this treatment is to reduce the bioavailability of pollutants

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[13,14]. The best way to immobilize heavy metals is to use a sorbent with the least negative impact on the biochemical condition of the tank. Many studies have been carried out using various additives to sludge contaminated with metals. The addition of iron-based binders such as hematite and zero-valent iron has been investigated in soil remediation [13,15,16]. Other studies tested the two main methods of stabilizing metals in the Novosol (Solvay, Brussels, Belgium) process using phosphoric acid and liming using CaO [17]. The studies conducted showed satisfactory effects in reducing the mobility of trace elements in soils and marine sediments contaminated with many elements.

The aim of this work was to conduct a pilot study of metal immobilization in lake's bottom sediments using natural sorbents (bentonite and chitosan). Mobile and bioavailable forms of heavy metals in raw sediments and with the addition of sorbents were determined. The study assessed the impact of natural sorbents on the stabilization of trace metals in bottom sediments. The research was aimed at assessing the sorption efficiency of natural sorbents and determining their effectiveness in the immobilization of selected trace elements (Cu, Ni, Cd, Zn and Pb). Adsorption was carried out in the solid–liquid/solution system. The scientific novelty of our work is the determination of changes in the speciation pattern of metals before and after the sorption process. This practical relevance can contribute to the development of effective remediation strategies that are environmentally friendly and cost-effective.

## 2. Materials and methods

The bottom sediments used in the study were collected from a lake located in the Warsaw agglomeration, which belongs to the Natura 2,000 area. In the area of the lake, 9 samples of bottom sediments were collected. The sediments were mixed into an averaged sample used for further testing.

The water content (%) was determined by drying the sediment samples in triplicate at 105°C for 24 h. The texture of the precipitate was determined by measuring the particle size distribution using a Mastersizer Laser Granulometer (Malvern Instruments). The characteristics of the sludge were determined using analytical methods specified by the International Organization for Standardization (ISO). In the solution after mixing sediments, the pH of the sludge was measured by potentiometric method in a ratio of sediment/ water 1:5. Additionally conductivity and total organic carbon were measured with a conductivity meter and total carbon analyzer (Shimadzu TOC 5000A, Kyoto, Japan) were determined, respectively.

The content of macroelements calcium, magnesium were determined after soil extraction with 0.5 mol/L HCl by flame photometry. The content of chlorides was determined with Mohr's method and content of sulphates with the turbidimetric method.

Two sorbents were used in the research: bentonite and chitosan. Bentonite is a swelling clay named after the first mined deposit in Fort Benton, Wyoming, USA. It has unique physical properties. Geologically, bentonites are minerals of volcanic origin. Most of the exploited deposits were formed as a result of weathering of volcanic tuffs in an alkaline and highly saline environment. The main component of bentonite is a clay mineral – montmorillonite  $(Al_2O_3SiO_2 nH_2O - nH_2O)$ hydrated aluminum silicate). According to world standards, bentonite is a clay rock that contains not less than 75% of montmorillonite. Minerals containing 50%-75% montmorillonite are called bentonite clays. In nature, calcium bentonites with Ca2+ cations in exchangeable positions are the most common. However, due to the weak chemical bonds, it is possible to replace these ions with Na<sup>+</sup> ions in the process of the so-called activation (sodium compounds, for example, sodium carbonate Na<sub>2</sub>CO<sub>3</sub>). Sodium bentonite is widely known for its outstanding swelling capacity. It can adsorb 5 times more water than it weighs, and when fully saturated with water, it occupies a volume 12-15 times larger than in a dry state. This ability makes it very plastic and resistant to breakage and cracks, its liquidity limit is in the order of 600%-800%. An important property is also the ease of releasing adsorbed water at elevated temperature. The swelling capacity disappears if the drying temperature exceeds 500°C-600°C; the so-called separation of constitutional water [18].

Chitosan,  $(1\rightarrow 4)$ -2 amino-2-deoxy- $\beta$ -D-glucan, is a product of chitin deacetylation (Fig. 1). It is non-toxic, biocompatible and degradable, it has adsorption properties in relation to metal ions, cholesterol and proteins. These properties result from the fact that the molecule contains reactive amino groups and hydroxyl groups. In environmental protection, the adsorption properties of chitosan and the ability to form chelate compounds were used primarily for the separation of metal ions [19]. The deacetylation of chitin makes the chitosan obtained from it water-soluble and can take forms desirable from the point of view of some applications, for example, biopolymer used in tissue engineering, especially in orthopedics and bone regeneration. Chitosan is also found in many medical products, that is, gels, sponges, fibers or porous compositions of chitosan with ceramics, collagen or gelatin [19]. Chitosan is characterized by: the ability to form polymer films directly from the suspension, antibacterial effect, bioactivity, biocompatibility and non-toxicity, high value of the secondary swelling index, high sorption capacity and chelating capacity, high adhesiveness, good miscibility with a number of substances, including polymers [20].



Fig. 1. Preparation of chitosan from chitin [20].

The work uses Tessier's sequential scheme to determine the forms of metals and their mobility, described in previous study [18]. The pilot experiment was carried out using samples of raw bottom sediments and with the addition of sorbents. The pilot experiment consisted of three systems: (a) crude sludge, (b) sludge + 10% bentonite, (c) sludge + 10% chitosan. Each sample was thoroughly mixed and left under stable conditions for 7 d. After this time, tests were carried out to determine the content of metal fractions using the sequential extraction of the modified Tessier method:

- metal ion-exchange fraction (pH = 7);
- carbonate fraction (pH = 5);
- adsorption fraction (pH = 4);
- organic and sulphide fraction (pH = 2);
- residual fraction (pH = 1).

Cd, Cu, Pb and Zn concentrations were measured in the extracts using an AAS (atomic absorption spectrometer) (PinAAcle 900F PerkinElmer, Waltham, Massachusetts, USA). Detection limits were 0.01 g/L for Cd; 0.31 g/L for Cu and Pb; and 1.00 g/L for Zn. Calibration solutions were prepared by diluting a certified multi-element solution (10,000 g/L).

#### 3. Results

## 3.1. Characteristics of bottom sediments

The characteristics of bottom sediments is shown in Table 1. The granulometric composition of the sample is given in Table 2. It was found, based on X-ray diffraction analysis that, major mineralogical phases are: quartz  $(SiO_2)$ , calcite  $(CaCO_3)$ , feldspar, illite, kaolinite, smectite (<2 µm fraction).

## 3.2. Metal sorption

The collected samples of bottom sediments were subjected to speciation analysis of chemical fractions and the total content of Cd, Cu, Pb and Zn was also determined. In order to determine the metals in five fractions, the Tessier extraction scheme was used.

The largest share of cadmium (Fig. 2) in the total content in the sludge without the addition of sorbent was in the carbonate fraction (2nd fraction, 33%) and a slightly lower content was recorded in the ion-exchange fraction

Table 1

Main physico-chemical properties of the sediment sample

Parameter	Value
Initial pH-H <sub>2</sub> O (1:5 solid:liquid)	8.7 +/- 0.2
Conductivity, μS/cm	1325 +/- 5
Chlorides, mg/kg dry mass	126 +/- 5
Sulphides, mg/kg dry mass	69 +/- 1
Ca, mg/kg dry mass	33.2 +/- 0.5
Mg, mg/kg dry mass	6.7 +/0 0.3
Initial water content, %	65.3 +/- 0.4
Content of organic matter, g/kg	103 +/- 4

(1st fraction, 27%). The least amount of cadmium was found in fraction IV – organic (2%). The addition of chitosan to the sediment sample shifted the percentage of cadmium in the chemical fractions of the bottom sediment. The most noticeable change in the percentage of cadmium was observed in fraction V (from 13% to 27%). In the fraction of hydrated Fe/Mn oxides, its addition reduced the percentage of cadmium from 25% to 5%. The introduced bentonite into the sludge sample caused a significant increase in the share of cadmium in the ion-exchange fraction (from 27% to 48%). In the remaining fractions, the addition of bentonite immobilized the cadmium.

The percentage of copper in the five sludge fractions is shown in Fig. 3. Copper was most strongly bound in the organic and residual fractions. Low copper content was found in the mobile fractions (exchangeable, carbonate and adsorptive). The addition of chitosan caused a very large increase in copper binding in the organic fraction from 34% to 70%. A similar increase was observed in this fraction after the addition of bentonite (from 34% to 68%). In the

#### Table 2

Granulometric composition of the sample (in µm)

Fraction	%
<2	5.03
2–63	33.27
63–2,000	61.70



Fig. 2. Percentage of cadmium forms in chemical fractions of bottom sediments.



Fig. 3. Percentage of copper forms in chemical fractions of bottom sediments.

remaining fraction, both the addition of bentonite and chitosan reduced the copper content by more than half in the case of chitosan and 45% in the case of bentonite.

In the case of sludge without the addition of sorbent, lead (Fig. 4) was most strongly bound in the organic fraction (49%). Both the addition of chitosan and bentonite caused a decrease in lead mobility by about 14%–15%. The addition of natural sorbents reduced the metal mobility in the residual fraction, compared to the lead content in the sludge without sorbents. The addition of chitosan or bentonite in the ion-exchange fraction, and especially in the carbonate and adsorption fraction, slightly increased the percentage of lead in the given fractions.

The percentage of zinc in five sludge fractions is shown in Fig. 5. For all variants, zinc was most strongly bound in fraction III of hydrated Fe/Mn oxides, while it was least bound in the exchangeable fraction. The addition of chitosan increased the share of Zn in the fraction of hydrated Fe/Mn and organic oxides. In the carbonate fraction and the remaining fraction, this sorbent caused a decrease in the percentage of zinc.

The obtained results clearly indicate the effectiveness and efficiency of the sorption of the metallic elements on the sorbents used. The tests showed that the metals (Cu, Cd, Zn and Pb) reacted selectively with the sorbents. The best stabilization was found for lead and zinc. Copper and cadmium are immobilized to a lesser extent, which forces the use of a higher dose of sorbent or the use of a mixture that allows for more effective stabilization of the tested trace elements. The addition of natural sorbents to bottom sediments shifts the metal content between metal binding fractions in



Fig. 4. Percentage of lead forms in chemical fractions of bottom sediments.



Fig. 5. Percentage of zinc forms in chemical fractions of bottom sediments.

sediments. In the case of cadmium and copper, the addition of both sorbents caused an increase in the content of metals in immobile fractions, for zinc and lead, stronger binding was found in stable fractions IV and V.

Individual fractions of bottom sediment in terms of binding capacity can be ranked in the following order (Table 3).

The results of the speciation analysis without the use of sorbents and also with the use of sorbents for four heavy metals are presented in Figs. 6–9. The results of metal fraction studies in the lake sediments showed that the exchangeable fraction accounted for 27%–39% of the total cadmium content. The second metal with a significant share

Table 3 Individual fractions of bottom sediment in terms of binding capacity

	No sorbent	with bentonite	with chitosan
Cu	IV > V > III > II > I	$\mathrm{IV} > \mathrm{V} > \mathrm{I} > \mathrm{III} > \mathrm{II}$	$\mathrm{IV} > \mathrm{V} > \mathrm{II} > \mathrm{I} > \mathrm{III}$
Zn	III > II > IV > V > I	III > IV > V > II > I	$\mathrm{III} > \mathrm{V} > \mathrm{II} > \mathrm{I} > \mathrm{IV}$
Pb	$\mathrm{IV} > \mathrm{III} > \mathrm{V} > \mathrm{II} > \mathrm{I}$	$\mathrm{IV} > \mathrm{III} > \mathrm{V} > \mathrm{II} = \mathrm{I}$	III > IV > V > I > II
Cd	II > I > V > III > IV	II > I > III > V > IV	III > II > I > V > IV



Fig. 6 Percentage share of Zn in sediment fractions without and with the addition of sorbents.



Fig. 7 Percentage share of Cu in sediment fractions without and with the addition of sorbents.



Fig. 8. Percentage share of Cd in sediment fractions without and with the addition of sorbents.



Fig. 9. Percentage of Pb in sediment fractions without and with the addition of sorbents.

in this fraction was lead (7.7%-9.7%). For zinc and copper, the share in this fraction was much lower, 0.4%-0.7% and 0.1%-0.5%, respectively. Similarly, to the exchangeable fraction, the share of cadmium (31%–37%) was found in the carbonate fraction. The second metal with a significant share in the fraction was zinc (23.7%-26.1%). For lead and copper, the share was much smaller and amounted to: 6.5%–8.6% for lead and 0.7%–2.6% for copper. In the studies of the bottom sediments of the lake, a large share of zinc (44.2%-56.6%) and lead (19.4%-41%) was found in the fraction of released Fe/Mn oxides. In the organic fraction IV, copper had the largest share, as much as 34.2%–78%. In this fraction, the share of lead was found at the level of 23.1%-48.6%, and of zinc 9.5%-15.8%. A very small percentage share in the organic fraction IV was recorded for cadmium, 1%-5% only. The content of metals in the residual fraction, which is practically insoluble and inaccessible to aquatic organisms, varies. The metals in this fraction were associated with different strengths for copper (28.4%-50.6%), lead (11.4%-38.7%), cadmium (13%-25%) and zinc (3%-19.8%). This part of the metals should not be activated and is theoretically inaccessible to microorganisms.

The results of the study of metal fractions in the lake sediments showed that the addition of chitosan shifted the percentages of metals in individual fractions. The exchangeable fraction accounted for 28%-45% of the total cadmium content. The second metal with a significant share in this fraction was lead (7.1%-8.1%). For zinc and copper, the share in this fraction was much lower, 0.5%-0.7% and 0.2%–0.4%, respectively. Similarly, to the exchangeable fraction, the share of cadmium (17%–35%) was found in the carbonate fraction. The second metal with a significant share in the fraction was zinc (20.3%–23.9%). For lead and copper, the share was much smaller and amounted to: 5.4%-7.7% for lead and 0.4%–0.8% for copper. A very large share in the fraction of released Fe/Mn oxides was found for cadmium, copper and lead. In the organic fraction IV, copper had the largest share, as much as 66.5%–77.2%. In this fraction, the share of lead was found at the level of 26.2%-35.1%, and of zinc 16.3%-20.9%. A very small percentage was recorded for cadmium, only 5%-9%. The metals in the remaining fraction were associated with different strengths for copper (20.4%-28.5%), lead (19%-30.8%), cadmium (9%-27%) and zinc (1.5%–6.4%). The addition of bentonite also influenced the change in the percentage shares of individual metal fractions. The exchangeable fraction accounted for 20%-48% of the total cadmium content. The second metal with a significant share in this fraction was lead (7.1%-10.3%). For zinc and copper, the share in this fraction was much lower, 0.4%-1.2% and 0.2%, respectively. In the exchangeable fraction, the share of cadmium (18%-22%) was found in the carbonate fraction, and zinc showed a share of 16.4%-26.8%. For lead and copper, the share was much smaller and amounted to: 7.7%-10.3% for lead and 0.9%-4.7% for copper. The largest share in the fraction of released Fe/Mn oxides was found for zinc (49%–53.4%). In fraction IV (organic), copper had the largest share, as much as 24.4%-65.2%. In this fraction, the share of lead was found at the level of 21.4%–33.3%, and of zinc 7.6%-17.8%. A very small percentage was recorded for cadmium, only 5%-9%. Metals in the remaining fraction were associated with different strengths for copper (24.7%-74.2%), lead (23.8%-27.6%), cadmium (2%-9%) and zinc (1.5%-46%).

On the basis of the obtained results, the values of geoaccumulation indexes and were determined. The state of sediment contamination with heavy metals was also determined using Muller's classification (Table 4).

#### 4. Discussion

Sorption is a well-established mechanism for removing and immobilizing contaminants, including metals, from sediment matrices. Sorbents possess high surface areas and diverse surface chemistries, allowing them to efficiently bind and retain metal ions through various sorption mechanisms, including ion exchange, complexation, and surface adsorption [21]. This makes sorption an attractive option for remediating metal-contaminated sediments, as it directly targets the metals of concern and reduces their mobility and bioavailability. Metals in sediments can pose significant risks to aquatic ecosystems and human health when they become bioavailable and enter the food chain [22]. Sorption plays a crucial role in reducing the bioavailability of metals by

Metal	Average metal content	Geoaccumulation index	Classification of sediment according to Muller			
Without sorbent						
Cd	6.2	4.2	Class V – moderately extremely polluted			
Cu	205.5	5.7	Class VI – extremely polluted			
Pb	0.9	-2.9	Class 0 – practically not polluted			
Zn	81.2	1.3	Class II – moderately polluted			
With chitosan						
Cd	6.3	4.3	Class IV – heavily polluted			
Cu	176.0	5.2	Class VI – extremely polluted			
Pb	0.9	-3.0	Class 0 – practically not polluted			
Zn	86.8	1.1	Class II – moderately polluted			
		With bentonite				
Cd	6.4	4.3	Class V – moderately extremely polluted			
Cu	188.2	5.6	Class VI – extremely polluted			
Pb	0.9	-2.9	Class 0 – practically not polluted			
Zn	91.0	1.5	Class II – moderately polluted			

Table 4 Geoaccumulation index and classification of sediment according to Muller

immobilizing them within the sediment matrix. By adsorbing metal ions onto sorbent surfaces, sorption hinders their uptake by organisms, minimizing the potential for bioaccumulation and subsequent ecological and human health risks. This aspect is particularly important when considering the long-term effects of metal-contaminated sediments on the surrounding environment. Metal-contaminated sediments often suffer from poor physical and geotechnical properties, leading to erosion and resuspension, which can further spread contamination downstream [23]. The addition of sorbents can improve sediment stability by altering its physical properties, such as porosity and permeability. The sorbents can bind to fine particles and create a more cohesive matrix, enhancing sediment strength and reducing erosion potential. This stabilization effect can prevent the release and transport of metal contaminants, mitigating the environmental impact downstream and ensuring the longterm integrity of the sediment containment. Sorption-based approaches offer scalability and adaptability, making them suitable for a wide range of sediment management scenarios. The addition of sorbents can be implemented at various scales, from small laboratory experiments to large-scale field applications. Furthermore, different types of sorbents can be selected based on site-specific conditions, sediment characteristics, and target metals, allowing for tailored solutions. This flexibility enables engineers to design efficient and cost-effective remediation strategies that can be customized to meet specific project requirements [24]. Significant advancements in sorption technologies have been made in recent years, enhancing their efficacy and applicability [25]. Sorption-based approaches can offer cost-effective solutions compared to alternative remediation methods. While the specific costs depend on factors such as the type and quantity of sorbents required, their availability, and site-specific conditions, sorption generally provides a viable and competitive option [26]. Compared to techniques like dredging and removal, which are often costly and disruptive, sorption can be implemented without extensive excavation and transport, minimizing the associated expenses. The longterm benefits of stabilizing metals and preventing their further spread can outweigh the initial investment.

When sorbents are added to sediments, they can bind to contaminants or other substances present in the sediment, thereby altering their weight. The weight change caused by the addition of sorbents depends on the sorbent's density relative to the sediment and the concentration of sorbents added. If the sorbent's density is significantly higher than that of the sediment, the addition of 10% sorbents by weight could result in a noticeable increase in sediment weight. On the other hand, if the sorbent's density is similar to or lower than that of the sediment, the weight increase may be minimal. Bulk density of chitin and chitosan products was reported to be in the range of 0.20-0.38 g/mL, depending on porosity [27]. Furthermore, the type and properties of the sediments themselves play a crucial role. Sediments can vary widely in composition, grain size, moisture content, and organic matter content. These factors can influence the sorption capacity and behavior of the sediments [28]. Sediments with high organic matter content tend to have a higher sorption capacity due to the presence of reactive sites on organic molecules. Consequently, the weight change caused by sorbents might be more significant in sediments with higher organic matter content. Another aspect to consider is the specific purpose of adding sorbents to the sediments. The intention is to remediate contaminated sediments, the sorbents should help immobilize or remove pollutants, leading to a potential reduction in sediment weight if the contaminants are effectively trapped [29]. In addition to the weight change, other factors should be taken into account when considering the addition of sorbents to sediments. These include potential impacts on sediment characteristics, such as permeability, porosity, and nutrient cycling. Moreover, the long-term

stability and effectiveness of sorbents in retaining contaminants should be evaluated to ensure their sustainable use.

The cost of sorbents is an essential economic factor to consider. Different types of sorbents have varying costs, depending on factors such as availability, production processes, and demand. The amount of sorbents needed for a particular application is a crucial consideration. Adding 10% sorbents by weight to bottom sediments may require a substantial quantity of sorbents. Large-scale applications might entail significant costs, including procurement, transportation, and storage of the sorbents. The availability and accessibility of the required quantity of sorbents can also impact the overall economics of the process. The duration and frequency of sorbent applications can affect economic considerations. If sorbents need to be reapplied regularly or in large quantities, it can lead to increased costs over time. Evaluating the longevity and effectiveness of sorbents in retaining contaminants or fulfilling their intended purpose is crucial to ensure cost-effectiveness. Long-lasting or reusable sorbents can potentially reduce the economic burden of continuous reapplication. Assessing the potential economic benefits associated with sorbent use is essential. If the addition of sorbents leads to the remediation or improvement of contaminated sediments, it can have positive economic implications. Compliance with environmental regulations and potential liabilities should be considered from an economic standpoint [30]. Costs associated with ensuring compliance, monitoring, and proper disposal of sorbents and sediments should be factored into the economic analysis.

#### 5. Summary, prospects and direction of further research

The accumulation of heavy metals in the surface layer of sediments is a reflection of the ecological status of the lakes. The level of contamination of bottom sediments with heavy metals is a very important indicator for assessing the degree of contamination of water reservoirs. Performing an analysis of the content of heavy metals in the bottom sediments of the lake will allow to obtain extensive information about the water ecosystem under study. Control of the contamination of reservoirs allows for early identification of unfavorable changes in the water environment and counteracting them. The addition of natural sorbents may affect the immobilization of metals deposited in bottom sediments of water reservoirs. However, the behavior of metals in the presence of sorbents results from their properties and the nature of the sorbent. The positive effect of sorbents on metal immobilization was not observed in every case. The addition of the tested sorbents in the case of cadmium caused an increase in the content of Cd in the mobile fractions, for zinc, lead and copper, stronger binding of metals was found in the stable fractions IV and V. Chitosan stabilized metals more strongly than bentonite, which moved Zn, Pb and Cu to the first mobile fraction.

The obtained values indicate a strong contamination of sediments with cadmium and copper. Calculated values of geoaccumulation indices showed the natural content of Zn in the sediments and the average contamination of Pb.

The research have aimed to establish a proof of concept, determining whether the speciation pattern changes as a result of the use of sorbents. We have shown that the pattern of speciation changes, metals from individual fractions are sorbed with different efficiency. This proof of concept serves as a foundation for further investigations and more comprehensive studies in the future. The limitations of the initial study can inform the design of future research and guide researchers in expanding the scope of their investigations. We plan to undertake further research, which will include, among others: analysing the sorption mechanisms is fundamental to understanding how chitosan and bentonite interact with metal ions which provide valuable information about the chemical interactions and bonding between the sorbents and metal species. Understanding these mechanisms is crucial for optimizing sorption conditions, designing effective sorbents, and predicting sorption behaviour in various environmental scenarios. Additionally, sorbent modification and regeneration is planned. What is more, speciation and fate of sorbed metals will be investigated. Analysing the fate and speciation of sorbed metals is crucial for understanding their long-term behaviour and potential risks.

## 6. Conclusions

Based on the conducted research, the following conclusions were formulated:

- Accumulation of heavy metals in the surface layer of sediments is a reflection of the ecological status of water objects.
- The addition of natural sorbents to bottom sediments shifts the metal content between fractions.
- For different metals, the sorption strength is different and there may be a need to use different sorbents due to the properties of the metal.
- The use of a natural sorbent can immobilize metals and improve the chemical properties of sludge.

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