

Heavy Metals Removal from Simulated Wastewater using Horizontal Subsurface Constructed Wetland

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ABSTRACT

This study aimed to assess the efficiency of *Nerium oleander* in removing three different metals (Cd, Cu, and Ni) from simulated wastewater using horizontal subsurface flow constructed wetland (HSSF-CW) system. The HSSF-CW pilot scale was operated at two hydraulic retention times (HRTs) of 4 and 7 days, filled with a substrate layer of sand and gravel. The results indicated that the HSSF-CW had high removal efficiency of Cd and Cu. A higher HRT (7 days) resulted in greater removal efficiency reaching up to (99.3% Cd, 99.5% Cu, 86.3% Ni) compared to 4 days. The substrate played a significant role in removal of metals due to adsorption and precipitation. The *N. oleander* plant also showed a good tolerance to the uptake of Cd, Cu, and Ni ions from water. The highest removal of the heavy metals indicated that the HSSF-CW would be a promising technology for heavy metal contaminated wastewater as well as in electroplating and manufacturing industries.

Keywords: heavy metal removal, phytoremediation, horizontal subsurface constructed wetland, *Nerium oleander*, waste treatment.

INTRODUCTION

The environmental contamination with heavy metals is causing an increasing concern nowadays due to the industrial growth, agricultural practices, and transportation means. These metals include lead (Pb), chromium (Cr), cadmium (Cd), mercury (Hg), copper (Cu), nickel (Ni) and zinc (Zn). Cadmium, copper and nickel are among the major contaminants of water sources with heavy metals [Amarioarei et al., 2017]. Improper disposal of heavy metals into water bodies, even at low concentrations has become a major challenge due to their noxious impact on all creatures, persistence in nature

and difficulty in being transformed by microorganisms; therefore, they accumulate in the ecosystem [Miretzky et al., 2004]. Conventional remediation options, such as ion exchange, biosorption [Hasan et al., 2010; Hasan et al., 2016; Elham et al., 2018], chemical precipitation, electrochemical, adsorption [Mohammad et al., 2013; Abidin et al., 2020], and membrane treatment [Al-Hemiri et al., 2012; Abed, 2014] have been used for the removal of heavy metals. These techniques are expensive, have logistical problems and technical complexity.

Constructed wetlands (CWs) are an alternative treatment method with special merits of being sustained, efficient, economically and

environmentally friendly treatment that mimics the natural processes [Stefanakis, 2019; Said et al., 2020]. Researchers used different aquatic and terrestrial plants in their pilot or field studies to treat different contaminants by various mechanisms such as containment or contaminants removal into the upper plants parts or turn them into less harmful forms [Ismail et al., 2020]. CWs are comprised of chemical, physical, and biological processes that influence each other, resulting in properly treated water. Many plants have high potential for successful uptake of contaminants. They have the ability to absorb and accumulate metals which are essential for their growth (Cu, Ni, Fe, Mn, Zn, and Mg) as well as non-essential metals (Cd, Cr, Pb, Co, Ag, Se, Hg).

In this study, a pilot scale horizontal sub-surface flow constructed wetlands (HSSF-CWs) were investigated to remove Cd^{2+} , Cu^{2+} , and Ni^{2+} ions from simulated wastewater. A *Nerium oleander* plant was used in this study due to its potential to remove heavy metals. Oleander is a native ornamental plant that is found in almost different Iraqi regions. It is fast-growing, evergreen, has high biomass, withstands extreme temperature and is easily transplanted into most soils, although it grows well in poor, resistant to salt stress [Kumar et al., 2017]. This is an ever-green, non-edible, terrestrial plant which can endure the Iraqi climate. The main objectives of the study were to examine the performance of the HSSF-CW system in removing Cd^{2+} , Cu^{2+} , and Ni^{2+} from simulated water under the climatic condition of Iraq and to determine the effect of substrate in heavy metals retention.

MATERIALS AND METHODS

Simulation of heavy metal contaminated wastewater

Cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Tetnal photowerk GmbH, Germany), copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (BDH chemicals Ltd, UK), and nickel chloride $\text{Ni}(\text{Cl})_2 \cdot 6\text{H}_2\text{O}$ (Tetnal photowerk GmbH, Germany), all with purities above 98% were used to prepare simulated heavy metal contaminated wastewater by dissolving them with tap water. The concentrations of Cd^{2+} , Cu^{2+} , and Ni^{2+} ions were calculated and adjusted at pH value of 5 to maintain the soluble cation forms.

Pilot-Scale Horizontal Sub-Surface Flow - Constructed Wetland

In this study, four planted glass basins were constructed outdoor and operated continuously with a dimension of $70 \times 30 \times 30$ cm (LxWxD) and two different hydraulic retention times (HRTs) of 4 and 7 days were examined. A slope of (1%) was used to maintain the hydraulic gradient and aspect ratio of 2.3:1. Figures 1 and 2 show the photo and schematic diagram of HSSF-CW, respectively. Four storage tanks (each with 30 L capacity) were connected to four control tanks (each with 8 L capacity) with an opening to drain the excess simulated water that was fed from storage tanks to obtain constant water elevation throughout the whole study. The outlet valve of each control tank was attached to a stopcock to control the water flow into each basin. The flow rates were measured using a stopwatch and measuring cylinders. Each HSSF-CW

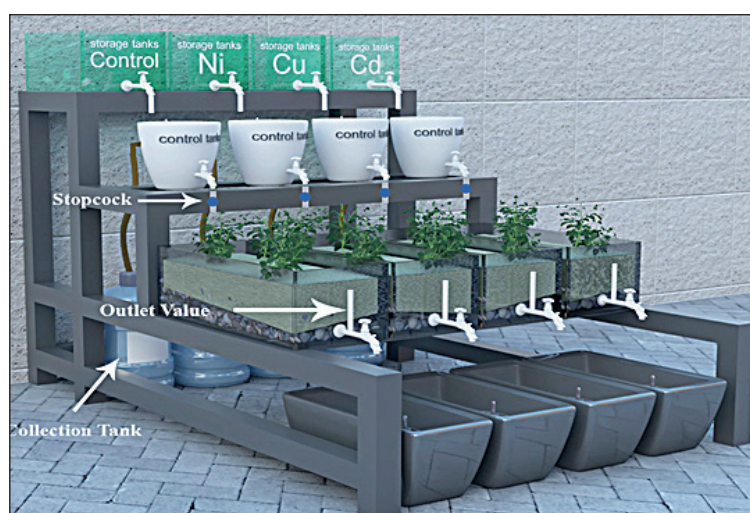


Figure 1. Photo of HSSF-CW

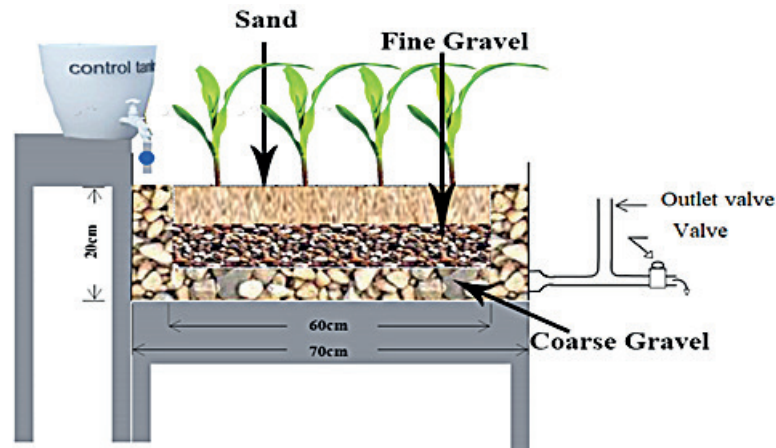


Fig. 2. Schematic diagram of HSSF-CW

was connected to a PVC pipe which controls water level within each bed as well as for periodic collection of samples from the effluent, and a valve to empty the basins. Coarse gravel with a size of > 4 mm was added at 5 cm length from the inlet and outlet zones with depth of 20 cm in each basin in order to obtain a uniform distributed flow. Then, the remaining area of the basins was filled with 7 cm sand, 7 cm fine gravel and 6 cm coarse gravel. The oleanders used in this study had an average height of 25 cm and a root length ranging from 10–12 cm.

Hydraulic retention time (HRT) is the actual volume of wastewater in the bed divided by the average design flow. Many studies found that HRT is not sufficient to achieve the required contaminants removal [EPA, 1993]. Many researchers suggested that it is more convenient to apply a nominal detention time (τ) as an alternative to HRT [Kadlec and Wallace, 2009]; [Rahi, 2019]. For all reactors, as the volume is known, nominal detention time (τ) was calculated according to the formula given in equation (1):

$$\tau = \frac{V}{Q} \quad (1)$$

where: τ - hydraulic retention time (days); V - volume of the constructed wetland (m^3); Q - flow rate (m^3/d).

The total quantity of simulated wastewater used during each experiment was 45 L and was fed manually into each storage tank. Each basin was treating a volume of 5 and 9 L/d for 4- and 7-days HRT, respectively. The three CW were irrigated with Cd^{2+} , Cu^{2+} and Ni^{2+} , respectively, while the fourth basin was irrigated with tap water as a control. Treated heavy metal contaminated wastewater was sampled and analyzed.

Analytical Methods

Heavy Metals Measurement in Simulated Wastewater

The wastewater samples were analyzed daily. The samples were filtered using (Whatman No. 45) filter paper for the estimation of heavy metals, collected in plastic test tube and then analyzed using atomic absorption spectrometry (ASS) (SensAA GBC Scientific Equipment, Malaysia). The percentage of Cd^{2+} , Cu^{2+} and Ni^{2+} removal on each sampling day was determined with Eq. (2):

$$\text{Removal} = \frac{(C_o - C_i)}{C_o} \times 100 \quad (2)$$

where: C_o - concentration of heavy metal entering the HSSF-CW (mg/l); C_i - concentration of heavy metal flowing out of the HSSF-CW (mg/l).

Heavy Metals Measurement in Sand Samples

The sand was sampled at the beginning and at the end of each experiment during the first and last day of the experiments. These samples were taken at different points of 5 cm depths and mixed to ensure representative sampling. After that, the samples were air-dried and digested. The total (Cd^{2+} , Cu^{2+} , Ni^{2+}) concentrations in sand was extracted using the hot aqua regia digestion procedure (ISO standard 11466). Then, the concentration of heavy metals was analyzed using ASS.

Heavy Metals Measurement in Plant Tissues

The plant tissues were analyzed on the first and last days of the experiments. Plant samples

were taken from the beginning and the end of each basin at each sampling time. The dried plant samples were ground, and about 1 g of each part (root, stem and leaves) was treated with 10 mL of concentrated HNO₃. The solution was placed on a hot plate for 30–45 min and left to cool. After that, 4 mL of 20% hydrogen peroxide (H₂O₂) was added. The solution was reheated on a hot plate until it became semi-dried and clear. Then, the suspension was allowed to cool and was filtered into a 50 mL volumetric flask and diluted with distilled water [Rashid et al., 2016].

Chemical Parameters

The parameters of pH, dissolved oxygen (DO), and total dissolved solids (TDS) were measured to observe the potential changes in water. The pH in the water samples was measured by means of a HANNA pH meter model (HI 98103), TDS was measured using a HANNA conductivity tester model (HI 98301), and DO was measured using a HACH meter (HQ430d, USA).

RESULTS AND DISCUSSION

Heavy Metals Removal from Water

The results of the Cd²⁺ concentration during the 4 and 7 days HRT are shown in Figure 3 (a) and (b), respectively. At 4 days HRT, the Cd²⁺ concentration in the effluent ranged from 0.213 to 0.626 mg/l, which exceeds the permissible limits for local river conservation criteria (< 0.01 mg/l). The average removal efficiency was 96.5%. At 7 days HRT experiment, the Cd²⁺ concentrations in the effluent were 1.59 mg/l at day-1, 0.17 at day-5 sampling, and decreased to meet the permissible limits starting from day-7 sampling to be 0.008 mg/l. The average removal efficiency was 99.3% which was higher than the removal efficiency at 4 days HRT.

The results of the Cu²⁺ concentration at 4 and 7 days HRT in the effluent are shown in Figure 4 (a) and (b), respectively. During the 4 days HRT, the Cu²⁺ concentration at day 1 sampling was 3.63 mg/l, ending by 0.661 mg/l, which exceeds the permissible limits for local river conservation criteria (< 0.2 mg/l). The average removal efficiency

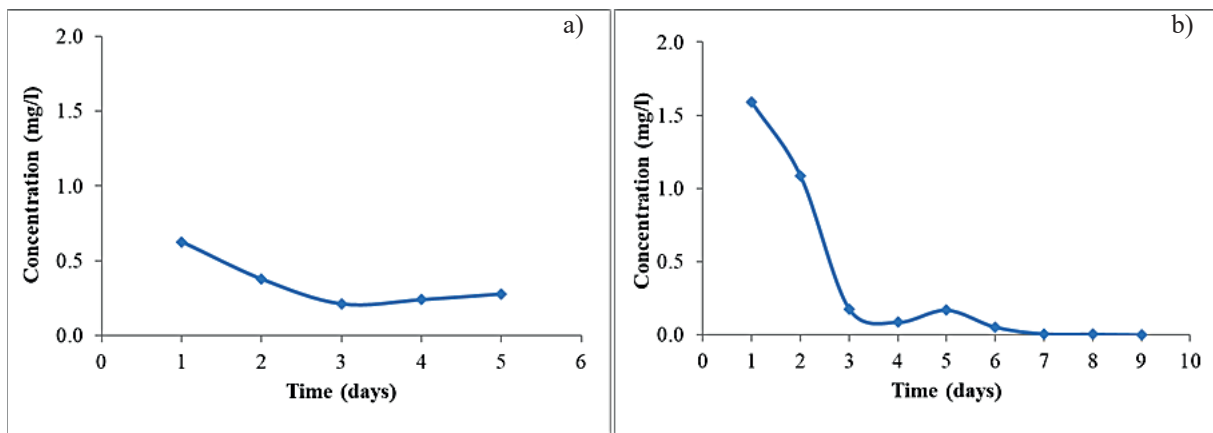


Figure 3. Cd concentration in the effluent water at a) 4 and b) 7 days HRT

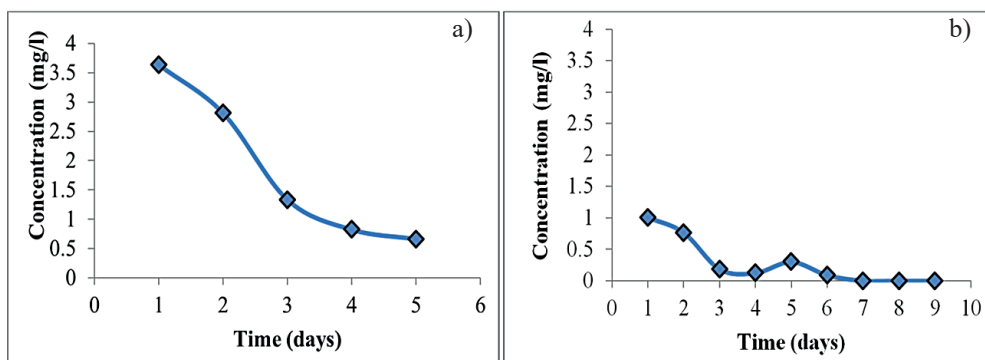


Figure 4. Cu concentration in the effluent water at a) 4 and b) 7 days HRT

was 96.3%. At 7 days HRT, the Cu²⁺ concentrations were 1.01 mg/l at day-1, 0.3 mg/l at day-5, and decreased to meet the permissible limits starting from day-6 with 0.088 mg/l. The average removal efficiency was 99.5%.

The results of Ni²⁺ concentration at 4 and 7 days HRT in the effluent are shown in Figure 5 (a) and (b), respectively. At 4 days HRT, the concentrations of Ni²⁺ exceeded the permissible limits for local river conservation criteria (< 0.2 mg/l) and ranged from 15.1–20.5 mg/l. The average removal efficiency was 71%. At 7 days HRT, the Ni concentration ranged of 7.6 to 9.41 mg/l, and also exceeded the permissible limits with an average removal efficiency of 86.3%.

Regression Models for Cd²⁺, Cu²⁺, and Ni²⁺ Removal in HSS-CW

The results of the regression analysis between the time (*t*) and effluent concentration (*C*) of the three metals are shown in Table 1. A square polynomial was used to calculate the concentrations

of Cd²⁺, Cu²⁺, and Ni²⁺ ions in the effluent water from the CW. The analysis showed a significant relationship between the variables *t* and *C* ($R^2 > 0.9$), and the quadratic equation can be used to predict the Cd²⁺, Cu²⁺, and Ni²⁺ concentration in the effluents of simulated wastewater by time.

Heavy Metals in Sand

The results of sand analyses are summarized in Table 2. The heavy metals were high on the last day for both experiments compared to the first day. This could be attributed to the gypsiferous and calcareous characteristics of the sand, in addition to the neutral pH, the presence of clay content and – to a lesser extent – organic matter [Pappalardo et al., 2010]. Moreover, it was clearly shown that higher HRT resulted in higher heavy metals accumulation in soil [Gola et al., 2016].

Heavy Metals Concentration in Plant Tissues

The results of the plant tissues analyses are summarized in Table 3. The oleanders planted near

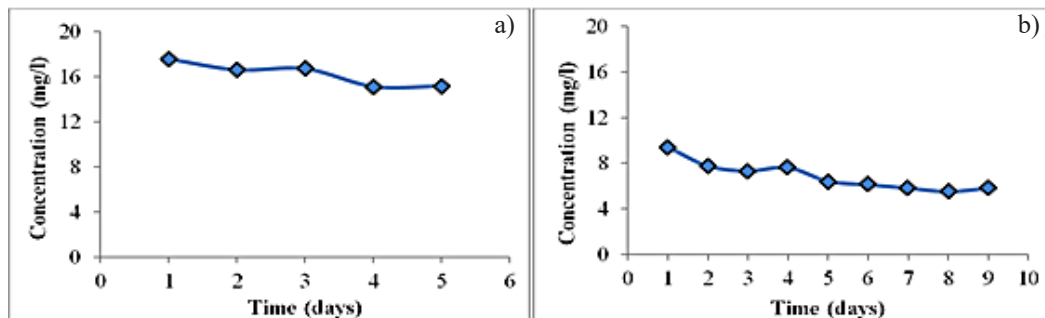


Figure 5. Ni concentration in HSSFCW effluent at a) 4 and b) 7 days HRT

Table 1. Regression of Cd²⁺, Cu²⁺, and Ni²⁺ concentration in the effluent with time

Metals	HRT	Regression equation	R ²	F-value	P-value
Cd ²⁺	4	$C = 0.055t^2 - 0.411t + 0.979$	0.9844	63.0	> 0.05
	7	$C = 0.049t^2 - 0.652t + 2.075$	0.8978	26.4	> 0.05
Cu ²⁺	4	$C = 0.163t^2 - 1.773t + 5.376$	0.9749	38.8	> 0.05
	7	$C = 0.057t^2 - 0.996t + 10.028$	0.9292	21.0	> 0.05
Ni ²⁺	4	$C = 0.451t^2 - 3.934t + 23.659$	0.9102	7.2	> 0.05
	7	$C = -0.033t^2 + 0.521t + 7.2584$	0.8709	20.2	> 0.05

Table 2. Concentration of Cd²⁺, Cu²⁺, and Ni²⁺ in sand at 4 and 7 days HRT

HRT (d)	Sampling time	Cd (mg/kg)	Cu(mg/kg)	Ni (mg/kg)
4	1 st day	8	21	30
	Last day	21	10	48
7	1 st day	7	17	41
	Last day	44	63	287

Table 3. Heavy metals accumulation in oleander at the beginning and the end of CW with HRT of 4 and 7 days

HRT (d)	Sampling time	Cd (mg/kg)		Cu (mg/kg)		Ni (mg/kg)	
		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
4	1 st day	67	23	90	36	52	44
	Last day	81	38	154	105	329	126
7	1 st day	57	33	101	59	289.84	186
	Last day	109	89	279	164	493.29	240

the HSSF-CW inlet showed higher concentrations accumulated in their tissues than those planted near the outlet. This could be attributed to the metal ions absorbed by the plant along with their flow through the HSSF-CW, in addition to the metal sorption capacity of the sand. At 7 days HRT, the oleander plant accumulated higher Cd²⁺, Cu²⁺, and Ni²⁺ than at 4 days HRT. Moreover, it was obvious that oleander accumulated more Cd²⁺, Cu²⁺, and Ni²⁺ at the last day of the experiments than the first day.

Monitoring of pH, DO and TDS

The pH, DO and TDS were recorded for each metal throughout the study and the profiles are shown in Figures 6, 7, and 8, respectively.

Throughout the 4 days HRT, the pH values ranged from 7.1 to 7.6 for Cd²⁺, 6.7 to 7.5 for Cu²⁺, 7.1 to 7.5 for Ni²⁺, and 7.2 to 7.8 for control. At the 7 days HRT, the pH ranged from (7.5–7.8) for Cd²⁺, (7.4–7.5) for Cu²⁺, (7.4–7.6) for Ni²⁺, (7.5–7.91) control. The results did not show any significance between the different CWs and both HRTs.

The DO ranged between 5.1 to 7.2 mg/l for Cd²⁺, 4.3 to 6.7 mg/l for Cu²⁺, 3.6 to 6.4 mg/l for Ni²⁺, and 6.1 to 7.4 mg/l for control during the 4 days HRT. At 7 days HRT, the DO ranged between 3.4 to 6.2 mg/l for Cd²⁺, 3.3 to 5.4 mg/l for Cu²⁺, 4.1 to 5.8 mg/l for Ni²⁺, and 4.3 to 7.2 mg/l for control. According to Po-dedworna and Zubrowska-Sudol [2010], these

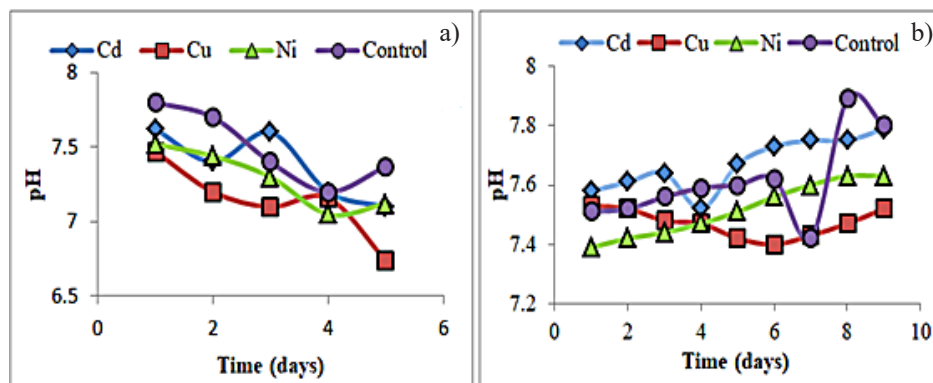


Figure 6. The pH values measured at the effluent of HSSFCW with HRT of a) 4 days b) 7 days

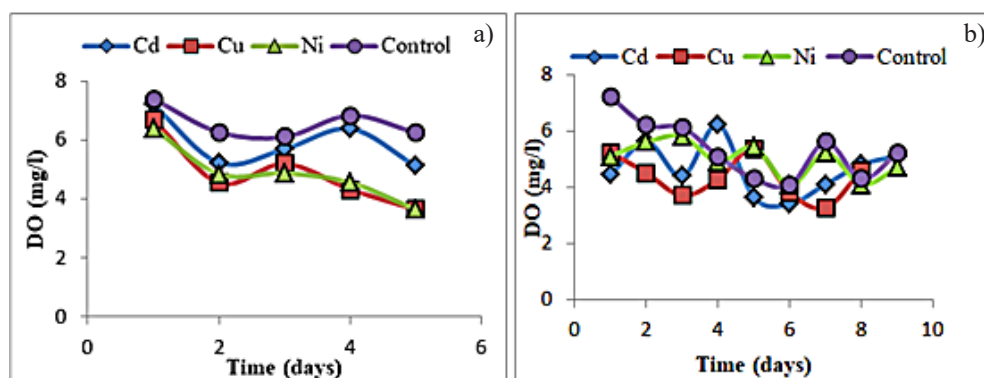


Figure 7. The DO values measured at the effluent of HSSFCW with HRT of a) 4 days b) 7 days

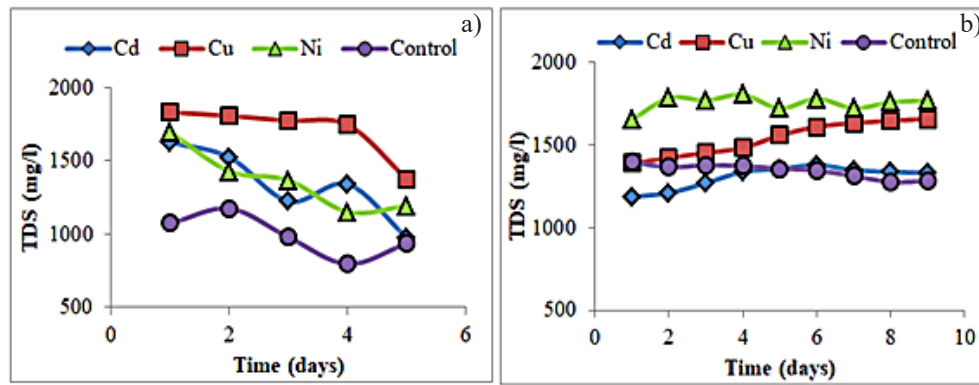


Figure 8. The TDS values measured at the effluent of HSSFCW with HRT of a) 4 days b) 7 days HRT

results indicated that all test were conducted under aerobic conditions. The TDS values during the 4 days HRT experiment ranged from 974 to 1830 mg/l in the effluent of the HSSF-CWs irrigated with Cd^{2+} , Cu^{2+} and Ni^{2+} and 973 to 1174 mg/l for control. At 7 days HRT, the TDS values ranged from 1187 to 1781 mg/l for the CWs irrigated with Cd^{2+} , Cu^{2+} and Ni^{2+} and 1277 to 1396 mg/l in the control. In general, the TDS values were higher for HSSF-CWs treated with Cd^{2+} , Cu^{2+} , and Ni^{2+} . This result agrees with Borker et al., [2013] who found that TDS in water increased due to the metal ions added to water addition.

CONCLUSIONS

Higher removal efficiencies from simulated wastewater were observed in 7 days HRT with an average removal efficiency of 99.3, 99.5, and 86.3% for Cd^{2+} , Cu^{2+} , and Ni^{2+} , respectively. At 4 days HRT, the removal efficiencies were only 96.5 (Cd^{2+}), 96.3 (Cu^{2+}), and 71% (Ni^{2+}). This indicated the essential role of HRT on the treatment efficiency of heavy metals in HSSF-CWs. The HSSF-CW was able to reduce the Cd^{2+} and Cu^{2+} concentrations to meet the permissible limits at 7 days HRT, while increasing HRT has a slight contribution on the removal of Ni^{2+} ions and it is obvious that the metal concentrations were higher than the permissible limits at both HRTs.

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