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Feasibility Studies for Reuse of Constructed Wetlands Treating Simulated Nickel Containing Groundwater

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Abstract:
Constructed wetlands are considered as low cost treatment option for domestic and industrial wastewater in the recent decades. The presence of toxic heavy metals in wastewater is a problematic issue, since these heavy metals have potential to accumulate in the treatment systems. Thus heavy metals greatly influence the efficiency of constructed wetlands. Therefore a feasibility study was proposed for long term usage of constructed wetlands as treatment systems. Initially sediment in a constructed wetland was contaminated with simulated nickel containing groundwater followed by using suitable leaching solution to rejuvenate the heavy metal contaminated sediment. A batch study was performed to identify the optimum pH for nickel adsorption on sand. The efficiency of different leaching solutions to remove the adsorbed nickel from sand was studied. Following this a Pilot scale study was carried out in constructed wetland treatment plant (vertical flow) at Anna University, Chennai, India. The amount of nickel solution charged into the Control Cell (sand) and Test Cell (sand planted with *Arundo donax*) was 29000 mg/cell. The concentration of nickel adsorbed to sand increased from 0.2mg/Kg to 4.34 mg/Kg in the control cell whereas the increase in test cell was 4.08mg/Kg. Leaching the wetland with EDTA solution resulted in removal of nickel up to its background concentrations on the sand. It can be concluded that the proposed feasibility study can be used to rejuvenate the sediment in a constructed wetland for its long term usage as treatment systems.

Keywords: Constructed Wetland, Ethylene Diamine Tetraacetic Acid, Leaching, Nickel, Rejuvenate.

1. Introduction:
Constructed wetlands treatment systems are human-made, engineered wetland areas specifically designed for water quality improvement by optimizing physical, chemical and biological processes that occur in natural aquatic wetland systems (Yeh *et al.,* 2009). They are cheap and alternative to expensive treatment technologies like trickling filters and activated sludge processes. Horizontal and vertical flow wetlands constructed based on soil, sand or gravel is used extensively to treat domestic and industrial wastewater (Kadlec and Knight 1996). The processes that contribute for pollutant removal in a constructed wetland are chemical networks, microbially mediated processes, volatalisation, sedimentation, sorption, photodegradation, plant uptake, vertical diffusion of soil and sediments, transpirational flux, seasonal cycles and accretion (Kadlec and Wallace 2009). Trace metals present in environment are essential micronutrients to the biota but accumulation of these metals leads to bioaccumalation, a term referred to toxicity of pollutants. The presence of heavy metals in the domestic wastewater (Sorme and Lagerkvist 2002, Ellis and Revitt, 1991) is due to disposal of electronic wastes, traditional medicines, amalgam, detergents, car washes, copper roofs, galvanized steel, pipes and taps which contain heavy metals in trace proportions.

The use of constructed wetlands as treatment system for domestic wastewater has gained wide acceptance in the recent decades (Vymazal *et al.,* 2011). The metal removal processes in constructed wetlands is very complex and these processes include a combination of biotic and abiotic reactions such as sedimentation, flocculation, adsorption, precipitation, co-precipitation, cation and anion exchange, complexation, oxidation and reduction, microbial activity and plant up-take (Kosopolov *et al.,* 2004; Ujang *et al.,* 2005; Yalcuk and Ugurlu. 2009). The metals cannot be destroyed but their chemical and physical characteristics are modified (Ujang *et al.,* 2005). However if constructed wetland is used as a treatment system for metal containing domestic wastewater, the treatment design should be done cautiously. The trace proportions of heavy metals present in the wastewater will accumulate in the constructed wetland's sediment causing significant damage to microbial flora and fauna in the system. It is not possible to dig up the contaminated sediment from the constructed wetland and replace with fresh sediment when treatment system is in full operation. To prevent this problem constructed wetland designers adopt different alternatives. The first alternative was to pre-treat the wastewater to remove the heavy metals. This alternative may be feasible for industrial wastewater but not fit in the case of domestic wastewater where the heavy metals are present in low concentrations (Vymazal *et al.,* 2007). A second alternative is to minimize the ingestion of heavy metals. This can be accomplished with subsurface flow wetlands. As an alternative, we carried out a feasibility study wherein we investigated the usage of leaching solution for the rejuvenation of heavy metal contaminated sediment in a constructed wetland during a short period. In the present study, Nickel was used for contamination; sand was used as sediment in the constructed wetland as well as to adsorb the nickel, and Ethylene Diamine Tetra Acetic acid (EDTA) was used as leaching solution to remove adsorbed nickel from the sand.

2. Materials and Methods:

2.1 Chemicals:

EDTA and Hydrochloric acid are purchased in bulk packs from Merck India. All the other chemicals used in the study were purchased from Merck India of highest purity available. A batch study was performed to identify the optimum pH for nickel adsorption by the sand. The adsorbed metal from the sand was leached using Hydrochloric acid (0.1 N) and Ethylene Diamine Tetra Acetic acid (EDTA) (0.01 M).

2.2 Description of Pilot Scale Constructed Wetland System:

The pilot scale study was carried out in the constructed wetland treatment plant (vertical flow type) at Anna University, Chennai, India (Figure 1). Sand used in the study was collected from the Chengalpat River, Chennai, India. Before filling into the wetland cell, sand was sieved to remove the particles ≥2 mm. Particle size of the sand ≤ 2mm was filled into the wetland cell. The wetland plant used in the study was *Arundo donax*, which was collected from the Chengalpat River Basin, Chennai, India. *Arundo donax* is a rhizomatous perennial grass species belongs to *Poaceae* family reproduces by rhizomes and stem, also can essentially remain alive throughout the year. It grows in a number of freshwater riparian habitats such as irrigation ditches, streams, lakes, and wetlands. *Arundo* has the ability to survive in a number of different types of soils, ranging from heavy clays to lose sands and gravelly soils. Sandy soil is the most common type of soil in which it is found. It has hollow, segmented culms that measure anywhere from 1 to 4 centimeters in diameter, which will branch in the second year of growth. The rootstock bears fibrous roots that grow into the soil up to 5 meters in depth (Frandsen, 1997). The constructed wetland plant has a control cell and test cell in which control cell was filled with gravel and sand whereas the test cell has gravel, sand and planted with *Arundo donax* (Figure 2). Each cell fitted with a separate drainage pipe which was directed towards a trench to collect the effluent.

2.3: Pilot Scale Studies in the constructed Wetland System:

Pilot scale study was carried out after the plants were grown for a consistent period. Simulated nickel containing groundwater (hereafter described as Nickel solution) was prepared by dissolving Hydrated Nickel Nitrate in ground water filled in a plastic container of one hundred litres capacity. The pH of the nickel solution was adjusted to 6 using concentrated hydrochloric acid. EDTA solution was prepared by dissolving it in the ground water to a concentration of 0.01 M. Charging of Nickel or EDTA solution into the wetland was done manually using a shower to ensure the uniformity in distribution throughout the cell (Figure 3). During the nickel charging phase, volume of nickel solution passed to each cell was two hundred litres whereas in the leaching phase, one thousand litres of leaching solution was passed into the cell.

Figure 1: Pilot Scale Constructed Wetland System (Vertical Flow) at Anna University, Chennai-India

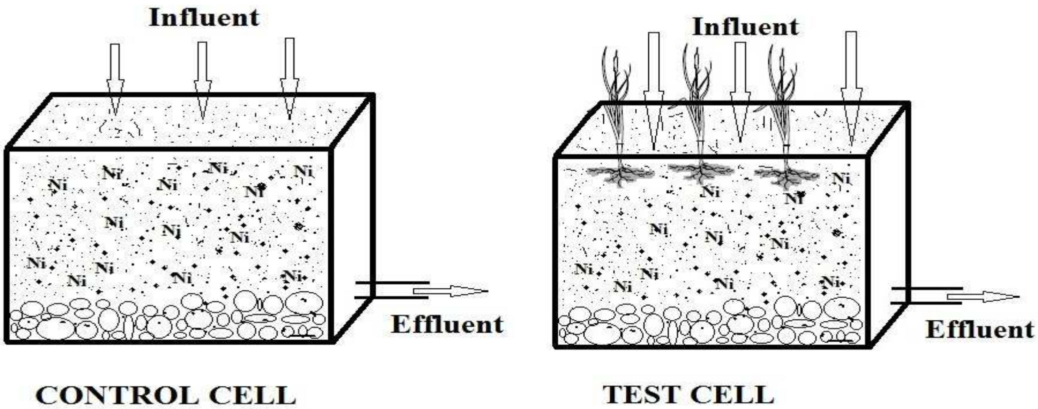

Figure 2: Design of Control Cell and Test Cell in Vertical Flow Constructed Wetland System

Figure 3: Charging of Nickel Solution or EDTA into the Constructed Wetland System

Table 1: Parameters and Techniques Used to Analyze the Samples

Sampling Approaches		**Parameters analyzed**	**Techniques**
Control cell (without *Arundo donax*)	**Test Cell (with *Arundo donax*)**		
Influent	Effluent	pH, Nickel	Electrode, AAS
Sand at surface, at a depth of 30 cm and 60 cm	Sand at surface, at a depth of 30 cm and 60 cm	pH, Nickel	Electrode, Aqua-regia Digestion, AAS
	Root and Shoot of *Arundo donax*	Nickel	Aqua-regia Digestion, AAS

2.4 Sampling Strategies:

Sand from each cell was sampled out using a hand steel auger and stored in air-tight polyethylene bags in order to account for the nickel adsorption. The auger was washed with water during every single sampling. Sand samples were taken from five different locations (four corners and a centre point) in each cell to ensure the uniformity in nickel adsorption by sand. In each location sand was sampled out at surface, 30cm and 60 cm in depth in order to know about the nickel adsorption at different depths. Root and shoot samples were collected from control cell at the end of Nickel charging phase (Table 1). To enhance leaching efficiency, both the cells were stagnated with leaching solution to remove the adsorbed nickel from the sand. Like charging phase, sand was sampled out to know the recovery of nickel by the leaching solution. Influent and effluent samples were collected in plastic containers and acidified to pH<2 with conc. nitric acid. Nickel analysis on sand, influent and effluent was done immediately after sampling.

2.5 Analytical Methods:

The pH of the influent, effluent and sand were measured with a pH meter (Elico). Sand samples were mixed with deionised water in the ratio 1:10 (w: w), and left for 24h at room temperature. The mixtures were centrifuged and the pH of the supernatant was measured (Sakata, 1987) using a glass electrode. Estimation of nickel in sand, plant, influent and effluent were done as per APHA, (1998) in Atomic absorption spectrophotometer (Analytik Jena, Germany).

3. Results and Discussion:

The pH of the sand was found to be 7.6 at 1:10 suspensions. The background concentration of nickel in sand and groundwater were found to be 0.2mg/kg and below detection limits respectively.

3.1 Batch Studies:

The mobility of trace elements in wetlands is highly influenced by redox potential and pH of the water-sediment system. Many trace elements such as Cu, Zn, Cd, Pd and Ni are not subject to change in oxidation state as result of redox reactions wetland systems (Khalid *et al.,* 1978). Sand was used as adsorbent based on previous work by Aslam *et al.,* (2004) who achieved 70-97% of removal efficiencies for copper removal. The discharge limits for nickel in the effluent was set as 3mg/L by the regulatory authorities, India (CPCB 1997). Hence, batch study was performed to identify the optimum pH for nickel adsorption, which was found to be 6 at 5mg/L of nickel. Selection of EDTA and HCl was done based on the research work carried out by different scientists to remove the contaminants from the polluted habitats (Matsumoto *et al.,* 1997, Blaylock *et al.,* 1997, Huang *et al.,* 1996, Reed *et al.,* 1996, Raskin *et al.,* 1997, Martell and Smith 1974). The leaching efficiencies of Hydrochloric acid (0.1 N) and Ethylene Diamine Tetra Acetic acid (EDTA) (0.01 M) are found to be 55% and 30.6% respectively. Since acidic properties of hydrochloric acid affect the sand properties such as Porosity and Texture, EDTA was used to leach out the nickel from the sand because of its less toxicity towards the wetland species and its biodegradability in the system.

3.2 Nickel Charging Phase during Pilot Scale Study:

Nickel solution charged into the test cell and control cell at a concentration of 5mg/L with pH maintained at 6 as per the batch study. There was a strong relationship between metal adsorption in response to pH of the adsorbent. During the initial charging, the nickel fed to the system get precipitated but later due to progress in charging the pH of the sand get decreased resulting in increased nickel adsorption. The concentration of nickel found in the effluent from test cell at the beginning was 6.8 mg/L, which gradually declined to 2.1 mg/L at the end of the nickel charging phase (Figure 2). The pH of the effluent from test cell had declined from 8.0 to 6.2 which lead to rapid decline in pH of the adsorbent (sand); the effluent nickel concentration from control cell was decreased from 7.9 mg/L to 2.3 mg/L (Figure 4).

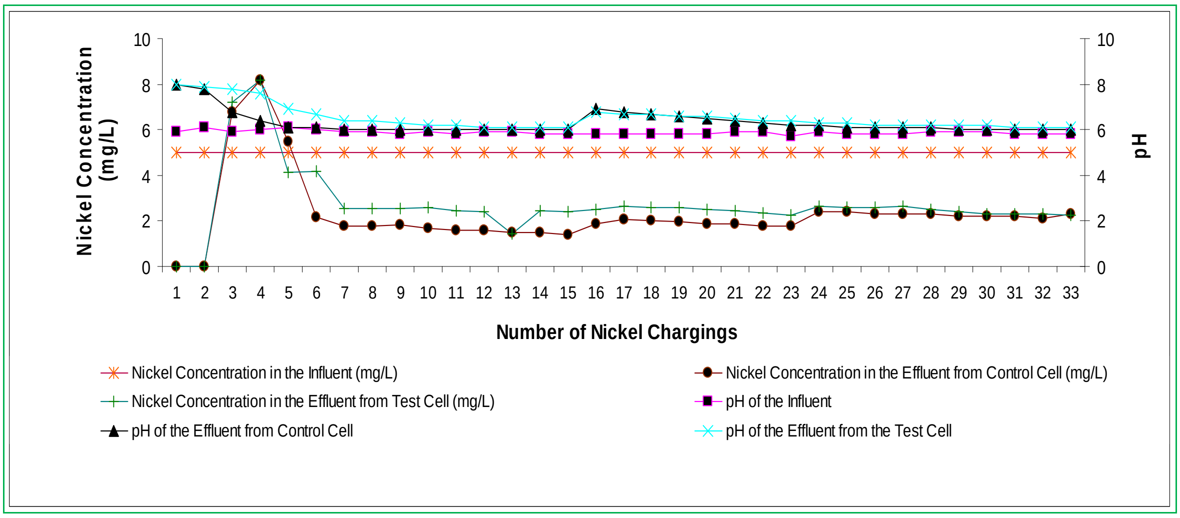

Figure 4: Nickel Concentration in Response to pH in Control Cell and Test cell

Sediment used in the constructed wetlands is the primary sink for metal accumulation (Lesage *et al.,* 2007). Karathanasis and Johnson (2003) used acid mine drainage water (pH-3.3) which decreased the pH of the sediment from alkaline to acidic nature which enhanced the metal retention in the wetlands. Mitchell and Karathanasis (1995) found that plant species did not influence the nickel retention, but the sediment significantly influenced the removal of nickel and other heavy metals during the surface flow experiments.

To account for nickel adsorption, sand was sampled in five locations at different depths and analysed for nickel at subsequent periods. The amount of nickel adsorbed by the sand kept increasing, as there was progress in the charging of nickel into the system. Adsorption of nickel was found greater in the top layers of the cell whereas only less amount of nickel adsorbed in the bottom layer of the cell. The variation could be due to the probability of contact between the nickel solution and sand, which was high in the top layers when compared with bottom layers (Data not Shown). Interestingly, the amount of nickel adsorbed by the sand in the middle layer was found to be the average of the obtained results. Similar results had been obtained, by Nolte *et al.,* 1997 in which 2-13 fold metal concentrated in the upper layer than the bottom layers (Dombeck *et al.,* 1998). Mitchell and Karathanasis (1995) found that metal retention was greater in the surface than in the deeper layers. The depth greatly plays a role in removing pollutants from domestic sewage (Ren *et al.,* 2011).

Analysis of nickel had been done four times during the course of the nickel charging phase. Due to decline in the pH of the sand more nickel got adsorbed to the sand. The nickel adsorption in the control cell increased from 0.71mg/kg of sand to 4.48 mg/kg of sand whereas in test cell the hike was from 0.68 mg/kg of sand to 4.08 mg/kg of sand (Figure 5). Analysis of Nickel in shoot and root of *Arundo donax* shown below detection limits for nickel which indicates that there was no significant accumulation of nickel in the plant.

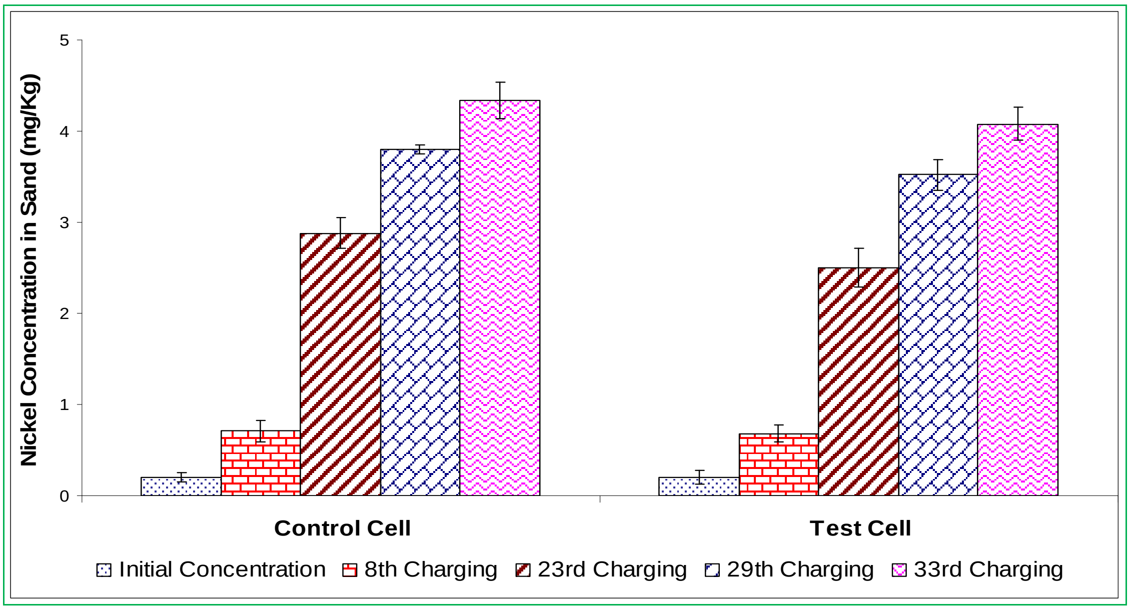

Figure 5: Increase in Nickel Concentration during the Charging Phase

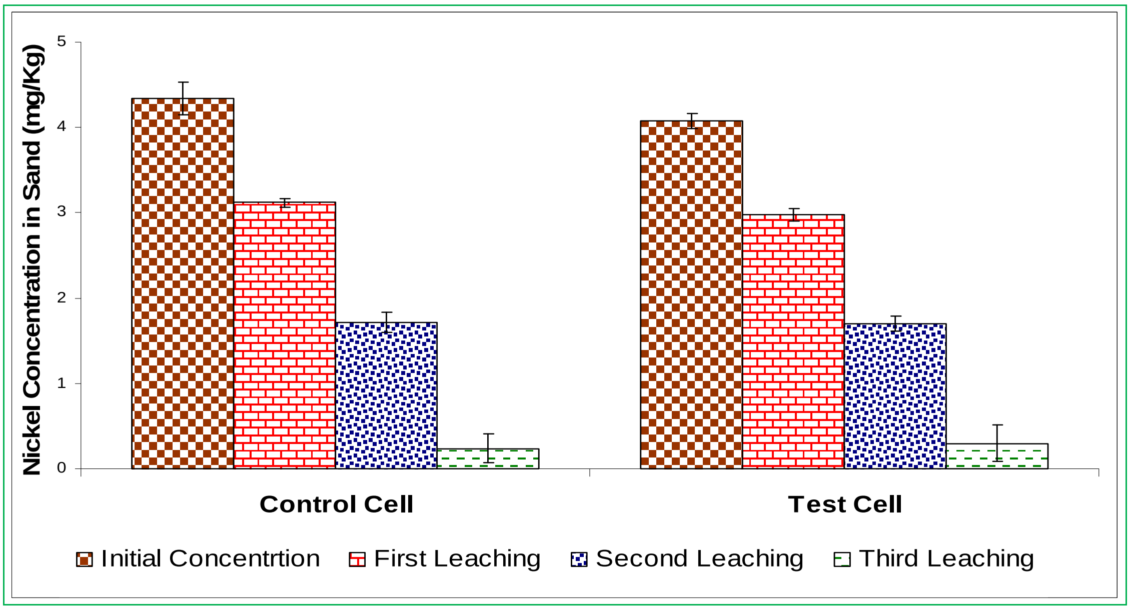

Figure 6: Concentration of Nickel in Sand at Leaching Phase

During the batch study, the amount of nickel adsorbed to 1 Kg of sand was found to be 18.2 mg. These observations were in agreement with the studies previously conducted by Ure and Berrow (1982) who calculated that the theoretical value of adsorption of nickel in 1 kg of sand was in the range of 0.8 mg to 100 mg.

3.3 Removal of Nickel during Leaching Phase:

During the leaching phase at the end of every EDTA charging, sand sampling was done as like Nickel charging phase to quantify the amount of nickel leached out from the sand. At the end of the first leaching, analysis on sand for nickel concentration showed a decline from 4.34 mg/kg to 3.12 mg/kg in the control cell. The observed decline in the test cell was from 4.08 mg/kg to 2.98 mg/kg. During second leaching, the nickel concentration on sand was found to be decreased from 3.12 mg/kg to 1.72 mg/kg in the control cell whereas the decline in the test cell was from 2.9 mg/kg to 1.7 mg/kg. This was due to more saturation of the adsorbent by the EDTA solution. At the end of the third leaching, analysis on sand for nickel concentration showed a decline from 1.72 mg/kg to 0.24 mg/kg in the control cell. The observed decline in the test cell was from 1.7 mg/kg to 0.3 mg/kg (Figure 6). The overall leaching efficiencies of Control Cell and Test cell were found to be 94.5% and 92.6% respectively.

Reed *et al.,* (1996) achieved removal efficiencies of 85%, 100% and 78% using 0.1 N HCl, 0.01 M EDTA and 1M $CaCl_2$ for leaching of Pb contaminated soil. Leaching was more effective in soils less than 10-20% clay and organic matter (Mulligan *et al.,* 2001). Heavy metals can be leached out of soils using mineral acids, organic acids, chelating agents or their combinations (Lestan *et al.,* 2008). In the present study EDTA was chosen because it is biodegradable and it enhances the leaching efficiency of the heavy metal from the wetland cell. The plants in the system seem to starve at the first day on the addition of leaching agent. On successive leaching, the plants gradually adapted to the condition. There was no significant effect of leaching agent on the wetland plant *Arundo donax*.

4. Conclusions:

From the present study it is evident that, constructed wetlands could remove trace metals from the wastewater. It can be concluded that the proposed feasibility study was efficient to rejuvenate the metal contaminated sediment in constructed wetlands during a short period. The further work was planned to find breakthrough for nickel and its absorption by the wetland plant in the charging phase during the pilot scale study.

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