

Efficient Removal of Nickel, Zinc, Chromium, and Cobalt from Acid Mine Drainage using Constructed Wetlands

Impact of Vegetation and Hydraulic Retention Time

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ABSTRACT

This study evaluates the effectiveness of Constructed Wetlands (CWs) in treating Acid Mine Drainage (AMD), focusing on the removal of Ni, Zn, Cr, and Co. Two CW configurations were tested: CW-I (unplanted) and CW-II (planted with *Alocasia odora* and *Spirodela polyrhiza*). Over 12 months, both systems operated at Hydraulic Retention Times (HRTs) of 24, 48, and 72 hours. CW-II consistently outperformed CW-I, achieving 88.1% Zn and 67.8% Cr removal at 72 hours. Ni removal improved to 44.3%, while Co, though less effectively removed, reached 28.3%. . The statistical analysis confirmed that both HRT and vegetation significantly influenced metal removal efficiencies. The enhanced performance of CW-II highlights the critical role of phytoremediation in the pollutant uptake. These findings demonstrate that vegetated CWs offer a scalable, eco-friendly alternative for AMD treatment, with potential applications in broader environmental remediation efforts. Further research should focus in plant optimization, real-world validation, and substrate and system design.

Keywords-constructed wetland; acid mine drainage; phytoremediation; hydraulic retention time; heavy metals

I. INTRODUCTION

AMD is a significant environmental challenge resulting from the oxidation of sulfide minerals during mining activities. This process releases heavy metals and acidity into aquatic systems, posing severe risks to ecosystems and human health [1]. Among these contaminants, nickel (Ni), zinc (Zn), chromium (Cr), and cobalt (Co) are of particular concern due to their toxicity and persistence in the environment [2]. Traditional AMD treatment methods, including chemical precipitation and lime neutralization, are effective but often come with high costs, substantial energy consumption, and the generation of secondary waste [2-4]. These drawbacks highlight the need for cost-effective and sustainable alternatives with minimal environmental impact [5, 6].

CWs have emerged as a promising solution for AMD remediation, utilizing natural processes, such as sedimentation, adsorption, microbial activity, and phytoremediation, to remove pollutants [3-6]. As engineered ecosystems designed to mimic natural wetland functions, CWs offer a low-maintenance and energy-efficient approach to water treatment. Unlike chemical methods, CWs integrate physical, chemical, and

biological mechanisms to achieve the simultaneous removal of multiple pollutants [7-9].

This study evaluates the performance of a three-chamber CW system for AMD treatment, specifically targeting the removal of Ni, Zn, Cr, and Co [9, 10]. The system consists of two configurations: CW-I (unplanted) and CW-II (planted with *Alocasia odora* and *Spirodela polyrhiza*). Prior research highlights the role of vegetation in enhancing pollutant removal through mechanisms, such as root-mediated microbial activity, nutrient uptake, and particulate trapping [11, 12]. *Alocasia odora*, a rhizomatous perennial, and *Spirodela polyrhiza*, a floating macrophyte, were selected for their demonstrated ability to tolerate and accumulate heavy metals, making them suitable candidates for AMD treatment [11-13].

HRT is a key design parameter in CWs, as it determines the contact time between pollutants and treatment media [14, 15]. Extended HRTs generally improve removal efficiencies by increasing interactions through adsorption, sedimentation, and biological processes [14-16]. In this study, three HRTs -24, 48, and 72 hours- were tested to assess their impact on heavy metal removal in both CW configurations over a 12-month period

[15, 16]. While previous research has examined individual aspects of CW performance, limited studies have explored the combined effects of HRT and vegetation on the simultaneous removal of multiple heavy metals [16-18].

This study addresses critical knowledge gaps by investigating the interactive effects of HRT and vegetation on heavy metal removal efficiency. It aims to demonstrate the superior performance of vegetated CW systems (CW-II) in achieving sustained pollutant removal compared to unplanted systems (CW-I) [18, 19]. The findings have important implications for scaling up CW technology for large-scale AMD remediation, reinforcing its potential as an eco-friendly and cost-effective solution. By integrating vegetation-assisted remediation with optimized HRTs, this study seeks to establish a robust framework for addressing the complex challenges associated with AMD treatment [19, 20].

II. MATERIALS AND METHODS

A. Synthetic Acid Mine Drainage Preparation

Synthetic AMD was prepared to simulate real-world conditions, incorporating heavy metals such as Ni, Zn, Cr, and Co, along with other common contaminants, including Cu, Mn, Al, Cd, Fe, and Mg. Metal sulfates were dissolved in deionized water to achieve target concentrations, following established AMD preparation protocols [1, 2]. The inclusion of Fe, Cd, and Mn ensured that the experimental conditions reflected the complexity of real-world AMD [3, 4].

B. Constructed Wetland System Design

The CW systems featured a three-chamber system design to maximize heavy metal removal through physical, chemical, and biological processes. Each chamber measured 300 mm, 600 mm, and 300 mm in length, with a height and width of 300 mm and 400 mm, respectively [5, 6]. A Free Surface Up Flow (FSUP) model was utilized to maintain continuous AMD flow, with effluent collected from the third chamber via a 15 mm pipe fitted with a ball valve [7, 8, 14, 15].

C. Media Layers and Vegetation

To optimize pollutant transformation, the substrate layers were arranged from bottom to top as follows:

- Gravel (12.5-10 mm, 30 mm layer)
- Gravel (10-6 mm, 40 mm layer)
- Sand (600 μ m to 2.36 mm, 100 mm layer)
- Local sandy-clay soil (100 mm layer)

CW-I (control) contained no vegetation, while CW-II was planted with *Alocasia odora* in the main chamber and *Spirodela polyrhiza* in the third chamber. *Alocasia odora* provided an extensive root network to enhance microbial activity, while *Spirodela polyrhiza* functioned as a nutrient absorber and particle trap [16-18].

D. Hydraulic Retention Times

Three HRTs (24, 48, and 72 hours) were evaluated for their effectiveness in removing Ni, Zn, Cr, and Co over a 12-month period. This timeframe captured both seasonal and long-term

variations in treatment performance. The water sampling followed BIS 3025 and APHA 2017 standards to ensure accuracy and reliability [17, 19-20].

E. Analytical Procedures

Effluent samples were analyzed using Atomic Absorption Spectroscopy (AAS) to quantify metal concentrations, adhering to APHA 2017 guidelines. Statistical analysis, including Analysis of Variance (ANOVA), was conducted to assess differences in removal efficiencies between CW-I and CW-II under varying HRTs [21, 22].

III. RESULTS AND DISCUSSION

Table I (sample count: 91) summarizes the key statistics for the unplanted system (CW-I) across different HRTs of 24, 48, and 72 hours for Ni, Zn, Cr, and Co removal. The mean influent concentration of Ni was 0.79 mg/L, with moderate reductions, most effective at 24 hours (0.55 mg/L). Zn had an initial concentration of 0.84 mg/L, with a significant reduction to 0.21 mg/L at 24 hours, though longer HRTs yielded diminishing returns. Cr concentrations decreased from 0.31 mg/L to 0.14 mg/L at 24 hours and remained stable thereafter. Co showed minimal removal, fluctuating around 0.36 mg/L, regardless of increasing HRTs.

TABLE I. DESCRIPTIVE STATISTICS OF CW-I

Parameter	Mean	Std	Min	25 %	50 %	75 %	Max
S1_Ni_Input	0.79	0.11	0.52	0.72	0.79	0.89	1.08
S1_Ni_24H	0.55	0.10	0.37	0.47	0.55	0.62	0.86
S1_Ni_48H	0.59	0.10	0.35	0.52	0.59	0.67	0.82
S1_Ni_72H	0.58	0.14	0.12	0.50	0.57	0.68	1.06
S1_Zn_Input	0.84	0.12	0.49	0.76	0.83	0.94	1.07
S1_Zn_24H	0.21	0.06	0.06	0.17	0.20	0.26	0.36
S1_Zn_48H	0.16	0.05	0.05	0.13	0.15	0.20	0.29
S1_Zn_72H	0.19	0.05	0.06	0.16	0.19	0.23	0.30
S1_Cr_Input	0.31	0.07	0.11	0.26	0.31	0.37	0.49
S1_Cr_24H	0.14	0.05	0.02	0.11	0.15	0.18	0.28
S1_Cr_48H	0.13	0.04	0.03	0.10	0.13	0.15	0.25
S1_Cr_72H	0.14	0.05	0.06	0.11	0.14	0.17	0.32
S1_Co_Input	0.39	0.05	0.20	0.36	0.39	0.42	0.50
S1_Co_24H	0.36	0.07	0.17	0.32	0.36	0.41	0.66
S1_Co_48H	0.36	0.06	0.17	0.33	0.37	0.40	0.51
S1_Co_72H	0.36	0.04	0.21	0.33	0.36	0.39	0.45

Table II (sample count: 91) demonstrates the enhanced performance of CW-II (vegetated system). Ni concentrations decreased significantly to 0.44 mg/L at 72 hours. Zn showed exceptional removal, dropping to 0.01 mg/L at 72 hours. Cr concentrations were also reduced to 0.01 mg/L, while Co, although the least removed metal, decreased to 0.28 mg/L - indicating a clear improvement over CW-I. Table III and IV present the treatment efficiencies of CW-I and CW-II, respectively, CW-I achieved a peak Zn removal efficiency of 81% at 48 hours, while Ni and Cr removal remained inconsistent, and Co removal stayed below 8%. In contrast, CW-II demonstrated superior performance. Ni removal increased to 44.3%, Zn efficiency reached 88.1%, and Cr removal improved to 67.8% at 72 hours. Co removal, though still limited, improved to 28.3%, significantly higher than in CW-I.

TABLE II. DESCRIPTIVE STATISTICS OF CW-II

Parameter	Mean	Std	Min	25%	50%	75%	Max
S2_Ni_Input	0.79	0.11	0.52	0.72	0.79	0.89	1.08
S2_Ni_24H	0.48	0.04	0.36	0.45	0.48	0.51	0.60
S2_Ni_48H	0.47	0.06	0.32	0.43	0.47	0.52	0.62
S2_Ni_72H	0.44	0.07	0.29	0.39	0.44	0.48	0.60
S2_Zn_Input	0.84	0.12	0.49	0.76	0.83	0.94	1.07
S2_Zn_24H	0.16	0.03	0.08	0.14	0.16	0.18	0.25
S2_Zn_48H	0.12	0.03	0.04	0.10	0.12	0.14	0.20
S2_Zn_72H	0.10	0.02	0.05	0.09	0.10	0.11	0.15
S2_Cr_Input	0.31	0.07	0.11	0.26	0.31	0.37	0.49
S2_Cr_24H	0.12	0.03	0.04	0.10	0.12	0.14	0.19
S2_Cr_48H	0.12	0.03	0.04	0.10	0.12	0.14	0.19
S2_Cr_72H	0.10	0.02	0.06	0.08	0.10	0.12	0.13
S2_Co_Input	0.39	0.05	0.20	0.36	0.39	0.42	0.50
S2_Co_24H	0.31	0.02	0.25	0.30	0.31	0.33	0.35
S2_Co_48H	0.30	0.03	0.23	0.28	0.30	0.32	0.37
S2_Co_72H	0.28	0.03	0.22	0.26	0.28	0.30	0.35

TABLE III. TREATMENT EFFICIENCIES OF CW-I

Parameter	Efficiency (%)	Efficiency Std Dev (%)
Ni_S1_24H	30.32	13.48
Ni_S1_48H	25.31	13.23
Ni_S1_72H	26.59	18.18
Zn_S1_24H	75.04	13.01
Zn_S1_48H	80.97	13.11
Zn_S1_72H	77.45	12.64
Cr_S1_24H	54.77	20.43
Cr_S1_48H	58.11	18.72
Cr_S1_72H	54.81	20.63
Co_S1_24H	7.74	18.07
Co_S1_48H	7.71	15.53
Co_S1_72H	7.82	10.49

TABLE IV. TREATMENT EFFICIENCIES OF CW-II

Parameter	Efficiency (%)	Efficiency Std Dev (%)
Ni_S2_24H	39.16	7.49
Ni_S2_48H	40.44	9.52
Ni_S2_72H	44.27	10.89
Zn_S2_24H	80.86	12.18
Zn_S2_48H	85.70	12.82
Zn_S2_72H	88.12	12.90
Cr_S2_24H	61.30	17.09
Cr_S2_48H	61.30	17.03
Cr_S2_72H	67.83	16.78
Co_S2_24H	20.74	5.98
Co_S2_48H	23.14	8.26
Co_S2_72H	28.31	8.53

Table V provides a statistical overview of the effects of HRT and system type (CW-I vs. CW-II) on metal removal efficiencies employing ANOVA. The results indicate that both the HRT and system type significantly influence removal efficiencies for all metals. The extremely low p-values for both factors confirm their substantial impact. Additionally, the interaction between HRT and system type was statistically significant, demonstrating that CW-II's performance is greatly benefited from the extended HRT, particularly for Ni and Zn.

Figures 1-8 illustrate that CW-II consistently outperformed CW-I across all metals, especially at longer HRTs. The key findings include:

- Nickel (Ni): CW-II reduced concentrations from 0.79 mg/L to 0.44 mg/L at 72 hours, whereas CW-I achieved a lower reduction to 0.58 mg/L.
- Zinc (Zn): CW-II exhibited the most pronounced improvement, lowering Zn concentrations to 0.10 mg/L at 72 hours, achieving 88.1% removal efficiency, compared to 77.4% in CW-I.
- Chromium (Cr): CW-II reduced Cr concentrations to 0.10 mg/L at 72 hours, significantly outperforming CW-I, which only reduced Cr to 0.14 mg/L.
- Cobalt (Co): Although the least removed metal, CW-II achieved a greater reduction from 0.39 mg/L to 0.28 mg/L, while CW-I exhibited only a minimal decrease to 0.36 mg/L.

Figures 9-16 present time-series data, displaying CW-II's superior and consistent performance over time. Ni concentrations in CW-II steadily declined, highlighting the benefits of phytoremediation, whereas CW-I plateaued early, indicating a limited removal capacity.

Figures 17-24 confirm CW-II's superior performance through post-hoc analyses. Tukey's Honest Significant Difference (HSD) test revealed that CW-II's removal efficiencies at 72 hours were significantly higher than those of CW-I, underscoring the crucial role of vegetation in enhancing pollutant removal.

Tukey's HSD tests demonstrated that CW-II's Zn removal at 72 hours was significantly higher, with a mean difference of 0.11 mg/L compared to CW-I. Ni removal efficiency in CW-II increased to 44.3% at 72 hours, while CW-I's peak was only 30.3% at 24 hours. The interaction between system type and HRT underscored the importance of vegetation in maximizing pollutant removal efficiency.

TABLE V. TWO WAY ANOVA RESULTS

	Metal	sum_sq	df	F	p-value
Ni	C(HRT)	10.08	3	359.38	1.3E-142
	C(System)	1.23	1	131.49	4.47E-28
	C(HRT):C(System)	0.53	3	18.79	9.57E-12
	Residual	6.73	720	-	-
Zn	C(HRT)	63.99	3	4242.46	0
	C(System)	0.36	1	71.96	1.24E-16
	C(HRT):C(System)	0.18	3	12.25	7.95E-08
	Residual	3.62	720	-	-
Cr	C(HRT)	4.68	3	656.46	1.7E-205
	C(System)	0.06	1	23.77	1.33E-06
	C(HRT):C(System)	0.04	3	5.70	0.000734
	Residual	1.71	720	-	-
Co	C(HRT)	0.55	3	82.72	5.47E-46
	C(System)	0.41	1	187.84	3.71E-38
	C(HRT):C(System)	0.16	3	23.93	9.07E-15
	Residual	1.59	720	-	-

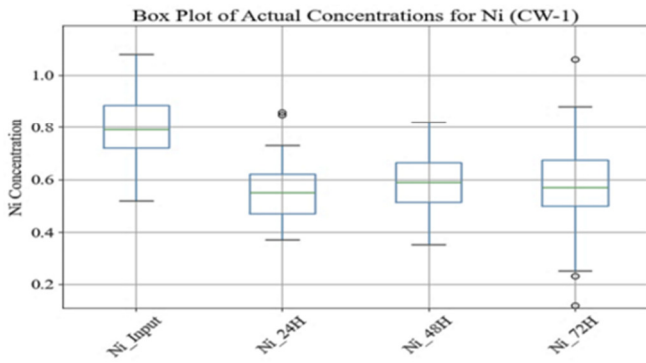


Fig. 1. Actual concentrations for Ni (CW-I).

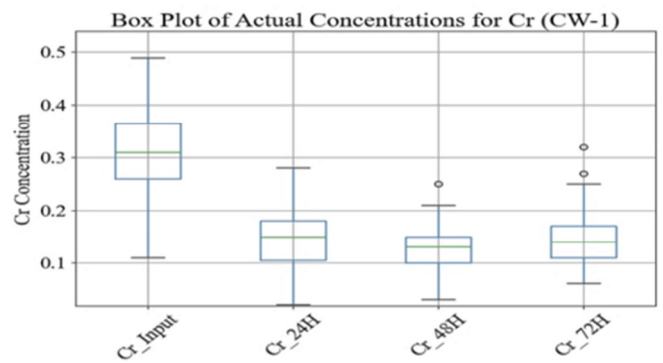


Fig. 5. Actual Concentrations for Cr (CW-I).

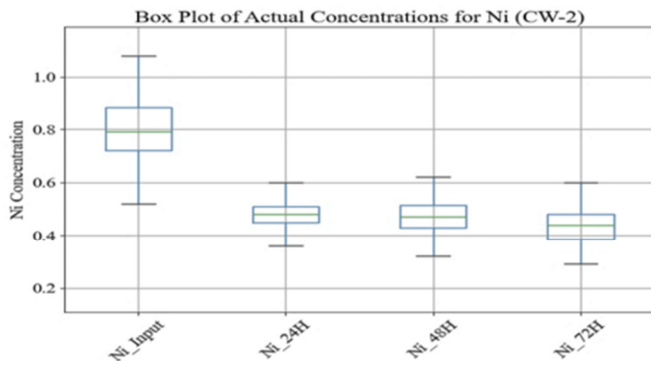


Fig. 2. Actual concentrations for Ni (CW-II).

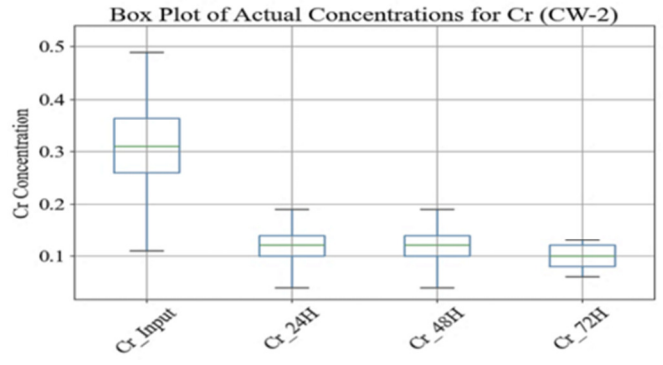


Fig. 6. Actual concentrations for Cr (CW-II).

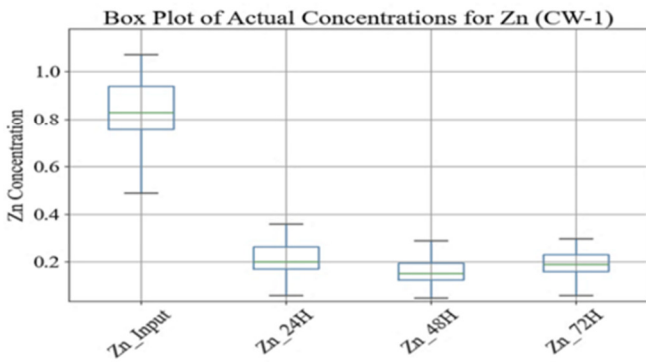


Fig. 3. Actual Concentrations for Zn (CW-I).

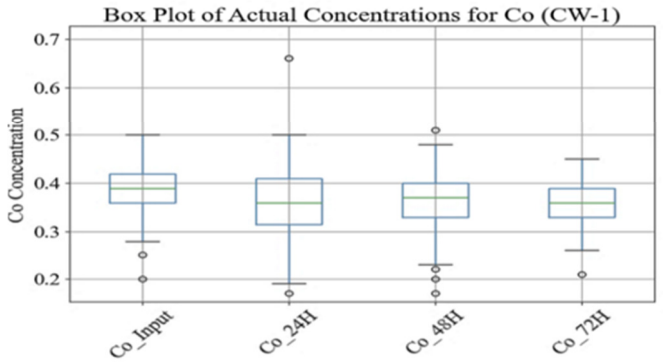


Fig. 7. Actual concentrations for Co (CW-I).

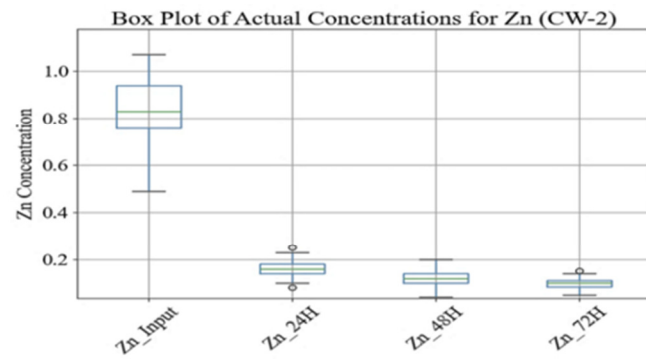


Fig. 4. Actual Concentrations for Zn (CW-II).

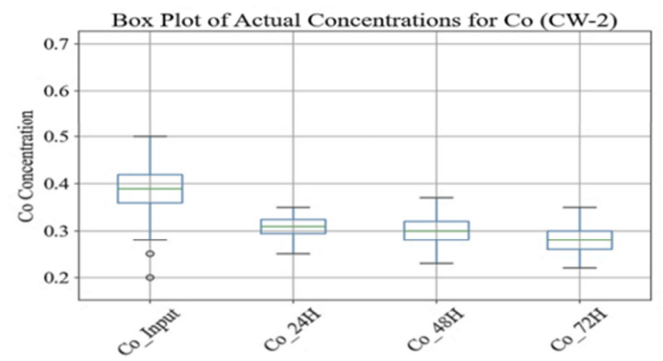


Fig. 8. Actual concentrations for Co (CW-II).

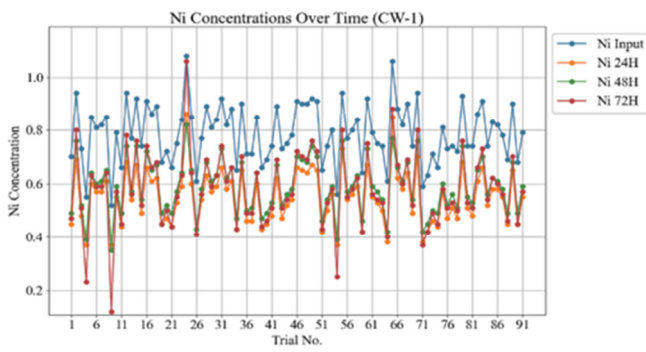


Fig. 9. Time-Series chart of Ni (CW-I).

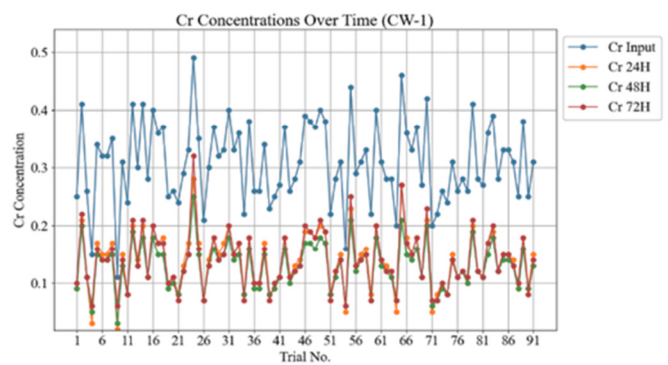


Fig. 13. Time-Series chart of Cr (CW-I).

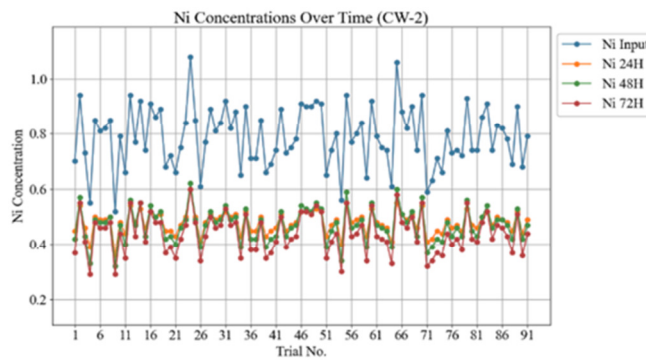


Fig. 10. Time-Series chart of Ni (CW-II).

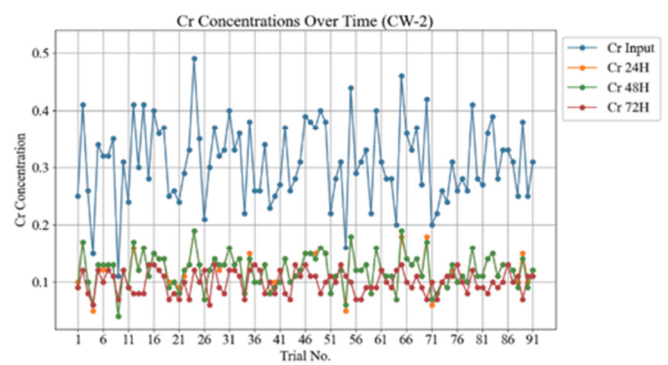


Fig. 14. Time-Series chart of Cr (CW-II).

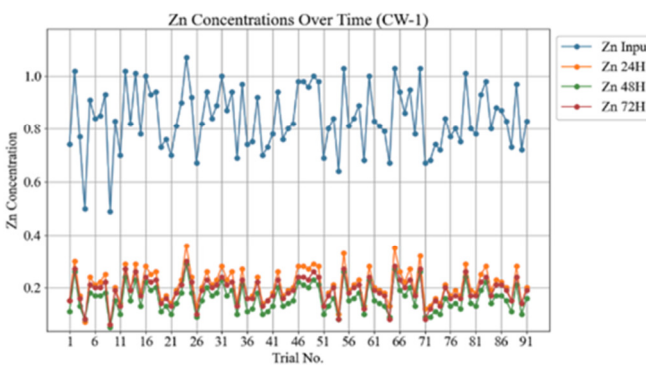


Fig. 11. Time-Series chart of Zn (CW-I).

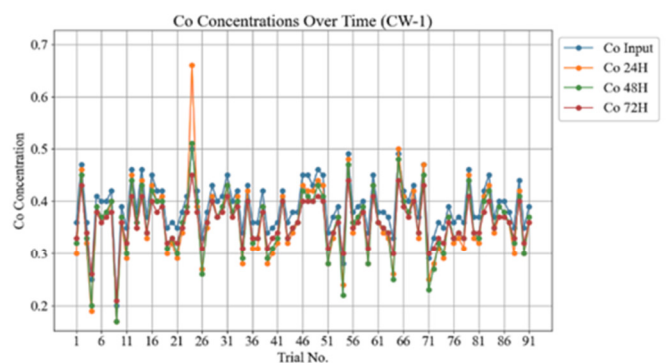


Fig. 15. Time-Series chart of Co (CW-I).

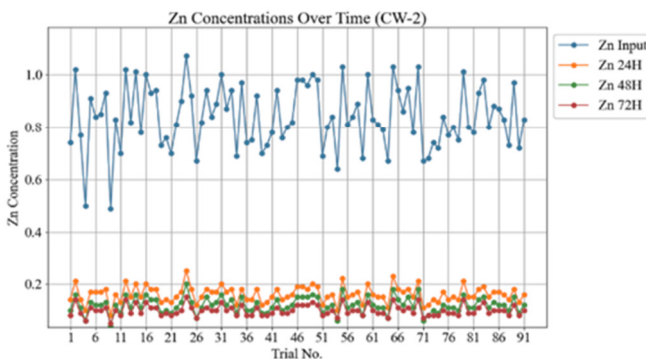


Fig. 12. Time-Series chart of Zn (CW-II).

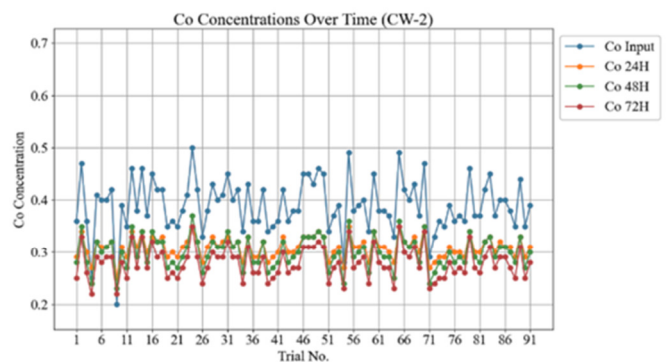


Fig. 16. Time-Series chart of Co (CW-II).

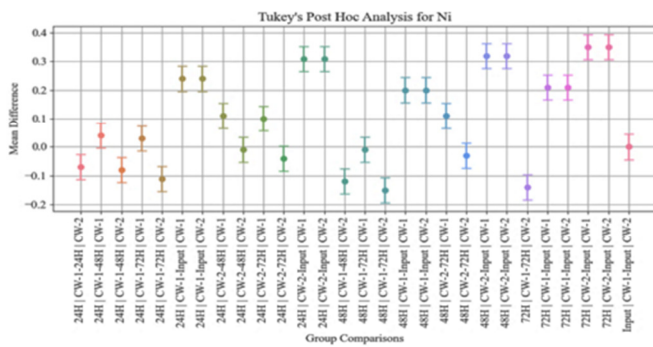


Fig. 17. Group comparison of mean differences of Ni.

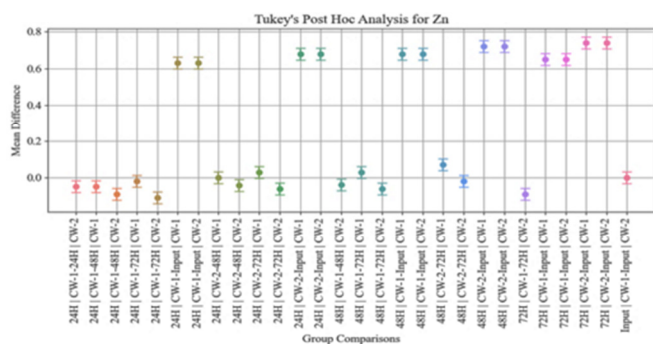


Fig. 18. Group comparison of mean differences of Zn.

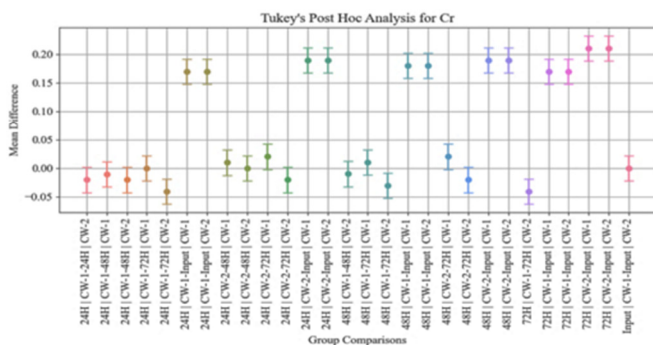


Fig. 19. Group comparison of mean differences of Cr.

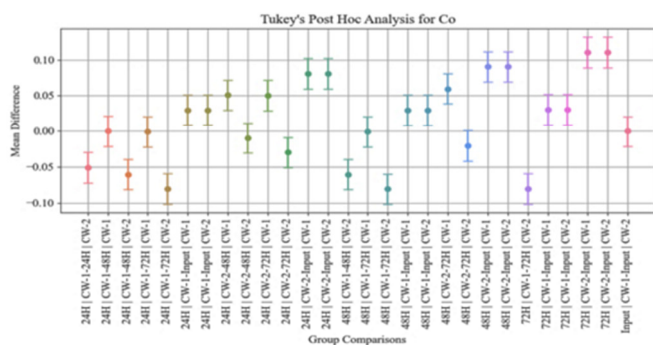


Fig. 20. Group comparison of mean differences of Co.

IV. CONCLUSION

This study highlights the effectiveness of Constructed Wetlands (CWs) for treating Acid Mine Drainage (AMD) by

comparing an unplanted system (CW-I) with a vegetated system (CW-II) across Hydraulic Retention Times (HRTs) of 24, 48, and 72 hours. The results demonstrate that CW-II, incorporating *Alocasia odora* and *Spirodela polyrhiza*, consistently outperformed CW-I in heavy metal removal, particularly for Nickel (Ni), Zinc (Zn), and Chromium (Cr). Zn removal efficiency peaked at 88.12%, while Cr reached 67.83% at the 72-hour HRT. Although cobalt (Co) removal remained challenging, CW-II achieved a maximum efficiency of 28.31%, significantly surpassing CW-I's performance.

The statistical analysis, including Two-Way Analysis of Variance (ANOVA), confirmed that the system type, HRT, and their interaction had a statistically significant impact on removal efficiencies ($p < 0.001$). The planted system was benefited from extended retention times, facilitating sustained pollutant removal through phytostabilization and phytoextraction. These findings underscore the importance of integrating biological processes with optimized HRTs to enhance treatment efficiency. It is concluded that CW-II is capable of a scalable and sustainable solution for AMD remediation, combining physical, chemical, and biological processes to achieve superior results. Future research should focus on:

- Plant Optimization: Exploring diverse vegetation to improve the removal of challenging metals, like Co.
- Real-World Validation: Assessing long-term performance under varying environmental conditions.
- Substrate and System Design: Optimizing media configurations to further enhance removal efficiencies.

By aligning design and operational parameters, CW-II offers cost-effective and eco-friendly alternatives to conventional chemical treatments. These findings provide a solid foundation for advancing CW technology to address the complex challenges of AMD remediation efficiently and sustainably.

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