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Removal of chromium and nickel from aqueous solution in constructed wetland: Mass balance, adsorption–desorption and FTIR study

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ABSTRACT

The present study was conducted to investigate the chromium and nickel removal from aqueous solutions in constructed wetland microcosms using *Canna indica* Lin. species. Effects of different hydraulic retention times (HRTs), initial metal concentrations and depth of gravel beds on removal of chromium and nickel were studied. Maximum removal of chromium and nickel was found to be 98.3(±0.32) and 96.2(±1.52) %, respectively, at initial concentrations of 10 mg l^{-1} and at an HRT of 48 h in 0.95 m gravel bed depth constructed wetland microcosms. The attempt was made to know the possible mechanism of metals removal and their mobility within the plant. In order to reuse the exhausted gravel, desorption possibilities were tested. Desorption of 35, 25 and 33% of chromium and 60, 98 and 100% of nickel from gravel were achieved with 0.50 mM EDTA, 0.1 M HNO_3 and 0.1 M $CaCl_2$ solutions, respectively.

1. Introduction

Heavy metals are potentially hazardous to public health. They may damage nerves, liver, bones, block functional groups of vital enzymes and are possible human carcinogens (group 2B) [1,2]. Various industrial processes result in the production of metal bearing waste streams. The removal of toxic heavy metals from industrial wastewaters using conventional chemical approaches such as adsorption, oxidation and reduction and chemical precipitation, among others, proves to be costly. These processes require large quantities of reagents and result in the production of considerable amounts of toxic sludge and secondary pollutants, thus raise questions about the sustainability of these technologies. Operational costs for wastewater treatment processes increase for waste streams with complex characteristics like complex organic matters and relatively low metal concentrations [3].

In recent years, there has been a growing interest in treating wastewaters through constructed wetlands as an alternative to conventional treatment technologies [4,5]. Constructed wetlands are comparatively inexpensive to construct and operate. They utilize solar energy for treatment, produce relatively smaller amounts of sludge, and involve less operational and maintenance costs. They are also more tolerant to varying environmental conditions and pollutant shock loadings [6]. Field applications of these systems have been reported for the management of domestic wastewaters agricultural wastewaters, stormwater and industrial wastewaters, especially industries like mining, pulp and paper and textile [7,8]. However, this technique has not been sufficiently tested for treatment of industrial wastewaters contaminated with a variety of pollutants like heavy metals and organic pollutants in concentrations that fluctuate with time.

The potential of constructed wetlands for the removal of BOD, COD, suspended solids and nutrients from wastewaters is well documented, but less studied with respect to their capacity for the removal of heavy metals and persistent organic substances [9,10]. Mechanism of heavy metal removal in constructed wetlands include sedimentation, filtration, binding to substrata, precipitation as insoluble salts such as sulphides or oxyhydroxides and accumulation by plants, algae, and bacteria [11]. Constructed wetlands have been shown to be sinks for metals [6,12–15].

The main objectives of this work were to explore heavy metal removal potential of *Canna indica* Lin. in vertical flow constructed wetlands. The selected plant species has not yet been tested extensively for use in treatment of wastewaters containing heavy metals. The selection of one anion as chromium and one cation as nickel for this study was based on Indian industrial wastewater scenario, where these ions are found abundantly. The present work studied the effect of different HRTs, initial concentration of selected metals and depth of the gravel beds on removal of chromium and nickel from aqueous solution in constructed wetlands microcosms. It also

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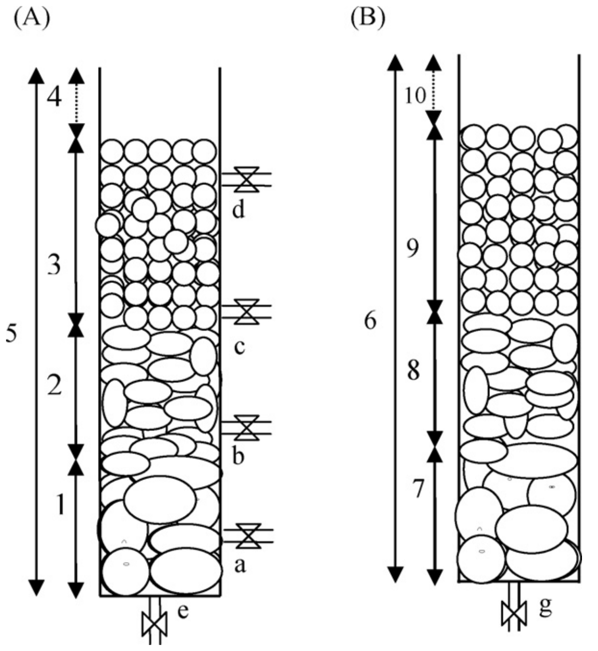

Fig. 1. Schematic of large (A) and small (B) vertical flow constructed wetlands microcosm (not scaled) [(A) 1 = 20 cm with fill up 40–50 mm gravel; 2 = 30 cm fill up with 20–25 mm gravel; 3 = 45 cm fill up with 5–7 mm gravel; 4 = 5 cm vacant space; 5 = 100 cm; a–d = sampling ports; e and g = outlet; empty volume of the reactor = 16.7 l; void volume after filling up gravel = 7.6 l. (B) 6 = 70 cm; 7 = 20 cm fill up 40–50 mm gravel; 8 = 20 cm fill up 20–25 mm gravel; 9 = 25 cm fill up with 5–7 mm garvel; 10 = 5 cm vacant space; empty volume of the reactor = 11.7 l; void volume after filling up gravel = 3.8 l].

studied the accumulation of these metals in gravel, roots, stem and leaves of *C. indica* Lin. in order to know the removal mechanism and mobility of these metals in constructed wetlands. FTIR study of gravel were also done to know the removal mechanism. The adsorption capacities of gravel and desorption of exhausted gravel were also studied for chromium and nickel by using different solutions in order to explore their reuse possibilities. Attempts were also made to study the metal removal mechanism in constructed wetlands.

2. Materials and methods

2.1. Constructed wetlands microcosm

Vertical flow constructed wetlands microcosm were constructed using cylindrical plastic pipes of internal diameter 0.15 m. Length of large bed columns were 1.0 m long and small bed columns were 0.7 m long. These were filled with gravel of three different particle sizes as outlined in Fig. 1. All gravels were washed with tap water before use. The top of the column was open to atmosphere; the bottom was sealed with valved. Four sampling ports were also installed for collecting samples from different depth of the bed. The smaller size gravel (5–7 mm) was mainly used to fill the microcosms; other bigger size gravel was placed in small amount at bottom of the column to avoid the clogging. Type of smaller gravel was sandstone, irregular in shape and uneven surfaced. It has 0.7 $m^2\,g^{-1}$ BET specific surface area, 6.04% porosity and 1.25 $g\,cm^{-1}$ bulk density.

2.2. Solutions

(i) Macro-nutrient solution: 29.7 mg NH_4Cl, 17.75 mg KH_2PO_4 and 1026 mg of $MgSO_4{\cdot}7H_2O$ were dissolved in 1 l tap water. This macro-nutrient solution contains 400 $mg\,l^{-1}$ of $SO_4{}^{2-}$, 12.4 $mg\,l^{-1}$ of $PO_4{}^{3-}$ and 10 $mg\,l^{-1}$ of $NH_4{}^{+}$.

(ii) Trace nutrients solution: trace nutrient solution was prepared by dissolving the chemicals listed in Table 1 in 1 l of tap water.

(iii) Stock solution: $K_2Cr_2O_7$ and $NiSO_4{\cdot}6H_2O$ were used for preparing 1000 $mg\,l^{-1}$ of Cr and Ni, respectively.

(iv) Working solution: working solution of desired concentration of metal was prepared by diluting the appropriate volume of stock solution with macro-nutrient solution for metal removal experiments.

10 ml of the trace nutrient solution was added to 1 l of macro-nutrient solution to prepare a final nutrient solution.

Table 1
Composition of micronutrients solution.

Substance	$mg\,l^{-1}$
EDTA-Na/TitriplexIII	100
$FeSO_4{\cdot}7H_2O$	100
$MnCl_2{\cdot}4H_2O$	100
$CoCl_2 \times 6H_2O$	170
$CaCl_2{\cdot}6H_2O$	100
$ZnCl_2$	100
$CuCl_2{\cdot}5H_2O$	20
H_3BO_3	10
$Na_2MoO_4{\cdot}2H_2O$	10
H_2SeO_3	1
H_2SO_4	3 ml

2.3. Plant species

C. indica L. plant species (also known as Indian shot or Kelli) was selected for this study. Plants were collected from a local nursery. *C. indica* belongs to the mostly tropical, monocotyledonous Canna Family (Cannaceae). It is a robust perennial herb that grow up to three feet tall, it can be grown from a thick, branching, underground rhizome. The large green leaves taper into slender petioles that form a sheath around the main stem.

2.4. Experimental details

One large and one small constructed wetland microcosm were used for each experiment on Cr and Ni metal. Mixed metals experiments were also done in all constructed wetlands microcosms. *C. indica* were planted in all microcosm. 400–450 g of *C. indica* were planted in each microcosm after cleaning with tap water. After planting, the columns were fed twice with final nutrient solution for a period of 2 months in order to allow the plants to adapt to the new environment. 500 ml of digested anaerobic slurry (1:1 cowdung and water) collected from an operating biogas plant were added in every constructed wetland during this period. The purpose of adding digested slurry was to seed active anaerobic microbes in the experimental constructed wetland. Sodium benzoate as carbon source was used to stimulate anaerobic conditions in the microcosm for promoting the growth of anaerobic microbes. All experiments were performed in same experimental condition and in batch mode, i.e. once fed and once draw mode. All experimental constructed wetlands were fed from the open end and after the desired HRT the whole solution was emptied and stirred. 60 ml composite samples were collected in plastic bottles then acidified and kept in a refrigerator until analysis. Samples were filtered using Whatman-42 filter paper before analysis. The pH of fed solution was found to be 6.4. Temperature of the atmosphere was recorded between 20 and 27 °C during the experiment period. Two run of each experiments were performed. Triplicate samples were taken for analysis. The background concentration of Cr and Ni was analyzed in roots, stems and leaves of plants and gravel and were found

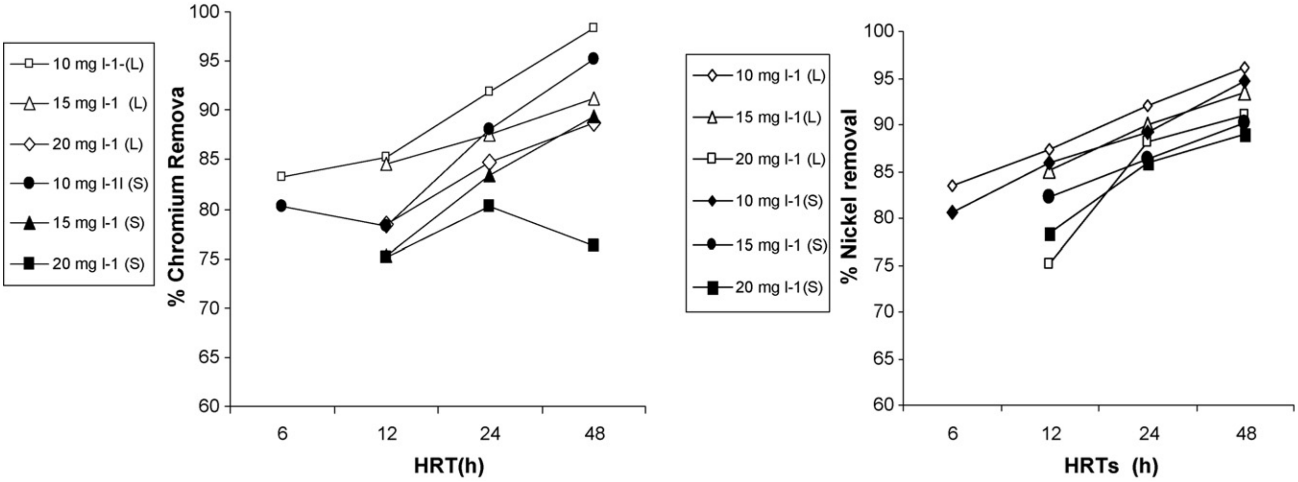

Fig. 2. Effect of HRTs on chromium and nickel removal.

to be below prescribed detection limit of instrument, i.e. 0.006 and 0.01 mg l^{-1} for Cr and Ni, respectively.

To study the accumulation of heavy metals in plants, the concentration of heavy metals were analyzed in roots (belowground biomass) and stems and leaves (aboveground biomass) of plants before and after the study. Heavy metal analysis was done on atomic absorption spectrophotometer (PerkinElmer, Model No. AAnalyst 200, USA). The water loss by evaporation was calculated by placing a small flat plastic tub filled with known amount of water. It was placed near the columns and water loss due to evaporation was calculated by difference in volume of water per unity area during daily basis. Loss of water by evaporation in 1-day time was calculated for each experimental columns and same volume of water was added per day for avoiding experimental errors due to evaporation loss.

2.5. Sample preparation

Plant samples were analyzed for metals before and after the treatment period. Roots, stems and leaves of the plants were dried at 105 °C. One gram of dried plant material was digested in 10 ml concentrated HNO_3 (35% pure) at 60 °C for 2 h in a water bath [16]. The amount of chromium and nickel that had adsorbed on the gravel was analyzed by digesting 50 g sample of gravel in 50 ml of 1 M HNO_3 at (60 °C) for 2 h in a water bath, which was filtered through Whatman no. 42 filter paper, made up the volume and analyzed [16]. Experimental blank of gravel were also performed.

2.6. Adsorption and desorption properties of gravel

Three different concentrations of 10, 30 and 100 mg l^{-1} of chromium and nickel were prepared from stock solution. 40 g of gravel was mixed with 250 ml of each solution in a flask. The flasks were allowed to stand for 48 h at room temperature. Metal concentration was measured at the beginning and end of the experiment. The sample was filtered with Whatman no. 42 filter paper before analysis.

The adsorption capacity of the gravel was determined by following the method used for soil adsorption capacity [17]. The experiment adsorption capacity was calculated with the following equation:

$$q = (C_f - C_i) \times \frac{V}{M} \tag{1}$$

where q is adsorption capacity; C_f is the final concentration; C_i is the initial concentration; V is the volume of the solution; M is the mass of the gravel.

Desorption tests were performed in plastics bottles with 50 ml 0.50 mM EDTA, 0.1 M HNO_3 and 0.1 M $CaCl_2$ solutions. Flasks were kept for 12 h, after which the solutions were filtered with Whatman no. 42 filter paper and analysed for Cr and Ni.

The concentration of metal desorbed from the surface of the gravel (q_{des}, mg g^{-1}) was calculated as

$$q_{des} = C_{des} \times \frac{V}{M} \tag{2}$$

where C_{des} is the metal concentration in the solution at the end of the desorption experiment (mg l^{-1}), V the volume and M is the mass of sorbent.

2.7. Fourier transform infrared analysis

The infrared spectra of the gravel samples with and without metal adsorption were recorded on Fourier transform infrared spectrometer (PerkinElmer Precisely Spectrum One). Gravel samples were prepared by dispersing in dry KBr pellets and recorded within the range 400–4000 cm^{-1}.

3. Results and discussions

3.1. Effect of different HRTs on chromium and nickel removal

Fig. 2(A) shows the effect of different HRTs on chromium removal at initial chromium concentrations of 10, 15, 20 mg l^{-1}. Maximum chromium removal was found to be 98.3 (±0.32) and 95.2 (±0.98) % at an HRT of 48 h with initial concentration of 10 mg l^{-1} in large and small bed depth, respectively, while lowest removal was observed as 75.1 (±0.95) % in small bed depth in the concentration of 20 mg l^{-1} at an HRT 12 h. Percentage removal of chromium increased with HRT in all studied concentrations except 20 mg l^{-1} in small bed depth. Chromium removal increased from 83.2 (±1.11) to 98.3 (±0.75) % at an HRT of 6–48 h in case of 10 mg l^{-1} initial metal concentration in large bed microcosm. Similar trend was observed in 15 and 20 mg l^{-1} initial metal concentrations. For 15 mg l^{-1} initial concentration, 84.6 (±1.04) and 91.2 (±0.7) % chromium removal was achieved at an HRT of 12 and 48 h, respectively, while at 20 mg l^{-1} initial concentration, 78.5 (±1.17) and 88.7 (±0.69) % chromium removal was achieved at an HRT of 12 and 48 h, respectively, in case of large bed microcosm.

Fig. 2(B) shows the effect of different HRTs on nickel removal at initial concentrations of 10, 15 and 20 mg l^{-1}. Maximum removal of 96.2 (±1.52) % nickel was observed at 48 h HRT in the large bed depth microcosm at initial concentration of 10 mg l^{-1}, while lowest removal was observed as 75.2 (±1.24) % in large bed depth microcosm at an HRT of 12 h at 20 mg l^{-1} initial concentration. In all studied concentrations, percentage removal of nickel increased with HRT. Although overall removal percentage of metal decreased with higher initial metal concentration, observed trend was the same for all concentration. It is evident from the results that even at low HRTs, percentage heavy metal removal from 15 mg initial metal is quite sufficient for meeting Indian wastewater discharge limit which is 3 mg l^{-1} for nickel. Therefore, it is possible for the constructed wetland systems to achieve acceptable treatment results at less HRT. If this finding can be confirmed by further studies, a shorter HRT in constructed wetland systems might suffice for treating heavy metal-loaded wastewaters and the land devoted to constructed wetland systems could be reduced.

3.2. *Effect of initial metal concentration on chromium and nickel removal*

Fig. 2(A) and (B) shows the effect of initial metal concentrations on removal of chromium and nickel. The results reveal that as the initial concentration of the metal increased, percentage removal decreased. Overall amount of removed metals increased at high initial concentration. The drop in percentage removal at higher initial metal concentration was because the number of metals ions increased at higher concentrations but the active sites for adsorption on gravels and plant surface remained the same. At lower initial metal concentrations, sufficient adsorption sites were available for the sorption of metal ions. Hence, the percent removal of metal ion depends on the initial metal concentration and decreases with increase in initial metal concentration. The difference in percentage removal of different metal ion at the same initial metal ions concentration may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent [18].

3.3. *Effect of different depth of gravel beds on chromium and nickel*

Two different depths of gravel beds, i.e. 0.95 m (large) and 0.65 m (small) were studied. The depths of gravel beds change the aerobic and anaerobic zone of reactor as well as amount of the gravel filled in. This may be important for metal removal. Results presented in Fig. 2 show that in most of the cases large reactor perform better as compared to the smaller reactor. This is due to enhancement of effective surface area of adsorbent with enhancement of the bed size. Another reason for better performance of large microcosm may be development of anaerobic conditions due to large bed size. The anaerobic condition is very much suitable for reduction of sulphate into sulphide by sulphate reducing bacteria in the presence of organic carbon. Sulphide then reacts with metals to form insoluble metal sulphide precipitates. Similar mechanism for metal removal has been described by other workers [19–21]. It is noticed from the results that there is a near-linear relationship between bed depth and percentage heavy metal removal. If this finding can be confirmed by further studies, use of large bed depth can give better performance and the land requirement for constructed wetland systems could be reduced.

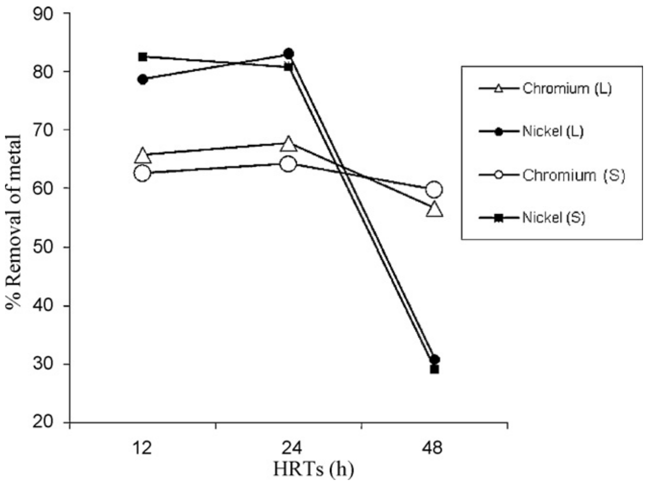

Fig. 3. Chromium and nickel removal from mixed metal solution.

3.4. *Performance of vertical flow constructed wetland reactors in case of mixed metal solutions*

Performance of both types of the microcosm for mixed metal solutions of 10 mg l^{-1} of chromium and 10 mg l^{-1} of Ni were studied in order to assess the performance of both type of microcosms in a complex situation. Maximum 67.75% (±0.86) chromium removal was achieved in 24 h HRT in large bed microcosm while 56.62% (±2.00) was the lowest removal percentage in 48 h in small bed microcosm. In case of Ni maximum removal was 83 (±0.39) % in

Table 2

Concentration in mg kg^{-1} of chromium and nickel in leaves, stem, roots (dry biomass) and gravel [small (S) and large (L). All microcosm is used for mixed as well as individual metals removal experiments].

Microcosm	Sample description	Concentration of Ni	Concentration of Cr	Mixed concentration (Cr + Ni)
Cr (L)	Roots	125.06	1160.8	1285.86
Cr (S)	Roots	79.3	986.7	1066
Cr (L)	Stem	35.8	76.2	112
Cr (S)	Stem	21.3	62.3	83.6
Cr (L)	Gravels	20.63	56.9	77.53
Cr (S)	Gravels	25.86	60.2	86.06
Cr (L)	Leaves	11	12.2	23.2
Cr (S)	Leaves	5.3	8.4	13.7
Ni (L)	Roots	862.6	449	1311.6
Ni (S)	Roots	976.8	446	1422.8
Ni (L)	Stem	42.5	10.7	53.2
Ni (S)	Stem	38.6	9.2	47.8
Ni (L)	Leaves	19	3.6	22.6
Ni (S)	Leaves	16.2	4.4	20.6
Ni (L)	Gravels	63.6	23.1	86.7
Ni (S)	Gravels	68.2	34.4	102.6

Table 3
Adsorption and desorption of properties of gravel.

Metal	Initial concentration, C_i (mg l^{-1})	Final concentration, C_f (mg l^{-1})	Adsorption capacity (experimental) (mg kg^{-1})	% Desorption		
				EDTA (0.50 mM)	HNO_3 (0.1 M)	$CaCl_2$ (0.1 M)
Chromium	10	8.86	7.16	35.27	24.94	33.26
	30	26.22	23.63	25.27	23.74	33.03
	100	79.45	128.42	19.925	25.27	25.04
Nickel	10	8.39	10.07	60.19	98.25	99.9
	30	24.75	32.83	27.02	92.59	95.09
	100	85.60	89.99	16.20	76.01	85.10

24 h HRT in large bed microcosm while lowest was 29.12 (±1.04) % in 48 h HRT in small bed microcosm (Fig. 3).

3.5. *Accumulation of heavy metals in gravels, roots and leaves and their mobility*

Accumulation of chromium and nickel in gravels, roots, stem and leaves were estimated and are presented in Table 2. Concentrations of both metals were found to be below detection limit for chromium and nickel in fresh gravel, roots, stems and leaves of fresh plants. In case of chromium large bed microcosm, the maximum accumulation of chromium was found to be in roots followed by stems, gravel and leaves and maximum nickel accumulation was found to be highest in roots followed by stem, gravel and leaves. In case of chromium small bed microcosm, the maximum chromium accumulation was found to be in roots followed by stems, gravel and leaves and maximum nickel was found to be in roots followed by gravel, stem and leaves. The maximum concentration of chromium was found to be 1160.8 mg kg^{-1} in the plant root of chromium large bed microcosm. The plant root of chromium small bed microcosm accumulated 986.7 mg kg^{-1} of chromium. It is higher than previous reports in which *Vallisneria spiralis* L., a root submerged plant, accumulated Cr to about 57.5 mg kg^{-1} dry weight of root after 10 days of exposure to 100% tannery wastewater [22]. It may be due to plant species difference and exposure to higher initial concentration of metal. Similarly maximum nickel concentration was found to be 976.8 mg kg^{-1} in plant root of nickel small bed microcosm while plant roots of nickel large bed microcosm have 862.6 mg kg^{-1}. The general trend from Table 2 shows that the root tissue accumulates greater concentration of metals than stem and leaves. It indicates high availability and limited mobility of metals inside the plant. The observation in this study is in agreement with the experiment undertaken by previous workers [15,23].

The accumulation of nickel followed the trend, i.e. roots fallowed by gravel, stems and leaves in both small and large bed nickel microcosms. To check the mobility of metals, translocation factors (TF) of each metal in plants were calculated. The TF for metals within a plant was expressed by the ratio of the metal concentration in the above and belowground biomass [24]. It was also expressed by the ratio of the metal concentration in belowground biomass and gravel. The TF of chromium from belowground to aboveground biomass was found to be 0.072 and from gravel/aqueous solution to root was found to be 16.39 in case of small bed microcosm, while it was found to be 0.076 from belowground to aboveground biomass and 20.40 from gravel to root in the case of large bed microcosms. The TF for nickel from belowground to aboveground biomass was found to be 0.056 and from gravel to root it was found to be 14.32 in the case of small bed microcosm, while it was found to be 0.071 form belowground to aboveground and 13.56 form gravel to root for the case of large bed microcosms. These results show that mobility of chromium and nickel are less within the *C. indica* plant species as TF < 1. The TF for gravel to roots was always found to above than one which indicates its metal accumulator nature. It is also noticed that plant is very effectively grown on gravel bed with supporting nutrients with continuous growth and production of new biomass.

3.6. *Adsorption and desorption properties of gravel*

The chromium and nickel adsorption capacities of gravel and desorption are summarized in Table 3. In this study, as the initial concentration changed between 10 and 100 mg l^{-1}, the adsorption capacities of gravel varied between 7 and 128 mg kg^{-1} for chromium and 10 and 89 mg kg^{-1} for nickel. Higher adsorption capacities were obtained for higher initial metal concentrations. This can be explained by greater driving force of a higher concentration gradient pressure [25]. Similar observation was also reported for phosphorous removal by [26].

Vohla et al. [27] reported decreasing trend of phosphate removal due to saturation process in filter media for long-term constructed wetlands. They also reported several alterative potential filter media with high phosphorus sorption capacity, sorption characteristics and particle size distribution of several local sands, gravels, glauconite-sandstone, LWA, and calcareous waste products from oil-shale industry of Estonian region. Similarly, Brown et al. [28] has reviewed peat for various heavy metal removal which may also be utilized as potential filter media in constructed wetlands.

The maximum desorption of chromium (33%) and nickel (99%) was achieved with 0.1 M $CaCl_2$. The EDTA solution showed poor

Table 4
Percentage contribution in heavy metals removal by different parts of constructed wetlands microcosm.

Different component	Percentage metal removal in different constructed wetlands microcosms			
	Chromium (L)	Chromium (S)	Nickel (L)	Nickel (S)
Effluent	17.09	21.03	14.68	14.66
Gravels	68.51	72.22	74.68	79.77
Leaves	0.0188	0.026	0.03258	0.01
Stems	0.0698	0.096	0.0033	0.1184
Roots	1.744	3.012	0.133	0.5929
Other	9.356	3.616	10.4711	4.8487
Total	100	100	100	100

Concentrations of both metals were found to be below detection limit in fresh gravel, roots, stems and leaves of fresh plants.

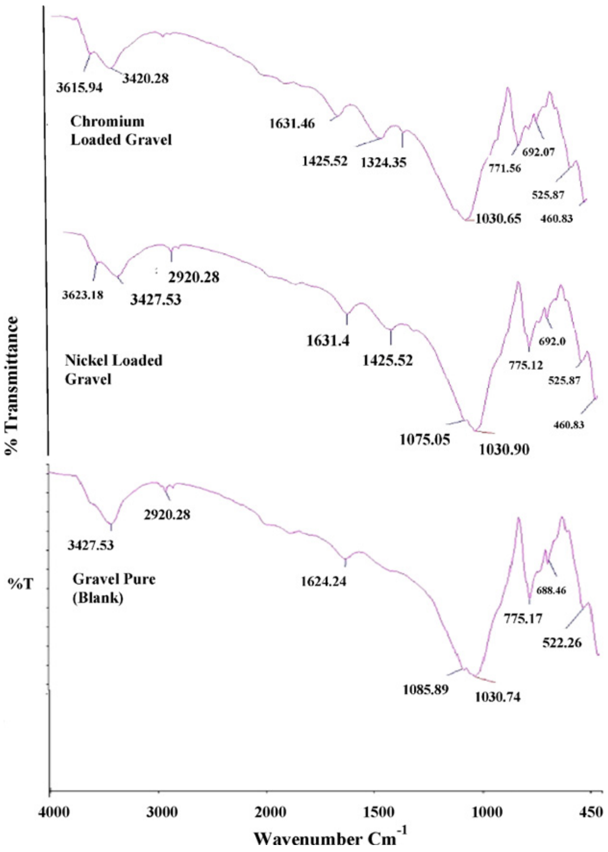

Fig. 4. FTIR analysis of gravel with and without metal adsorption.

desorption quality among all studies desorption solution for both metals.

3.7. *Mass balance of heavy metals removal*

Table 4 shows relative percentage contribution of each component in the wetland microcosm towards overall metal removal. The contribution of the aboveground biomass was less than 1% in all cases, while belowground biomass contributed between 1.744 and 3.012% in the overall chromium removal, and between 0.133 and 0.592% in the overall nickel removal. The low contribution of plant uptake in treatment wetlands has been reported several times [15,29–31]. The gravel plays a major role in overall removal of chromium and nickel.

3.8. *FTIR analysis*

The FTIR spectra of the unloaded gravel and gravel loaded with chromium and nickel is shown in Fig. 4 where the new peaks appear at 1324 and 1425 cm^{-1} in case of chromium loaded gravel while in case of nickel loaded gravel new peaks appear at 1425 cm^{-1}. These peaks were not observed in the unloaded gravel. This may be attributed to interaction between the functional groups and metal ions as a result of adsorption or chemical reaction. The probable functional groups corresponding to these peaks may –O–Si=O, SO_2OH group [32,33].

4. Conclusions

This study concluded that

(1) Maximum removal of chromium and nickel was found to be 98.3(±0.32) and 96.2 (±1.52) %, respectively, at initial concentrations of 10 mg l^{-1} and at an HRT of 48 h in large bed depth constructed wetland microcosms. Lowest chromium removal was found to be 75.1 (±0.95) % in small bed depth in the concentration of 20 mg l^{-1} at an HRT 12 h and lowest nickel removal was found to be 75.2 (±1.24) % in large bed depth microcosm at an HRT of 12 h at 20 mg l^{-1} initial concentration. Results of this study reveal that in most of the cases large reactor performs better as compared to the smaller reactor.

(2) Adsorption capacities of gravel varied between 7 and 128 mg kg^{-1} for chromium and 10 and 89 mg kg^{-1} for nickel with varying initial concentration. The maximum desorption of chromium (33%) and nickel (99%) from exhausted gravel was achieved with 0.1 M $CaCl_2$.

(3) The contribution of the aboveground biomass was found to be less than 1% in all cases, while belowground biomass contributed between 1.744 and 3.012% in the overall chromium removal, and between 0.133 and 0.592% in the overall nickel removal. The TF of chromium from belowground to aboveground biomass was found to be 0.072 and 0.076 and from gravel/aqueous solution to root it was found to be 16.39 and 20.40 for small bed and large bed microcosm, respectively. TF for nickel from belowground to aboveground biomass was found to be 0.056 and 0.071 and from gravel to root it was found to be 14.32 and 13. 56 for small and large bed microcosm, respectively.

(4) In case of chromium large bed microcosm, the maximum accumulation of chromium was found to be in roots followed by stems, gravel and leaves while in case of small bed microcosm, the maximum chromium accumulation was found to be in roots followed by stems, gravel and leaves. The accumulation of nickel followed the trend, i.e. roots fallowed by gravel, stems and leaves in both small and large bed nickel microcosms.

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