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INSIGHTS INTO PH DYNAMICS, DISSOLVED OXYGEN VARIABILITY, AND ION REMOVAL EFFICIENCY IN FLOATING TREATMENT WETLAND

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Abstract: *This paper aims to analyse the dynamic responses within FTW constructed on the riverbank, focusing on pH, dissolved oxygen (DO), and the dynamics of calcium and magnesium concentrations. While some research has been carried out on Ca and Mg behavior in constructed wetlands no papers specifically addressed the removal mechanisms of these ions in FTWs have been found. Results showed that both polluted and treated water exhibited characteristics consistent with a mildly alkaline environment. Extremely low DO levels in cells with floating islands were increased after water passing through cell with algae. Ca removal efficiency in cells with floating island cells ranged from 2% to 6%, while the cell with algae achieved 23% to 49% efficiency. Modest Mg removal (1-6%) could indicate potential challenges in Mg removal processes within the FTWs. The analysis of plant responses to polluted water exposure reveals species-specific variations in Ca and Mg concentrations in shoots and roots. Ca concentration in algae tissue increased over time contrasting the marked decrease of Mg content. The study also revealed a gradual decrease of Ca and Mg concentration in stone wool corresponding to exposure duration. This research contributes to a better understanding of the complex dynamics of water treatment in FTWs, emphasizing the need for continued investigation into ion removal mechanisms, plant responses to increased Ca and Mg concentrations, and the role of algae in these biological systems.*

Keywords: polluted water, calcium, magnesium, macrophytes, water treatment

UVIDI U DINAMIKU pH, VARIJABILNOST RASTVORENOG KISEONIKA I EFIKASNOST UKLANJANJA JONA U BIOLOŠKOM SISTEMU SA PLUTAJUĆIM OSTRVIMA

Sažetak: *Cilj ovog rada je analiza dinamičkih procesa u biološkom sistemu sa plutajućim ostrvima (FTW) konstruisanog na obali reke, sa fokusom na pH, rastvoreni kiseonik (DO) i promenu koncentracija kalcijuma i magnezijuma. Iako je manji broj istraživanja sproveden o ponašanju Ca i Mg u konstruisanim akvatičnim ekosistemima, nisu pronađeni radovi koji bi se posebno bavili mehanizmima uklanjanja ovih jona u FTW.*

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Rezultati su pokazali da su i zagađena i prečišćena voda imale karakteristike slabo alkalne sredine. Ekstremno nizak nivo DO u bazenima sa plutajućim ostrvima povećan je nakon prolaska vode kroz bazen sa algama. Efikasnost uklanjanja Ca u bazenima sa plutajućim ostrvima se kretala od 2% do 6%, dok je u bazenu sa algama postignuta efikasnost od 23% do 49%. Slabo uklanjanje Mg (1-6%) može da ukaže na potencijalne probleme u procesima uklanjanja Mg u FTW. Analiza reakcije biljaka na izlaganje zagađenoj vodi je pokazala varijacije specifične za vrste u koncentracijama Ca i Mg u nadzemnoj biomasi i korenu. Koncentracija Ca u tkivu algi se vremenom povećavala, dok se sadržaja Mg izrazito smanjivao. Studija je takođe ukazala na postepeno smanjenje koncentracije Ca i Mg u kamenoj vuni u skladu sa trajanjem izlaganja supstrata zagađenoj vodi. Ovo istraživanje doprinosi boljem razumevanju složene dinamike prečišćavanja vode u FTW i naglašava potrebu za kontinuiranim istraživanjem mehanizama uklanjanja jona, reakcije biljaka na povećane koncentracije Ca i Mg i uloge algi u ovim biološkim sistemima.

Ključne reči: zagađena voda, kalcijum, magnezijum, makrofite, tretman vode

1. INTRODUCTION

Clean rivers play a crucial role in urban environments, contributing to the overall well-being of cities and their inhabitants. Rivers serve as essential water sources, providing drinking water, supporting agriculture, and sustaining diverse ecosystems. Moreover, they enhance the aesthetic appeal of urban landscapes, offering recreational spaces for residents and promoting biodiversity. However, the escalating pollution of urban rivers poses a significant threat to both the environment and public health. Contaminants such as industrial runoff, untreated sewage, and various pollutants from urban activities can compromise water quality, adversely impacting aquatic life and ecosystems. Furthermore, polluted rivers contribute to the degradation of downstream water bodies and thus affect communities beyond city limits. Addressing river pollution is imperative for ensuring sustainable urban development. Mitigating water pollution involves implementing effective waste management practices, enhancing wastewater treatment infrastructure, and promoting public awareness about the responsible disposal of pollutants.

In this context, floating treatment wetlands (FTW) emerge as a green and cost-effective technology that can help in the treatment of polluted water in urban areas. FTWs, with their innovative use of floating islands planted with vegetation, provide an eco-friendly approach to water remediation. As a crucial part of the biological system, the floating islands can be placed in existing reservoirs and cells or directly on the lake or river. By imitating natural processes, without the use of chemicals or additional energy, and due to the symbiotic relationships between plants, algae, small invertebrates, zooplankton, microorganisms, substrate, and water (Chen et al., 2017; Stottmeister et al., 2003; Yeh et al., 2015) FTWs can be used for the treatment of leachate and field runoff, stormwater, municipal, domestic, industrial, agricultural, and animal wastewater (Cule et al., 2021a; Di Luca et al., 2019; Kadlec and Wallace, 2008; Shahid et al., 2018). Integrating FTWs into urban water management strategies represents a sustainable solution to combat river pollution.

This study analyses the dynamic responses within FTW constructed on the riverbank, focusing on pH, dissolved oxygen (DO), and the dynamics of calcium and magnesium concentrations.

The pH value is an important parameter in assessing water quality, as it, like temperature, influences biological and chemical processes in water (Chapman and Kimstach, 1996). Additionally, an essential indicator of water quality is the concentration of DO, which is influenced by factors such as temperature, salinity, turbulence, atmospheric pressure, and the photosynthetic activity of algae and plants (Rajwa-Kuligiewicz et al., 2015). Calcium (Ca) and magnesium (Mg) are essential elements found in natural waters, contributing significantly to their overall chemistry, and influencing the environment and living organisms. While necessary for ecosystems, their presence in excessive amounts can pose significant challenges for both water quality. Within FTWs, Ca and Mg can play a significant role in facilitating phosphorus precipitation in anaerobic conditions and natural to the basic environment (Verhoeven and Meuleman, 1999). In that sense, the present study provides valuable insights into the dynamics of Ca and Mg within the FTW, revealing the influence of treatment cycles on Ca and Mg concentration and removal efficiency. However, it is important to acknowledge the dearth of existing research on this topic. To date, no research papers have specifically addressed the fate and removal mechanisms of these ions in FTWs. While some studies (Maine et al., 2006; Maine et al., 2009) have investigated Ca and Mg behavior in constructed wetlands, the direct comparison of results remains challenging due to construction differences in the systems.

2. MATERIAL AND METHODS

A floating treatment wetland (FTW) was established along the Topciderka riverbank in Belgrade, Serbia, to explore the potential of employing a nature-based solution for the effective revitalization of contaminated waters during a single vegetation period (May-October).

The FTW setup included a pump for drawing water from the river, a closed 5.0 m³ collection tank, four open rectangular cells with floating islands (3.0 m² surface area, 3.0 m³ volume each), and one open rectangular cell with algae (3.0 m² surface area, 1.5 m³ volume) (Čule et al., 2022). Water meters controlled precise water distribution from cells I-IV to cell V. With 100% cell coverage planned, anaerobic conditions were expected in cells I-IV. The inlet of cell V was positioned 50 cm above the ground to enhance oxygen introduction (Čule et al., 2017). Each of cells I-IV had three floating islands with 25 (in the first three cells) or 30 (in cell IV) seedlings, using stone wool as a substrate. Non-invasive and plants suitable for rhizofiltration (Blaylock and Huang, 2000; Cule et al., 2016; Dushenkov et al., 1995; Kumar et al., 1995; Salt et al., 1995) were selected and obtained from local nurseries. Species *Phragmites australis* (Cav.) Trin. ex Steud (PA) was planted in cell I, while *Canna indica* L. (CI) was in cell II. A mix of *P. australis* and *C. indica* seedlings was established in cell III, with planting a ratio of 12:13. A mix of *Iris pseudacorus* L. (IP; 8 seedlings), *Iris sibirica* 'Perry's Blue' (IS; 5), *Alisma plantago - aquatica* L. (APA; 5), *Lythrum salicaria* L. (LS; 5) and *Menyanthes trifoliata* L. (MT; 6) was planted in cell IV. This planting approach ensured consistent microclimatic conditions for each species within the FTW, facilitating their comparative analysis based on the obtained results (Čule et al., 2021). Algae were introduced directly from the river to cell V.

The FTW start-up phase lasted 45 days, involving regular water changes twice a week and the introduction of new polluted water from the river. Subsequent monitoring focused on four treatment cycles (C1, C2, C3, C4). Each cycle involved pumping water to the collection tank, gravitational transport to four cells with floating islands, 6-day retention, and simultaneous transfer to cell V for an additional 6-day polishing before release into the river. The cycles overlapped, with a new cycle beginning immediately after sampling water, plants, and substrate from the floating islands after the initial 6-day treatment.

Sampling, analysis, and data processing followed internal QA/QC procedures. Polluted water samples were obtained at the beginning of each treatment cycle at the pump outlet, while treated water was sampled every 6 days in cells I-IV and at the end of each treatment cycle in cell V. The composite water sample represented 1L of water collected from 5 spots within each cell (each angle and middle) at approximal 30 cm depth. Initial plant, algae and substrate sampling were done just before the beginning of water treatment (C0) to assess baseline nutrient concentrations. Subsequent plant sampling was done at the end of each cycle in cells I-IV, with roots and shoots separated, washed, dried (Campbell and Plank, 1998), and milled for chemical analysis. One composite plant sample represented one vegetative part of one plant species on one floating island within one cell. The algal samples were collected at the end of each treatment cycle and prepared for analysis according to the same methodology as for plants. The composite algal sample represented algae tissue collected from 5 spots within cell 5 (each angle and middle). The sampling of the substrate was done along with plant sampling. The composite substrate sample represented stone wool collected from 5 spots of one floating island (each angle and middle).

Microwave digestion (CEM MDS 2000, Berghof, Germany, Mod. Speedwave MWS3+) was used for the extraction of Ca and Mg from plant and algae tissue (Șenilă et al., 2011). The extraction of Ca and Mg from the air-dried substrate was done in aqua regia according to the ISO 11466:1995 method.

Temperature, pH, and dissolved oxygen (DO) were measured (HACH HQ 40d Digital Multi 2-channel Meter with automatic temperature calibration) at the beginning of each treatment cycle at the outlet of the pump and directly in cells (each angle and middle) at the end of each treatment cycle. The concentrations of Ca and Mg in water, plants, algae, and stone wool, were analyzed using ICP-OES (Varian Vista-PRO, CCD Simultaneous ICP-OES) according to standard methodology (ISO 11885:2009).

When appropriate, statistical analysis was performed using Analyses of Variance (one-way ANOVA). Significant differences between the groups were determined by a subsequent comparison using Fischer's LSD test ($p < 0.05$). Summary statistics and ANOVA tests were carried out using Statgraphics Centurion XVI (Statpoint Technologies, Inc., Warrenton, VA, USA).

3. RESULTS

The results of the pH analysis of both polluted and treated water are displayed in Table 1. The influent pH ranged from 7.66 to 8.46. Following the initial six days of treatment, a decline in the pH values was observed in the effluent of all cells with floating islands, falling within the range of 7.29 to 7.91. However, upon passing through cell V with algae in all treatment cycles, the pH values of the water increased and were within the limits of 7.79 to 8.43.

Table 1. *pH value of polluted and treated water during experimental period.*

Treatment cycles		C1	C2	C3	C4
Influent to FTW (mg/L)	Tank	8.46	8.38	8.29	7.66
Effluent of single cell (mg/L)	Cell I	7.61	7.52	7.68	7.33
	Cell II	7.85	7.81	7.91	7.29
	Cell III	7.52	7.37	7.42	7.37
	Cell IV	7.57	7.55	7.50	7.33
	Cell V	7.79	8.43	8.14	8.15

Each value represents the value of a composite sample taken from the tank and 5 spots in each cell. C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle. Cell I - *Phragmites australis* (Cav.) Trin. ex Steud., Cell II - *Canna indica* L., Cell III - *P. australis* and *C. indica*, Cell IV - *Iris pseudacorus* L., *Iris sibirica* 'Perry's Blue', *Alisma plantago - aquatica* L., *Lythrum salicaria* L. and *Menyanthes trifoliata* L.

The water temperature (t) showed two different trends during the water treatment period (Figure 1). Temperatures of the influent into the FTW were 24.0°C and 22.5°C at the end of C1 and C2, respectively. Water temperature rose above initial temperatures in cells with floating islands (26.8°C -28.3°C and 22.6 °C-23.1°C in C1 and C2, respectively) but declined again in the cell with algae (19.2°C and 15.5°C in C1 and C2, respectively) till the end of these treatment cycles. Following lower air temperatures in late September and early October, temperatures of influent were lower with values of 18.0°C and 14.5°C at the end of C3 and C4, respectively. Water temperature then further declined in cells with floating islands (16.0°C - 16.6°C and 12.1°C -12.8°C in C3 and C4, respectively) but raised above initial temperatures of influent in the cell with algae (22.5°C and 15.0°C in C3 and C4, respectively) till the end of these treatment cycles.

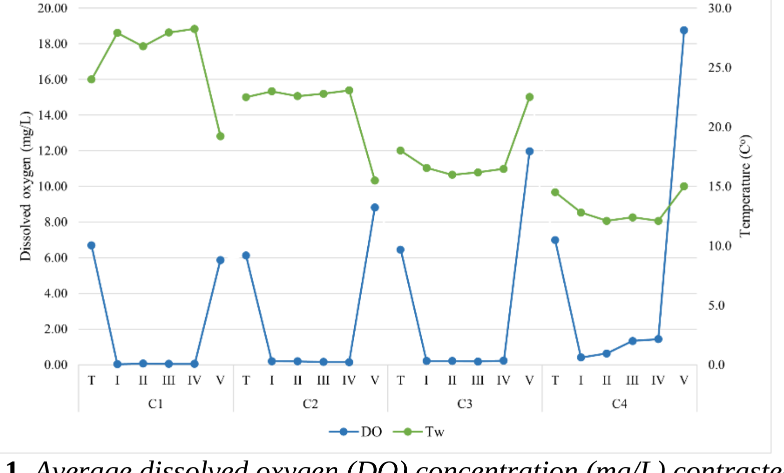

Figure 1. *Average dissolved oxygen (DO) concentration (mg/L) contrasted with water temperature (Tw) during water treatment.*

T - tank, C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle; Cell I - *Phragmites australis* (Cav.) Trin. ex Steud., Cell II - *Canna indica* L., Cell III - *P. australis* and *C. indica*, Cell IV - *Iris pseudacorus* L., *Iris sibirica* 'Perry's Blue', *Alisma plantago - aquatica* L., *Lythrum salicaria* L. and *Menyanthes trifoliata* L.; Each value represents the value of the composite sample of water taken from the tank or 5 spots in the cell.

Figure 1 further reveals that dissolved oxygen (DO) concentration maintained relatively constant in influent into the FTW with average values of 6.11-6.98 mg/L during the water treatment period. There is a clear trend of decreasing DO levels after six days of water treatment in cells with floating islands in all treatment cycles. The DO levels declined far below 1.0 mg/L resulting in anaerobic conditions in all cells except in cell III and cell IV in C4 (1.33 mg/L and 1.43 mg/L, respectively). The concentration of DO increased in cell V with algae till the end of each treatment cycle. The DO levels in cell V were higher than the initial DO in influent at the end of C2 (8.81 mg/L), C3 (11.96 mg/L), and C4 (18.77 mg/L), and slightly below in C1 (5.87 mg/L). Even water supersaturation occurred in cell V at the end of C3 and C4 with oxygen saturation of 140% and 183%, respectively.

Table 2 presents the results obtained from the analyses of Ca concentration in both polluted and treated water, alongside the Ca removal efficiency of FTW. The influent Ca concentrations entering the FTW varied from 7.61 mg/L to 8.12 mg/L. Table 2 further reveals that there was a slight increase in Ca concentration in all cells after the first six days of treatment in C1 and C2, except for cells II and III exhibiting very low Ca removal efficiency of 2% and 1%, respectively, at the end of C2. Gradual efficiency increase was noted across all cells with floating islands in C3 and C4. Throughout these treatment cycles, the Ca removal efficiency ranged from 2% to 6%, with the highest efficiency recorded in C4 in Cell II planted with *C. indica*. A significant reduction of the Ca content in the water occurred only in the cell with algae (Cell V) at the end of all treatment cycles (C1-C4). The calcium concentrations in the FTW effluent ranged from 3,99 to 6.22 mg/L resulting in 23% to 49% FTW Ca removal efficiency. The most notable reduction in Ca concentration was observed at the end of C3.

Table 2. *Calcium concentration in polluted and treated water and efficiency of the floating treatment wetland.*

Treatment cycles		C1	C2	C3	C4
Influent to FTW (mg/L)	Tank	7.92	8.12	7.86	7.61
Effluent of single cell (mg/L)	Cell I	8.15	8.21	7.60	7.46
	Cell II	8.07	7.98	7.60	7.18
	Cell III	7.96	8.02	7.64	7.21
	Cell IV	8.25	8.21	7.71	7.48
Reduction of Ca in single cell (mg/L)	Cell I	-0.23	-0.09	0.25	0.15
	Cell II	-0.15	0.14	0.26	0.43
	Cell III	-0.04	0.10	0.22	0.40
	Cell IV	-0.33	-0.09	0.14	0.13
Single cell efficiency (%)	Cell I	-3	-1	3	2
	Cell II	-2	2	3	6
	Cell III	0	1	3	5
	Cell IV	-4	-1	2	2
Influent to Cell V (mg/L)	Cells I-IV	8.11	8.10	7.64	7.33
Effluent of single cell (mg/L)	Cell V	6.13	6.22	3.99	4.99
Reduction of Ca in single cell (mg/L)	Cell V	1.97	1.88	3.65	2.34
Single cell efficiency (%)	Cell V	24	23	48	32

Each value represents the value of a composite sample taken from the tank and 5 spots in each cell. C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle.Cell I - *Phragmites australis* (Cav.) Trin. ex Steud., Cell II - *Canna indica* L., Cell III - *P. australis* and *C. indica*, Cell IV - *Iris pseudacorus* L., *Iris sibirica* 'Perry's Blue', *Alisma plantago - aquatica* L., *Lythrum salicaria* L. and *Menyanthes trifoliata* L.

The results of Mg concentration in both polluted and treated water, along with the Mg removal efficiency of FTW are shown in Table 3. What stands out in this table is the notable absence or low reduction rate of Mg content in all cells. The influent Mg concentrations varied from 7.61 mg/L to 8.12 mg/L. A slight increase in Mg concentration was observed in Cell I and Cell IV at the end of C1 as well as in all cells with floating islands at the end of C2. There was a slight reduction of Mg content in subsequent cycles (C3 and C4) in Cell I-IV with the Mg removal efficiencies ranging from 1% to 4%. Upon passing through the cell with algae, Mg concentrations in treated water surpassed those in the influent, reaching the highest recorded concentration of 2.66 mg/L by the end of C1. The highest Mg removal efficiency of 6% was achieved in Cell V at the end of C4.

Table 3. *Magnesium concentration in polluted and treated water and efficiency of the floating treatment wetland.*

Treatment cycles		**C1**	**C2**	**C3**	**C4**
Influent to FTW (mg/L)	Tank	2.18	2.06	1.99	1.86
Effluent of single cell (mg/L)	Cell I	2.21	2.14	1.96	1.84
	Cell II	2.17	2.11	1.96	1.80
	Cell III	2.13	2.10	1.97	1.78
	Cell IV	2.33	2.16	2.00	1.83
Reduction of Ca in single cell (mg/L)	Cell I	-0.03	-0.08	0.03	0.02
	Cell II	0.01	-0.05	0.04	0.06
	Cell III	0.05	-0.04	0.02	0.08
	Cell IV	-0.15	-0.10	0.00	0.03
Single cell efficiency (%)	Cell I	-1	-4	2	1
	Cell II	1	-3	2	3
	Cell III	2	-2	1	4
	Cell IV	-7	-5	0	2
Influent to Cell V (mg/L)	Cells I-IV	2.21	2.13	1.97	1.81
Effluent of single cell (mg/L)	Cell V	2.66	2.21	2.04	1.75
Reduction of Ca in single cell (mg/L)	Cell V	-0.45	-0.08	-0.06	0.06
Single cell efficiency (%)	Cell V	-20	-4	-3	3

Each value represents the value of a composite sample taken from the tank and 5 spots in each cell. C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle; Cell I - *Phragmites australis* (Cav.) Trin. ex Steud., Cell II - *Canna indica* L., Cell III - *P. australis* and *C. indica*, Cell IV - *Iris pseudacorus* L., *Iris sibirica* 'Perry's Blue', *Alisma plantago - aquatica* L., *Lythrum salicaria* L. and *Menyanthes trifoliata* L.

The results obtained from the analysis of the effects of treatment cycles on the concentration of Ca and Mg in shoots (CaS and MgS, respectively) and roots (CaR and MgR, respectively) of selected plant species are presented in Figure 2 A-G. As evident from the data, there was no significant difference ($p>0.05$) in the Ca concentration of *P. australis* shoots (3.44-4.83 g/kg) concerning the duration of reed exposure to polluted water (Fig. 2A). The same trend was also noted in *M. trifoliata*, with Ca concentration falling within the range of 13.76-16.63 g/kg (Fig. 2G). Figure 2 further reveals that species *C. indica*, *I. pseudacorus* and *I. sibirica* 'Perry's Blue' contained significantly more Ca in their shoot at the end of C4 (15.78 g/kg, 37.78 g/kg and 25.03 g/kg, respectively) compared to treatment cycles that preceded it. At the end of C2, *A. plantago-aquatica* contained a significantly higher Ca concentration of 28.79 g/kg in shoots, while *L. salicaria* had a concentration of 44.19 g/kg at the end of C3, surpassing levels observed in other treatment cycles (Fig. 2E and Fig. 2F, respectively).

Concerning the Mg content in the shoots of selected plants, Figure 2 illustrates that there was no significant difference (p>0.05) in the Mg concentration of *I. pseudacorus* shoots (4.22-5.35 g/kg) and *A. plantago-aquatica* shoots (2.74-3.94 g/kg) concerning the period of exposure of these species to polluted water (Fig. 2C and Fig. 2E, respectively). *I. sibirica* 'Perry's Blue' was the only species that contained significantly higher Mg concentration in shoots (4.36 g/kg) at the end of C4 compared to the preceding treatment cycles (Fig. 2D). Significantly lower Ca concentrations were determined in *C. indica* shoots (4.58 g/kg) sampled at the end of C3 compared to those sampled at the beginning of the experimental period (C0) and at the end of C1 (Fig. 2B). Furthermore, there is a significant decrease in Ca content in the shoots of *P. australis*, *L. salicaria*, and *M. trifoliata* (1.20 g/kg, 3.75 g/kg, and 3.23 g/kg, respectively) at the end of C4 in contrast to the prior treatment cycles.

The present study revealed no significant difference (p>0.05) in the Ca concentration of *I. pseudacorus* and *I. sibirica* 'Perry's Blue' roots (14.92-26.88 g/kg and 18.16-27.50 g/kg, respectively) concerning the duration of species exposure to polluted water (Fig. 2C and Fig. 2D, respectively). Moreover, across the experimental period (C1-C4), there was no significant difference (p>0.05) in the Ca concentration of *P. australis* roots (15.47-20.47 g/kg) (Fig. 2A). However, these Ca concentrations were significantly higher compared to the Ca concentrations in roots (5.15 g/kg) sampled before the beginning of the experiment (C0) (Fig. 2A). *C. indica* roots contained significantly higher Ca concentrations (35.55 g/kg) at the end of the experimental period (C4) compared to all other treatment cycles (Fig. 2B). Conversely, significantly lower Ca concentrations were detected in *A. plantago-aquatica* roots (25.43 g/kg) compared to other treatment cycles (Fig. 2E). Calcium concentrations in the roots of *L. salicaria* significantly increased toward the end of the experiment compared to the Ca concentrations in roots (19.99 g/kg) sampled before the experiment began (C0) (Fig. 2F). In contrast, Ca content in *M. trifoliata* roots (16.72 g/kg) significantly decreased at the end of C4 compared to C1 (Fig. 2G).

Similar to the Ca content, there was no significant difference (p>0.05) in the Mg concentration of *I. pseudacorus* and *I. sibirica* 'Perry's Blue' roots (14.92-26.88 g/kg and 18.16-27.50 g/kg, respectively) concerning the duration of species exposure to polluted water (Fig. 2C and Fig. 2D, respectively). The same trend was also noted for Mg concentration in *P. australis* roots (3.39-4.13 g/kg) (Fig. 2A). A significant decrease in Mg concentration in *C. indica* roots at the end of C1, C2, and C3 was observed when compared to the Mg content in roots (9.85 g/kg) sampled before the beginning of the experiment (C0) (Fig. 2B). However, at the end of the experimental period (C4), there was no significant difference (p>0.05) in root Mg concentration compared to C0 (Fig. 2B). Species *A. plantago-aquatica* contained significantly higher Mg concentration in roots (6.73 g/kg) at the end of C4 compared to C3 (Fig. 2E). Significantly lower Mg concentrations were detected in roots of *L. salicaria* and *M. trifoliata* (2.60 g/kg and 2.12 g/kg, respectively) at the end of C4 compared to the first treatment cycle (C1) (Fig. 2F and Fig. 2G).

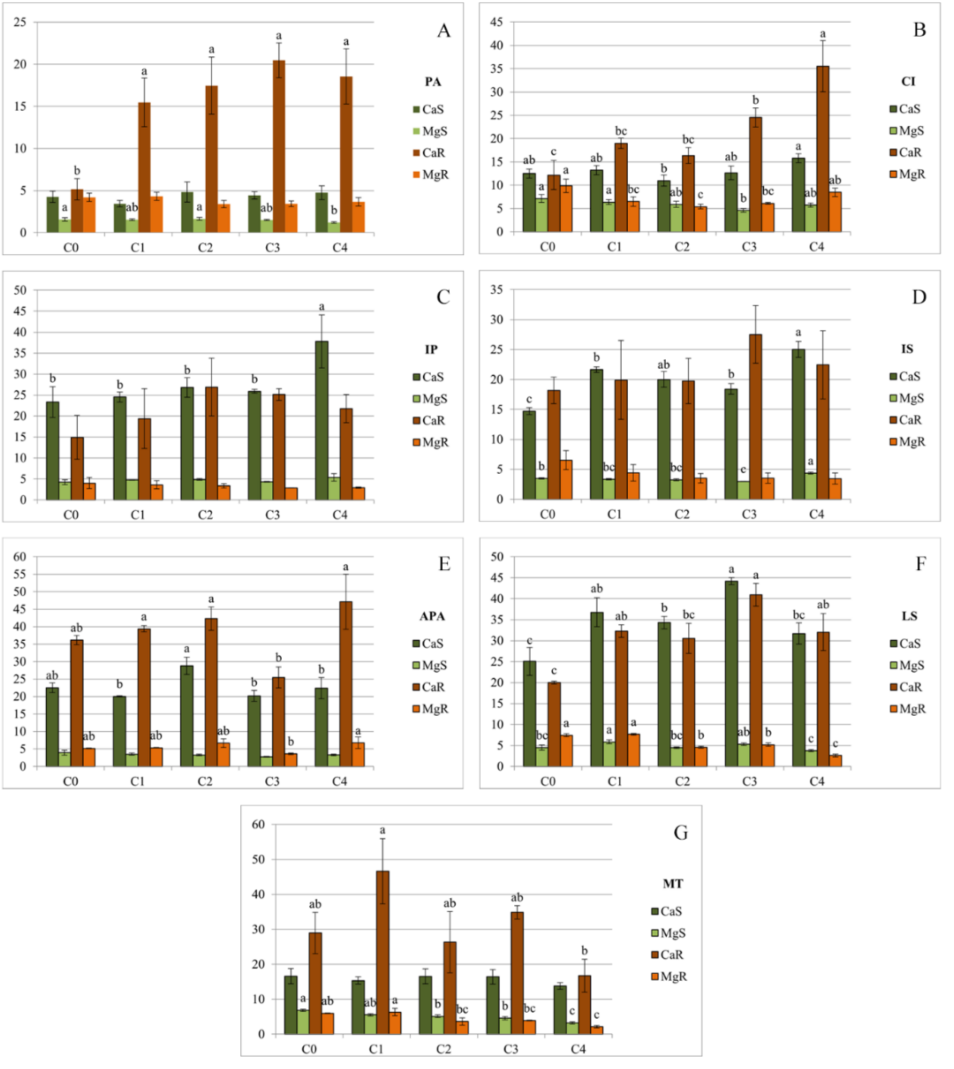

Figure 2 A-G *The concentration of Ca and Mg in shoots and roots (g/kg) of selected plant species in relation to treatment cycle.*

One-way analysis of variance (ANOVA I). Factor treatment cycle with 5 levels: C0 - the beginning of the experiment, C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle; plant species: PA - *Phragmites australis* (Cav.) Trin. ex Steud., CI - *Canna indica* L., IP - *Iris pseudacorus* L., IS - *Iris sibirica* 'Perry's Blue', APA - *Alisma plantago-aquatica* L., LS - *Lythrum salicaria* L., MT - *Menyanthes trifoliata* L.; CaS - concentration of Ca in the shoot, MgS - concentration of Mg in the shoot, CaR - concentration of Ca in the root, MgR - concentration of Mg in the root. Each value represents the mean value ± SE; Within each series mean values with a different letter are significantly different ($p<0.05$).

Table 3 presents the results obtained from the analysis of Ca and Mg concentrations in algae of the genus *Cladophora* sp. across different treatment cycles. There is a noticeable increase in Ca concentration in *Cladophora* sp. corresponding to the duration of exposure to polluted water. The highest Ca concentration, reaching 255.00 g/kg, was observed in C1. Conversely, a marked decrease in Mg concentration in algal tissue was observed from one treatment cycle to the next. At the end of the experimental period (C4), *Cladophora* sp. had the lowest Mg content of 2.67 g/kg.

Table 3. *Concentration of Ca and Mg in algae in relation to treatment cycle.*

Treatment cycles	C0	C1	C2	C3	C4
Ca concentration (g/kg)	186.45	255.00	234.84	197.27	252.80
Mg concentration (g/kg)	6.96	6.30	5.06	3.39	2.67

Each value represents the value of a composite sample taken from 5 spots in Cell V. C0 - the beginning of the experiment, C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle.

Table 4 provides the results obtained from the analysis of Ca and Mg concentrations in stone wool in relation to the treatment cycle. As data reveals there has been a gradual decrease in both Ca and Mg concentrations in substrate concerning the period of exposure to polluted water. Stone wool sampled just before the beginning of the experiment (C0) contained significantly higher Ca and Mg than substrate sampled at the end of the treatment cycles C3 and C4.

Table 4. *Concentration of Ca and Mg in stone wool in relation to treatment cycle.*

Treatment cycles	Ca concentration (g/kg)	Mg concentration (g/kg)
C0	130,75±3,657ab	51,66±1,356a
C1	149,06±11,056a	57,21±1,922a
C2	129,41±4,080ab	50,99±2,239a
C3	115,32±5,721c	39,57±3,646b
C4	100,17±8,647c	37,51±3,529b
	$^{A}F_{4,54}$=6,38*	$F_{4,54}$=9,71*

One-way analysis of variance (ANOVA I). Factor treatment cycle with 5 levels: C0 - the beginning of the experiment, C1 - 1st treatment cycle, C2 - 2nd treatment cycle, C3 - 3rd treatment cycle, C4 - 4th treatment cycle. Each value represents the mean value ± SE; Within each series mean values with a different letter are significantly different ($p<0.05$). ^{A}= *F*-test indicator with a number of degrees of freedom; ns = not significantly different ($p>0.05$); * = significantly different ($p<0.05$).

4. DISCUSSION

The observed changes in pH values throughout the FTW provide valuable insights into the water treatment process. The presented results indicate that both polluted and treated water exhibited characteristics consistent with a mildly alkaline environment. The influent pH established the initial conditions of the water under study. The observed decline in pH values within the effluent of all cells with floating islands during the initial six days of treatment suggests a dynamic response to the introduced phytoremediation processes. These results reflect those of White and Cousins (2013) who also observed lower pH in planted FTWs in their experiments. The decrease in pH values indicates the removal of alkaline substances from the polluted water. This could be attributed to various factors associated with the treatment mechanisms, such as microbial activity, plant uptake, or chemical reactions occurring within the floating treatment wetlands. According to Gao et al. (2017), one of these mechanisms involves nitrification, where the conversion of ammonium to nitrate by nitrifying bacteria results in proton consumption, ultimately causing a decrease in pH. Additionally, the breakdown of organic matter releases protons, augmenting the decline in pH (Ijaz et al., 2015). This alteration may also be attributed to the discharge of CO_2 and acidic exudates during plant root system respiration (Iamchaturapatr et al., 2007). Lastly, Sharma et al. (2021) propose that floating islands host diverse microorganisms capable of exchanging cations (e.g., H^+ for Ca^{2+} or Mg^{2+}) with the surrounding water, potentially leading to a reduction in pH. The subsequent increase in pH values upon passing through cell V with algae in all treatment cycles indicates the potential role of algae in modifying water chemistry. Algae are known to influence pH through photosynthetic activity, where carbon dioxide uptake during photosynthesis can elevate pH levels (Kadlec and Wallace, 2008). Also, algae utilize various nutrients from the water, including bicarbonate ions (Gao, 2021). Removal of these ions can shift the carbonate equilibrium towards the less acidic forms, increasing pH. The pH values ranging from 7.79 to 8.43 demonstrate the buffering effect of algae within the treatment system, contributing to the restoration of a more neutral pH range.

The presented results provide valuable insights into the dissolved oxygen (DO) dynamics within the floating treatment wetland. The dissolved oxygen content in water depends on water temperature, salinity, turbulence, atmospheric pressure and photosynthetic activity of algae and plants (Chapman and Kimstach, 1996). The solubility of oxygen in water decreases with increasing salinity and temperature (Marks, 2008). Looking at Figure 1, there is no clear evidence that water temperature had a decisive influence on DO levels in cells with floating islands. A possible explanation for extremely low DO levels is a lack of aeration and free water surface in these cells. These results reflect those of (Chance and White, 2018) who also found that DO level in non-aerated FTW was less influenced by temperature but more by cell coverage percent. The higher the cell coverage percent, the more atmospheric diffusion is restricted by vegetation, and therefore the DO concentration is lower (Pavlineri et al., 2017). It can thus be suggested that 100% coverage of cells with floating islands, as well as the high consumption of oxygen during the decomposition of organic matter (Radwan et al., 2003), led to extremely low DO levels. Chance and White (2018) further suggested that as temperatures declined DO in non-aerated FTW appeared to be more influenced by temperature. This fact can explain the higher DO concentration in cell III and cell IV in the last treatment cycle (C4) when the water temperature was below 15°C. Another possible explanation for this is that at temperatures below 15°C, the activity of microorganisms that decompose organic matter slows down (Kumarathilaka et al., 2017), so the consumption of oxygen is lower. Treated water was enriched with additional amounts of oxygen after passing polishing treatment in cell V. Several factors can explain this fact. In addition to removing various pollutants, algae can enhance oxygen levels in water through photosynthesis (Kadlec and Wallace, 2008) and the most oxygen is released during the period of rapid algal growth (Marks, 2008). Algal biomass was not monitored during the water treatment. However, based on the photo documentation from the beginning and the end of the treatment period, it can be stated that the algae had a significant increase in biomass. Even lower water and air temperatures in early October did not hinder the algae growth resulting in the highest DO levels in this period. It is also possible that higher DO levels occurred as a result of water inlet construction which led to good aeration of cell V. Furthermore, the large free water surface could also enable the additional introduction of oxygen into this cell through the creation of numerous opportunities for contact between water and air (Wu et al., 2001). Taken together, these factors simultaneously with the influence of lower temperature can explain the occurrence of supersaturation in the last two treatment cycles (C3 and C4).

The findings of this study provide insights into the dynamics of Ca and Mg within the FTW, illustrating the influence of treatment cycles on the concentration and efficiency of Ca and Mg removal. It is worth noting that limited knowledge exists regarding the fate and removal mechanisms of these ions in FTWs. Additionally, direct comparisons with the behavior of Ca and Mg in constructed wetlands are not meaningful due to fundamental differences in the systems. Constructed wetlands typically employ a substrate of gravel, sand, or soil to support plant growth and microbial activity. However, FTWs utilize floating islands with plant roots directly submerged in the water column. This distinct configuration likely influences the processes and pathways associated with Ca and Mg removal.

The influent Ca concentrations establish the starting point for evaluating the treatment efficiency. The initial observation of a slight increase in Ca concentration across all cells after the first six days of treatment in C1 and C2 could indicate a potential adjustment phase in the FTW. Notably, cells II and III show low Ca removal efficiency, emphasizing the need for further investigation into the specific factors affecting these cells. A positive trend emerges in subsequent treatment cycles (C3 and C4), with a gradual increase in Ca removal efficiency across all cells with floating islands. The range of 2% to 6% efficiency indicates an improving trend, culminating in the highest efficiency recorded in C4, particularly in Cell II planted with *C. indica*. This could underscore the influence of plant species on enhancing the removal of Ca from water. An interesting finding is the significant reduction in Ca content observed exclusively in the cell with algae (Cell V) at the end of all treatment cycles (C1-C4). This emphasizes the unique contribution of algae to Ca removal, potentially through biological interactions or specific biochemical processes. In contrast to Ca, the results for Mg reveal a notable absence or low reduction rate in all cells. A slight reduction in Mg content is noted in C3 and C4 in cell I-IV, with Mg removal efficiencies ranging from 1% to 4%. This modest reduction could suggest challenges or limitations in Mg removal within the FTW. The highest Mg removal efficiency of 6% is achieved in Cell V at the end of C4, indicating the potential efficacy of algae in Mg removal. Despite the limited research, this study demonstrates the potential of FTWs for Ca removal, achieving overall efficiencies ranging from 23% to 48%, with the most significant reduction observed at the end of C3. The findings suggest that microbial activity, plant uptake, and algal bioremediation all contribute to this removal process. However, Mg removal efficiency remained significantly lower, ranging from 1% to 6%, highlighting the need for further research to improve Mg removal in FTWs.

The analysis of the effects of treatment cycles on the concentration of Ca and Mg in the shoots and roots of selected plant species provides valuable insights into the response of these plants to exposure to polluted water over different treatment periods. The results revealed significant variations in the concentrations of both elements across different plant species and treatment cycles.

P. australis and *M. trifoliata* exhibited a consistent Ca concentration in shoots throughout the exposure, suggesting resilience to the duration of exposure to polluted water. Conversely, *C. indica*, *I. pseudacorus*, and *I. sibirica* 'Perry's Blue' displayed a significant accumulation of Ca in their shoots by the end of C4, signifying a potential adaptive response or physiological adjustment (Barker and Pilbeam, 2006) to prolonged exposure. *A. plantago-aquatica* demonstrated a spike in shoot Ca concentration at the end of C2. Similarly, *L. salicaria* exhibited a substantial increase in Ca concentration at the end of C3, surpassing levels observed in other treatment cycles. These differences underscore the dynamic nature of plant responses to water quality conditions and varying rates of Ca supply, with different species manifesting unique adaptations (Loneragan and Snowball, 1969). The roots of *I. pseudacorus* and *I. sibirica 'Perry's Blue'* maintained consistent Ca levels across the treatment cycles, emphasizing a stable response to polluted water exposure. In contrast, *P. australis* roots exhibited a significant increase in root Ca concentration throughout C1-C4, indicating an efficient uptake mechanism. *C. indica* roots displayed a notable accumulation of Ca at the end of C4, suggesting a potential role in the remediation process. Conversely, *A. plantago-aquatica* roots showed a decline in Ca concentration, possibly indicating a dynamic response unique to this species. *L. salicaria* roots exhibited an increase in Ca content toward the end of the experiment, emphasizing the species-specific dynamics of root ion accumulation (Barker and Pilbeam, 2006).

Turning to Mg concentrations, the study found consistent levels in *I. pseudacorus* and *A. plantago-aquatica* shoots, highlighting their stability in the face of varying exposure periods. A notable increase in Mg concentration was observed only in *I. sibirica* 'Perry's Blue' shoots at the end of C4, signifying a species-specific response (Barker and Pilbeam, 2006; Schwab et al., 2000). *C. indica* shoots exhibited a decline in Mg concentration at the end of C3, suggesting a potential influence of treatment cycles on Mg dynamics. The observed decrease in Mg content in the shoots of *P. australis*, *L. salicaria*, and *M. trifoliata* at the end of C4 could also indicate a dynamic species-specific response to prolonged exposure. Regarding this, prior studies have highlighted that the uptake and accumulation of magnesium can vary across distinct phases of physiological development (Schwab et al., 2000; Mills and Scoggins, 1998). Additionally, these processes can be influenced by an antagonistic relationship between magnesium ions and other cations, including hydrogen, ammonium, calcium, potassium, aluminum, or sodium (Mills and Jones, 1996). The investigation into Mg concentrations in roots revealed consistent levels in *P. australis*, *I. pseudacorus* and *I. sibirica* 'Perry's Blue'. *A. plantago-aquatica* roots displayed an increase in Mg concentration at the end of C4, indicating a distinct pattern in root ion uptake dynamics. Conversely, *C. indica* roots exhibited a decrease in Mg content at the end of C1-C3, emphasizing the variability in root responses. *L. salicaria* and *M. trifoliata* roots showed a decline in Mg concentration at the end of C4, signifying a nuanced response to prolonged exposure. The observed species-specific patterns in root Mg accumulation highlight the complex interplay between plant physiology and environmental conditions (Barker and Pilbeam, 2006).

The results of this study highlight the contrasting dynamics of Ca and Mg accumulation in algae belonging to the genus *Cladophora* sp. exposed to polluted water for different durations. *Cladophora* sp. exhibited an increase in Ca concentration over time, with the highest content of 255.00 g/kg observed in the first treatment cycle (C1). This suggests a rapid uptake and accumulation of Ca by the algae, as algae are known to exhibit rapid responses to their environmental conditions. The reasons for this increased Ca accumulation could include active uptake, passive adsorption, and precipitation. Although algae, unlike plants, need calcium only as a micronutrient (Knight et al., 1973) *Cladophora* sp. may actively take up Ca for various metabolic processes, such as cell wall formation and calcium carbonate precipitation (Barker and Pilbeam, 2006). Also, Ca ions in the polluted water may bind to the surfaces of *Cladophora* sp. cells through passive adsorption processes or precipitate on the surface of algae cells due to changes in water chemistry or biological processes within the algae (Chen et al., 2023). In contrast to Ca, *Cladophora* sp. displayed a marked decrease in Mg concentration throughout the experiment. This finding was unexpected, and the lowest Mg content of 2.67 g/kg was observed at the end of the final treatment cycle (C4).

The presented results offer insights into the dynamics of Ca and Mg concentrations in stone wool concerning different treatment cycles. The data indicates a significant reduction in both Ca and Mg concentrations within the substrate corresponding to the duration of exposure to polluted water. Specifically, stone wool sampled at the beginning of the experiment (C0) exhibited significantly higher concentrations of both Ca and Mg compared to samples taken at the end of treatment cycles C3 and C4. It could be argued that the observed decrease in Ca and Mg concentrations in stone wool could be attributed to either the leaching of these elements into the water or the reduced concentration in the substrate resulting from the uptake of these elements by plants. However, drawing a definitive conclusion from the findings of this study proves challenging.

5. CONCLUSION

This study provided a comprehensive examination of the dynamic responses within a floating treatment wetland, focusing on pH, dissolved oxygen, and the dynamics of calcium and magnesium concentrations.

The observed changes in pH values reflect the influence of phytoremediation processes on water quality. The initial decline in pH within the effluent of FTW cells with floating islands during the early treatment days suggests active remediation processes, potentially involving microbial activity, plant uptake, and chemical reactions. The subsequent increase in pH values upon passing through cells with algae highlights the buffering effect of algae, contributing to the restoration of a more neutral pH range. The dissolved oxygen dynamics reveal the complex interaction of various factors, including temperature, cell coverage, and organic matter decomposition. The low DO levels in cells with floating islands and full coverage indicate challenges in oxygen diffusion. The increase in DO after passing through the cell with algae underscores the role of algae in enhancing oxygen levels through photosynthesis and nutrient uptake. The investigation into the dynamics of Ca and Mg concentrations in both water and selected plant species sheds light on the complexities of ion removal within the FTW. The study identifies a lack of research on Ca and Mg removal in FTWs, emphasizing the need for further exploration in this area. The observed increase in Ca removal efficiency across treatment cycles suggests an adaptive phase in the FTW, with notable contributions from plant species (particularly in Cell II planted with *C. indica*) and algae. However, Mg removal efficiency remains modest, indicating potential challenges in Mg removal processes within the FTWs. The analysis of plant responses to polluted water exposure reveals species-specific variations in Ca and Mg concentrations in shoots and roots. The study highlights the resilience of certain species to varying exposure periods, while others exhibit dynamic adjustments in ion accumulation. The unique patterns in root ion uptake underscore the complex interaction between plant physiology and environmental conditions. Notably, the research into algae belonging to the genus *Cladophora* sp. demonstrates a rapid uptake and accumulation of Ca, suggesting active processes such as metabolic utilization or passive adsorption. The unexpected decrease in Mg concentration in *Cladophora* sp. prompts further inquiry into the mechanisms involved in Mg dynamics within algae exposed to polluted water. The study also explores changes in Ca and Mg concentrations in stone wool, revealing a gradual decrease corresponding to exposure duration. However, the exact mechanisms leading to this reduction, whether leaching or plant uptake, remain inconclusive.

This research contributes to a better understanding of the complex dynamics of water treatment in FTWs, emphasizing the need for continued investigation into ion removal mechanisms, plant responses, and the role of algae in these biological systems. The findings provide a foundation for future research aiming to optimize FTWs for enhanced water treatment efficacy.

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INSIGHTS INTO PH DYNAMICS, DISSOLVED OXYGEN VARIABILITY, AND ION REMOVAL EFFICIENCY IN FLOATING TREATMENT WETLAND

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Summary

The escalating pollution of urban rivers poses a significant threat to both the environment and public health. Addressing river pollution is imperative for ensuring sustainable urban development. In this context, floating treatment wetlands (FTW) emerge as a green and cost-effective technology that can help in the treatment of polluted water in urban areas. The aim of this paper is to analyse the dynamic responses within FTW constructed on the riverbank, focusing on pH, dissolved oxygen (DO), and the dynamics of calcium and magnesium concentrations. The pH value is an important parameter in assessing water quality, as it, like temperature, influences biological and chemical processes in water. Additionally, an essential indicator of water quality is the concentration of DO, which is influenced by factors such as temperature, salinity, turbulence, atmospheric pressure, and the photosynthetic activity of algae and plants. Calcium (Ca) and magnesium (Mg) are essential elements found in natural waters. While necessary for healthy ecosystems, their presence in excessive amounts can pose significant challenges for both water quality and life. While some studies have investigated Ca and Mg behavior in constructed wetlands, no research papers have specifically addressed the fate and removal mechanisms of these ions in FTWs. Results showed that both polluted and treated water exhibited characteristics consistent with a mildly alkaline environment. Decline of pH values within all cells with floating islands was noted. The subsequent increase in water pH values upon passing through cell with algae, ranging from 7.79 to 8.43, indicated the important role of algae. Extremely low DO levels of 0.03 mg/L - 1.43 mg/L were detected in cells with floating islands. Treated water was enriched with additional amounts of oxygen after passing polishing treatment in cell with algae resulting in DO concentrations of 5.87 mg/L - 18.77 mg/L. Calcium removal efficiency ranged from 2% to 6% in cells with floating islands. A significant reduction of the Ca content in the water occurred in the cell with algae resulting in 23% to 49% FTW Ca removal efficiency. The modest FTW Mg removal efficiency of 1-6% could indicate potential challenges in Mg removal processes within the FTWs. The analysis of plant responses to polluted water exposure reveals species-specific variations in Ca and Mg concentrations in shoots and roots. The research highlights the resilience of certain species to exposure periods, while others exhibit dynamic adjustments in ion accumulation. Algae demonstrated a rapid uptake and accumulation of Ca, with the increase Ca concentration in algae tissue over time. However, an unexpected decrease in Mg concentration occurred. The study also revealed a gradual decrease of Ca and Mg concentration in stone wool corresponding to exposure duration. The exact mechanisms leading to this reduction, whether leaching or plant uptake, remain inconclusive. This study offers valuable insights into the dynamics of FTW water treatment, demonstrating the need for continued research on ion removal mechanisms, plant-pollutant interactions, and the role of algae.

UVIDI U DINAMIKU pH, VARIJABILNOST RASTVORENOG KISEONIKA I EFIKASNOST UKLANJANJA JONA U BIOLOŠKOM SISTEMU SA PLUTAJUĆIM OSTRVIMA

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Rezime

Sve veće zagađenje urbanih reka predstavlja značajnu pretnju i životnoj sredini i zdravlju. Rešavanje problema zagađenja reka je imperativ za osiguranje održivog urbanog razvoja. U tom kontekstu, biološki sistemi sa plutajućim ostrvima (FTW) se pojavljuju kao zelena i isplativa tehnologija, koja može da pomogne u tretmanu zagađene vode u urbanim područjima. Cilj ovog rada je analiza dinamičkih procesa u FTW konstruisanog na obali reke, sa fokusom na pH, rastvoreni kiseonik (DO) i promenu koncentracija kalcijuma i magnezijuma. pH vrednost je važan parametar u proceni kvaliteta vode, jer kao i temperatura, utiče na biološke i hemijske procese u vodi. Takođe, značajan indikator kvaliteta vode je koncentracija DO, na koju utiču faktori kao što su temperatura, salinitet, turbulencija, atmosferski pritisak i fotosintetička aktivnost algi i biljaka. Kalcijum (Ca) i magnezijum (Mg) su esencijalni elementi, koji se nalaze u prirodnim vodama. Iako su neophodno za održivost ekosistema, njihovo prisustvo u prevelikim koncentracijama može da predstavlja značajne izazove za kvalitet vode. Iako su neke studije istraživale ponašanje Ca i Mg u konstruisanim akvatičnim ekosistemima, nijedna se nije posebno bavila mehanizmima uklanjanja ovih jona u FTW. Rezultati su pokazali da i zagađena i prečišćena voda pokazuju karakteristike slabo alkalne sredine. Uočen je pad pH vrednosti u svim bazenima sa plutajućim ostrvima. Naknadno povećanje pH vrednosti vode pri prolasku kroz bazen sa algama, u rasponu od 7,79 do 8,43, ukazuje na značajnu ulogu algi. Ekstremno nizak nivo DO od 0,03 mg/L - 1,43 mg/L detektovan je u bazenima sa plutajućim ostrvima. Tretirana voda je obogaćena dodatnim količinama kiseonika nakon prolaska tretmana poliranja u bazenu sa algama što je rezultiralo koncentracijom DO od 5,87 mg/L - 18,77 mg/L. Efikasnost uklanjanja Ca kretala se od 2% do 6% u bazenima sa plutajućim ostrvima. Do značajnog smanjenja sadržaja Ca u vodi došlo je u bazenu sa algama, što je rezultiralo efikasnošću uklanjanja Ca od 23% do 49% u FTW. Mala efikasnost uklanjanja Mg u FTW od 1-6% mogla bi da ukaže na potencijalne probleme u procesima uklanjanja Mg unutar ovih bioloških sistema. Analiza odgovora biljaka na izlaganje zagađenoj vodi otkriva varijacije specifične za vrste u koncentracijama Ca i Mg u izdancima i korenu. Istraživanje naglašava otpornost određenih vrsta na dužinu izlaganja zagađenoj vodi, ali i dinamička prilagođavanja drugih vrsta u akumulaciji jona. Alge su pokazale brzo usvajanje i akumulaciju Ca, uz povećanje koncentracije Ca u tkivu algi tokom vremena. Međutim, došlo je do neočekivanog smanjenja koncentracije Mg. Istraživanje je takođe pokazalo postepeno smanjenje koncentracije Ca i Mg u kamenoj vuni u skladu sa trajanjem izlaganja. Tačni mehanizmi koji dovode do ovog smanjenja, bilo da se radi o ispiranju ili usvajanju od strane biljke, ostaju nejasni. Ova studija daje uvid u dinamiku tretmana vode u FTW, ukazujući na potrebu za kontinuiranim istraživanjem mehanizama uklanjanja jona, interakcija biljaka i zagađivača i uloge algi.