Paweł KREMS[1*], Małgorzata RAJFUR[1], Maria WACŁAWEK[1] and Andrzej KŁOS[1]

THE USE OF WATER PLANTS IN BIOMONITORING AND PHYTOREMEDIATION OF WATERS POLLUTED WITH HEAVY METALS

WYKORZYSTANIE ROŚLIN WODNYCH W BIOMONITORINGU I FITOREMEDIACJI WÓD ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: The publication is a synthetic review of many years of research on the possibility of using water plants (macrophytes) to assess pollution of surface waters and the possibility of using the biomass in phytoremediation processes. The results of the research of kinetics and equilibria of heavy metals sorption and desorption conditions were presented in order to repeatedly use the biomass, as well as the research on the influence of abiotic factors on sorption processes. Defence mechanisms of macrophytes, which enable them to vegetate in considerably polluted waters, have been discussed. The results presented herein and carried out in many countries demonstrate that macrophytes can be successfully used in the biomonitoring of water environments and phytoremediation of waters and sewage; however, validation of these procedures requires more detailed research of the mechanisms, which accompany them.

Keywords: water plants, heavy metals, sorption, biomonitoring, phytoremediation

Introduction

The concept of a "water plant" is a matter of convention. It is difficult to build a coherent definition of these groups of organisms, due to the connections of both higher and lower water plants with various transitory forms of land plants. One of the definitions describes water plants (hydrophytes) as the organisms, which by way of natural selection adapted to a water environment and are inseparably connected with it. Another term defines water plants, also referred to as *macrophytes*, as the plants belonging to different systematic groups, excluding single-cell and colonial algae. Macrophytes are often regarded as the group of plants including vascular plants, water moss and algae generating macroscopic thallus. Macrophytes are quite a differentiated group of plants from a morphological point of view. In Poland, the group includes all chara (*Charophyta*), some mosses (*Bryophyta*), a few ferns (*Pteridophyta*) and a small group of spermatophytes (*Spermatophyta*) [1-5].

[1] Chair of Biotechnology and Molecular Biology, Opole University, ul. kard. B. Kominka 6, 45-032 Opole, Poland, phone +48 77 401 60 42, fax +48 77 401 60 50, email: aklos@uni.opole.pl
* Corresponding author: kremspawel@gmail.com

Water plants have many common features, which result from the fact that they are perennial plants, which lose their assimilation organs in winter [1]. They inhabit the littoral zone of rivers and water reservoirs, from the banks to the light penetration zone, which indicates that macrophytes live in differentiated habitats [6, 7].

The research of the accumulative properties of water plants have been carried out for many years in order to use them in biomonitoring and phytoremediation of waters contaminated by heavy metals. The research focuses on, among others, sorption mechanisms, the factors influencing the process kinetics and equilibrium as well as mutual relations between concentrations of pollution accumulated in their structure and habitat. Macrophytes' resistance to pollution and the possibility of their repeated use in water and sewage phytoremediation processes have been tested.

The most frequent immersed and floating types and species of water plants in Poland tested for the possibility of using them in biomonitoring of water ecosystems and water and sewage phytoremediation are *Elodea canadensis* L., *Ceratophyllum demersum* L., *Myriophyllum spitacum* L., *Potamogetonaceae* and *Lemna minor* L. [8-12].

The objective of the research was to systematise the obtained results and conclusions regarding sorption properties of various types of water plants, in particular the immersed and floating plants, published in science magazines accessible in *Science Direct* base. The results of research regarding the use of macrophytes for biomonitoring and phytoremediation of waters were presented.

Biosorption and bioaccumulation of heavy metals by macrophytes

In order to assess sorption qualities of macrophytes, research has been in progress on sorption kinetics and equilibrium parameters. The assessment includes also the possibility of desorption of the accumulated heavy metals from plants biomass in order to reuse it in phytoremediation processes.

The immersed and floating water plants can absorb heavy metals from bottom sediments via their root systems, if they have one, or via their whole surface directly from water. It was confirmed that concentrations of the analytes accumulated in water plants are correlated with their concentrations in water and/or bottom sediments [13].

It is assumed that the process of sorption of metals via the surface of water plants by ions exchange [14, 15]; however, it was also noticed that the sorption mechanism can have different characteristics, which is confirmed by low energy of the sorption process activation and, in certain cases, fast and easy desorption processes [16, 17].

The process of ions exchange, as the main mechanism of cations sorption, is indicated by the studies carried out with *Potamogeton natans*. It was confirmed that, among others, this macrophyte sorbs hydrogen cations at low pH values of the solution and then desorbs with the increasing pH of the solution, which it was in contact with [18]. Similar conclusions were made on the basis of the research results, which show that heavy metals cations sorption is simultaneous with desorption of cations naturally bound in macrophytes: H^+, Na^+, K^+, Ca^{2+} and Mg^{2+} [19, 20].

Veglio and Beolchini declared that there are many ways of metals absorption by plant cells. They divided biosorption processes into surface sorption as well as extra- and intracellular accumulation [21]. Another division differentiates biosorption as a fast and reversible process, based on physical and chemical binding of metals cations (complexing

and chelation, ions exchange, microprecipitation and adsorption) and bioaccumulation, as a slow and irreversible process, which takes place in living organisms only and which mainly influences a cell's metabolic activity [22-24].

Mainly the model of the pseudo-second order reaction [23, 25-30] and, less frequently, the model of the pseudo-first order (the Lagergren model) [19] is used to describe sorption kinetics. The studies of kinetics aim at establishing the reaction speed constant. This parameter assists in being able to assess the sorption efficiency in time, also in dynamic equilibrium status.

The research results show that the time needed to achieve equilibrium depends on the plant type but also on the type of sorbed cations. The example is the study of nickel and chromium sorption in *Elodea canadensis*. It was confirmed that, depending on the initial concentration of the solution, *E. canadensis* accumulates in the same time from 25 to 40 times more Ni than Cr. For example, after 24-hour sorption, Ni content in the plant biomass amounted to 0.037 mmol/g d.m., and Cr 0.0016 mmol/g d.m. (d.m. - dry mass) [31].

One of the examples of the studies of surface sorption kinetics is the studies of copper, zinc and lead cations in macrophytes: *Myriophyllum spicatum* and *Ceratophyllum demersum*. The results of studies of the sorption from solutions of these metals with volume of 250 cm^3 and initial concentrations of 10 mg/dm^3 show that the time required to achieve dynamic equilibrium is approximately 20 minutes [25]. This was confirmed by other tests on the same plant species [23, 26, 29]; however, it is emphasised that the equilibrium status during sorption of copper in *Myriophyllum spicatum* is achieved after 35 minutes [30]. Other studies of lead sorption with the same macrophyte show that after 10 minutes, 66% of lead cations present in initial solution were sorbed, whereas in dynamic equilibrium achieved after 20 minutes, 85% of Pb cations were sorbed [28]. Studies of mercury sorption kinetics in *Potamogeton natans* show that after 30 minutes approximately 90% Hg was sorbed from solutions [18].

Studies of sorption kinetics and efficiency relate also to the above-mentioned bioaccumulation - a slow process lasting many days.

The example is cadmium bioaccumulation studies in the plants *Myriophyllum*. Sorption was carried out from the solutions with concentrations from 0.018 to 0.14 mmol/dm^3. After 96 hours, from 81 to 95% of Cd cations were sorbed, depending on the plant type and initial concentration of cadmium in the solution [32]. Macrophyte *Ceratophyllum demersum* kept in selene solution with concentration of 0.13 mmol/dm^3, after 31 days sorbed 0.0062 ±0.0011 mmol/g d.m., whereas *Myriophyllum spicatum* after 13 days sorbed 0.0027 ±0.0001 mmol/g d.m. of the analyte [33]. In other studies, *Ceratophyllum demersum,* after 24 h in arsenic solution with initial concentration of 0.04 mmol/dm^3 sorbed 0.003 mmol/g d.m. of this element, and after 48 hours 0.004 mmol/g d.m. [34]. After 7 days, from the solution with initial lead concentration of lead of 0.1 mmol/dm^3 this macrophyte accumulated 0.008 mmol/g d.m. Pb (95.8%); however, most of the lead was accumulated already after day 1: 0.0059 mmol/g d.m., *ie* 70% of the available lead cations [35].

Studies of heavy metals sorption efficiency by *Potamogeton pectinatus* and *Potamogeton malaianus* showed that they accumulate on average 92% Cd, 79% Pb, 86% Mn, 70% Cu and 67% Zn, present in the initial solution [36]. A comparison of sorption properties *Elodea canadensis* and *Salvinia* sp. was carried out [37] and sorption

characteristics of *Lemna minor*, in which from the solution with initial concentration of 10 mg/dm^3 the sorbed volumes were 98.83% Pb, 94.07% Cd, 72.78% Cu, 69.03% Ni and 63.42% Zn. It was confirmed that the efficiency of sorption of most metals was greater in the solutions with the initial concentrations of 10 mg/dm^3 in comparison with the solutions with twice as large concentrations, which probably results from filling the active centres by the sorbed metals [19].

The presented research results show that the equilibria resulting from surface sorption, the main mechanism of which is the ions exchange, stabilise after approximately 30 minutes. In the case of bioaccumulation in extra- and intracellular structures, studies of sorption processes can even last several dozen days [38].

Table 1

Equilibrium parameters of the selected types of water plants: c_{max} - sorption capacity,
t - time needed to achieve equilibrium, pH of the solution in equilibrium

Aquatic plants	Heavy metal	c_{max}		t [min]	pH	References
		[mg/g d.m.]	[mmol/g d.m.]			
Myriophyllum spicatum	Cu	10.37	0.163	120	5.0-6.0	[23]
	Zn	15.59	0.238			
	Pb	46.49	0.224			
	Cu	6.20	0.098	120	5.0-6.0	[25]
	Zn	14.00	0.214			
	Pb	45.00	0.217			
	Pb	41.14	0.199	120	5.0	[28]
	Cu	12.07	0.190	-	-	[29]
	Cu	10.80	0.170	120	5.0-6.0	[30]
	Co	2.30	0.039	120	8.0	[39]
	Ni	3.00	0.051			
	Zn	6.80	0.104			
	Cu	12.90	0.203	60	-	[40]
	Zn	13.50	0.206			
	Pb	55.60	0.268			
Myriophyllum alterniflorum	Cu	13.90	0.219	120	5.0	[27]
	Cd	11.10	0.099			
Ceratophyllum demersum	Cu	6.17	0.097	120	5.0-6.0	[25]
	Zn	13.98	0.214			
	Pb	44.80	0.216			
	Cu	6.17	0.097	120	5.0-6.0	[26]
	Zn	13.90	0.213			
	Pb	44.80	0.216			
Potamogeton lucens	Cu	40.80	0.642	-	-	[15]
	Zn	32.40	0.495			
	Pb	141.00	0.681			
Potamogeton natans	Hg	180.00	0.897	180	7.2	[18]
Spirogyra sp.	Cu	137	2.16	40	5.0	[41]

The Langmuir isotherm model is mainly used to describe dynamic equilibrium [23, 25-27, 29]. It assumes the existence of a definite number of active locations, in which sorption of only one chemical substance is possible. The maximum sorption capacity is equal to filling all active locations. The authors also point out good correlations between the experimental data and calculations from the model [23, 25, 28, 29]. The equilibrium status

is also described by other isotherm models, among others, Freundlich isotherm [38] and Spis isotherm (generalised Freundlich isotherm) [28].

The results of laboratory tests of sorption capacity of different macrophyte types, defined on the basis of Langmuir isotherm, are presented in Table 1. For comparison, the table includes the sorption capacity of *Spirogyra* sp. referring to copper.

The presented values of sorption capacities in mmol/g d.m. show differences resulting from physical and chemical properties of the sorbed cations. Most of the data presented in the Table show that, after conversion to mol, sorption is most difficult with regard to copper and similarly to zinc and lead cations. These results also show considerable differences in assessment of sorption capacity of the same plant, with reference to one metal. For example, the capacity of *Myriophyllum spicatum* with regard to copper cations was assessed at 0.098 mmol/g d.m. [25] and at 0.203 mmol/g d.m. [40]. The problem is that authors rarely provide uncertainty of the sorption capacity determination. Tests of copper sorption by *Spirogyra* sp., within the small initial metal concentrations in solution of 10^{-3}-10^{-2} mmol/dm^3, showed that the standard error in sorption capacity determination, depending on the experiment conditions, may amount even to 10^4% [42].

There are also differences regarding sorption capacity of immersed and floating plants. The data included in Table 2 show that the best sorption characteristics for Cu, Zn and Pb is the floating leaves plant - *Potamogeton lucens*. However, numerous other studies emphasise the reverse effect. The comparison of sorption characteristics of several types of macrophytes, with reference to accumulation of Ni, Cu and Cd shows that immersed plants have superior sorption characteristics. Among these plants, *Ceratophyllum demersum* presented the best sorption characteristics. In experimental conditions, it accumulated 0.0030 mmol/g d.m. of Ni, 0.0041 mmol/g d.m. of Cu and 0.00071 mmol/g d.m. of Cd. In the same conditions, macrophyte *Potamogeton natans* with floating leaves accumulated 0.0012 mmol Ni/g d.m., 0.0024 mmol Cu/g d.m. and 0.00037 mmol Cd/g d.m. [43]. Similar correlations are confirmed by other experiments [43-46]. It is supposed that better sorption characteristics of immersed plants are related to the specific structure of these macrophytes. Their leaves have underdeveloped skin (sometimes none) and lamina, which support a fast exchange of matter with the environment [43].

The presented results of research show, in some cases, considerable differences, which may result from different experiment conditions and a lack of recognition of abiotic and biotic factors, which influence sorption processes.

The influence of abiotic and biotic factors on sorption characteristics of macrophytes

Accumulation of heavy metals by water plants in natural conditions is influenced by a number of abiotic factors, among others pH, presence of other cations in the waters of the reservoir, temperature, intensity of photosynthetic light and the exposure period, as well as biotic factors, among others, specific features (*eg* hyperaccumulation capacity and resistance to high concentration of pollution), metal storage and detoxification forms by a plant as well as interaction with other compounds present in a cell [47].

The influence of abiotic factors on sorption characteristics of macrophytes

The pH of solution is one of the most frequently tested parameters. Hydrogen cations influence solubility of heavy metal compounds; they locate themselves in active centres and influence the ionisation degree of the sorbate during the process. The tests carried out with the use of *Myriophyllum spicatum* showed that the maximum efficiency of lead cations sorption (76%) was achieved at pH = 5. Efficiency of Pb cations sorption at pH 2.0 was only 37%. It was noticed that the very competitive hydrogen cations sorption causes reduction of lead cations sorption [28]. Similar results were obtained when analysis sorption processes of Se(VI) by *Lemna minor* within pH changes range from 2.0 to 8.0. The maximum sorption efficiency is achieved at a solution pH of 6 [48].

General salinity of a solution has a similar influence on heavy metals sorption. The research carried out with *Elodea canadensis* and *Potamogeton natans* showed that with lower salinity, sorption efficiency of Cu, Zn and Cd increases in these macrophytes. The research also showed that temperature influences sorption of metals by macrophytes. It was confirmed that with the increase of temperature within the range from 278 to 293 K, sorption efficiency increases. It is supposed that temperature influences the change of cell membrane lipids composition, which may support metals sorption [49].

Macrophytes resistance and reactions to the presence of heavy metals in their environment

Heavy metals, among others Fe, Mn, Cu, Zn, Mo and Co, in physiological quantities perform important functions in living organisms; they make up metal-organic compounds, *eg* metalloproteins and are necessary to maintain the appropriate structure and operation of enzymes. However, they are toxic in greater concentrations. They cause, among others, damage to root cells and limit their growth, change permeability of cell membranes and slow down the transport of electrons in photosynthesis process [50, 51].

Water plants, which live in the environment with a high concentration of heavy metals, developed effective defence systems including, among others, a mechanism to avoid metal ions, stopping metals in the cell membrane, *eg* by organic acids and amino acids, by the increase of glutathione biosynthesis, production and activation of various antioxidant particles and enzymes [35].

Elodea canadensis is the example of a macrophyte, which was many times analysed for anatomical, morphological and physiological changes, caused by the influence of heavy metals. It was found, among others, that *Elodea canadensis* has a large tolerance to the presence of some metals, without any symptoms of oxidative stress or damage to cell membrane [52]. The plant, incubated briefly in the solutions with large lead concentrations (0.24 and 0.48 mmol/dm^3), did not show reduction of *chlorophyll a* and *chlorophyll b*, and the "ageing" symptoms occurred only after 168 hours [53]. It was also confirmed that after 5 days of incubation in Ni solution with concentration of 0.01 mmol/dm^{-3}, there was no slowing down of growth or reduction of the quantity of photosynthetic dyes; at greater concentrations of this metal, the plant activates defence mechanisms, among others, the increase of biosynthesis of the compounds containing thiols [54]. Macrophytes *Elodea canadensis* and *Salvinia* sp. immersed in a ferrous solution with concentration of

0.09 mmol/dm^{-3} after 10 days did not show reduction of growth or any other symptoms of toxic influence of the metal, contrary to Ni and Cu solutions, which after 5 days caused morphological changes in the tested macrophytes [30]. Laboratory tests also showed that Ni cations, within concentration range from 0.07 to 1.7 mmol/dm^{-3}, slow down metabolism of nutritive compounds, among others, phosphorus and nitrogen [55].

Monthly observations of the external changes in *Elodea canadensis* kept in the solution with gradually increasing cadmium concentration up to 0.1 mmol/dm^{-3} showed that the plant growth was stopped, compared with the control sample. The macrophyte had thinner stems and less developed leaves. Division and growth of chloroplasts were also slowed down, photosynthesis activity was reduced and organisation of cell membrane build up was disturbed [56]. Similar tests showed that slowing down the growth of *Elodea canadensis* could also be noticed in copper salts solutions, within concentration range from 0.016 to 0.16 mmol/dm^{-3}, in which the tested samples were incubated for 25 days [57]. Toxic influence of Cu on this macrophyte was also confirmed by other experiments [54].

Tests were also carried out of the influence of cadmium and lead on cellular ultrastructures of *Elodea canadensis*. It was confirmed that these metals cause changes in the cellular organisation of the plant. Also swelling of chloroplasts was noticed, in consequence of the changes in thylakoids structure. It was also noticed that the stress caused by cadmium cations activated proteins induction - HSP 70 antibodies, belonging to chaperones, the so called chaperone proteins. At a concentration of Cd 0.01 mmol/dm^{-3}, there was a 25% increase of antibodies and at the concentration of Cd 0.1 mmol/dm^{-3}, the antibodies increase was 70%. The authors assume that the chaperones can be responsible for the resistance of *Elodea canadensis* on the toxic influence of Pb and Cd. This gives it an advantage over other macrophytes and the possibility to survive in the conditions lethal to other water plant species [58].

Other tests showed that *Elodea canadensis* binds in its cell membranes approximately 70% Cd from the solution with concentration of 0.6 μmol/dm^{-3}, 30% Zn from the solution with concentration of 30 μmol/dm^{-3} and 50% Cu from the solution with a concentration of 1.0 μmol/dm^{-3}. It was confirmed that most of the accumulated zinc and copper is transported through a cell membrane inside a cell, whereas cadmium remains in the cell membrane of the plant. Zn and Cu are used, among others, to produce the enzyme needed in synthesis of other, physiologically active particles [52].

Myriophyllum spitacum is another frequently tested macrophyte. With the use of infrared spectroscopy with Fourier transformation (FT-IR) on the example of lead, the function groups present on the surface of this macrophyte were identified. Carboxyl, carbonyl and hydroxyl groups were identified, responsible for fixing cations. Involvement of aromatic fatty acids in the process was also suggested [28]. Thanks to the same method, it was confirmed that carboxyl groups in cell membrane of *Myriophyllum spitacum* are responsible for fixing copper [29].

In macrophytes *Myriophyllum aquaticum* collected from the river Xanaes in Argentina, polluted by waters from fields containing, among others, Co, Cu, Fe, Mn, Ni, Pb and Zn, a decrease in photosynthetic pigments quantity in *chlorophyll a* and *b* and damage of its structure were observed. It was stated that the phenomenon may be caused by replacement of magnesium ions by heavy metals in chlorophyll particles, which results in reduced catchment of photons and limited photosynthesis process. Some heavy metals, even at low concentrations, can cause oxidative stress, which stops chlorophyll biosynthesis and

accelerates lipids pre-oxidation, which leads to damage of cellular membranes. The influence of heavy metals on the changes of physical and chemical parameters of the tested organisms was also emphasised [59].

A relatively high resistance of *Elodea canadensis* and *Myriophyllum aquaticum* to the content of heavy metals in their environment and the fact that they can sorb cations via all surface directly from water (similarly to lichens and mosses used in biomonitoring of atmospheric aerosol pollution [60, 61]) shows that they can be used in the biomonitoring of surface waters pollution with these analytes.

Use of macrophytes in biomonitoring of surface waters

Numerous bioindicators and biomonitors, among others algae [62, 63], water animals [64, 65] and macrophytes [54, 66] are used to assess pollution of water environment. The main objectives of biomonitoring research of surface waters are the assessment of reservoirs pollution, identifying sources of pollution, long-term monitoring in order to define the dynamics of the changes, defining consequences of pollution for biocenosis and comparative studies between different elements of the ecosystem.

Water plants used in biomonitoring should meet the defined criteria, among others, collect large amounts of pollution without damaging themselves, be common in the studies area, be easy to identify and collect for the purpose of studies and, in order to asses seasonal changes, should have a relatively long vegetation period [67-69]. Quantitative assessment of reservoirs pollution also requires that a biomonitor shows statistically relevant correlations between concentration of analytes collected in it, and the concentration in water and/or bottom sediments.

There is a variety of different fresh water reservoirs in nature. They can be divided into natural ones, such as lakes, rivers, streams, natural ponds and marshes, and anthropogenic reservoirs, such as dam reservoirs, artificial ponds, canals and melioration ditches [7]. Many biomonitoring studies of fresh water ecosystems have been carried out with the use of immersed or floating water plants as indicators.

One of the objectives of such studies is to compare the correlations between concentrations of analytes accumulated in various plants and their anatomical parts with concentrations of these analytes in water and bottom sediments. The example includes studies of heavy metals pollutions, *ie* Cu, Zn, Cd and Pb of rivers and water reservoirs in western and central Slovakia. During these studies 21 types of water plants were used, among others: *Batrachium aquatile, Batrachium penicillatum, Ceratophyllum demersum, Elodea nuttallii, Lemna minor, Myriophyllum spicatum, Potamogeton nodosus* and *Potamogeton pectinatus*. The obtained results show differentiated level of plants pollution in the studied water reservoirs. The largest average concentrations of Cu, Zn and Cd were identified in *Batrachium aquatile*, whereas Pb in *Fontinalis antipyretica*. From the studied types, higher concentrations of heavy metals were observed in the immersed plants, in comparison with the free-floating surface plants [70]. This has been confirmed by the studies published in other works [44, 45].

Elodea canadensis Michx. was used during the studies carried out in four eutrophic lakes in southern Finland. In the leaves, sprouts and roots of this macrophyte as well as in bottom sediments of these reservoirs, concentrations of Cr, Mn, Fe, Ni, Cu and Zn were analysed. The obtained results show that concentrations of heavy metals are different in

different parts of plants. *Elodea canadensis* accumulates Fe and Cu best in roots and Cr, Mn and Ni in leaves. Zn concentration was similar in all parts of the plant. Concentration of the analysed metals in bottom sediments was comparable to their concentration in plants, except for Mn [71].

In Moldavia, the river Dniestr waters were analysed for mercury contamination. Several water plants were used for that purpose: *Potamogeton pectinatus* L., *Myriophyllum verticillatum* L., *Potamogeton perfoliatus* L., *Elodea canadensis* Michx. and *Ceratophyllum demersum* L. The studies showed that these plants can be successfully used as bioindicators of Hg pollution in surface waters. It was also shown that there is an important correlation of Hg content in bottom sediments, water and biomass of the studied plants [72].

Pollution with Cu, Zn, Cd and Pb of the river Nile waters was analysed in Egypt. The metals were studied in six water plants: *Ceratophyllum demersum* L., *Echinochloa pyramidalis* (Lam.), *Eichhornia crassipes* (Mart.), *Myriophyllum spicatum* L., *Phragmites australis* (Cav.) and *Typha domingensis* (Pers.) as well as in bottom sediments and water. Concentrations of heavy metals in water, sediments and plants were changing in line with the following order: Zn > Cu > Pb > Cd. Seasonal nature of concentration changes of the studied analytes was pointed out. The ability to accumulate metals by the studied plants was changing in line with the following order: *C. demersum* > *E. crassipes* > *M. spitacum* > *E. pyramidalis* > *T. domingensis* > *P. australis*. On the basis of the obtained results, it was confirmed that in comparison with sprouts, the roots of all studied plant types contain greater concentration of Cu and Zn, whereas the leaves contain the largest concentrations of Pb. Cd concentrations in different plant organs are comparable, except for *M. spicatum*, in which the largest Cd concentrations were observed in leaves [66].

Another example is the studies carried out in south-eastern France, where the plants *Elodea canadensis* and *Elodea nuttallii* to assess pollution with S, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb were used. Concentration of the analytes was assessed for two years in water (a stream and two ponds), bottom sediments and biomass of the studied plants. It was found out that the analytes accumulation was influenced by the location of samples taking but also the analyte type and season of the year. It was also shown that the sorption characteristics of *E. canadensis* and *E. nuttallii* are comparable [73].

Another example of biomonitoring studies with the use of water plants are the studies carried out in New Zealand, which covered waters in the volcanic region of Taupo (geothermal area Tokaan and upper and lower section of the river Waikato). During these studies, 16 types of water plants were used, among others *Ceratophyllum demersum, Elodea canadensis, Lemma minor, Myriophyllum propinquum, Polygonum hydropiper, Callitriche petriei, Egeria densa*. Arsenic concentration was assessed in plants, bottom sediments and water. It was discovered that As concentration in *Ceratophyllum demersum* was 100 times larger than in bottom sediments and 1000 times larger than in water. Moreover, it was confirmed that As concentration in water, bottom sediments and the studied plants was twice larger than the water quality standard applied in New Zealand [74].

In Poland, similar studies have been carried out with the use of *Elodea canadensis* Michx. Contamination with heavy metals was studied in three small rivers in the river Odra catchment area: Row Polski, Kanal Polski and Row Slaski. An increased concentration of the following metals was identified: Al, V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb. It was found out that they originate mainly from communal sewage discharged to the rivers. Also the positive correlations between concentrations of Al, Cr and Cu in bottom sediments, water

and the studied macrophytes were emphasised [75]. Studies were carried out near Wroclaw with the use of several types of water plants, aiming at assessment of water quality and identifying potential sources of contamination. It was found out that average concentration of the identified heavy metals (Cr, Co, Ni, Cu, Zn, Cd, Hg and Pb) exceed the allowed concentrations for waters, which are the source of potable water. They originate mainly from a pesticide factory in Brzeg Dolny and from a power plant and steel mill sewage. Comparison of concentrations of the studied analytes in the individual groups of water plants showed that the largest concentrations of Cr, Co, Ni, Cu and Zn were present in totally immersed plants with root systems. In turn, the largest concentrations of Pb were observed in the plants floating under the water surface. The largest concentrations of Cd and Hg were observed in the macrophytes, where leaves float on the water surface. Also, the correlation between concentration of Cu, Zn and Cd in the plant biomass and concentration of Cu in water and between concentration of Ni and Cd in the plants and concentration of Ni in water were pointed out [76]. Biomonitoring studies of two small rivers were carried out: Olobok and Pilawa, located in south-western Poland. The following macrophytes were used in the studies: *Elodea canadensis*, *Callitriche verna*, *Potamogeton crispus*, *Potamogeton natans*, *Ceratophyllum demersum*, *Polygonum amphibium* and *Veronica beccabunga* [77].

Studies of surface waters pollution with the use of macrophytes were also carried out in Czech Republic, where on the basis of the analytes concentrations accumulated in: *Potamogeton crispus, Potamogeton. pectinatus, Myriophyllum spicatum, Elodea canadensis* and *Polygonum amphibium assessment* of the pollution of the river Dyi and its catchment area [78], in Romania (samples of *Ceratophyllum* sp., *Myriophyllum* sp., *Potamogeton* sp. were taken from waters in the Danube delta) [65], in the former Yugoslavia *(*samples*: Ceratophyllum demersum* L., *Myriophyllum spicatum* L. and *Nymphoides flava* Hill. were taken in the Provala lake waters) [45], in Serbia, in the canal system Danube - Tisa - Danube (samples for tests collected: *Ceratophyllum demersum* L., *Nymphaea alba* L., *Phragmites communi*s Trin., *Trapa longicarp*a Jank., *Typha angustifolia* L., *Elodea canadensis* L., *Phragmites communi*s Trin. *Potamogeton pectinatus*) [79] and waters of the Danube (samples taken: *Potamogeton perfoliatus, Potamogeton pectinatus, Potamogeton lucens, Ceratophyllum demersum* [80], in Moldavia (samples: *Myriophyllum verticillatum* L., *Potamogeton perfoliatus* L., *Potamogeton pectinatus* L., *Elodea canadensis* Michx. collected in a reservoir in Dubossary) [81], in Greece (samples taken: *Ceratophyllum demersum, Myriophyllum spicatum, Potamogeton nodosus* and *Lemna minor*) [82], in Turkey, where on the basis of analytes accumulated in *Potamogeton pectinatus L.,* pollution of marshes in the central region was studied [83], in China (samples: *Potamogeton pectinatus L.* and *Potamogeton malaianus Miq.* taken from the river Donghe) [36] and in Argentina, where from the river Xanaes near Cordoba samples of *Myriophyllum aquaticum* were taken [59].

As evident from the quoted examples, at the current stage of the studies, it is essential to identify correlations between the concentrations of analytes accumulated in various plants and their anatomical parts, with concentrations of these analytes in water and bottom sediments. The studies show that different parts of plants demonstrate sorption preferences regarding different metals present in the form of ions in water and accumulated sediments, which permits selective assessment of contamination with heavy metals of these ecosystem components. However, it is hard to definitely asses the correlations presented in the articles,

due to lack of information on the errors count; however, the authors clearly declare that macrophytes can be successfully used in biomonitoring of heavy metal pollution in surface waters and bottom sediments.

Use of water plants for removal of heavy metals from water and sewage

Phytoremediation is a technology of purification based on the use of higher plants and the related microorganisms in order to clean or stop spreading pollution in the environment [84]. Phytoremediation techniques use natural processes, during which plants together with their risospheric symbiants accumulate, deactivate, detoxify or evaporate pollution from soil, water or air [85-88], however, in reality, these processes are much more complex [85, 86].

The water plants used in phytoremediation processes should be tolerant to a large concentration of xenobiotics and should have the ability to accumulate several contaminants simultaneously, high level of pollution biodegradability, even at a relatively low pollution level, fast growth, large biomass production, resistance to diseases and pest as well as difficult environment conditions. Certain plants have the ability to accumulate pollution by fixing it in the structure of own cells; others, in turn, can absorb toxins as a natural effect of adjustment to difficult conditions in a polluted environment [86].

In recent years, more attention is paid to the use of various types of water plants in the processes of cleaning waters and sewage, mainly from heavy metals. The biggest advantage of the phytoremediation process, as the method for removing heavy metals, is low costs versus classical cleaning methods, its simplicity, which improves efficiency and makes it economically feasible. There are no special requirements regarding the supply of nutritive elements to the plants, which take part in the cleaning process [89].

The studies regarding the use of water plants to clean water and sewage aim at assessing the ability of water plants to remove heavy metals from solutions, the speed of the process, the influence of large concentrations of analytes on their morphology and physiology and assessment of the possibility of desorption of heavy metals from plants, in order to reuse the same biomass several times.

Laboratory tests were carried out, which showed that certain types of water plants are capable of hyperaccumulating heavy metals from solutions. One of the plants with such characteristics is *Elodea canadensis* Michx. The plant accumulates large amounts of Cu, Zn and Cd and, as was also confirmed, large concentration of Cu and Zn in its cells does not stop growth of the plant and further accumulation of metals [52]. Other studies also showed the ability of this macrophyte to hyperaccumulate Cr [90]. Good sorption characteristics of Cu, Zn, Cd and Pb from solutions are demonstrated by: *Lemna minor, Elodea canadensis* and *Leptodictyum riparium* [91]. Studies were also carried out with *Ceratophyllum demersum*. From the solution with initial concentrations: 4.866 µmol Cr/dm^3, 6.63 µmol Mn/dm^3, 74.91 µmol Fe/dm^3, 1.338 µmol Cu/dm^3 and 7.784 µmol Pb/dm^3, after 15 days of exposure, the plant accumulated 92% Cr, 80% Mn, 95% Fe, 90% Cu and 70% Pb [28].

Good sorption characteristics can also be attributed to *Lemna minor*. Using this macrophyte, from lead solution with initial concentration of 0.024-0.048 $mmol/dm^3$ on average 76% Pb was removed, whereas from nickel solutions with initial concentrations of 0.43-0.86 $mmol/dm^3$ on average 82% of the metal was removed [92]. Other studies show

that *Lemna minor* can also be used to remove Cu and Cd from solutions [93] and with low concentrations, Cr, Zn and As [38, 94].

Table 2 presents information on macrophyte studies regarding sorption characteristics of selected metals and literature containing descriptions of the studies.

Table 2

Studies of macrophytes in order to assess their ability to accumulate heavy metals

Aquatic plants	Heavy metal	References
Ceratophyllum demersum	Cu, Zn, Pb	[26]
Elodea canadensis	Cr	[90]
	Pb	[95]
	Cu, Zn, Cd	[52]
	Cu, Zn, Cd, Pb	[91]
Lemna gibba	As, U	[96]
	As	[97]
Lemna minor	Cu, Zn, Cd, Pb	[91]
	As	[98]
	Cr, Cu, Zn, Cd	[38]
	Pb	[92]
	Cu, Cd	[93]
	As, Hg	[94]
Myriophyllum spitacum	Cr, Co, Ni, Cu, Zn, Pb	[23]
	Cu	[30]
Potamogeton natans	Cu, Zn, Cd, Pb	[99]
Potamogeton pectinatus	Cr, Ni, Cu, Zn, Cd, Pb	[100]

Together with the studies related to the use of sorption characteristics of water plants to clean waters, studies have been carried out regarding the multiple use of biomass. This results from the fact that dead biomass does not lose its surface sorption characteristics. In order to reactivate the surface and deactivate heavy metals, desorption of metal cations and their precipitation in insoluble form are carried out by, for example, bathing biomass in H_2S, carbonate or sodium bicarbonate and in solutions with metal chelating factor, *eg* EDTA. Also desorption of metals in acids solutions is carried out [101, 102]. One of the most frequently used desorbing agents is hydrochloric acid. It was confirmed that in HCl solution with concentration of 0.1 mol/dm^3, approximately 55% Cu, 60% Ni and 71-72% Co and Zn desorbed from *Myriophyllum spitacum* [39]. Selenium desorption efficiency from *Lemna minor* in HCl solution with the same concentration amounted to 18% [48]. Hydrochloric acid (0.5%) was successfully used in multiple desorption of copper from the biomass of *Ceratophyllum demersum*, *Myriophyllum brasiliensis*, *Eichhornia crassipes*, *Potamogeton lucens* and *Salvinia herzogii* [15].

The presented studies results show that phytoremediation of water and sewage with the use of immersed and floating water plants can be an effective and economically feasible method of cleaning surface waters and additional cleaning of industrial sewage.

Summary and conclusions

Biomonitoring studies have become more and more popular in assessing pollution of different environment matrices during recent years. The method has many advantages, among others availability of research material, easy and cheap method of sample taking and

the fact that biomonitors accumulate bioaccessible forms of pollution. Studies regarding the use of plants in the remediation processes of soil, air and water have been under way for many years. Similarly, it is a cheap and environment-friendly cleaning method based on, among others, accumulation in plants or deactivation of pollution.

It was confirmed that certain water plants, thanks to their anatomical structure, good sorption characteristics and great resistance to pollution, can be used for both biomonitoring and phytoremediation processes of water and sewage.

The main objectives of the studies of the use of macrophytes in biomonitoring is assessment of water quality, identification of pollution sources and assessment of quality changes of water ecosystems in time. The most frequently used macrophytes in biomonitoring are *Elodea canadensis*, *Ceratophyllum demersum*, *Lemna minor* and the types within the *Potamogeton* and *Myriophyllum genus.* Also, the possibilities of using these plants in phytoremediation processes are analysed.

Still, the correlations between concentrations of pollution in water plants and waters, in which they vegetate, are being studied. The presented examples of research show, in some cases, considerable differences of results, which may depend on different the experiment conditions and lack of recognition of abiotic and biotic factors, which influence sorption processes. However, the authors clearly point out that macrophytes can in future be successfully used in the biomonitoring of heavy metals pollution in surface waters and bottom sediments.

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WYKORZYSTANIE ROŚLIN WODNYCH W BIOMONITORINGU I FITOREMEDIACJI WÓD ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

[1] Samodzielna Katedra Biotechnologii i Biologii Molekularnej, Uniwersytet Opolski

Abstrakt: Publikacja jest syntetycznym przeglądem prowadzonych od wielu lat badań, dotyczących możliwości zastosowania roślin wodnych (makrofitów) do oceny zanieczyszczenia wód powierzchniowych oraz możliwości

wykorzystania ich biomasy w procesach fitoremediacji. Przedstawiono wyniki badań dotyczących kinetyki i równowag sorpcji metali ciężkich, warunków desorpcji, w celu wielokrotnego wykorzystania biomasy, oraz badań dotyczących wpływu czynników abiotycznych na procesy sorpcji. Omówiono mechanizmy obronne makrofitów, umożliwiające im wegetację w wodach o znacznym zanieczyszczeniu. Zaprezentowane wyniki badań, prowadzonych w wielu krajach świata, wskazują, że makrofity mogą być w przyszłości z powodzeniem wykorzystywane w biomonitoringu środowiska wodnego oraz w fitoremediacji wód i ścieków, przy czym walidacja procedur wymaga dokładniejszego poznania mechanizmów, jakie towarzyszą tym procesom.

Słowa kluczowe: rośliny wodne, metale ciężkie, sorpcja, biomonitoring, fitoremediacja