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Water hyacinth (*Eichhornia crassipes* and *Epipremnum aureum*) - a potent tool for the removal of cadmium and chromium from industrial discharges

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ABSTRACT

Industrial discharge is one of the major reasons for increasing heavy metal intoxication in the ecosystem and is a cause of global apprehension. The introduction of policies for periodically limited duration shutdown of industries might provide a way forward for reducing the pollutant loads in river bodies. Further, hyper-accumulator plants could serve as cost-effective alternatives to conventional sewage treatment facilities but comparative studies with native water hyacinth as natural water filtration systems with limnological studies and risk assessment remain to be determined. We here investigated the most polluted industrial effluent among ten industries during SARS-CoV-2 pandemic confinement (pre- and post-lockdown, that is, February 2020 and October 2020) in Mathura industrial area, India in terms of chromium and cadmium toxicity. Besides, the biosorbent potential of native *Eichhornia crassipes* and *Epipremnum aureum* plants was also estimated by triplicate batch experiments (7 d) from the most polluted industrial effluent. For risk assessment, the Metal Quality Index (MQI), Pearson's correlation coefficient analysis, and Heavy Metal Pollution Index (HPI) were calculated, while the students' paired sample *t*-test was employed to determine the statistical significance of changes in HPI and MQI. The findings revealed that the mean HPI for Cr (166,545 and 53,797) and Cd (96.11 and 9.78) were found to be extremely high during the pre-lockdown period which reduced significantly in the post-lockdown period. For student's *t*-test analysis, the *p*-values for the investigated sites were initiated to be considerably below the 0.05 level of significance. While results demonstrate removal efficiency of 67.66% and 61.22%, respectively in *E. crassipes*, whereas it was 44.26% and 38.90% in *E. aureum*. Low levels of student's *t*-test and *p*-values suggest a transient statistical impact of pandemic confinement on the water quality of studied sites and may help to alter pollution control policies and actions to make sure the environment is sustainable and safe. In addition, information makes it possible to conclude that money plants and water hyacinths both are effective candidates for removing chromium and cadmium from industrial effluents. This paper also summarizes the prospects for the scientific area of biosorption and bioaccumulation, focusing on its underlying assumptions, potential environmental benefits, and practical applications.

Keywords: Heavy metals; Biosorption; *Eichhornia crassipes; Epipremnum aureum;* Industrial effluents

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1. Introduction

Every single component of the environment (soil, air, water, etc.) has been severely contaminated with numerous toxins in today's fast-paced society due to rapid industrialization and urbanization [1]. Cities have been subjected to severe soil and water pollution as a result of their function as sinks for a variety of pollutants (including heavy metals) released into the ecosystem [2,3]. Another factor that has increased pressure on the system is the growth of human populations and activities along rivers. As a result, the water quality has declined and the environment is getting more polluted [4]. Pollution is the act of introducing dangerous compounds for living things into the environment [5]. Pollutants are dangerous liquids, solids, or gases that are produced in greater quantities than usual and to a greater extent than our ecosystem [2]. This leads to environmental breakdown which is a growing concern worldwide. There an is urgent need for immediate interventions to halt environmental pollution. According to the United States Environmental Protection Agency (USEPA), heavy metals have been highlighted as a key concern pollutant as a result of rising urbanization and industrialization. This is because heavy metals can heavy metals can accumulate in the environment over time. Heavy metals and toxicants emitted in industrial effluents, such as Cd, Cu, Zn, Pb, Cr, and others, eventually find their way into aquatic water bodies such as ponds, lakes, and rivers [6]. Water pollution is a significant subclass that comprises wastewater from various industries that contain hazardous materials such as radioactive materials, toxic heavy metals, volatile organic compounds, polycyclic aromatic hydrocarbons, petroleum contaminants, etc. [7]. Tenacious heavy metal contaminants such as Tl, Pb, Cd, Cr, Hg, Zn, U, etc. have the potential to adversely affect all life forms as indicated in Table 1. Cadmium is one of the heavy metals that has been linked to a variety of various forms of exposure during the past century [8]. Cadmium is present in the environment as a result of anthropogenic activities, and these activities have contributed to the presence of cadmium in the environment [9]. The use of cadmium in the industry as a corrosive reagent, as well as its use as a stabilizer in PVC products, color pigments, and Ni-Cd batteries, are the primary ongoing sources of cadmium contamination [10]. Cadmium exposure increases the risk of several potentially fatal illnesses, including renal and hepatic failure, pulmonary edema, testicular damage and osteomalacia, and damage to the adrenal glands and the hemopoietic system [4].

Besides, Cr is another heavy metal that can be toxic even at very little concentration and is found naturally in rocks volcanic dust, and as well as industrial effluents [7]. The most prevalent types of Cr found in natural water resources are trivalent chromium (Cr-III) and hexavalent chromium (Cr-VI). In addition to being created by several industrial processes, Cr-VI can also be formed naturally in the environment when natural chromium deposits erode [14]. There are documented cases of Cr being released into the environment due to leaks, poor storage methods, or insufficient industrial waste disposal techniques [7]. Production of chromate, metal processing, stainless steel welding, tannery facilities, and the manufacture of ferrochrome and chrome pigments are the primary contributors to chromium emission. The metallurgical, refractory, and chemical industries are the main contributors to the rising chromium levels in the environment through their use of the element in both air and wastewater. Once it has made its way into the body, Cr is capable of causing a variety of chronic respiratory conditions (CRCs), such as chronic respiratory failure, cystic fibrosis (CF), asthma, pulmonary hypertension (PH), interstitial lung diseases (ILD), chronic obstructive pulmonary disease (COPD), sarcoidosis, chromium ulcers, skin ulcers, vascular damage, nervous system disorders, cancers and allergic contact dermatitis in humans [15]. Table 2 illustrates various disorders in humans due to cadmium and chromium.

The traditional methods of eliminating heavy metals from tainted water are costly, time-consuming, and environmentally hazardous. Conventional methods prove to be useless over larger areas. Thus, in recent years, engineers and scientists have begun to develop low-cost methods that use biomass or living plants to clean up polluted regions. The search for innovative technologies to remove harmful heavy metals from contaminated water led to the development of a process referred to as "biosorption", which is dependent on the binding of toxic heavy metal abilities of a wide variety of living things. This mechanism was created as a result of the hunt for new technologies [10]. A metal sink's microbial biomass is influenced by pigments, extracellular polysaccharides, intracellular aggregation, and biosorption to cellular walls. There are two ways to get rid of metals: biosorption and buildup. The biosorption process needs a liquid phase (solvent) and a solid phase (biosorbent) that both contain a melted species that has to be sorted [19]. Studies have shown that plants may be able to recover metals in addition to removing heavy metals from polluted sites. It is an efficient and useful "natural" cleanup technique for polluted water and soil systems. The term "biosorption" refers to

Table 1
Pollutants and disorders in humans

Pollutant	Disorders	References
Heavy metals	Coronary heart disease, depression, anxiety Conduct disorder and associated antisocial behavior	[11]
Pesticides	Neurotoxicity and carcinogenic effect	[12]
Polycyclic aromatic hydrocarbons	Chronic stress, cardiovascular disease	[13]
Radioactive compounds	DNA damage and cancer Mental retardation, estrogenic effect	[5]

Table 2
Cadmium and chromium toxicity with associated disorders

Heavy metals	Disorders	References
Cadmium	Cancer, kidney, and liver malfunction	[16]
	Osteomalacia, renal and hepatic dysfunction, testicular damage	[4]
	Testicular injury, pulmonary edema, and cancer	[9]
Chromium	Osteomalacia, and damage to the adrenals and hemopoietic system	[17]
	Nervous system disorders, skin ulcers, vascular damage	[7]
	Chronic respiratory failure, chronic respiratory diseases (CRDs), pulmonary disease	[15]
	Asthma, cancer, skin ulcers	[18]

"the engineered use of green plants to remove, contain, and render non-toxic environmental toxicants such as organic chemicals, heavy metals, trace elements, and radioactive substances in water". The Water Hyacinth (*Eichhornia crassipes*) is an inexhaustible marine macrophyte that is regarded as a metal accumulator, a quickly emerging, freely floating aquatic plant, and it is also attributed to its bioaccumulation effectiveness, which can be defined as the accumulation of toxicant heavy metals or other chemicals in a living being [20]. Similarly, *Epipremnum aureum* has immortal creepers with green stems and striped with white or hardy interior foliage plant, and yellow heart-shaped leaves. It belongs to the arum family (Araceae) and to the genus Kirin, a large perennial vine that grows in the tropics and is instinctive to southeastern Asia. They are known to eradicate trace organic toxicants in the home and they also carry biosorption potential [9,21].

Therefore, monitoring followed by the removal of such lethal environmental toxicants from the ecosystem is an area of concern in front of mankind. Hence the paramount requirement of living organisms is to control this kind of undesirable disastrous pollution [22]. For this regular monitoring of heavy metals in the ecosystem is needed; to attain a sustainable future [14,22]. Keeping these things in view we deliberate to use this broad research theme to emphasize the current status of the existing trials of heavy metal toxication in the environmental biome for reducing the potential severances of the well-known concept of "environmental pollution" and for the attainment of defensible improvement in the future. In present study chromium and cadmium concentrations were analysed from ten industrial effluents at Mathura industrial area, India during pre- and post-lockdown SARS-CoV-2 periods (February 2020 to October 2020). In addition to the Metal Quality Index (MQI) and the Heavy Metal Pollution Index (HPI), the students' paired *t*-test was utilized to analyze the statistically significant changes in HPI and MQI. To identify the pollutant that contributed the most to the pollution indices, an examination based on Pearson's correlation coefficient was carried out. An unprecedented lockdown of global transportation was caused by the novel coronavirus (SARS-CoV-2) outbreak, which was mediated by the COVID-19 disease pandemic. This led to a rapid reduction in industrial and urban development with potential impacts on environmental pollution. Although lockdown can never be the remedial resolution to diminish environmental pollution. However, studying the impact of lockdowns on pollution levels in aquatic ecosystems can help to propose new management strategies, and redesign and readjust policies, for control of water pollution in future pollution control schemes. Thus, we strategically studied the chromium and cadmium contamination during pre- and post-lockdown SARS-CoV-2 phases.

2. Material and methods

2.1. Studied area

Mathura, the latitude and longitude lines of 27°41′North and 77°41′East (Fig. 1). This holy city is well known for its religious and historical significance and is Uttar Pradesh's fastest-growing and one of the most polluted industrialized regions [23]. For the present research effluent samples were taken from ten different industrial sites from the Mathura region which are categorized under the following industrial groups: refinery, polish plant, textile, chemical, and manufacturing industries. Many large and small-scale industries were categorized under these groups. Industrial sites namely refinery, chrome polish plant, metal factory, ATV company, Anuradha textiles, CP plant, Ni polish plant, silver polish, tap factory, and Laxmi chemicals are all essential industries that financially support many human workers. Contradictory these are also responsible for polluting the environment using their industrial discharges with their moieties and pollutants. The study was carried out in the industrial area of Mathura city, India during pre- and post-lockdown SARS-CoV-2 periods (February 2020 to October 2020). The industrial area is spread over 330.02 hectares of land comprising many extensive and medium-scale industries like oil refineries, polish plants, chemical units, pharmaceutical units, textile industries, ATV companies, etc as shown in Fig. 1. Discharged water from industries like these is continuously inclined off into aquatic ecosystems and soil. Populations around these areas are at risk of environmental pollution since toxic contaminants from effluents of various industries are regularly drained off into the natural ecosystem.

2.2. Sample collection

Ten industries were selected for determining the impact of COVID-19 pandemic confinement (February and October 2020) on Cr and Cd concentration in industrial effluents (Table 3). Effluent samples were collected aseptically in 5 L sample collecting screw cap bottles from clearing points of instigated industries outlets. Details of ten sampling sites

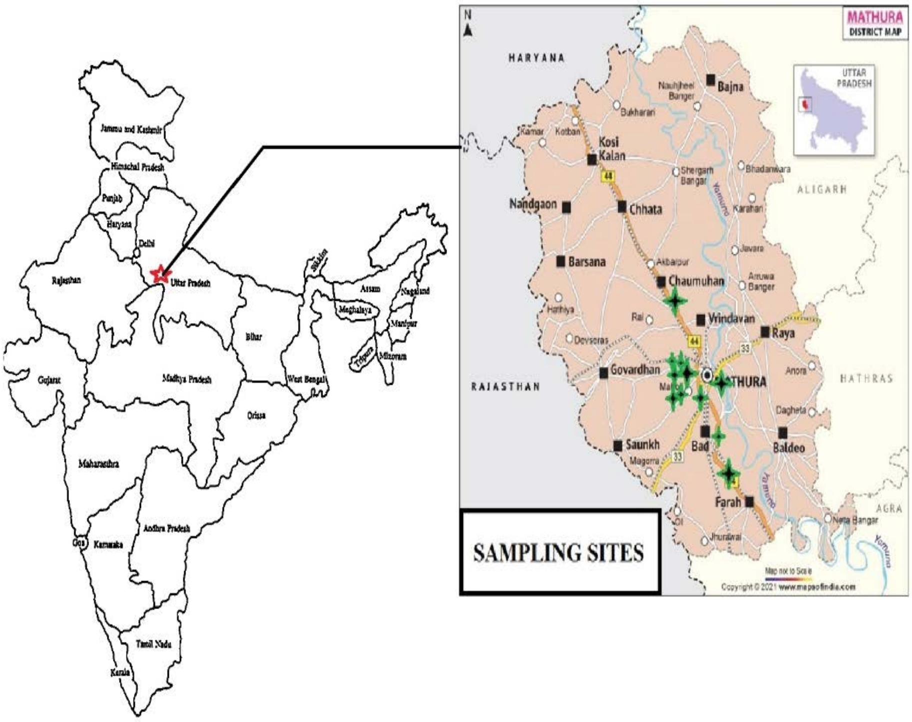

Fig. 1. Study area - Industrial Area, Mathura City, India.

Table 3
Latitude and longitude of the sampling sites

S. No.	Industrial groups	Site	Latitude	Longitude
1	Refinery	Mathura refinery (S1)	27.3772161	77.6860254
2	Polish plant	Cr. polish plant (S2)	27.5012223	77.6459568
		Silver polish (S8)	27.4999	77.6486
		Ni polish plant (S7)	27.4999	77.6437
3	Textile	Anuradha textile (S5)	27.509677	77.6480345
4	Chemical	Laxmi chemicals (S10)	27.4972	77.661
		CP plant (S6)	27.4993306	77.6637382
5	Manufacturing	Tap factory (S9)	27.5233	77.6529
		Metal factory (S3)	27.4989951	77.6634398
		ATV Company (S4)	27.463209	77.664856

(S1–S10) including latitude and longitude are shown in Table 2. All of the collected samples were delivered to the Biotechnology Department of GLA University, Mathura (U.P.) for further investigation.

2.3. Plants

E. aureum and *E. crassipes* were chosen to reduce the levels of cadmium and chromium found in industrial wastewater. The effluent samples were collected in screw-cap bottles with a volume of 50 L each and were obtained in a sterile manner from the clearance points of the initial industry outlets. Additionally, aseptically harvested plant samples were made from several water bodies in the Mathura region. The harvested plant samples were brought to the Department of Biotechnology at GLA University for further analysis.

2.4. Physicochemical analysis

The several physicochemical parameters of industrial effluents, such as pH, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), and total dissolved solids (TDS), were measured by the Standard Methods of the 23rd edition of the Renowned Water Handbook [24]. *In-situ* pH measurements of the samples were taken with portable pH meters (Systronics Digital pH Meter 335). The COD and BOD of the collected effluents were executed as per the standard protocols described by Rume and Islam [25]. While TSS and TDS values were determined by the protocols mentioned by Butler and Ford [26].

2.5. Experimental setup

The methodology implemented in the current study comprises a phytoremediation setup at the Department of Biotechnology, GLA University, itself. Both the selected plant species (*E. aureum* and *E. crassipes)* each about 20 kg were soaked for 7 d (starting on December 19, 2021) in the tubs filled with chrome polish plant effluent (50 L) in triplicates for their phytoremoval efficacy. The exceptional metabolic, hydrodynamic, and transport mechanisms that enable plants to specifically absorb nutrients and toxins from their physical surroundings make them distinctive beings.

2.6. Sample digestion and AAS analysis

Each sample that was obtained had 1 L of effluent removed separately for processing. 3 mL of 1N HNO_3 was added to each sample, which was then well mixed and filtered through filter paper (Sartorious Whatman filter paper - grade 292). The 100 mL filtered sample was then gently combined with 15 mL of the diacid solution HNO_3/$HClO_4$ (9:4). The conical was allowed to cool to room temperature after the solution had fully evaporated. Lastly, each powdery deposit received 100 mL of triple-distilled water before the AAS examination [27]. Varian Spectra AA55B, Australia - atomic absorption spectrophotometer was used for the determination of metal concentrations in processed samples [24].

2.7. Index for heavy metal pollution

The HPI is a useful tool for determining the overall quality of water based on the levels of various heavy metals present in the water. An HPI grade is a grade that represents the aggregate impact of a number of different heavy metals that have dissolved [28]. A total score of 100 HPI is required to conclude that the water quality is good. HPI can be determined by making use of Eq. (1) which was provided by Mohan et al. [29].

$$\text{HPI} = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{1}$$

where $W_i = K/S_i$ denotes the unit weight of the ith parameter. Q_i calculated as per Eq. (2) shows the sub-index of the ith parameter; K is the proportionality constant, and n is the total number of parameters M_i, S_i, and l_i are the measured levels of heavy metals, the reference levels, and the optimum levels, respectively.

$$Q_i = \sum_{i=1}^{n} \frac{M_i}{S_i} \times 100 \tag{2}$$

where M_i symbolizes the calculated amount of heavy metal. and S_i symbolizes the standard factor of ith in PPM (µg/L).

2.8. Index of metal quality

The MQI was intended with the help of standard Eq. (3). Where M_i is the amount of heavy metals discovered S_i denotes the standard ith parameter in PPM (µg/L). The vilest sample quality can be seen when a metal concentration is amplified and exceeds its permitted limit. MQI > 1 is a verge of cautionary [30].

$$\text{MQI} = \sum_{i=1}^{n} \frac{M_i}{S_i} \tag{3}$$

2.9. Modeling and analytical statistics

The overall results from the aforementioned equations were statistically analyzed by using the R software tool to determine the standard deviation, average, vivid t-statistics, and degree of significance for Pearson's correlation coefficient p 0.05. A paired students' sample t-test was performed to determine the effect that the lockdown had (both before and after the lockdown periods of COVID-19) on the quality of the industrial effluent [31]. The data were taken three times to ensure accuracy, and the outcome was determined by taking the mean.

2.10. Determination of histological studies for metal accumulation site in plant tissues through TEM

E. crassipes plants under metal stress were poured into tubs with industrial effluent for 7 d. After which they were cut down with their roots still attached, wrapped in moist tissue paper, placed in plastic bags, and tagged appropriately. Thereafter, the infected rootlets were taken to the laboratory of SAIF AIIMS Delhi, for supplementary TEM investigation.

3. Results and discussion

Cadmium, chromium, copper, lead, zinc, and other heavy metals and toxicants released in industrial effluents eventually make their way into aquatic water bodies like lakes, rivers, and ponds. Nowadays rapid industrialization and urbanization have become the prominent key to economic development but on the other hand, it has also majorly contributed to air, soil, water, and sediment pollution which has drastically affected humans thereby pulling them back to diseases and deaths [32]. Cadmium is a hazardous toxic metal that is lethal to living organisms and non-essential biological metals and causes diseases like associated anti-social behavior, and conduct disorder [8]. Chromium, a highly toxic metal pollutant, enters the human body through the gastrointestinal tract, skin, and lungs and causes deadly diseases like cancer, hypersensitivity, coronary heart disease, anxiety, depression, etc. [33]. Therefore, routine monitoring for the presence of these toxicants in industrial effluents is need of the time for a sustainable future. The present investigation aims to impact the assessment of COVID-19 pandemic confinement (February and October 2020) on Cr and Cd concentrations in ten industrial effluent samples at Mathura of Brij region, India, and explore the biosorption potential of *E. aureum* and *E. crassipes* for Cr and Cd removal.

3.1. Physico-chemical analysis

The evaluated results of the physicochemical parameters of ten sites during the impact assessment of the confined pandemic (February 2020 and October 2020) are presented in Table 4. In the present study, a slight acidic shift was observed in the pH values of effluent samples during the pre- and post-lockdown period, that is, 4.0–10.9 and 3.65–10.65, respectively as shown in Table 4. Similar results were revealed by Karunanidhi et al. [34] during the study conducted on groundwater pollution in a commercial area of southern India with humanoid vigor hazards impact of COVID-19 confinement. Besides, Bogler et al. [35] also reported the associated risks of wastewater and the impact of the COVID-19 pandemic. The pH of industrial effluents was not statistically different ($p > 0.05$) and was found above permissible limits for most of the effluent (5.5–9.5) as per Environment Protection Rules, 1986 (2021). The nickel polish plant (S7) and chromium polish plant (S2) effluents had the lowest and highest pH values during the pre- to post-lockdown period, respectively. Hence this alkaline effluent wastewater proves to be toxic and unsafe for humans as it draws them to many obnoxious and lethal diseases and ultimately after entering through the food chain disrupts the whole human cycle and leads to many complications which seems to be unsafe for the attainment of sustainable development.

Biological and chemical oxygen demand (COD and BOD) often reflect the magnitude of organic pollution in water and wastewater [36]. The COD and BOD readings of effluent samples gradually decreased for all of the selected sites during the pre- and post-lockup periods of COVID-19. As is revealed from Table 4 the lowest and highest values for all of the sites studied were in the range from 260.6 to 235,892.6 mg/L and 257.05 to 230,383.6 mg/L for COD while 15.60 to 43,122.85 mg/L and 15.25 to 42,619.7 mg/L for BOD, respectively. Similar results were disclosed by Bharathiraja and Ramanujan [13] in an Indian multi-state investigation for assessment of COVID-19 lockdown's effects on industrial effluent physicochemical parameters revealed a decrease in BOD, COD, and total coliform levels with an increase in average DO levels. Yazdian and Jamshidi [33] evaluated the performance of wastewater treatment plants in the face of the sewage variations imposed by COVID-19 spread prevention measures. They revealed that there was a gradual reduction in the values of COD and BOD, respectively. Rume and Islam [25] mentioned in their literature about the environmental characteristics of the COVID-19 epidemic and projected strategies of sustainable development that there was a modest drop in the values of COD and BOD. According to Yashvardhini et al. [18], BOD and COD have decreased dramatically over the course of a month during to lockdown while the samples from Delhi have also emphasized the favourable effects of COVID-19 on the environment.

In the present study, COD and BOD values for most of the effluents were found above standard values as per Environment Protection Rules (1986), that is, 250 and 100 mg/L. The tap factory (S9) and refinery (S1) effluents had the lowest and highest COD values during the pre-lockdown era, respectively, whereas the tap factory (S9) and ATV company (S4) had the lowest and highest values during the post-lockdown time. As indicated in Table 4, the effluents from the metal factory (S3) and refinery (S1) had the lowest and highest BOD values for the time before and after the shutdown.

Aquatic ecosystems get hampered badly by altered properties (COD and BOD) and develop a low dissolved oxygen environment due to which aquatic organisms are prone to suffocate and conditions become stressed, ultimately disrupting the whole aquatic life. Hence monitoring of such vital parameters becomes an important initiative for an individual to build effective wastewater treatment plants and come up with innovative strategies for sustainability [37].

Both TSS and TDS measure the quantity of particulate matter fluctuating in water. A few instances of withdrawal-related occurrences that could result in the formation of TSS and TDS include crushing, storage of materials, sorting, mine site preparation, and washing of materials that may be showing to precipitation [26]. As displayed in Table 4, the effluent sample's TSS values steadily decreased for all of the selected locations during pandemic confinement. The lowest and highest range in terms of TSS for all of the studied sites were from 175.5 to 3,735.0 mg/L (during

Table 4
Heavy metal physico-chemical properties (mg/L) pre- and post-lockdown SARS-CoV-2

	Physico-chemical properties									
Site	Pre-lockdown Feb-20					Post-lockdown Oct-20				
	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	TDS (ppm)	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	TDS (ppm)
S1	6.8	235,892.6	43,122.85	226.5	18,716.5	6.8	220,882.18	42,619.7	225.5	18,147.5
S2	10.9	11,674.5	7,250.0	222.5	8,872.0	10.65	9,848.00	6,717.5	220.95	7,710.0
S3	7.4	625.00	15.60	175.5	3,806.0	7.0	522.00	15.25	174.0	3,300.0
S4	7.25	235,385.17	42,752.45	3,735.0	149.5	7.2	230,383.6	41,726.35	3,684.0	82.0
S5	7.6	2,185.00	736.75	225.95	8,890.5	7.35	2,082.5	636.1	220.4	8,289.0
S6	7.8	261.35	41.00	231.8	3,545.5	7.35	257.3	39.45	224.6	2,435.5
S7	4.0	875.45	26.90	626.0	3,805.0	3.65	818.45	25.25	427.0	3,699.5
S8	8.1	836.00	568.15	1,235.0	3,329.5	7.95	784.00	551.8	1,180.0	2,765.0
S9	8.0	260.6	40.9	227.5	1,199.55	7.6	257.05	38.5	217.0	693.0
S10	5.8	939.3	7,662.65	461.0	525.5	5.7	882.7	4,024.05	405.0	465.0

pre-lockdown) and from 174 to 3,684.0 mg/L (during post-lockdown). Similarly, TDS values ranged from 149.5 to 18,716.5 ppm and from 82 to 18,147.5 ppm from lowest to highest during pre- to post-lockdown periods, respectively. Das et al. [38] reported similar patterns in TSS and TDS values during a study on COVID-19 lockdown on surface water quality. Besides they also found that during the lockdown period, there was a significant increase in the normalized difference turbidity index (NDTI), while the values of total suspended matter (TSM) decreased, as did the values of normalized difference water index (NDWI), normalized difference vegetation index (NDVI), nitrogen content index (NI), and normalized difference chlorophyll index (NDCI). In another study, Mohamed et al. [39] also demonstrate a significant reduction in TSS, TDS, and heavy metal concentrations among industrial effluents in the Mahanadi industrial belt of India during COVID-19 confinement. Various studies illustrated, that environmental reviews were lax in India and many other nations when it came to maintaining clean habitats close to industrial areas. The significant reductions in water, air, and noise pollution seen in several places are almost certainly attributable to the lockdowns brought on by COVID-19 and the combustion of industrial fossil fuels [40–42]. In the present research work, TSS and TDS values for most of the effluents were found above standard values as per Environmental Protection Rules (1986), that is, 100 and 2,100 mg/L. TSS values for effluents from the Metal Factory (S3) and ATV Company (S4) were lowest and highest during the pre- and post-lockdown periods, respectively. ATV Company (S4) and refinery (S1) effluents were found to have the lowest and highest TDS values for the pre- and post-confinement periods (Table 4). Therefore, to have ever ever-lasting cherished nature, adjustment of such severe and innovative plans will lead to a pollution-free environment and only then we can attain a sustainable balance in nature [43].

3.2. Heavy metal analysis

Since the industrial revolution, anthropogenic activities have been gradually changing the environment's natural biogeochemical cycles [3]. The occurrence of toxic heavy metals such as Pb, Hg, Cd, Sn, Cr, Zn, U, Th, and Cu, in industrial wastewater is unanimously contemplated as a big cover. These multiple toxicants exist in environmental media and are widely dispersed in areas surrounding sites of rigorous industrial and agricultural actions. These pollutants have toxic effects on the biological atmosphere and human health and display multifaceted behavior that differs from the existing condition [14]. Industrial discharges contain higher concentrations of toxic components including heavy metals, organic pollutants, pesticides, PCBs, phenolic components, petrochemicals, etc. which may lead to deadly and lethal diseases in humans [10].

There is chromium present in both the crust of the earth and in saltwater (Cr). In manufacturing processes, it can be found in its naturally occurring heavy metal state. Chromium can infiltrate natural streams through a variety of different processes, including the weathering of rocks that contain Cr, direct industrial discharge, and soil leaching. Cr may undergo reduction, oxidation, sorption, desorption, dissolution, and precipitation in an aqueous environment [7]. Even though cadmium (Cd) is a toxic, non-essential transition metal that endangers the health of both people and animals, it is widely used in industrial processes. It is a pollutant that occurs naturally in the environment and has its origins in both industrial and agricultural processes and products. Cadmium being a hazardous toxic metal turns out to be silver, white, malleable, and ductile metal. It is lethal to living organisms and is a non-essential biological metal that may cause diseases like associated antisocial behavior, conduct disorder etc [8]. Silver Polish Plant (S8) > Tap Factory, Anuradha Textile, ATV Company (S9, S5, S4) > CP Plant (S6) > Nickel Polish Plant (S7) > Metal Factory (S3) > Chromium Polish Plant (S2) > Refinery (S1) > Laxmi Chemicals (S10) pattern for Cr and Silver Polish (S8) > Tap Factory (S9) > CP Plant (S6) > Nickel Polish Plant, Refinery, Metal Factory, ATV Company (S7, S1, S3, S4) > Laxmi Chemicals (S10) > Anuradha Textiles (S5) > Chromium Polish Plant (S2) pattern for Cd, respectively, were the percentage reduction in effluent samples during the pre- and post-lockdown periods. During the pre- and post-confinement period, effluents from Laxmi Chemicals (S10) and Silver Polish Plant (S8) had the lowest and highest reduction percentage of chromium, whereas Chromium Polish Plant (S2) and Silver Polish Plant (S8) had the lowest and highest reduction percentage of cadmium concentrations (Table 5). Similar trends were revealed by Chanchpara et al. [44], in their work with bioaccumulation of heavy metals in ambient air and coastal water. The metal concentration in the samples of coastal sediments revealed a substantial reduction during the pandemic. Besides, research conducted by Rao et al. [45] during COVID-19 confinement reported the daily geochemical record of the Ganga River and observed a significant reduction (50%) of heavy metal concentrations in industrial discharge. According to Ahmed et al. [23], a case study in the Mathura district revealed that there is deterioration in the groundwater quality, due to excess withdrawals without sustainable planning makes drinking water unsafe for drinking and other household purposes. According to research that was conducted by the International Agency for Research on Cancer (IARC) in 2018, hexavalent chromium was designated as a carcinogen that falls under category I for occupational exposure [46].

The Cr and Cd standard values (Cr - 0.05 and Cd - 0.03) of industrial effluent samples were found over acceptable limits for most of the cases as per Common Effluent Treatment Facilities (Environment Protection Regulations, 1986) as indicated in Table 5. It is also evident from the results obtained that Chromium Polish Plant (S2) proves to be the most polluting industry for chromium during pre- and post-confinement periods with the concentrations of (49.89 ± 0.20 mg/L) and (14.46 ± 0.73 mg/L), respectively. While in the case of the cadmium Tap Factory (S9) showed the highest results (0.11 ± 0.009 mg/L) for pre-lockdown and the CP plant (S6) was found to be the most polluting industry (0.01 ± 0.003 mg/L) for post confinement period. Chromium Polish Plant (S2) and CP Plant (S6) proved to be the most polluting industry for chromium and cadmium toxicity during the post-confinement period and were chosen off-site for further studies. But cadmium concentration in the CP Plant was found to be under permissible limits therefore effluent from the chrome polish plant was selected for further phytoremediation studies. Hence it becomes very important for mankind to monitor the bad consequences and toxicity of such heavy metals to attain sustainability in the environment.

3.3. Student's t-test analysis

The descriptive t-statistics and the investigation of Pearson's correlation coefficient were utilized to analyze the studied data. A statistical test using students' paired sample *t*-tests was conducted to see how the lockdown influenced the quality of the industrial effluent. The null hypothesis, also known as H_0, and the alternate hypothesis, usually known as H_1:

H_0: Lockdown has no impact on the water quality of industrial effluents, as there was no appreciable difference in water quality before and throughout the lockdown period.

$$H_0 : \mu_1 = \mu_2 \tag{4}$$

H_1: The water quality of industrial effluents differed significantly before and after the lockdown phase, indicating that the lockdown had a significant positive impact.

$$H_1 : \mu_1 > \mu_2 \tag{5}$$

This right-tailed paired *t*-test was performed. The null hypothesis (H_0) will be rejected in the situation where the calculated *t*-value (t) exceeds the tabulated or critical value at a predefined level of significance (α = 0.05). On the other hand, if the calculated *t*-value is lower than the tabulated *t*-value, the null hypothesis is assumed to be true [45]. The formula given below is used to calculate the *t*-value for a paired sample.

$$t = \frac{\sum d}{\sqrt{\frac{n\left(\sum d^2\right)-\left(\sum d\right)^2}{n-1}}} \tag{6}$$

where n is the number of samples and d is the difference between each matched value. *R* software was used to conduct all statistical analyses, which are presented in Table 6.

The above Table 6 shows that the null hypothesis is significantly rejected for both the heavy metal concentrations. This suggests that the lockdown has an effect that is statistically significant on the water quality of the locations that

Table 5
Heavy metal concentrations (mg/L) pre- and post-lockdown SARS-CoV-2

Site	Cr (mg/L)			Cd (mg/L)		
	20-Feb	20-Oct	% Reduction	20-Feb	20-Oct	% Reduction
S1	1.40 ± 0.10	0.43 ± 0.07	69.28	0.01 ± 0.003	0.002 ± 0.001	80.00
S2	49.89 ± 0.20	14.46 ± 0.73	71.02	0.01 ± 0.004	0.004 ± 0.002	60.00
S3	1.30 ± 0.002	0.36 ± 0.06	72.30	0.005 ± 0.003	0.001 ± 0.00	80.00
S4	0.09 ± 0.005	0.02 ± 0.02	77.77	0.005 ± 0.002	0.001 ± 0.00	80.00
S5	0.54 ± 0.03	0.12 ± 0.04	77.77	0.003 ± 0.002	0.001 ± 0.00	66.66
S6	3.95 ± 0.04	1.08 ± 0.03	72.65	0.057 ± 0.01	0.01 ± 0.003	82.45
S7	1.71 ± 0.01	0.47 ± 0.05	72.51	0.01 ± 0.00	0.002 ± 0.001	80.00
S8	0.10 ± 0.005	0.02 ± 0.05	80.00	0.05 ± 0.008	0.001 ± 0.00	98.00
S9	0.63 ± 0.04	0.14 ± 0.06	77.77	0.11 ± 0.009	0.003 ± 0.002	97.27
S10	32.41 ± 0.47	12.18 ± 0.50	62.41	0.01 ± 0.003	0.003 ± 0.001	70.00
Permissible limit	0.05			0.03		

Table 6
t-values for chromium and cadmium concentration of the studied sites

	Chromium		Cadmium	
	20-Feb	20-Oct	20-Feb	20-Oct
Mean	1.215792	0.331542	0.028833	0.002933
Variance	1.581799	0.123025	0.0013	0.000011
Observations	8	8	10	10
Pearson correlation	0.997615		0.320422	
Hypothesized mean difference	0		0	
Degree of freedom	7		9	
t-stat	2.754124		2.331488	
P(*T* <= *t*) one-tail	0.014167		0.022319	
t-critical one-tail	1.894574		1.833112	

were studied. In other words, it has led to a considerable improvement in the water quality at every location that was examined. The level of Cr and Cd concentration has fallen to an excessive amount, which has led to an improvement in the water quality (*p*-value less than 0.05) [30]. Heavy metals are toxic to biological systems because they produce reactive oxygen species (ROS) and interact negatively with sulfhydryl groups of proteins. In addition to oxidative stress and glutathione depletion, this results in the inactivation of important macromolecules. Following hazardous metal exposure and entry into the body, several events occur, including the interaction or inhibition of some metabolic pathways.

Another investigation conducted in India in 2021 found that those who were exposed to groundwater contaminated with Cr(VI) had an elevated incidence of gastrointestinal and dermatological issues [47]. One of the known mechanisms that contributes to the toxicity and carcinogenicity of Cr is the formation of reactive oxygen species (ROS). Other mechanisms include genomic instability and DNA damage. Both the (VI) and (III) oxidation states of chromium are capable of producing reactive oxygen species (ROS). The creation of the crosslinks Cr-Asc (ascorbate), Cr-GSH, and Cr-Cys leads to the depletion of cellular antioxidants and the induction of oxidative stress (cysteine). During the COVID-19-induced lockout times, it was found that, as a result of reduced pollution load, the base of the majority of the discharge canals (red arrow) were identifiable with crystal blue water, as stated by [48,49]. Additionally, as a result of the cessation of industrial effluent discharge during lockdown periods, canals shrunk and dried up (indicated by the red arrows). This was followed by the appearance of clear, visible water in the catchment region that was the subject of the study, which demonstrated an improvement in the quality of the water [50].

Khan et al. [51] analyzed the water quality depletion that is reported in several prior literatures, stressing the uniqueness of its water quality indicator (WQI). Also, the problem of domestic sewage discharge from numerous drains without sufficient treatment or with poor treatment, industrial effluent discharge from several drains, and the consumption of river water for drinking and other home uses were all issues that were discussed and resolved [51–53]. Ultimately, the distribution of chromium and cadmium concentration between pre- and post-lockdown are displayed through boxplots. This can be easily seen that, in the case of chromium concentration values, two sites (S1 and S10) have shown exceptionally higher values or this observation is beyond the upper or lower whisker (outlier), in pre- and post-lockdown while only one outlier is present in Cadmium concentration in post-lockdown. Therefore, these two values are discarded for calculating the *t*-value. Moreover, the medium values and the spread of values are shifted towards the left side (negatively skewed about the center) for chromium and cadmium concentration in both cases, that is, pre- and post-lockdown as is clearly shown in Fig. 2a and b.

3.4. Metal Quality Index and the Heavy Metal Pollution Index

The effects of various heavy metals on the caliber of industrial effluent were determined using HPI. Using the provided equation, the HPI was determined [29].

$$\text{HPI} = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{7}$$

where $W_i = K/S_i$ denotes unit weight of the *i*th parameter. $Q_i = \sum_{i=1}^{n} \frac{M_i - I_i}{S_i - I_i} \times 100$ shows sub-index of the *i*th parameter; n is the number of parameters overall; K the proportionality is constant; M_i, S_i and l_i are, in turn, the ideal, standard, and measured values of the parameter for heavy metals. The HPI values were determined using mean sample levels from all the studied locations. The mean HPI for Cr was initiated to be very high, that is, 166,545.27 and 53,797.13 for pre- and post-lockdown, respectively, showing increased contamination with chromium in the studied sites. Similarly, in the case

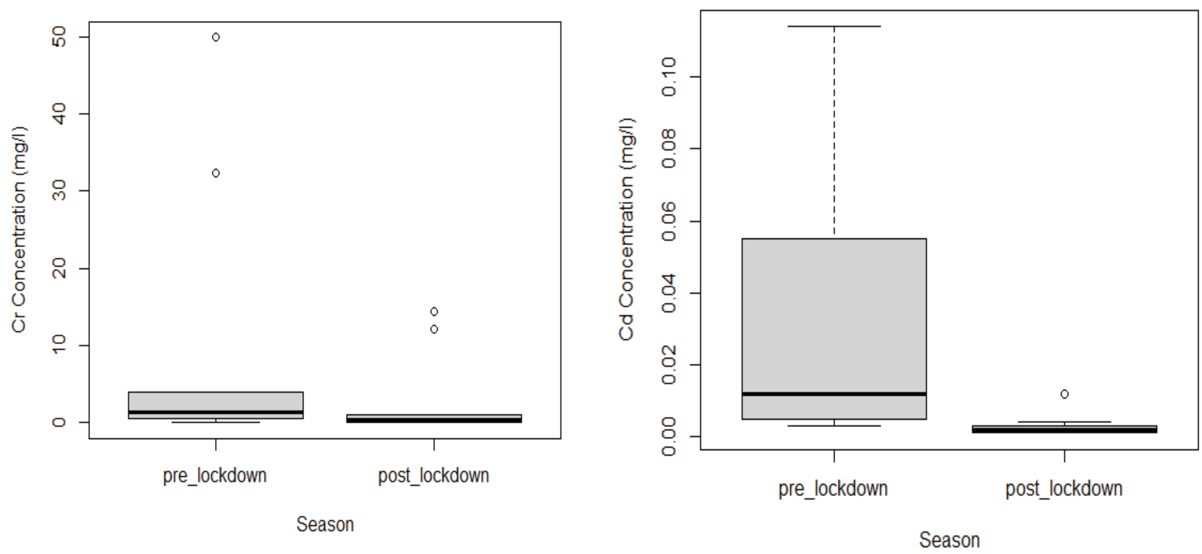

Fig. 2. (a) Boxplot showing the central value and (b) spread of the distribution.

of Cd, the mean HPI value was found to be 96.11 and 9.78 for pre- and post-lockdown, respectively as shown in Table 7.

The index of metal quality, also known as the MQI, was computed to analyze the total chromium poisoning in the industrial water. For both the pre- and post-lockdown periods, the chromium contamination risk was extremely high at every place along the stretch that was investigated. The HPI values and metal concentrations have been reviewed in several different literature, and the results reveal a large reduction, which is consistent with our findings. As, Cd, Cr, Fe, Mn, and Pb concentrations all clearly show a substantial reduction, highlighting the impact of the closure of agricultural, industrial, and commercial activities, according to an assessment of the effects of the COVID-19 lockdown on the heavy metal concentration and pollution analysis in the River Gomti in Lucknow city, India [51]. The study was conducted to determine how the lockdown affected the heavy metal concentration and pollution analysis in the River Gomti. The HPI readings at every location have decreased, and the overall quality of the environment at every site that was investigated has significantly enhanced. Studies conducted by Rahman et al. [3], as well as other researchers, came to the same conclusion (2020). Even though Cr is an essential nutrient for humans and is required for the metabolism of sugar and fat, exposure to high levels of Cr by inhalation, ingestion, or skin contact may create negative consequences on one's health. This was discovered in the research titled "Heavy metal pollution assessment in the groundwater of the Meghna Ghat industrial area, Bangladesh by using water pollution indices approach", which was conducted in Bangladesh. Cd, in contrast to Cr, is not a required element for agricultural plants; yet, these plants can rapidly absorb it from contaminated or supplemented soils, which allows it to enter the food chain and negatively impact the health of both humans and plants. According to Das et al. [38], the discharge of heavy metals from a variety of enterprises (including those that produce fertilizer, pigments, paper, and so on) located along the Halda River could be to blame for the high levels of pollution index values. It ought to be made abundantly clear that copper and arsenic were probably responsible for some portion of the high pollution index value that was caused by all of the heavy metals. The water was found to be contaminated with a variety of dangerous heavy metals, six of which (Cd, Cr, Fe, Pb, Cu, and As) were found to be significantly beyond the safe limit (for drinking water) established by the World Health Organization (WHO). It is believed that the direct discharge of effluents from local businesses is the primary contributor to the presence of heavy metals in the water of the Halda River. It was previously reported by Jayaweera et al. [40] for the Mathura and Agra regions, respectively, that the metal pollution index was high

Table 7
HPI and MQI of Cr and Cd at the studied sites

Sample	Cr		Cd	
	HPI	MQI	HPI	MQI
Pre-lockdown	166,545.27	1,665.45	96.11	0.96
Post-lockdown	53,797.13	537.97	9.78	0.10

when the MQI was greater than one. Bashir et al. [54] evaluated the MQI values for the assessment of total Cr pollution in the Yamuna environment and reported that the MQI > 1 is significant. This indicates a high metal pollution index. In developed nations, this issue is being sorted and solved to some extent by using "green remediation processes" involving metal-tolerant plants to wipe out and clean up contaminated sites. Nowadays rapid industrialization and urbanization have become the prominent key to economic development but on the other hand, it has also majorly contributed to air, soil, water, and sediment pollution which has drastically affected humans thereby pulling them back to diseases and deaths [32]. Mining and industrial processing used to extract mineral resources, followed by their use for agricultural, industrial, and economic development, has increased the amount of these elements mobilized in the environment and disrupted their biogeochemical cycles [55].

3.5. Biosorption efficacy

Ever since the industrial revolution, anthropogenic activities have been gradually changing the environment's natural biogeochemical cycles [7]. The presence of hazardous heavy metals like Hg, Pb, Zn, Cd, Sn, Cr, U, Th, and Cu, etc in industrial effluent is universally regarded as a major concern. Strohmeyer discovered cadmium in 1817, it is a malleable, polished silver-white metal [10]. This biological metal is toxic to both plants and animals. Environmental cadmium emissions are produced by nickel-cadmium batteries, electroplating, plastic stabilizers, and phosphate fertilizers [15]. The second most frequent metal to enter the pastoral ecosystem as a result of the introduction of wastes containing Cr is chromium, a hazardous heavy metal pollutant [10,56]. The current study aims to determine the phytoremoval effectiveness of *E. crassipes* and *E. aureum* on Cr and Cd concentrations in chrome polish plant effluent in the Brij region, India, for 7 d (starting on December 19, 2021). The experimental setup was done in triplicates and the average was calculated for the percent removal or the remediation process (Fig. 3). *E. crassipes* showed reductions in chromium and cadmium of 67.66% and 61.22%, respectively. *E. aureum* had a removal efficiency of 38.90% for cadmium and a removal efficiency of 44.26% for chromium. Irrespective of the plants the biosorption for Cr was greater and *E. crassipes* performed better in comparison to *E. aureum*. This is because of the characteristic fibrous and taproot system with long roots with thick root hairs which provides the advantage of increased biosorption of heavy metals from contaminated water systems. Similar findings were made by Chauhan and Singh [41], they disclosed that *E. crassipes* not only accumulates a wide range of toxic heavy metals (Cd, Zn, Cu, Pb, Cr, etc.) but also increases their translocation and uptake mechanisms in the more intoxicated sites, demonstrating that it has a high capability for removing toxic heavy metals from polluted water.

Hemalatha et al. [20] assessed the phytoremediation potential of dried *E. crassipes* biomass (roots, leaves, and petioles) for Zn and Cr heavy metallic ions from electroplating industry polluted water and their results revealed dried WH biomass Cr removal (96.4 percent) was found to be an effective and reasonably priced adsorbent. Furthermore, Bogler et al. [35] assessed the *E. crassipes*' phytoremedial characteristics, including its high growth rate, low maintenance costs, and renewability make it a practical substance for phytoremediation in the treatment of hazardous waterways, including domestic and commercial effluents.

Numerous publications have stated that a study has already been done to observe *E. aureum*, which was chosen because of its bioavailability and because environmentalists have an increasing interest in using it to seize harmful substances like chromium and lead [14]. According to Qing et al. [21], *E. aureum* proves to be a profitable hyperaccumulator plant to be planted in contaminated water or industrial waste. As a result, *E. aureum* falls within the category of pollution resistance plant. The phytoremedial capacity of four plant species, *E. aureum*, *C. alternifolius*, *C. indica*, and *C. rotundus*, was examined by Kinuthia [57] for the elimination of heavy metal fluoride up to 95%, 52%, 65%, and 56%, respectively from media at the strength of 10 ppm within 10 d. Our findings indicate that both *E. aureum* and *E. crassipes* are fast-growing, free-floating aquatic weeds that can be excellent biosorbents for the exclusion of Cr and Cd heavy metals. Further, these test plants can be used for the biomonitoring of pollution in river bodies.

3.6. TEM analysis of E. crassipes root tissue

E. crassipes was chosen for histological studies since it was found to be the most effective marine macrophyte for phytoremoval effectiveness. It was also determined to be the most effective marine macrophyte based on the effectiveness of both plants evaluated in terms of removing metal toxicants from the environment. Therefore, *E. crassipes* root samples were chosen for histological research using transmission electron microscopy. The metal toxicity in the root tissues of *E. crassipes* was investigated using TEM analysis. The consequences of stress brought on by heavy metals in plants are well-known to include morphological and structural changes at the cortical level. The most notable ultrastructural changes observed in the epidermal cells from the adaxial foliar tissue utilizing the plants analyzed were shown by TEM analysis to be the absence of epicuticular waxes and reduction in cortical layer cells from the media. In the root tissue, mucilage, microbes, and clay particles were also seen beneath the root epidermal cell boundaries (Fig. 4). Similar results were shown by our results and were revealed by many researchers. Chauhan and Singh [41] reported similar findings, revealing that *E. crassipes* not only accumulates a

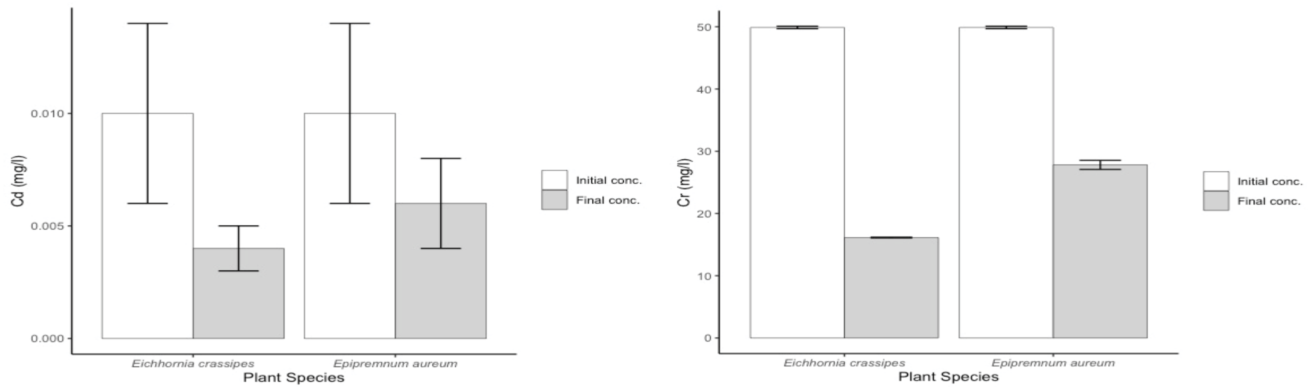

Fig. 3. Percent reduction of Cd (a) and Cr (b) for *Eichhornia crassipes* and *Epipremnum aureum*.

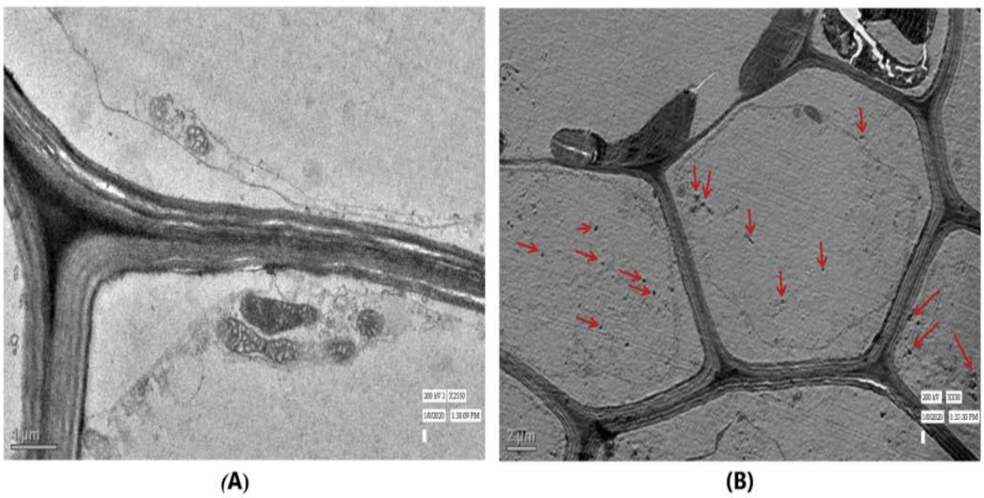

Fig. 4. Metal accumulation in ultrastructure of root of *Eichhornia crassipes* (A) 1 μm and (B) 2 μm.

wide range of toxic heavy metals (Cd, Zn, Cu, Pb, Cr, etc.) but also increases their translocation and uptake mechanisms in the more intoxicated sites, demonstrating that it has a high capability for removing toxic heavy metals from polluted water. Besides they also concluded that roots accumulated more metal than shoots and leaves. Additionally, Hayyat et al. [58] reported that the elimination of both Cr and Li was greatly aided by the roots, leaves, and shoots of *E. crassipes* as was depicted through TEM. Hemalatha et al. [20] evaluated the phytoremediation potential of dried *E. crassipes* and reported that metal accumulated more in roots than in leaves and stems. In addition to this, they also revealed that heavy metallic ions from electroplating industry polluted water showed dried weight biomass Cr removal (96.4%) was found to be an efficient and cost-effective adsorbent.

Because of its extremely adaptable and fibrous root structure, *E. crassipes* may have a higher biosorption potential for metal accumulation [58]. The rhizomes and pendant roots that are not attached to the substrate are often dark purple in color and made up of roughly 70 lateral roots, giving them a feathery look. *E. crassipes* can exploit nutrients in a low-nutrient water body because each lateral root has a root tip, which causes the lateral roots to grow longer and denser at low phosphorus concentrations [20,41].

4. Conclusion

Heavy metals are well-known to be harmful to the environment for a variety of reasons, including their toxicity, extended half-lives in the environment, and capacity for bioaccumulation. An effective and workable "natural" cleanup method for industrial wastewater may be phytoremediation. To extract or eliminate inert metals and metal pollutants from contaminated locations, a technological solution is already available that is both efficient and economical. The present study indicated that during pre- to post-lockdown times there were low levels of heavy metals in the study area in all of the studied parameters be it physicochemical, environmental modeling, or metal analysis. In addition to this modeling analysis also indicated significant chromium contamination in the examined sites, the mean HPI and MQI values for Cr and Cd were found to be quite high and starkly decreased from pre- to post-confinement. Student's *t*-test analysis markedly improved the water quality at all of the investigated sites. Stringent measures such as lockdowns imposed to contain COVID-19 cannot be a one-shot solution for controlling heavy metal pollution of river bodies.

Additionally, biosorption potential revealed that regardless of the plants, there was a larger biosorption of chromium and cadmium, and *E. crassipes* outperformed *E. aureum. E. crassipes* root tissue (TEM analysis) showed the absence of epicuticular waxes, and reduction in cortical layer cells from the medium were the most significant ultrastructural changes seen in the epidermal cells from the adaxial foliar tissue using plants sampled. Roots revealed lower cellular turgor and a reduction in the root hair numbers in the plants. However, evidence gathered from this study can help in planning and policy recommendations for environmental monitoring and control of unprecedented pollution situations through periodical shutdown of industries that could be considered in future schemes. Moreover, information enables the conclusion that money plants and water hyacinths are suitable plants for the removal of chromium and cadmium from industrial effluents. The scientific field of biosorption and bioaccumulation's prospects are also summarized in this study, with an emphasis on its fundamental principles, prospective environmental advantages, and real-world applications.

Conflict of interest

The study's authors affirm that there were no financial or commercial ties that might be viewed as having a potential conflict of interest.

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