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RESEARCH ARTICLE

Hexavalent Chromium (VI) Removal Efficiency From Petroleum Refinery Effluent Using Hybrid Constructed Wetlands Planted with *Arundo donax* L. in Erbil, Iraq

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ABSTRACT

This work assessed the efficacy of *A. donax* L. (giant reed) in outdoor hybrid-built wetland (HCW) experiments for the removal of the Cr (VI), from KCPS refinery effluents (32 km southwest of Erbil, Iraq). Results showed that *A. donax* L. macrophyte experienced an excellent adaptation and tolerance of the highly polluted effluent by Cr (VI), based on their significant biomass output and perfect survival rate over the entire 91-day experiment. The Cr (VI) concentrations taken from the outlet samples of HCWs (planted with *A. donax* L.) ranged from (0.04 to 0.12 mg/l), with a mean value of (0.07 $\pm$ 0.057 mg/l), which approached the Cr (VI) safe limit set by international guidelines. The HCWs planted with *A. donax* L. showed a high Cr (VI) removal rate of (88.12%) with a removal capacity of (3.34 mg/day/g). The highest accumulated Cr (VI) concentration was (925.11 mg/plant) in roots, (193.71 mg/plant) in stems and (115.1 mg/plant) in leaves. The phytoextraction potential of *A. donax* L. by both bioaccumulation factor (BAF) and translocation factor (TF) also underwent evaluation. Bioaccumulation factor values of (14.24), (8.46) and (68.02) were calculated for stems, leaves and roots, respectively, and the TF value was (0.33), proposing that *A. donax* L. has a good capacity of Cr (VI) phytostabilization from the KCPS refinery effluent, as revealed in elevated BAF (>1) and TF value (< 1) in plant parts, which showed that the *A. donax* L. is not a Cr-hyperaccumulator under these conditions of the experiment.

Keywords: *Arundo donax*, Chromium, Oil refinery effluent, Removal capacity, Wetland

Introduction

Petroleum refinery effluents (PRE) can have substantial environmental consequences, including toxicity in aquatic and terrestrial ecosystems and adverse effects on human health.[1] These waste substances flow into streams and impact the quality of water systems.[2] The mechanism of extracting crude oil necessitates the use of substantial quantities of generated water. Consequently, a substantial amount of effluent is generated. The quantity of PRE generated during processing is 0.4–1.6 times the amount of crude oil products treated. The global production of effluent amounts to 33.5 million barrels per day, based on the recent yield of 85 million barrels per day of crude oil.[3] Therefore, special attention should be paid to the handling and preservation of natural freshwater that will continue to be the primary source of both residential and agricultural water supplies, especially in arid and semi-arid developing countries such as Iraq.[4]

The more toxic metals in PRE include cadmium, lead, chromium (as hexavalent [VI]), and cobalt. As compared to Cr (III), aqueous hexavalent chromium, Cr (VI), is the most oxidized, mobile, reactive, and toxic form with no sorption in most sediment at pH $>$ 7. Also, Cr (VI) is more mobile than Cr (III) and is commonly linked with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions.[5] Cr (VI) levels in PRE must be reduced to (0.05 mg/l) before

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being released into the environment for public water systems. Accordingly, the highest permissible Cr (VI) discharge into surface and potable waters is set at ($<$ 0.05 mg/l),[6] while World Health Organization (WHO)[7] has set the admissible Cr (VI) discharge limit in wastewater at (0.05 mg/l).

Although, the bioavailability of the Cr (VI) introduced into the environment by the PRE is very low, it has been identified as carcinogenic, especially if ingested or inhaled where it can cause lung cancer. Furthermore, Cr (VI) could irritate the nose, throat, and lungs as well. Prolonged or repeated exposure leads to distract the mucous membranes of the nasal passages.[7,8] The toxicity of Cr (VI) to plants is contingent upon its valence state. Chromium (VI) exhibits significant toxicity and mobility. Plants do not have a specific transport mechanism for Cr; thus, it is absorbed *via* carriers that also transport important ions such as sulfate or iron.[9] On the other hand, the pronounced health issues seen in animals following ingestion of Cr (VI) compounds included stomach and small intestine (irritation and ulcer) and the blood (anemia).[6,8,9]

Various treatment methods exist for removing chromium, particularly hexavalent chromium, from both water and wastewater. These include biological treatment using bacteria, yeast, fungi and algae, as well as physicochemical processes such as ion exchange, chemical precipitation, reverse osmosis, membrane technologies, adsorption, and activated carbon. However, it is worth noting that these treatment methods may sometimes result in residual concentrations that surpass legal limits. In addition, alternative treatment procedures including reverse osmosis, ion exchange resins, and electrolysis, have been suggested, but their expenses are frequently prohibitive.[10]

Phytoremediation is an emerging technology that harnesses the power of plants to break down, absorb, process, or remove metals from industrial wastewater.[11,12] In addition, phytoremediation has demonstrated its effectiveness in the treatment of soil and wastewater contaminated with Cr (VI) due to its straightforward operation and high removal efficiency.[13–15] It offers a sustainable treatment approach that harnesses solar energy. In recent years, numerous research investigations have been conducted to comprehend the process mechanism. Furthermore, constructed wetlands (CWs) have been implemented near industrial facilities to treat effluents that contain high levels of pollutants.[16–18] Phytoremediation relies on constructed wetlands (CWs) as an essential component for treating wastewater. Constructed wetlands (CWs) utilize similar mechanisms as those found in natural wetlands, but in a more regulated setting. Compressed air energy storage (CW) systems are more efficient and have much lower initial investment costs compared to conventional systems. Additionally, CW systems require less land, labor, and energy usage. Hybrid systems that mix several types of constructed wetlands (CWs), such as vertical and horizontal CWs, are now being used. This is because these hybrid systems have the highest capacity for removing pollutants and produce superior treatment performance.[19,20] Hybrid constructed wetlands (HCWs) can be a promising option for treating polluted and contaminated water (PRE) in order to restore it for reuse.[16]

More specifically, HCWs are considered a nature-based solution for pollution and waste management. They are known for being sustainable systems that offer efficient treatment while having a minimal impact on the environment. Additionally, they provide several ecosystem services.[17] The primary premise of HCWs is the integration of different types of this mechanism (vertical and horizontal) arranged in a sequential manner. This configuration allows for the efficient treatment of various forms of industrial wastewater, including PRE.[18,19] Furthermore, the nutrients that remain after the wastewater treatment process have the potential to be used as fertilizers for crops.[20] As demonstrated by,[21] phytoremediation involves five primary actions: phytoextraction, phytostabilization (capturing contaminants in the root zone), rhizofiltration (filtering contaminants through the root system), phyto-transformation (breaking down organic contaminants into less harmful forms by the plant), and rhizosphere bioremediation (microbial metabolism in the plant root zone for breaking down organic contaminants). Phytoextraction and rhizofiltration are methods of remediation primarily observed in plants that float freely in water, while phytostabilization is linked to plants that are submerged or emergent.[21] Multiple investigations suggest that different aquatic macrophytes should be recognized as phytoremediators for diverse pollutants due to their ability to accumulate significant amounts of trace metals in their tissue.[22–24] Numerous plants have the ability to amass an exceptionally elevated quantity of pollutants from their surroundings and concentrate them within their roots, branches, and/or leaves.[25,26] The macrophyte *Arundo donax* L. (giant reed), being a candidate in this study, has been demonstrated as a good accumulator for Cr (VI).[13] Furthermore, the macrophyte *A. donax* L. is the most known utilized plant as a trace element bio-accumulator (specifically in phytoremediation approaches) for its ability to absorb pollutants such as Cr (VI) that cannot be easily biodegraded. The macrophyte *A. donax* L. is an aquatic plant species invader in Iraq. The plant is a species with minimal soil requirements, low nutrient demands, great resilience to diseases and parasites, as well as water and heat stressors. It has the ability to adjust to unfriendly and marginal places, such as locations with high levels of salt or heavy pollution. *A. donax* L. is unpalatable to animals, hence preventing the dissemination of hazardous and persistent chemicals throughout the food chain.[13]

The *A. donax* L. accumulation is linked to the activation of hyper tolerance mechanisms.[27] This sheds light on the different pathways that plants use to resist toxicity. The technology of CWs on PRE pretreatment could be improved.[28–30] Additionally, further efforts are required to enhance the management and sustainability of CWs. Further investigation is required to optimize phytoremediation in artificial wetlands, considering the technology's site-specific and climate-dependent nature.[31–33] However, it is a challenging issue for environmental engineers to reduce the concentration of toxic metals including Cr (VI) in effluents to meet the maximum permissible contaminant level.[34–36] Research on the phytoremediation of chromium-contaminated environments is experiencing tremendous growth. There is a lack of information about which native plants are effective in removing Cr (VI) through bioremediation. This topic requires more research and investigation.[37]

In Iraq, typically only 60 to 75% of discharged petroleum refinery effluent undergoes treatment.[1] However, the traditional treatment methods employed are inadequate in effectively reducing the presence of heavy metals in surface waters. Therefore, it is imperative to explore other solutions, such as utilizing aquatic plant species, as a cost-efficient and environmentally benign method in phytoremediation of heavy metals from PRE. Hence, the current study aimed to evaluate the operational efficiency of a full-scale hazardous chemical waste (HCW) treatment system in removing chromium (VI) from the KCPS (Khormala Central Processing Station) refinery in Erbil, Iraq. The system utilized giant reed (*A. donax* L.) as the plant species for treatment. The harvested plants were then analyzed to determine their survival rate, rate of growth, bioaccumulation factor (BAF), translocation factor (TF), metal uptake (MU), accumulation, and capability for removing metals. Special attention was given to understanding the mechanism(s) involved in the removal of metals.

Materials and methods

Study area

This study was performed at the KCPS refinery, located about 32 km southwest of Erbil, Iraq, Fig. 1.

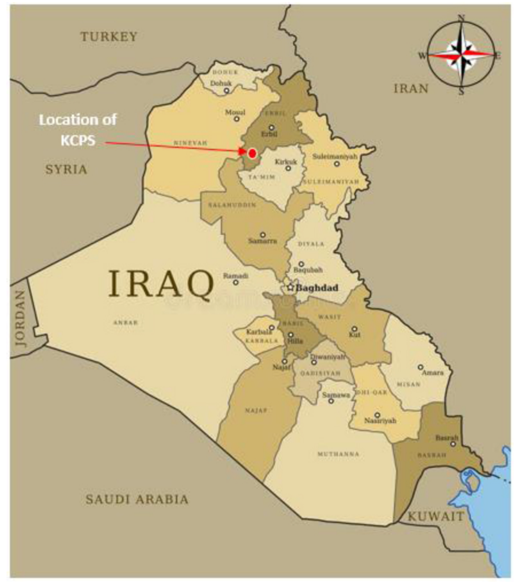

Fig. 1. Location map of the (KCPS) refinery (source: Atlas online).

The study area (i.e., Erbil province) has a subtropical semi-arid climatic condition, characterized by wide diurnal and annual ranges of temperature, low relative humidity, and cloudless summer months. In the summer, average daily maximum temperatures surpass 42°C, while average daily low temperatures are 24°C. In the winter, average daily temperatures vary from 8°C to 12°C. Temperatures fluctuate greatly throughout the year, with a high temperature of 46°C and a low temperature of −4°C. The average annual rainfall is between 250 and 400 mm, and prevailing wind directions are from northwest.[11,21] The KCPS refinery treats its effluents by chemical addition, clarification, oxidation, oil skimming and filtration before being discharged via drainages into the evaporation ponds.[4]

A. Donax L. preparation

The young, uniform and healthy *A. donax* L. (giant reed) plants were gathered at wetland habitats downstream of the KCPS, where receiving refinery's discharge, in June 2022. The plant specimens, Fig. 2, are identified either through or *via* comparing to the preserved specimens of the herbarium in the department of biology and duly authenticated from the college of science, Salahaddin University-Erbil, Iraq.

The macrophyte *A. donax* L. is a tall perennial aquatic reed. *A. donax* L. (long leaf) is an invasive plant species found in Iraq. However, it is now being recognized as a sub-cosmopolitan species because of its widespread and global distribution.[13] The

Fig. 2. The experiment plant *Arundo donax* L. (photos taken during acclimation stage of this study).

A. donax L. plant species used in this study is described in Table 1 below;

Plant specimens were acclimated, prepared and planted according to.[4,21] Prior to the experiment, the initial dry biomass and Cr (VI) concentrations in the plant shoot (stems and leaves) and root (rhizomes) are measured.

Hybrid-CW setup and the study assessment steps

The raw effluent from the KCPS (before discharging into evaporation ponds) was directly collected in a polyethylene pre-sedimentation tank capacity of 3000 liters, as a physical treatment (particulate settling) unit. The effluent from the pre-sedimentation tank was subsequently dispersed *via* 1 Inch PVC pipelines (with control flow taps between treatments) over three replications of HCWs (non-planted) as a control and HCWs (planted with *A. donax* L.). The vertical CW was set up in (LWH = 50 × 40 × 100 cm, respectively) galvanized (rust proof) containers, while the horizontal CW dimensions were (LWH = 120 × 80 × 100 cm, respectively) galvanized containers. The vertical type of CWs were filled with four stratified filtration media (20 cm thickness of each); a cobble layer size = 8-10 cm from the bottom (to prevent blockage by sediments and sludge), followed by medium gravel size = 5–16 mm, fine gravel size = 2–5 mm and quartz sand (size = 0.05–2 mm), respectively. On the other hand, the horizontal type of CWs were filled by only two stratified layers 40 cm thickness of each of medium gravel layer from the bottom, then supplemented by a fine sand layer, Fig. 3. The filtration media were prepared as described in.[4,21]

The whole system (CWs) was set at 35° slope, to ensure smooth (self-acting/ gravity dependent) flow of the effluent throughout treatment units (no peristaltic pump was needed), and intermittent batch loading (hydraulic loading), 8–10 doses per day (for oxygen transfer enhancement) with 2 days resting duration (hydraulic retention time, HRT).[21] The flow rate of effluents passing throughout the system was fixed approximately at 25 liters per hour (using flow control taps). In order to ensure the stability of the systems, the wetland areas were operational for a period of 5 days before the beginning of the experiment.

The current study was executed in three assessment steps, as summarized below:

- **Step I:** Acclimation step (duration = 6 weeks): During this step (i.e., before the start of the experiment) plants were acclimatized at the field (the new habitat), under natural conditions, for 6 weeks, and this was done to facilitate adaptation and promote robust plant growth before the commencement of the experiment. Additionally, an analysis was conducted to determine the initial dry biomass and Cr (VI) content in *A. donax* L. plant parts (stems, leaves and roots) as well.
- **Step II:** Monitoring step (duration = 7 weeks): During this step the Cr (VI) content and some other related water quality assessment parameters, namely: pH, redox potential (mV), temperature (°C), electrical conductivity μs/cm, chemical oxygen demand (mg/l), dissolved oxygen (mg/l), sulphate (mg/l) (data is not given here) were monitored on a weekly basis in the PRE and the outlet of the HCWs (non-planted and planted).

Table 1. Description of *Arundo donax* L. species collected around the KCPS refinery, Erbil, Iraq.

Name	Common name	Order	Family	Type	Habitat	Herbarium* accession number/ date (DD-MM-YY)	Conservation status
Arundo donax L.	Giant reed	Cyperales	Poaceae	Emergent	Aquatic	102/(16-08-1994)	Lest concern (LC)

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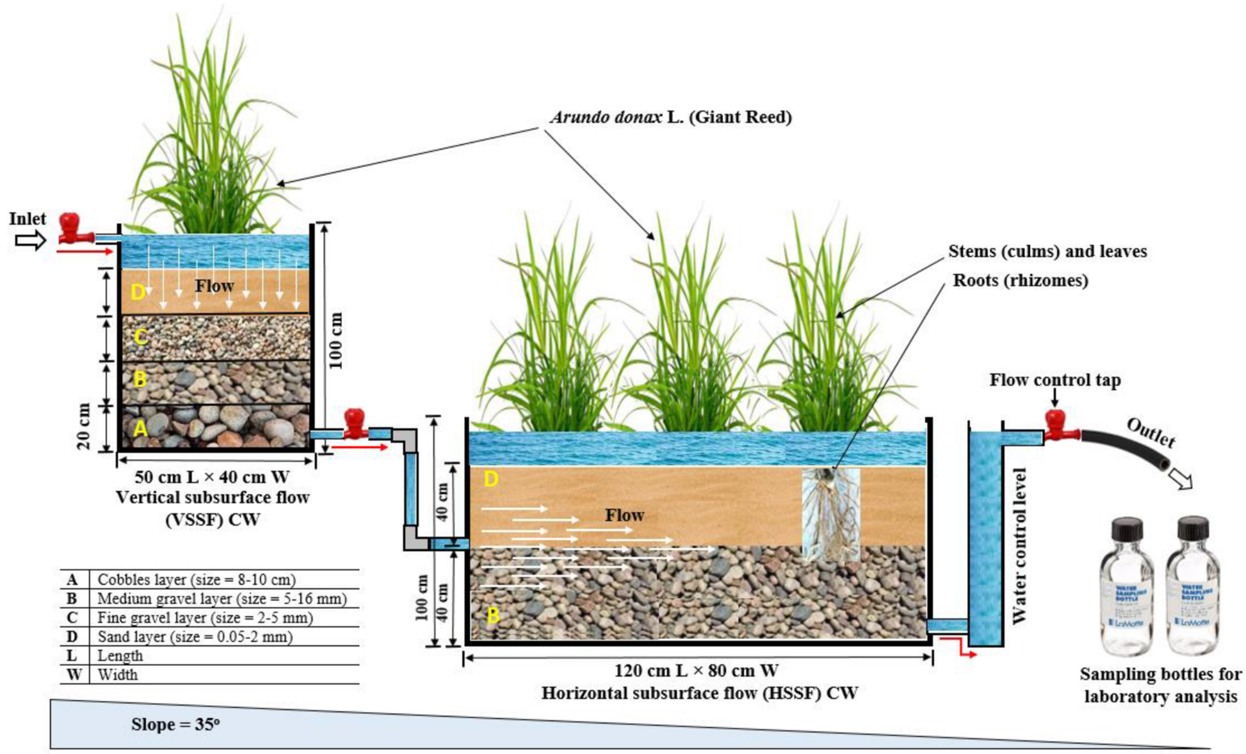

Fig. 3. The hybrid constructed wetland (HCW) set-up used for the treatment of Cr (VI) in the KCPS refinery's effluent, Erbil, Iraq.

- **Step III:** Bioassay step: Throughout this step, growth rate (GR), bioaccumulation factor (BAF_{root} and BAF_{shoot}), metal uptake (MU), translocation factor (TF), metal accumulation and metal removal capacity (RC) were analyzed for the plant of concern.

Chromium (VI) analysis in water samples

Cr (VI) in water samples was detected using UV-*Vis* spectrophotometer (JENWAY model 6300; China) at a wavelength of 540 μm. A violet color is produced in responsiveness to the presence of Cr (VI) after reacting an acidified sample with 1N H_2SO_4 and a 0.5% solution of a 1,5-diphenyl-carbazide (DPC).[10] Samples for Cr (VI) analysis were collected from the inlet (raw effluent/ before treatment) and the outlet (after treatment) once a week and preserved by addition of concentrated nitric acid (to reduce an adsorption of metal on the sampling bottle walls). Subsequently, water samples are transported to the laboratory under controlled conditions of low temperature and absence of light.[11,12] In the laboratory, the Cr (VI) concentration in water samples have been measured following the procedure described by.[38] Briefly, the water samples were filtered first *via* 0.45 μm filters, then digested with Aqua regia (HNO_3 67%: HCl 37% = 3).[4] Samples were read in triplicate with flame atomic absorption spectrophotometry (FAAS, [210/211 AAS 220 GF] graphite furnace and 220 AS auto sampler, U.S.A), with a detection limit less than 0.05 mg/l. Standards were prepared with the same wastewater (i.e., refinery's effluent) and carried through the same process as the samples. A calibration curve for Cr (VI) ions was constructed by analyzing multiple samples with known and specific concentrations of Cr (VI), correlating each concentration with its corresponding absorbance value.[21,38]

Chromium (VI) analysis in sand and plant parts

At the end of the 7th week of the experiment, *A. donax* L., were obtained from each HCW, and they were divided into roots (rhizomes), stems (culms) and leaves; these have been dried (60°C, oven, until constant weight) and extracted to analyze Cr (VI). The method as described by[4,21,38] was followed up properly. Briefly, sand samples were collected from vertical profiles manner (subsurface to $\geq$ 20 cm depths) of the HCWs. Each sample was operated *via* a homogenization of 5 sub-samples per HCW. The sand samples were also dried with air at standard temperature, followed by digestion with aqua regia (HCl: HNO_3 in 3:1). After that, the solution was evaporated up to 2 ml, filtered into a volumetric flask (20 ml), and the final volume was generated to mark with a double deionized water (dH_2O). On the other hand, the mineralization of samples was performed using Bergh's MWS-2 microwave digester (Germany) for each plant component and respective sand, implementing a tailored heating regimen for each individual sample. Furthermore, each sample of roots 1 g, stems 1 g and leaves (1 g) was put in a respective Teflon vessel of 7 ml HNO_3 65% and 1 ml of H_2O_2 30% at 200 °C for 20 min period; each soil sample 1 g was placed in a Teflon vessel of 7 ml of HNO_3 65% and 1 ml of H_2O_2 30% at 200 °C for 30 min period. After mineralization, the digested sample was brought to a volume of 20 ml with dH_2O followed by 0.45 μm nitrocellulose filtration. The analyses were performed by FAAS; ICP-MS Model 4500 Elan DRC, Perkin Elmer Company (U.S.A). Finally, the validity confirmation of the measurements was operated by three standard reference materials, NIST SRM 1643e – Trace Elements, NIST SRM 1515 – Apple Leaves, and NIST SRM 4354 – Sediment Powder, for sand, water and plant samples, respectively.[21]

The calculation of the growth rate, metal uptake and the removal indices

The total number of surviving plants has been counted at the end of experiments to assess mortality rates; the rate of plant survival was selected by dividing the final surviving number by the planted amount.[21] During the experiment steps, *A. donax* L. plants had been visually examined for any indications of toxicity.[4] The calculation of metal uptake indices was computed using the formulas, as described in;[4,21]

$$\text{Growth Rate (GR)} = DBP_{ah} - DBP_{bp}/T_{ah} - T_{bp} \quad (1)$$

Where:
DBP_{ah} is dry biomass produced right after harvesting.
DBP_{bp} is dry biomass produced before planting.
T_{ah} (time in days) and T_{bp} (time in days) are the cultivation intervals prior to and after harvesting.

The GR result has been turned to (% GR) percentages of growth rate.

$$\text{Metal Uptake (MU) (mg/plant part dry biomass)} = Metal_{pp} \times DB_{pp} \quad (2)$$

Where;
$Metal_{PP}$ is amount of metal concentration found in a plant's part (root or shoot),
DB_{pp} is dry biomass produced by the root or shoot tissues.

$$\text{Removal Capacity (RC) (mg/day/g)} = (C_i - C_f) \times VDB \quad (3)$$

Where;
C_i is the initial metal level; C_f is the final metal level, and
V is the volume, D is the number of days, and B is the dry biomass average.

$$\text{Percentage Removal Rate (\%)} = (C_i - C_f)/C_i \times 100 \quad (4)$$

Where; C_i is the initial (inlet) metal level, and C_f the final (outlet) metal amount.

$$\text{Translocation Factor (TF)} = MC_{shoot}/MC_{root} \quad (5)$$

Where; $MC_{shoot/root}$ is the concentration of metal in a plant part (root or shoot).

$$\text{Bioaccumulation Factor (plant parts) } (BAF_{pp}) = C_{PP}/C_{WW} \quad (6)$$

Where;
C_{PP} is the plant part's metal concentration; C_{WW} is the metal concentration in the wastewater.

Statistical analysis

The study was conducted with three replicates (n = 3), and the results were reported as the means ± standard deviation (mean ± SD). The obtained data was analyzed using the SPSS software (version 24). Statistically significant changes ($P < 0.05$) between the average values of various treatments were assessed and compared using Duncan's multiple range tests by one-way ANOVA. The correlation analysis was conducted to assess the relationship between the metal concentration in water and the corresponding metal content in plant parts, specifically the roots and shoots.

Results and discussion

Plant growth, survival rate and dry biomass

In this study, despite the *A. donax* L. plants being transplanted from outside the KCPS refinery premises (i.e., original habitat), it has experienced a high growth rate (218.5% or 3.6X) and survival rate 98–100% in the HCWs over the period of the experiment 7 weeks, Table 2. Both growth and development of *A. donax* L. in this study depended on the height and number of nodes recorded every week, which elevated with the time over the experiment period to range about (0.62 to 1.63 m) and (16 to 35 nodes) for the height and nodes number, respectively, Fig. 4. The

Table 2. Growth, survival rate and initial dry biomass of the *Arundo donax* L. over the experiment duration.

Treatment	Survival Rate (%)	Growth Rate (%)	Dry Biomass (g/plant dw)	
			Initial	Final
HCWs (planted)	98–100	218.5 or 3.6X	44.3	117.4

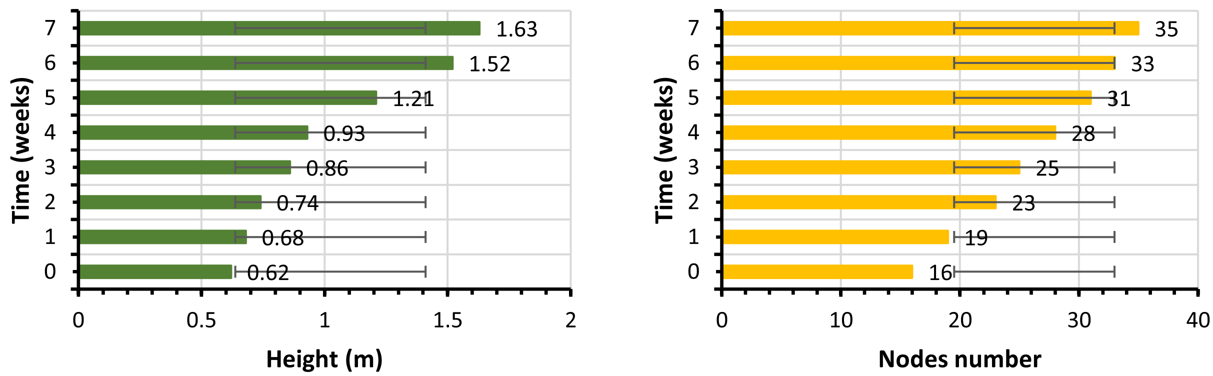

Fig. 4. The measurement of height (m) and node number of *Arundo donax* L.

initial dry biomass (dry weight) of *A. donax* L., was also considered and showed a higher value of (44.3 g/plant), while the final dry biomass reached 117.4 g/plant after the end of the 7th week, Table 2. Accordingly, the *A. donax* L. macrophytes grew without showing visible signs of Cr toxicity (e.g. chlorosis and stunting). This indicates *A. donax* L. plants adaptation and tolerance of the highly polluted effluent by Cr (VI).

A notable attribute of *A. donax* L. is its substantial rhizomes, which possess elongated and dense hairs and a taproot morphology.[13,30,32] In Erbil governorate, *A. donax* L. species are highly invasive. The *A. donax* L. plant species emerges and proliferates in untreated industrial effluent, exhibiting a high distribution along riverbanks and pond edges.[21] *A. donax* L. is a highly desirable choice for studying phytoremediation treatments due to its capacity to thrive in harsh environmental circumstances and its fast and robust development.[13] Utilizing plants to extract pollutants from contaminated soil and water might be a beneficial approach, particularly for remediating metals (such as Cr) that are typically challenging to eliminate effectively.[11,12] The study, referenced as,[13] assessed the capacity of *A. donax* L. to thrive in the chromium condition. The results suggested that the plant had a remarkable ability to develop in a nutrient solution containing progressively higher levels of chromium (Cr), up to 900 μg/l, during a three-week period in a greenhouse setting. According to,[13,27] *A. donax* L. exhibits exceptional capacity to absorb and accumulate harmful metals (such as Cr) from water without any detrimental impact on its health and growth. *A. donax* L. is commonly used as a bio-accumulator for heavy metals because it has the ability to absorb metal pollutants that cannot be easily broken down by biological processes. *A. donax* L. is capable of thriving in settings characterized by severe pH levels, high salt concentrations, and limited water availability, while also being able to absorb metals without experiencing any detrimental impacts on its growth. Moreover, it has been shown that *A. donax* L. can thrive in settings contaminated with trace metals. These trace metals, despite being present, did not cause any stress to the plant, and as a result, they did not hinder the opening of stomata or impact the functioning of *A. donax* L.'s photosynthetic machinery.[13,27] The same may be true for *A. donax* L. in this study.

The current findings indicate that the *A. donax* L. plants remained in a healthy state. The ability of *A. donax* L. to maintain good health and sustained growth, as indicated by the large number of nodes and plant height observed throughout the experiment, is a significant factor in selecting *A. donax* L. for phytoremediation purposes. Overall, the growth and development of *A. donax* L. grew over time for the entire duration of the experiment, as observed by the increase in height and number of nodes measured on a weekly basis. The results are consistent with those obtained in a prior investigation.[13] However, they observed a significant difference ($P < 0.05$) in the height and number of nodes of *A. donax* L. when growing in industrial effluents. The hypothesis was that *A. donax* L. (long leaf) with more biomass would have a higher capacity to extract chromium (Cr) compared to *A. donax* L. (short leaf) with lower biomass. The justification for this idea is that the *A. donax*

L. variations with higher biomass exhibit more root development, longer stems, and a higher leaf count in comparison to the varieties with lower biomass. Therefore, a greater amount of plant biomass (similar to what was observed for *A. donax* L. with long leaves in this study) is accessible for the uptake, movement, and accumulation of chromium. Additionally, it is shown that the chromium uptake efficiency by *A. donax* L. is enhanced under moderate pH conditions. The reason behind this notion is that plant Cr is present in the PRE within the pH range of 5.0–7.0.[21,38]

The present study also considered the dry biomass of *A. donax* L., which exhibited a higher value of 44.3 g/plant. By the end of the 7th week, the final dry biomass reached 117.4 g/plant, as indicated in Table 2. Consequently, *A. donax* L. (long leaf) plants were classified as belonging to the high dry biomass group in this study, which is a characteristic commonly observed in these native plant species in their natural habitat. Aquatic plants are strongly capable of reproducing and exhibit rapid growth, resulting in the accumulation of a substantial amount of biomass in a short span of time. Quantifying total plant biomass is crucial in phytoremediation studies, as it helps assess the ability of plants to withstand challenging environmental circumstances.[4,11,12] The reference[13] reached a similar conclusion, stating that *A. donax* L. is the top energy crop in terms of biomass output. It can provide approximately 50–80 dry tons of biomass/hectare/year, depending on the climate and the agricultural technique. This makes it a valuable source of renewable energy.[27] Moreover, as indicated by,[13,27] the *A. donax* L. genus, also known as long leaf, has a remarkable growth rate of 2.5 to 3 inches per day. It may reach a height of 20 ft. under ideal conditions. This plant is one of the fastest-growing species and has the capacity to produce about 50 tons of aboveground dry biomass per hectare annually. The growth, survival rate, and biomass production capacities in *A. donax* L. (long leaf) may depend on the adaptation of its genotype variations to harsh environments.[13,27,39]

Chromium (VI) concentration in inlet and outlet of HCWs with the percentage removal rate

The weekly Cr (VI) concentrations in the inlet (i.e., raw refinery's effluent) and outlet of HCWs (i.e., final/treated effluents), namely, the control (non-planted HCWs) and vegetated (planted HCWs) samples, were analyzed. Additionally, the percentage Cr (VI) removal rate by HCWs, along with the retained Cr (VI) concentrations by sand substrates in the HCWs, after 7 weeks of the experiment were analyzed as well (whereas, no/or little change in Cr reduction was seen afterward), Table 3 and Figs. 5 and 6.

Results showed that the Cr (VI) concentration in the inlet samples, varied from 9.87 to 14.63 mg/l, with a mean value of 13.60 ± 0.54 mg/l, which severely exceeded the safe limit of 0.05 mg/l set by international guidelines, Table 3. The Cr (VI) concentration in the outlet of the control HCWs (non-planted) samples, fluctuated between 7.32 to 10.86 mg/l, with a mean value of 11.74 ± 0.42 mg/l. Meanwhile, the Cr (VI) concentration in the outlet of the HCWs (planted) with *A. donax* L. samples, ranged from (0.04 to 0.12 mg/l), with a mean value of 0.07 ± 0.057 mg/l, which approached the legislative limit of 0.05 mg/l. The variations of the Cr (VI) concentration in the outlet samples of HCWs (planted) were dramatically lower ($p < 0.05$) over control (non-planted) outlet. The outlet from the planted HCWs suggested a dramatic ($p < 0.05$) decline in Cr (VI) concentrations from control (non-planted) HCWs. Meanwhile, non-significant differences ($p < 0.05$) were exhibited in the outlet Cr (VI) concentrations between the triplicate non-planted HCWs (control) and planted HCWs as well.

On the other hand, results showed that the percentage Cr (VI) removal rate (%) was 12.32 ± 4.2% and 88.12 ± 2.3%, recorded for HCWs (non-planted) and HCWs (planted) with *A. donax* L., respectively, over the experiment duration, Fig. 5. Meanwhile, the amount of Cr (VI) retained by sand substrate was estimated at 1.67 mg/g and 0.93 mg/g recorded for HCWs (non-planted) and HCWs (planted), respectively, over the period of the experiment, Fig. 6.

From Table 3, it seems that the initial (raw refinery effluent/before treatment) mean Cr (VI) concentrations in the KCPS refinery effluent recorded over the experiment duration severely exceeded safe limits, compared with the maximum allowed limit of 0.05 mg/l set by international standards. These limited options do not meet the necessary criteria for wastewater disposal. The KCPS employs a treatment process for its effluents that includes clarifying, oxidation, oil skimming, and filtration. These treated effluents are then discharged through drainage into evaporation ponds.[4] Petroleum refinery effluents are industrial wastewaters that are generated during the extraction of crude oil and the production of fuel, lubricants, and other petroleum-derived goods. This product contains various pollutants, including Cr (VI) and other contaminants.[37] In a previous investigation,[1] data on treatment of petroleum refinery effluents in Iraq was collected. They concluded that Iraqi petroleum refinery's effluents contain numerous pollutants in different levels, including Cr (VI) and the content of the products varies based on the type of crude oil being operated and the treatment procedures

Table 3. Inlet and outlet concentrations (mg/l) (mean ± SD) of Cr (VI) in the non-planted and planted HCWs with *Arundo donax* L., over 7 weeks of remediation.

Treatment	Cr (VI) concentration (mg/l)
Inlet (raw refinery's effluent)	13.60 ^{b} ± 0.54
Outlet of the control HCWs (non-planted)	11.74 ^{b} ± 0.42
Outlet of HCWs (planted)	0.07 ^{c} ± 0.057
Maximum permissible limit (EU; US EPA; WHO)	0.05
Iraqi safe limit for Cr (VI)	NA

The limit is for sanitary water set by EU (European Union), US EPA (U.S.A, Environmental Protection Agency), WHO (World Health Organization), NA means (not available). Values are means ± Standard Deviation of triplicate planted HCWs (n = 7) taken over the experiment period. Values with the same mean are non-significantly different ($p \geq 0.05$).

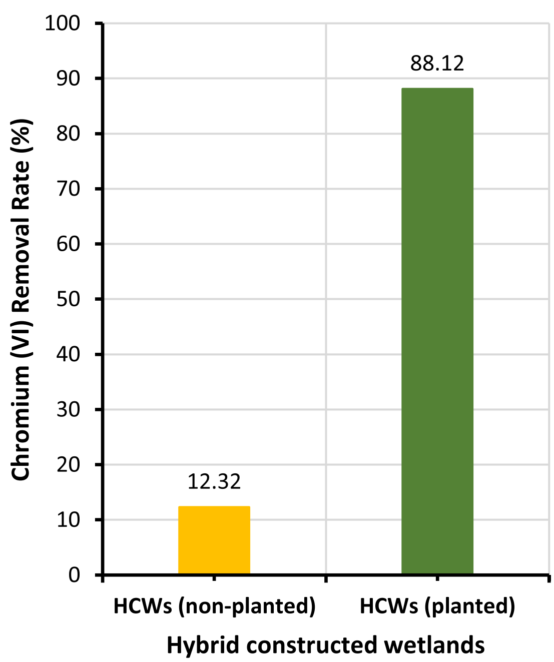

Fig. 5. Percentage removal rate (%) of Cr (VI) by HCWs (non-planted) and (planted) with *Arundo donax* L. over (7) weeks of phytoremediation (n = 3).

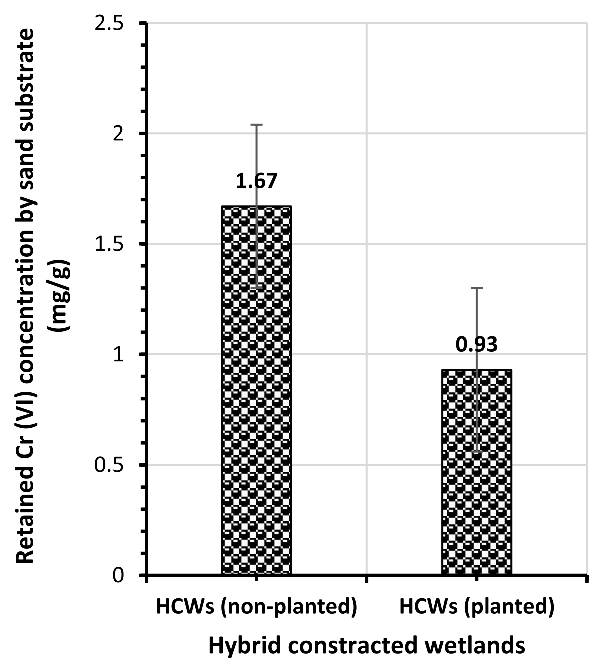

Fig. 6. Retained Cr (VI) (mg/g) by sand substrate in HCWs (non-planted) and (planted) with *Arundo donax* L. over (7) weeks of phytoremediation (n = 3).

being used, such as distillation and thermal cracking. In this context, similar trends can be observed with respect to the KCPS refinery. The levels of Cr (VI) from the KCPS refinery's effluent were higher than those obtained by[1] for 13 refineries investigated in Iraq, namely, Basra, Qayyarah, Kasak, Baiji, Haditha, Dora, Samawah, Kirkuk, Diwaniyah, Alsinsinah, Najaf, Dhi Qar and Maysan refineries. However, the results obtained from the investigation of 79 PREs from 67 refineries in 22 European nations, ranging from Portugal in the southwest to Romania in the east and Norway in the north, were similar to those found in other parts of the world.[39]

The removal percentage rate is the expression of the CWs overall ability to eliminate contaminants from wastewater for the investigation. The studied hybrid constructed wetland (HCW) planted with *A. donax* L. evinced a high level of Cr (VI) removal percentage rate (%). The removal of Cr (VI) amounted to 88.12 ± 2.3%, this system's removal efficiency values for various metals are comparable to previous hybrid systems that use horizontal and vertical filters in sequence, including Cr (VI).[4,21] Furthermore, a significant increase in Cr (VI) concentrations in the outlet of HCWs may be due to the fluctuation of pH toward the acidity level (< 7) observed throughout the experiment duration (date is note given here). It is widely recognized that total chromium can exist in several environmental forms, which are determined by pH and redox conditions. Cr (III) and Cr (VI) are the most stable forms due to their inherent chemical and physical characteristics. Chromium (III) has lower solubility at pH 5 and tends to precipitate because of its strong attraction to organic compounds.

On the other hand, Chromium (VI) is extremely soluble in water, and its solubility is dependent on pH, increasing as pH decreases.[5,38,39]

Constructed wetlands have proven to be highly effective in the treatment of heavy metals and metalloids found in wastewater.[4,21,39] Previous studies[4,8,17] showed HCWs planted with several macrophytes (including *A. donax* L.) can be utilized to treat secondary refinery wastewater to eliminate heavy metals such as cadmium, chromium, lead, zinc, and copper. Hybrid systems are now being developed by combining several types of built wetlands to improve the efficiency of pollution removal, specifically for substances like Cr (VI).[17,19,20] In addition, hybrid-built wetlands are sophisticated systems that are meticulously designed by mixing various types of constructed wetlands to enhance treatment efficiency.[19,20] Furthermore, hybrid systems typically consist of vertical-flow and horizontal-flow built wetlands organized in a stepwise fashion,[16,18,21] additionally, these technologies are currently being implemented in other countries across the globe. The treatment of (HCWs) relies on biological and physical mechanisms such as adsorption, precipitation, filtration, predation, nitrification, and decomposition. As a result, HCWs are more efficient in removing metals compared to other types of constructed wetlands (CWs). Unfortunately, there is a scarcity of information regarding the methods of removing Cr (VI) and the kinetics of the process in outdoor HCWs. Prior research[16,21,39] maintains that in a complex system like (HCWs), multiple pathways for elimination (such as volatilization, photochemical oxidation, sedimentation, sorption, and biodegradation) can occur simultaneously. Plants can contribute to this process by directly absorbing and accumulating contaminants, releasing them through phytovolatilization, and facilitating metabolic transformation. Additionally, plants can create conditions that are favorable for pollutant remediation within treatment systems. The same conclusions might be inferred for the present configuration of (HCWs).

In this study, sand and gravel substrate (filtration media) were used to construct the filter body. The studied HCWs evinced a moderate level of Cr (VI) retained by filtration media, Fig. 6. The retention rate of Cr (VI) is like that of previous hybrid systems utilizing horizontal and vertical sand/gravel filters.[4,21] The high efficiency of artificial wetlands in removing pollutants, including heavy metals, is mostly attributed to the filtering processes that take place throughout the entire wetland filter body. Overall, the findings indicated that Cr (VI) was predominantly concentrated within the uppermost 5 cm of the sand column depth, in both the vertical and horizontal constructed wetlands (CWs). Significant progress has been made in the research and development of slow sand filters and gravel for the purpose of removing particles. However, there have been few studies conducted on the application of these filters in the context of removing Cr (VI) from refinery effluents in HCWs. The results in this context are in accordance with the previous studies that suggested that the amount of Cr (VI) retained by sand filtration media is influenced by the initial concentration of Cr (VI) in the inlet, the flow loading rates, and the depth of the column. This can be attributed to the fact that the removal of Cr (VI) in HCW systems primarily occurs through non-living processes, such as adsorption to substrate media and roots. Parallel observations were noted by;[4] however, they also showed that the ability and effectiveness of sand and gravel substrates (specifically, the filter body) to remove heavy metals in (HCWs) is influenced by the initial concentration of metals in the inlet, the rate at which the flow is loaded (i.e., the number of intermittent batch loading doses per day), the duration of rest periods, and the depth of the substrate.

A. donax L. and contribution to Cr (VI) removal in HCWs

This study examined the variation in Cr (VI) concentrations across different portions of the *A. donax* L. plant, specifically the shoots (stems and leaves) and roots, following harvest. The focus was on determining the rates of metal accumulation (mg/g dw), Fig. 7. Furthermore, the absorption of Cr (VI) (mg/plant dw) in both the start and end sections of the plant was also examined, as shown in Fig. 8.

Results revealed that the emergent *A. donax* L. plant accumulated a significant ($p < 0.05$) amount of Cr (VI) in its tissues; (1.65 mg/g dw) in stems, (0.98 mg/g dw) in leaves, and 7.88 mg/g dw in roots, as compared to the initial Cr (VI) concentration of 0.35 mg/g dw in stems, 0.34 mg/g dw in leaves and 1.13 mg/g dw in roots, Fig. 7. On the other hand, a higher Cr (VI) uptake value was found in roots 925.11 mg/plant dw as compared to the shoots; (193.71 mg/plant dw) in stems and 115.1 mg/plant dw in leaves as compared to the initial Cr (VI) uptake of 50.1 mg/plant dw in roots, 15.51 mg/plant dw in stems and 15.12 mg/plant dw in leaves, respectively, Fig. 8. It means that *A. donax* L. plants were able to accumulate the highest Cr (VI) content in their roots, rather than shoots. In this study, Cr (VI) accumulation was greater at week 7 in *A. donax* L. plants receiving KCPS refinery's effluent. However, minimal or no alterations were seen subsequently.

The current study revealed that *A. donax* L. has a higher capacity to absorb Cr (VI) in its roots

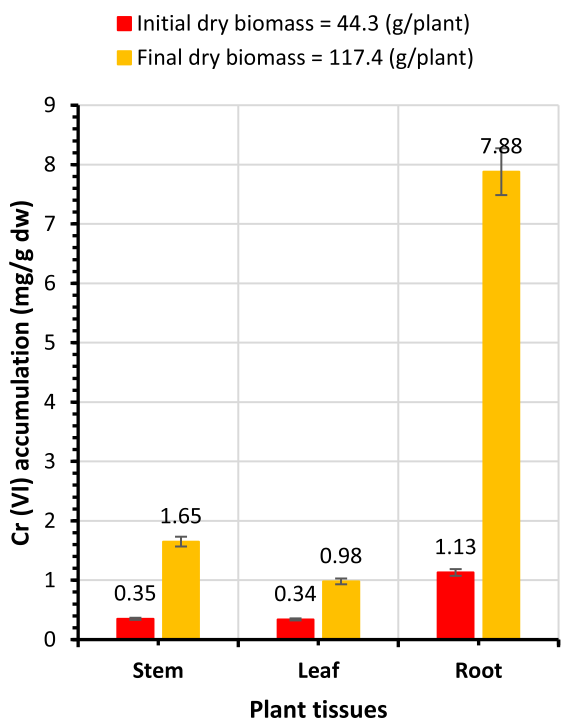

Fig. 7. Chromium (VI) accumulation (mg/g dw) by *Arundo donax* L. in the HCWs receiving KCPS effluents, over (7) weeks of phytoremediation (n = 3).

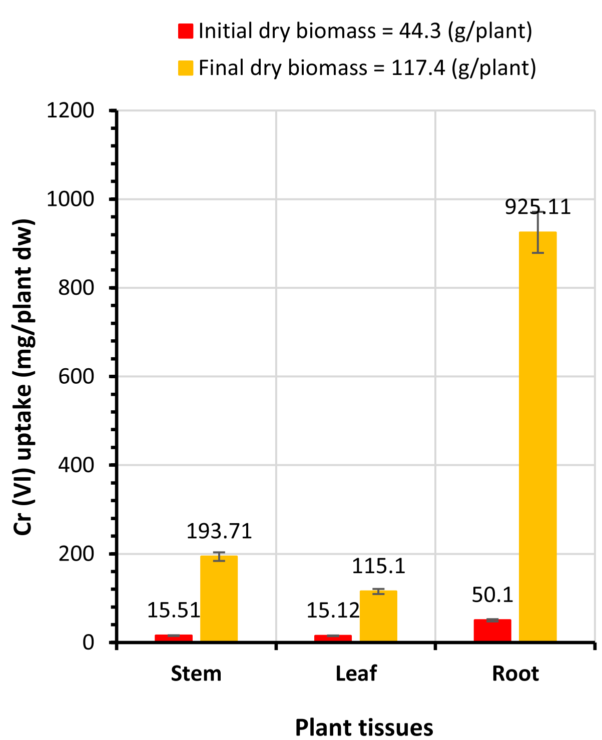

Fig. 8. Chromium (VI) uptake (mg/plant dw) by *Arundo donax* L. in the HCWs receiving KCPS effluents, over (7) weeks of phytoremediation (n = 3). Duration (n = 3).

compared to its shoots (stems and leaves), as shown in Figs. 7 and 8. This indicates that *A. donax* L. exhibits varying levels of Cr (VI) uptake in different tissues, with the highest uptake observed in the roots, followed by the stems and leaves. These findings are consistent with previous research on metal uptake in plants.[4,8,33] However, the reference[33] investigated wild plant species such as; *Cakile arabica, Capsella bursa – pastoris, Carrichtera annua, Diplotaxis acris, Diplotaxis haru, Eruca sativa* and *Erucaria hispanica*, grown in Wadi Al-Tib region northeast of Al-Ammara, Iraq, as indicators of certain toxic heavy metals, including Cr. They showed that the concentration of chromium (Cr) in all plant tissues surpassed the allowable limit. Their findings demonstrated that the observed plant species are capable of absorbing heavy metals without significant harm to their metabolic processes. The presence of a higher concentration of Cr (VI) in the effluent of the KCPS refinery resulted in an increased uptake of Cr (VI) by the *A. donax* L. plants, which is in line with prior research findings.[38,39] *A. donax* L. exhibits greater biomass production (refer to the findings shown in Table 2. Therefore, a greater amount of biomass is accessible to *A. donax* L. for the uptake and accumulation of a larger concentration of Cr (VI).

A study has shown that phytoremediation is an effective method for removing Cr (VI) from polluted soil and wastewater due to its straightforward operation and high removal effectiveness. It offers a sustainable treatment approach that harnesses solar energy.[10,12,15] In recent years, numerous research investigations have been conducted to comprehend the underlying process mechanism.[21,25,39] Constructed wetlands (CWs) have been implemented near industrial facilities to treat effluents with high loads of contaminants. As exemplified by,[4,11,14] plant species could gather heavy metals in their roots and subsequently transport them to the stem and leaves. Over the past three decades, there has been significant focus on the absorption of chromium by plants. A study involving 78 different plant species has demonstrated their ability to remediate soil and water, with *A. donax* L. being the most prominent. It is expected that advancements in biotechnology would enhance the efficiency of potential hyperaccumulators by transferring hyperaccumulating genes for heavy metals from the roots to the stems and leaves, resulting in the development of cultivable species. The cellular response to chromium (Cr) stress entails a complex interconnected system of pathways that are responsible for the detoxification of chromium and consequently contribute to the development of chromium tolerance.[39] In Cr accumulated plant species, several mechanisms have been demonstrated to account for their resistance to chromate. In addition, the cellular pathways that are observed to be upregulated in response to Cr (VI) stress include reactive oxygen species (ROS) signaling as well. Sources of ROS include mitochondria, auto-oxidation of glucose, and enzymatic pathways such as nicotinamide adenine dinucleotide phosphate reduced (NAD[P]H) oxidase. Additionally, there is an increase in the antioxidant system, production of phytochelatins, phytosequestration, and differential compartmentation. This assertion may be true for *A. donax* L. in the current investigation.

Furthermore, as outlined by,[10,27] various environmental factors affect the reduction of Cr (VI) in phytoremediation plants, including initial Cr (VI) concentration, biomass density, carbon source, organic matter content, pH, temperature, dissolved oxygen, competing electron acceptors, and effluent composition. One such plant is *A. donax* L. This observation is consistent with previous studies;[5,9,39] nevertheless, it was shown that the accumulation, uptake, and exudation of Cr (VI) in the roots of aquatic plants are controlled by factors such as pH, particle size distribution, and cation exchange between the soil and the roots. This is because Cr (VI) from wastewater does not easily move to the above-ground sections of the plants. Moreover, the absorption of Cr (VI) primarily occurs via canals and transporters located in the root plasma membrane. Meanwhile, most vascular plants absorb hazardous heavy metals, such as chromium (Cr), in different quantities through their roots.[27,39] Studies demonstrated the ability of *A. donax* L. species to uptake chromium.[13,27] However, they indicated that *A. donax* L. uptake Cr (VI) more easily than Cr (III); nevertheless, the pathway of Cr absorbed by *A. donax* L. plant tissues is not yet clarified.[39] The uptake of Cr (VI) by *A. donax* L. plant tissues is assumed to be an active mechanism achieved by carriers for the absorption of Cr (VI) by essential elements such as phosphate.[10,13,15] Moreover, the notable variations in the Cr (VI) levels found in the roots, stems, and leaves could be attributed to the limited solubility and bioavailability of Cr (VI). The solubility and bioavailability of chromium in wastewater are primarily regulated by factors such as pH, concentration of chromium cations, exchange capacity of cations, organic matter content, and oxidation state of the system. Only Cr (VI) is considered to have a noteworthy bioavailability to *A. donax* L. tissues in this study. Due to its reduced solubility and bioavailability, Cr (III) is less readily absorbed by *A. donax* L. compared to Cr (VI).[37,39] Within this context, the present study draws similar conclusions regarding the rate and mechanism of Cr (VI) accumulation by *A. donax* L. However, it is important to note that the timing of harvest may also impact the uptake of Cr (VI) by *A. donax* L. Consequently, it is necessary to conduct long-term harvesting in future to rectify the experiment and enhance the effectiveness of *A. donax* L. in remediating Cr (VI) in refinery effluents.

The current study aimed to explore the correlation coefficient (r) between the Cr (VI) content in the effluent and the plant tissues (shoot and root) of *A. donax* L. as well. The Cr (VI) content in water showed a strong and statistically significant correlation ($p < 0.05$) with the Cr (VI) content in both the shoot and root. The Pearson's correlation coefficient (r) was 0.357 for the shoot and 0.394 for the root, as shown in Fig. 9. Based on the analysis provided by,[5,9,27] there is a slight positive correlation between the presence of Cr (VI) in the effluent and the tissues of the *A. donax* L. plant (namely the shoot and root). This correlation is modest, as indicated by the obtained (r) values falling within the range of 0.1–0.39.

A. donax L. and phytoextraction capacity for Cr (VI)

The phytoextraction capacity (i.e., the phytoremediation efficiency) for Cr (VI) by *A. donax* L. in HCWs receiving KCPS refinery's effluent over 7 weeks of phytoremediation was evaluated by bioaccumulation factor (BAF) and translocation factor (TF). Additionally, the removal capacity (RC) (mg/day/g) was calculated also for *A. donax* L. during both the initial and final steps of the experiment, and the results are tabulated in Table 4.

Results showed that the bioaccumulation factor (BAF) values recorded for *A. donax* L. were generally high (i.e., > 1) in both initial and final treatments over the studied period of the experiment, and the values were 1.14 and 14.24 in stems (culms), 1.11 and 8.46 in leaves and 3.68 and 68.02 in roots (rhizomes) recorded between the initial and final step of the experiment, respectively. Meanwhile, the translocation factor (TF) values of the *A. donax* L. fell far below (<1) of 0.61 and 0.33 calculated for *A. donax* L. during the initial and final step of the experiment, respectively. However, lower removal capacity of 0.81 mg/day/g was recorded during the initial step of the experiment, which severely increased at the end of the experiment to 3.34 mg/day/g, Table 4. Generally, in contrast to TF, values for BAF coincided with the highest removal capacity (RC) recorded for *A. donax* L. over the experiment period.

From Table 4, the TF values of the *A. donax* L. plants were very low (i.e., <1), for all treatments throughout the experiment duration. It has been clarified that; the TF is a key index for determining metal transfer from the plant's belowground to aboveground sections (areal parts).[27] In contrast, the BAF values, which is a measure of the possibilities for

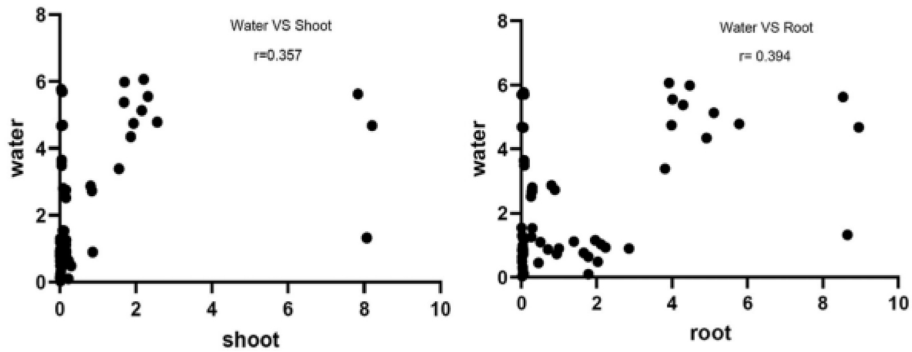

Fig. 9. Correlation r coefficient of Cr (VI) content between the effluent and *Arundo donax* L. tissues.

Table 4. Mean value of removal capacity (RC), bioaccumulation factor (BAF), and translocation factor (TF) with (mean ±SD) of *Arundo donax* L., planted in HCWs (n = 3) over the period of the experiment.

		BAF			
		Shoot		Root	
Treatment	Removal Capacity (RC) (mg/day/g)	Stem (culm)	Leaf	Rhizome	TF
Initial	0.81b ± 1.8	1.14a ± 0.2	1.11a ± 1.1	3.68c ± 6.6	0.61b ± 0.3
Final	3.34c ± 1.2	14.24ab ± 7.0	8.46ab ± 3.6	68.02ab ± 22.3	0.33b ± 0.1

heavy metal moving throughout various parts of a plant, were greater than (>1) in *A. donax* L. tissues (i.e., stem, leaf and root). It is known that the plant part tends to hold metal basically in roots for the process; whereas accumulation of metal is assumed to happen primarily in shoots in a plant extraction approach.[4,10,12] Furthermore, BAFs in whole plant parts (i.e., BAF_{root} and BAF_{shoot}) and TF are crucial indicators for demonstrating the effectiveness of plants used in the phytoremediation process.[4,12,27] It has been outlined that plants having BAF_{root} and BAF_{shoot} greater than one (>1) with TF less than one (<1), indicate good potential for Cr (VI) uptake from the effluent. However, TF < 1 indicates limited translocation of Cr (VI) to the areal parts of *A. donax* L., which may suggest that Cr (VI) is primarily retained in the plant roots (rhizomes). These values demonstrate that while *A. donax* L. can effectively absorb Cr (VI) from the refinery's effluent, its ability to translocate the Cr (VI) to the areal parts is relatively lower. This makes *A. donax* L. potentially useful for phytostabilization (trapping contaminants in the root zone), where contaminants are immobilized in the root zone rather than phytoextraction (extraction metal for removal). The effectiveness of phytostabilization depends on the amount of plant biomass, the concentration of chromium (VI) in the plants, and the availability of chromium (VI) in the effluent.[39] The bioavailability and solubility of Cr (VI) in the effluents of the KCPS refinery are mainly influenced by factors such as pH, the capacity of metal cations exchange, organic matter concentration, and the oxidation state of Cr (VI). In addition, plants must possess the ability to transport chromium from the roots to the shoots in order to facilitate the absorption of a harmful trace metal from the surrounding environment.[23,27] It has been outlined that root accumulation is considered a key characteristic of so-called excluder species.[4,12,27]

In the current study, *A. donax* L. plants stored Cr (VI) primarily in roots, and a smaller fraction was translocated to shoots. Such uptake data is a defining characteristic of excluder plants. Substantial metal immobilization may occur by metal binding to root cells, which may be regarded as a plant tolerance mechanism. Thus, *A. donax* L. in this study is considered suitable for phytoremediation of Cr (VI) *via* phytostabilization. Nevertheless, *A. donax* L. demonstrated a robust ability to exclude Cr (VI) by absorbing significant amounts of this compound through its roots. The findings align with prior research that hypothesized that metal excluders block the entry of metal into their above-ground sections or maintain a consistently low metal concentration across a wide range of metal concentrations in the environment. Their primary mechanism is to confine metal within their roots.[21,26,30] The plant could modify its membrane permeability, adjust the metal binding capability of its cell walls, or release an increased amount of chelating chemicals.[21] This assertion may be true for *A. donax* L. in the current investigation.

Generally, results showed that the *A. donax* L. plant accumulated approximately similar patterns of Cr (VI) in shoots and roots 193.71 and 115.10 mg/plant dw, respectively, Fig. 8, and showed suitability for Cr (VI) phytoextraction. Furthermore, *A. donax* L. adapted and lived well in the KCPS refinery's effluent over the study period (91 days), experienced high (growth rate 218.5 or 3.6X, and great dry biomass 117.4 g/plant dw) (see results in Table 2), with high removal capacity (3.34 mg/day/g) of Cr (VI), Table 4. Such data is a defining property of phytoextractor plants.[21,27] As cited by many studies (but in hydroponic systems),[28] their research mostly centered around the phytoextraction of various heavy metals, notably chromium (Cr). They have assessed over 500 plant species for this purpose. Several plants have been discovered to possess a significant ability to transport metals from their roots to different tissues through the xylem, which is a crucial trait of hyperaccumulator plants. Nevertheless, these metals are often stored in the vacuole of the leaves to prevent or minimize their deleterious effects.[27] On the other hand, many authors[4,21,27] demonstrated a strongly enhanced rate of heavy metal uptake, a faster root-to-shoot translocation (TF $>$ 1) and a greater ability to detoxify and sequester heavy metals in leaves (BAF_{shoots}). Furthermore, as demonstrated by[21,27] the most accumulator plants have the potential as hyperaccumulators, due to their intensive potential to accumulate a high level up to 0.1%, i.e. more than 1000 mg/g of Cr (VI) in the dry matter. In this context, during this study it is proposed that *A. donax* L. has a good capacity of Cr (VI) *via* phytostabilization, as revealed in lower TF value ($<$ 1) and elevated BAF ($>$ 1) in plant parts, which showed that the *A. donax* L. is not Cr-hyperaccumulator under the present conditions of the experiment.

Conclusions

Studies on phytoremediation of locations contaminated with Cr (VI) is expanding quickly. In Iraq, there is a lack of knowledge regarding indigenous plants that are suited for bioremediation of Cr (VI) in refinery effluents, and this area requires further investigation. The main conclusions are that the well-designed hybrid constructed wetland in the current study has the potential to offer an attractive solution to the treatment of petroleum refinery effluents for reclamation of Cr (VI) purposes. The macrophyte *A. donax* L. could be recommended for use in hybrid constructed wetlands technology due to its fast-growing and absorption and translocation of Cr (VI) capacity. Furthermore, it can be concluded that *A. donax* L. has a good capacity of Cr (VI) removal *via* phytostabilization, as indicated in lower TF factor ($<$ 1) and elevated BAF ($>$ 1) in plant parts, which showed that the *A. donax* L. is not Cr-hyperaccumulator under these conditions of the experiment. Genetic engineering techniques to implant a more efficient accumulator gene into *A. donax* L. have been suggested by the author.

Authors' declaration

- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Furthermore, any Figures and images, that are not mine, have been included with the necessary permission for republication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Salahaddin-Erbil, Iraq.

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كفاءة إزالة ايونات الكروم (سداسي التكافؤ) من النفايات السائلة الناتجة عن مصافي تكرير النفط باستخدام الأراضي الرطبة المنشاءة من النوع الهجين (HCWs) و المزروعة بنبات القصب العملاق، أربيل، العراق.

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الخلاصة

في هذه الدراسة، تم تقييم قدرة القصب العملاق (*A. donax* L.) في تجارب حقلية باستخدام تقنية انشاء الأراضي الرطبة من النوع الهجين (HCW) لإزالة أيونات الكروم سداسي التكافؤ من النفايات السائلة في مصفاة KCPS (32 كم جنوب غرب مدينة أربيل، العراق). أظهرت النتائج بأن القصب العملاق شهد تكيفًا ممتازًا وتحملًا عاليا للعيش في النفايات السائلة شديدة التلوث بعنصر الكروم، و كان هذا واضحا من خلال إنتاجها العالي من الكتلة الحيوية ومعدل البقاء على قيد الحياة بنسبة 100٪ خلال مدة التجربة (91 يومًا). من الجهة الأخرى تراوح تركيز الكروم سداسي التكافؤ المأخوذ من نهايات وحدات المعالجة (HCWs) (والمزروعة بـالقصب العملاق) بين (0.04 إلى 0.12) ملغم/لتر، بمتوسط قيمة 0.07 (± 0.057) ملغم/لتر الذي وصل الى الحد المسموح والموصى به من قبل المعايير الدولية. حيث تبين بأن هذه الوحدات والمزروعة بالقصب العملاق أظهرت قدرة عالية لازالة الكروم سداسي التكافؤ من النفايات السائلة للمصفى بمعدل إزالة وصل الى (88.12%) وبقدرة إزالة (3.34) ملغم/يوم/غم. حيث كان أعلى تركيز للكروم السداسي المتراكم (295.11 ملغم/نبات) في الجذور و(193.71 ملغم/نبات) في السيقان، و (115.1 ملغم/نبات) في الأوراق. فضلا عن ذلك تم تقييم قدرة الاستخلاص للقصب العملاق باحتساب كل من عامل التراكم الحيوي (BAF) وعامل النقل (TF). حيث كانت قيم (BAF) (14.24), (8.46) و (68.02) سجلت لكل من السيقان, الأوراق و الجذور على التوالي، وكانت قيمة TF (0.33) مما يشير إلى أن القصب العملاق لديه قدرة جيدة على استخلاص الكروم سداسي التكافؤ من النفايات السائلة عن طريق جذورها بظاهرة (phytostabilization)، في حين أظهرت قيمة عامل النقل (TF) التي كانت أقل من (1) و قيمة عامل التراكم الحيوي (BAF) في أجزاء النبات التي كانت أكبرمن (1)، لذا انه لا يمكن احتساب القصب العملاق من ضمن النباتات فرط التراكم (hyperaccumulator) لعنصر الكروم سداسي التكافؤ في ظروف التجربة الحالية.

الكلمات المفتاحية: *Arundo donax* ، الكروم ، النفايات السائلة لتكرير النفط ، قدرة الازالة ، الأراضي الرطبة.