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Application of Heavy metals pollution index on two types of constructed wetland

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Abstract

Two types of constructed wetland (CW), vertical subsurface flow (VSSF) and horizontal subsurface flow (HSSF), both planted with *Phragmites australis*, were established to treat wastewater. It was retained for three days in which the samples were collected 24, 48, and 72 hours after the initial filling. The present study aimed to evaluate the applicability of the HPI index using some heavy metals and investigate the degree of heavy metal pollution using this index. The dissolved metals declined in general throughout the operation days in both systems. Vertical and Horizontal subsurface flow systems effectively removed Al, Cd, Cu, and Ni. The decline in dissolved metals concentration was clearly observed in the HPI value. Therefore, HPI can be a very effective method and easy tool to review the level of pollution in heavy metals.

Keywords: heavy metals, wetland, pollution, treatment plant

Introduction

Urbanization and Industry during the past decades have increased the stress on the environment and ecosystems, especially in water resources contamination via wastewater that affects the human health in direct and indirect ways by introducing high amounts of pollutants more than its ability to sustain (Akpor & Muchie, 2011; Abdulredha *et al.*, 2021). Heavy metals are one of these pollutants, and the most important, they are divided into essential and non-essential elements. Zink, Iron, and Copper are described as essential nutrients for the biochemical processes which the flora can take, but at higher concentrations, it becomes toxic. Cadmium is non-essential and dangerous to health due to its carcinogenic nature and ability to accumulate and magnify throughout the food chain. However, there are species of plants called Phyto-hyper accumulators that can uptake significant amounts of heavy metals, one of which is Cadmium (Joan *et al.*, 2018). Natural wetlands, described as the kidneys of the landscape, are one of the most valuable ecosystems (Hussain *et al.*, 2015). These downstream receivers of water are vital through their services, including protection of shorelines, mitigating floods and droughts, a habitat for a variety of fauna and flora, cultural and aesthetic sites, and importantly the remediation ability of contaminated water through physio-chemical and biological processes (Mitsch *et al.*, 2015). These ecosystems are imitated to produce nature-driven technology through civil work to build constructed wetland that is gaining much attention in the recent decades to treat polluted water. This technology, which has been documented in Germany since 1952, is cheap and less demanding than conventional anthropogenic systems. Thus, it is an important approach for solving the lack of centralized treatment systems in developing and third world countries (AL-Maliky, 2018; Massoud *et al.*, 2008).

Water quality indices are an easy method to evaluate and understand the overall pollution and its influence (Al-Hejuje, 2014; Al-Hejuje *et al.*, 2017). These valuable tools are aimed to provide water quality executives, decision-makers, environmental managers, and potential users of a given water system with a comprehensible guide and clear view of the pollution levels. The heavy metal pollution index (HPI) is one of the most used approaches to assess and interpret metal pollution (Mohan *et al.*, 1996; Moyel *et al.*, 2015).

The present study aimed to evaluate the applicability of the HPI index using some heavy metals and investigate the degree of heavy metal pollution using this index.

Materials and methods

The experiment was conducted at constructed wetland research station (C.W.R.S.), located at coordinates (30.5557405 N, 47.7487667 E). C.W.R.S. was established as a pilot project in 2015 by (AL-Maliky, 2018) at the University of Basrah, Garmmat-Ali campus, near a wastewater treatment plant (WWTP). The WWTP collects its influent from various colleges, laboratories, workshops, and housing buildings; each contributes unique liquid wastewater. Therefore, WWTP was used as a source for the wastewater collected from the campus.

Constructed wetland research station (C.W.R.S.)

The station was rehabilitated and maintained as an operation-ready research station; the maintenance included the electricity wiring, pumps cleaning and replacing, storage tanks cleaning, and replacing basins substrate and plants with standardized layers of substrate and fresh plants.

C.W.R.S. consists of three tanks, each with 3 tons (3000 L) capacity sitting on a high platform, two for the wastewater and a middle tank for clean water. These tanks feed two identical operation lines. Each line includes a vertical subsurface flow system, a horizontal subsurface flow system, and a surface flow system made of fiberglass basins with the diminutions of 120 cm width, 300 cm length, and 100 cm high installed successively, which also can be operated as a hybrid system. The substrate was filled up to 60 cm with three standardized layers. The first layer was filled with 35 -55 mm cross gravel up to 10 cm in height; the second layer was filled with 15 mm gravel, making a 30 cm height layer. The third layer is filled with 20 cm height of 5 mm fine gravel forming the top layer.

Design of experiment

The experiment was conducted using two types of constructed wetland (CW), vertical subsurface flow (VSSF) and horizontal subsurface flow (HSSF), both planted with *Phragmites australis* collected from local marshlands. Wastewater was applied to the system to its full capacity and retained in the systems for three days, in which the samples were collected 24, 48, and 72 hours after the initial filling of the influent.

Sample collection, preparation, and analysis

Collected samples after each retention time were immediately filtered with vacuum filtration apparatus on a pre-washed, with 0.5N HCl, and weighted GF/C and Millipore 0.45µm filtration membrane. The filtered sample of two liters was then passed through ion exchange columns filled to an average depth of 11cm with fresh chelating ion exchange resin in hydrogen form (Purolite C 100). The resin was activated before use by passing 50 ml of 2N HNO_3 followed by 100 ml of deionized water, then passing 50 ml of 3N NH_4OH followed by 100 ml of deionized water.

The filtrated samples passed through the exchange columns with an average 8 ml/min flow rate. After the complete passing of the samples, 100 ml of deionized water was used to wash the resin in the column. Constrained heavy metals were eluted with 50 ml 2N HNO_3 into 100ml Polyethylene Tri Fluro Ethane (PTFE) clean beakers, which were then allowed on a hotplate at 70^oc until the sample became less than 25 ml. It was removed from the hotplate and completed 25 ml with deionized water. The samples were digested further, following the systems' sample preparation procedure, with a matrix of 2N HNO_3 and 0.5N HCl then diluted with deionized water and stored in a tight stopper polyethylene vial and analyzed with Inductively Coupled Plasma mass spectrometry (ICP-MS, ELAN 6100 DRC-e, Perkin-Elmer, USA).

Heavy metal pollution index (HPI)

Heavy metals can be assessed by rating or weighing each element with a value between zero and one to reflect its quality considerations and relative importance. HPI can be calculated in three steps as follow;

Step one is calculating the weight of ith parameter

$$\mathbf{Wi} = \frac{\mathbf{k}}{\mathbf{s_i}}$$

Wi: is the unit weightage.

Si: the recommended standard for an ith parameter.

k: is the constant of proportionality.

Step two is calculating the Individual quality rating

$$\mathbf{Q_i} = \mathbf{100} * \frac{|\,\mathbf{M_i} - \mathbf{I_i}\,|}{\mathbf{s_i} - \mathbf{I_i}}$$

Qi: is the sub-index of the ith parameter

Mi: is the monitored value of the ith parameter in µg/L

Ii: The maximum desirable value of the ith parameter.

Si: the standard or permissible limit for the ith parameter.

Step three is calculating the value of HPI

$$\mathbf{HPI} = \sum_{i=1}^{n} \mathbf{W_i Q_i} \Big/ \sum_{i=1}^{n} \mathbf{W_i}$$

Statistical analysis

Statistical analysis was conducted using the one-way ANOVA with the assumption of equal distribution at ($\alpha = 0.05$) significance level. Tukey post hoc test method for pairwise compresence analysis. The software used in the analysis was Minitab Ver.19.

Results and discussion

The collected results in table 1 showed pH levels ranging from neutral to alkaline. The systems and retention time affected the wastewater pH during the operation. The statistical analysis showed a significant difference among systems ($p \leq 0.05$), while the retention time effect was not significant ($p > 0.05$). Moreover, both retention time and systems had a significant effect on pH. The decrease in pH levels in VSSF and HSSF systems could be due to anaerobic conditions, consumption of organic matter, and releasing carbon dioxide, calcium carbonate $CaCO_3$, and free anions and other bicarbonates which can interact with H+ and OH- ions. (Gerla, 2013; Mitsch & Gosselink, 2015).

The electrical conductivity (EC) showed that operation EC measurements were higher than the applied wastewater into the systems during separated operations. The statistical analysis showed that the difference between systems and retention was significant ($p \leq 0.05$). EC levels were significantly affected by the system type and retention time. Depending on the organic and mineral content, wetland substrates have a cation exchange capacity (CEC). Mineral sediments have high CEC caused by major cations. Meanwhile, organic sediments have high CEC caused by hydrogen ions (Mitsch & Gosselink, 2015). Generally, the increase in dissolved pollutants and salinity such as NO_3^-, PO_4^{-3}, Cl^-, $SO4^{-2}$, Na^+, and K^+ increases the EC of the water (Moyel & Hussain, 2015). Both pH and EC results were similar to what had been observed in natural wetlands by Hussain and Abduljaleel (2020).

Dissolved Aluminium (Al) showed a decline in concentration, reaching a high removal rate on the third day of operation. The statistical analysis showed a significant difference between the systems and retention time ($p \leq 0.05$). The concentrations of dissolved Al were significantly different between the systems and retention time during the three-day operation. After 72 hours, the highest removal was 94.8% in VSSF planted with *P. australis*.

A rapid decrease in dissolved Cadmium concentration after 24 hours reached more than 99% removal across systems during the operation. The concentration in the following days was in a plateau phase. Statistical analysis for the dissolved concentration showed a significant difference between the systems during the operation ($p \leq 0.05$).

Also, the difference was significant ($p < 0.05$) between the retention time.

Copper (Cu) concentration reveals a high removal of dissolved Cu during the operation. The effect of retention time and the difference between system types was statistically significant ($p \leq 0.05$). The interaction of both system type and time significantly affected the removal of dissolved Cu.

A variance in dissolved Nickle (Ni) removal throughout the operation period was observed. The statistical analysis showed significant differences among systems ($p \leq 0.05$) and through the retention time.

Table 1: Results obtained from the experiment.

		pH	EC (mS/cm)	Al (µg/L)	Cd (µg/L)	Cu (µg/L)	Ni (µg/L)	HPI
VSSF	**RAW**	7.7	3.9	121.230	25.526	20.902	64.985	407.4
	24 Hours	7.4	5.95	44.293	0.225	0.492	1.820	5.47
	48 Hours	7.4	5.9	9.152	0.182	0.249	1.465	3.39
	72 Hours	7.39	6	2.322	0.171	0.161	1.724	2.98
HSSF	**RAW**	7.7	3.9	121.230	25.526	20.902	64.985	407.4
	24 Hours	7.4	6.62	73.209	0.186	1.193	3.324	6.32
	48 Hours	7.5	6.78	78.600	0.173	0.742	1.730	6.01
	72 Hours	7.5	6.77	12.925	0.192	0.399	2.289	3.84

The chemical precipitation of metals, alongside substrate filtration, rhizofiltration, phytoextraction, and remediation, play an important role in the removal process. The alkaline environment with high (OH-) could be interacted with the dissolved phase of the metal, producing a more insoluble precipitate of Aluminium hydroxide $Al(OH)_2$, thus lowering the dissolved concentration of Al released from the system (Krupińska, 2020; Lesage, 2007). The transformation of dissolved metals to particulate helped to precipitate and increase the immobilization in the system in which the Cd, and Cu, interact with sulfide and form different complexes (Shmaefsky, 2020). Nevertheless, plant uptake and accumulation of highly mobilized dissolved Cd in tissue contribute to a metal reduction in the wastewater and play an important role in the removal of the soluble, bioavailable Cu (Khan *et al.*, 2009). The adsorption and precipitation of Ni depend on the ion exchange capacity and the presence of other metals competing for the adsorption sites, which have greater adsorption ability than Ni (Seo, Yu, & DeLaune, 2008). Also, the decrease in the removal could be caused by pH change in which the increase of H+ ions and protons lead to Ni release from the systems (Nyquist & Greger, 2009).

Heavy metals concentration after treatment was similar to what had been observed by Al-hemidawi, Mohammed, and Al-saad (2020) in natural marshland. Heavy metal pollution index (HPI) was a calculation based on heavy metal concentrations that clearly showed highly polluted wastewater (HPI = 407.4), which reached a level similar to what had been observed in the natural wetland by Al-atbee *et al.* (2020). Over time, this pollution was decreased to more acceptable levels than Iraq river maintenance regulations (2011).

Conclusions

The dissolved metals declined in general throughout the operation days in both systems. Vertical and Horizontal subsurface flow systems effectively removed Al, Cd, Cu, and Ni. The decline in dissolved metals concentration was observed in the HPI value. Therefore, HPI can be a very effective method and easy tool to review the level of pollution in heavy metals.

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تطبيق دليل التلوث بالمعادن الثقيلة (HPI) في نوعين من الأراضي الرطبة المشيدة

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المستخلص

تم استخدام نوعين من الأراضي الرطبة المشيدة (CW) ، الاولى ذات التدفق العمودي تحت السطح (VSSF) والاخرى ذات التدفق الأفقي تحت السطح (HSSF) ، وكلاهما مزروع بنبات القصب *Phragmites australis* لغرض معالجة مياه الصرف الصحي التي تم تمريرها على النظام ولمدة ثلاثة أيام تم فيها جمع العينات بعد 24 و 48 و 72 ساعة بعد التعبئة الأولية.

هدفت الدراسة الحالية إلى تقييم تطبيق دليل التلوث بالمعادن الثقيلة (HPI) باستخدام بعض المعادن الثقيلة بالإضافة إلى دراسة درجة تلوث المعادن الثقيلة باستخدام هذا الدليل. انخفضت تراكيز المعادن الذائبة بشكل عام طوال أيام التشغيل في كلا النظامين، وكانت أنظمة التدفق الرأسي والأفقي تحت السطح فعالة في إزالة العناصر(Al، Cd، Cu، و Ni) وقد لوحظ بوضوح الانخفاض في تركيز المعادن الذائبة من خلال قيمة دليلHPI لذا يمكن أن يكون HPI طريقة فعالة للغاية وأداة سهلة لمعرفة مستوى التلوث بالمعادن الثقيلة.

كلمات مفتاحية: تطبيق دليل تلوث المعادن الثقيلة على نوعين من الأراضي الرطبة المشيدة