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# Toxicity of Chromium on Nitrogen and Biodegradable Compound Removal in Vertical Flow Constructed Wetlands

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**Abstract:** The objective of this study is to investigate the removal efficiencies of Chromium (Cr), Nitrogen and biodegradable organic compounds, as well as its interference of each other in vertical flow constructed wetlands with different bed media. Four laboratory-scale vertical flow constructed wetland (CW) units, each with dimensions of 750 x 635 m (diameter x height), were installed with different bed media: $CW_{C2}$ with 200 100, 100and 150 mm of charcoal, sand, small gravel and large gravel; $CW_{C1}$ with 100, 200, 100 and 150 mm of charcoal, sand, small gravel and large gravel; $CW_{C0}$ and CWControl with 200, 200 and 150mm of sand, small gravel and large gravel. Typha Angustifolia (Cattails) were planted at initial density of 50 shoots./$m^2$ in $CW_{C1}$, $CW_{C2}$ and $CW_{C0}$ units and fed with domestic wastewater spiked with Cr at the concentrations ranging from 10 to 100 mg/L at the Hydraulic Retention Time (HRT) of 4 days. Samples from CW units were taken once in 3 days throughout 115 days of operation for analysis of total Cr, nitrogen, pH. In addition, N accumulated in the plant biomass (roots and shoots) were analysed to identify the Cr toxicity for plant uptake of Nitrogen. For influent concentrations up to 30 mg/L, it was found that Cr mass removal efficiencies for all CW units were 99-100 %, resulting effluent concentrations below the industrial effluent standard which is 2 mg/L. Beyond 30 mg/L influent Cr concentrations, it was apparent that the CW unit with thick charcoal layer met the industrial effluent standard, even at an influent Cr concentration of 100 mg/L. Experimental data revealed that the CW units with charcoal layers could result in COD and N removals of 82 - 92 % and 57 - 87%, respectively. Possibly due to the inhibitory effect of Cr on N plant uptake, the N removal in CW units were decreased rapidly with increasing Cr loading. On the contrary, the increase in Cr loading did not affect the COD removal efficiencies in CW units.

**Keywords:** Vertical flow Constructed wetlands, Chromium toxicity, COD, Nitrogen

## 1. Introduction

Among the conventional treatment processes, the CWs are found to be efficient in treating industrial wastewater containing chromium due to various treatment mechanisms including biological, physical and chemical interactions of the soil-plant-micro-organisms. Most of the research findings ( Gersberg et al ,[7], Oke and Juwarkar [1]) reported that heavy metals such as Cu,Cd,Zn, Pb, Ni and Co could be readily removed by CW systems though the metal removal efficiency seems to be influenced by the types of media used and the types of wastewater to be treated.

The evaluation of the treatment potential of constructed wetlands appear to have focused separately on two types of pollutants, namely,

a). Biodegradable matters and organic nutrients
b). Toxic pollutant

However the effects of toxic pollutants on removal efficiency of organic compounds as well as nutrients are not yet focused widely among the researches.

Therefore, the goal of this research was to have a better understanding about the effect of Cr for the performance of nitrogen and COD removals, and to investigate Cr removal efficiencies with charcoal in the bed media in vertical flow constructed wetlands.

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## 2. Material and Methods

Four laboratory scale vertical flow CW units each with 750 mm in diameter and 635 mm in height were employed (Figure 1). Total bed media thickness for all the wetlands were kept as 550 mm but different bed materials with dissimilar layer thicknesses were employed.

During the start-up period, all CW units were fed with tap water for two weeks and then fed with domestic wastewater for another two weeks. During this time tracer study was carried out since there was no interference of Lithium ion ($Li^+$) with domestic wastewater. There the Lithium chloride was injected to make 5 mg/L of Lithium ion in the inlet, for each CW unit and effluent Lithium ion concentrations were measured to study the flow pattern inside the CW units. 5 mg/L of Cr concentration was spiked before feeding in the next week to acclimatize the soil microbes and the cattails. After that wastewater with 10mg/L, 30mg/L and 100mg/L concentrations was fed for 115 days,

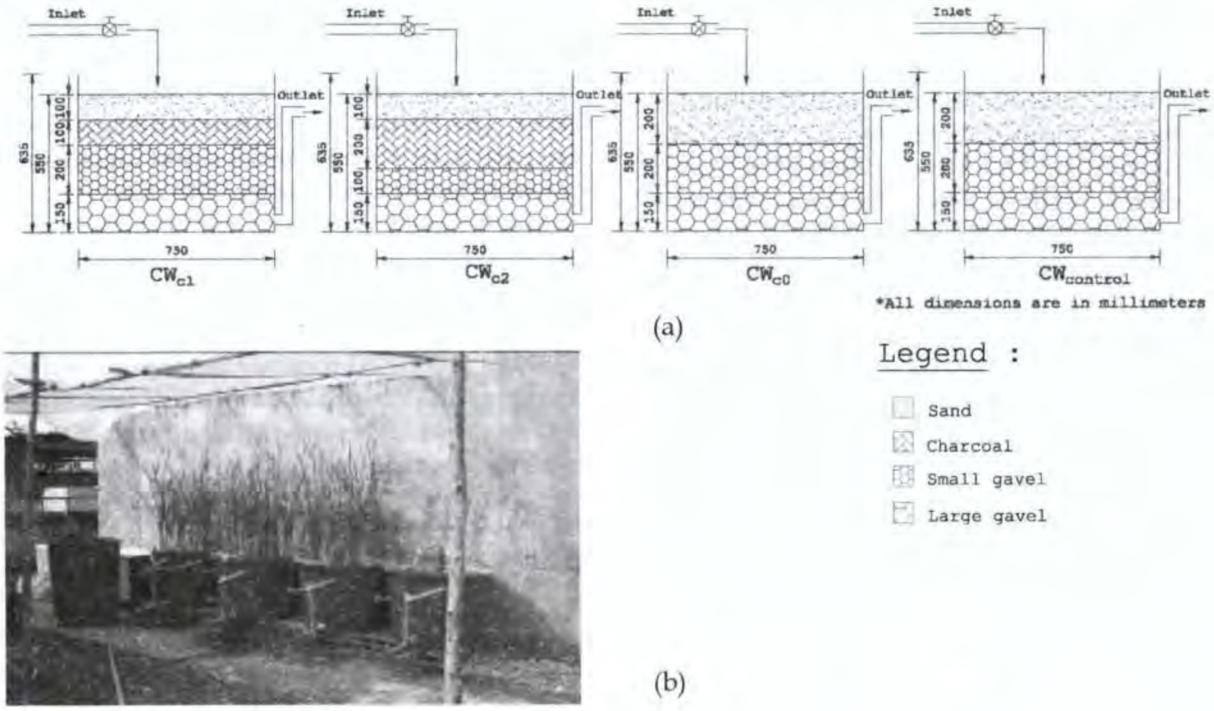


**Figure 1- Experimental Setup, (a) Sectional view, (b) Photo in the field**

The first CW unit ( $CW_{C1}$) has a 100 mm thick charcoal layer (3.36-4 mm media size) in between a sand layer (100 mm thickness with 2-2.38 mm media size) and a small gravel (200 mm thickness with 16-19 mm media size) layer, which act as chromium adsorbent to enhance the removal efficiency. A 150 mm thick large gravel (25-37.5 mm media size) layer was placed under the small gravel layer. Sand ($CW_{C2}$), charcoal, small gravel and large gravel layers of thickness 100mm, 200mm, 100mm and 150mm respectively were employed in the second CW unit from top to bottom. Here the charcoal layer thickness was increased by 100 to see the difference with increased thickness. The third ($CW_{C0}$) and fourth ( $CW_{Control}$) CW units followed the conventional wetland beds with sand and two graded gravel layers. Sand, small gravel and large gravel layer thicknesses were set to 200, 200 and 150 mm respectively for both of those units. The Cattail plant (Typha Angustifolia) was planted only in the first three CW units with initial density of 50 shoots/$m^2$ and the fourth one was employed without plants as a control unit.

The influent and the effluent samples were analysed for total Cr, COD, TN, $NH_4$-N, $NO_2$-N, and $NO_3$-N in all CW units once in three days. Experiments were performed under different concentration levels. It was 10mg/L at the beginning and increased up to 100mg/L stepwise. At last nitrogen uptake by plant was carried out by measuring the nitrogen in the plant components before and after the testing period to find whether there is any effect on Cr for nitrogen uptake by plant.

## 3. Results and Discussion

Based on the 115 days of experiential period, the Chromium, COD and nitrogen removals in the wetland system as well as the toxicity of Cr for removal of COD and Nitrogen is discussed in this section. From the tracer Study it was found that all CW units have the same flow patterns.

### 3.1 Chromium removal

Removal of Cr in wetlands may occur through a number of processes, including plant uptake and soil adsorption. Moreover chemical reactions between substances, especially metals, can lead to their precipitation from the water column as insoluble compounds.

It was found that Cr removal efficiency in all CW units were 99 % when influent Cr concentration was 30m/L. But for high concentrations such as 75mg/L the efficiency was remaining above 98% only in the wetland which had thinker charcoal layer in the bed material. This could be mainly due to the adsorption of Cr within the charcoal layer ( Figure 2).

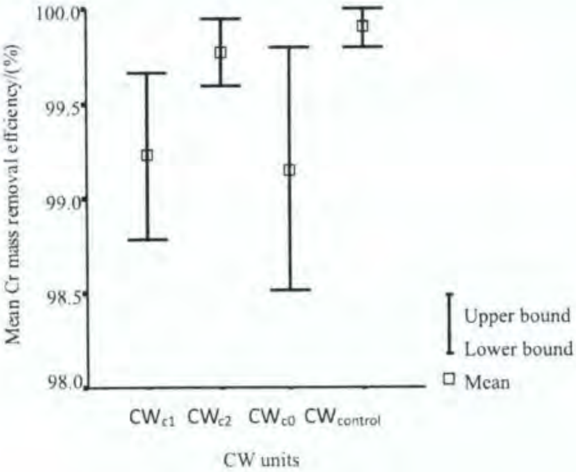


**Figure 2- Overall mean Cr mass removal efficiencies**

The overall mean Cr mass removal efficiencies in CW units were very high in all CW units. It was recorded as 99.2%±0.44, 99.7%±0.17, 99.1%±0.64 and 99.9%±0.11in $CW_{C1}$, $CW_{C2}$, $CW_{C0}$ and CWControl respectively. Among the planted CW units the one with the highest thickness of charcoal layer in the bed media shows the higher removal efficiency of Cr (Figure 2)

### 3.2 COD removal

An average value of 168 mg/L was fed during the operation period resulting an average loading rate of 115 kg of COD/ha.d. Effluent COD concentration in the first two months was same in all the units and afterwards there was a small increment. Mean values of COD mass removal efficiencies in all CW units were calculated using one sample T test and it is depicted in Figure 3. Highest mean COD removal was recorded from the CW unit having a 200mm thick charcoal layer ($CW_{C2}$). CW unit having a 100mm thick charcoal layer ($CW_{C1}$) gave the next highest and it was followed by other two CW units.

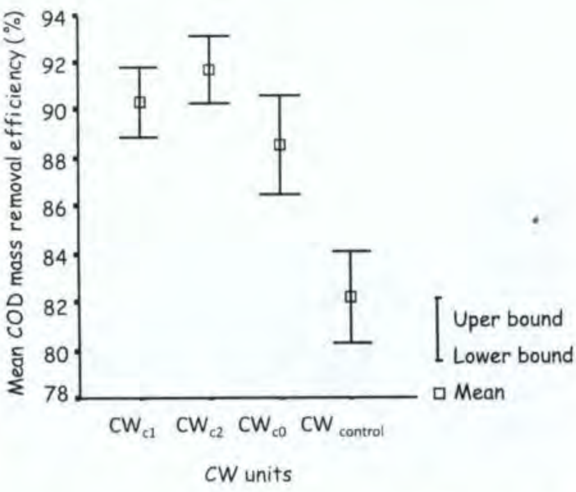


**Figure 3- Mean COD mass removal efficiency in CW units**

Analysis of Variance (ANOVA) tests were carried out separately for the three cases to see any significant effect on mass removal efficiency of COD. Three planted CW units were taken as a group and the functionality of bed media for COD removal efficiency was considered in the first case (Among these three units two of them have charcoals and the other has only sand and gravel.) It was found that there is a significant effect at 95% confident interval. Thus it can be said that CW units having charcoal perform differently for COD mass removal. Charcoal could act as adsorption of biodegraded compound and enhance the COD removal in these systems might be the reason.

In the second case two CW units having different thicknesses of charcoal layer were considered. Different thicknesses of charcoal layer in the wetland bed were not different in COD removal efficiencies, for 95% confident interval. Hence variation of charcoal layer thickness may not affect the COD removal efficiency. In the third case, two CW units having same bed media were considered ($CW_{C0}$ and $CW_{Control}$), to see whether there was a significant effect with and without plant in treating COD. Treating COD with and without plant in the CW unit was different for 95% confident intervals. As Figure 3 shows mean mass removal efficiency of these two were only different by 6%. Recently Chi-Yuan Lee et al [2] found that (52- 74%), and (26-48%) from the overall removal of COD were due to physical and biological mechanisms respectively. Since charcoal is a good absorbent COD removal efficiency can increase by physical mechanisms. This should be the reason for higher removal efficiency of COD in the CW units with charcoal layers.

At last, analysis of variance (ANOVA) test was carried out to find whether there is a significant effect of time on COD removal efficiency in CW units and it was found to be different with time for 95% confidence interval.

### 3.3 Nitrogen Removal

There was no difference in effluent TN in planted CW units for first 40 days and it was closer to zero. After 40 days it increased rapidly. In contrast unplanted CW unit had high effluent loading rate from the beginning and it was same even after 40 days. Nitrogen plant uptake was high until it became mature. That was the main reason to have very less TN in the effluent within first 40 days.

The highest TN, TKN, $NH_4$-N, Organic-N, $NO_3$-N and $NO_2$-N were recoded from $CW_{C0}$ unit. Those values were 79%, 79%, 82%, 69%, 71%, and 80% respectively. $CW_{C2}$ unit was the next and it was followed by $CW_{C1}$ unit and then fourth (WContral) as shown in Table 1. There was high removal efficiency in inorganic nitrogen compound such as $NH_4$-N, $NO_2$-N rather than organic nitrogen compound.

Because cattail plant readily uptake by inorganic-nitrogen compounds. Thus Organic nitrogen can be removed mainly by microbial actions. As suspended or attached growth microbial organisms play a significant role in biodegradation process of the CW units, the emergent plants provide supports of the boifilm growth and releases oxygen via the root system. (Reed et al.,[8], Polprasert et al.,[6]). TKN removal efficiency depends on both $NH_4$-N and organic -N contents. Table 1 shows that removal efficiency of $NH_4$-N is higher than that of organic-N. Thus $NH_4$-N removal is highly affected for TKN removal efficiency rather than organic-N.

### 3.4 Nitrogen Plant Uptake

Biomass of each CW units, after 4 months period were found to be 49.10, 58.94 and 64.53 ton/ ha in $CW_{C1}$, $CW_{C2}$ and $CW_{C0}$ respectively. It was 10.68 ton/ha for the initial period. Roots and leaves plus stem were separately analyzed for TN in each CW unit by taking two plants per CW unit. Results are illustrated in Table 2 below. It shows that Root and leaves took 1.4-1.92% and 8.7-10.5% of TN respectively and came up with a total TN uptake of 10-12% from the TN input. Breen [5] studied nitrogen mass balance in vertical flow CW units fed with domestic wastewater and reported 55% of nitrogen uptake by cattail plant. Compared to this value (55%), obtained TN uptake by plants in this study (10-12%) was very small since Cr in the inlet was greatly affected.

### 3.5 Effect of Cr for nitrogen uptake by cattail.

The dry biomass and TN content in the cattail plants at the initial period (before spiked Cr) of operation and after four months of operation were analysed. Accumulated nitrogen in Cattail plants and its uptake rates by the plants in all three wetlands are shown in Table 2.The data shows the estimated nitrogen uptake rates as 1.4-2kg/ha/day for all the CW units which received wastewater containing Cr. This range is lower than those reported CW units treating only the domestic wastewater 4.5-4.9kg/ha/day (Lim et al., [4]), 3.0 kg/ha/day (Koottatep and Polprasert, [9]) and 1.6-7.2kg/ha/day(Reddy and DEBusk,1987). Hence Cr exerted some inhibitory effect on the uptake on nitrogen by cattail plant.

Variation of COD and $NH_4$-N efficiencies with respect to the spiked Cr concentration in each CW unit are depicted in Figure 4 above. These results illustrate that, for all CW units, there was a slight decline of COD removal efficiency in the high Cr concentration (100mg/L). However, for less Spiked Cr concentrations, there was no observed effect on the COD removal efficiency.

**Table 1- Nitrogen removal efficiencies**

| Parameter | $CW_{C1}$ Mean (mg/L) | $CW_{C1}$ Removal ( % ) | $CW_{C2}$ Mean (mg/L) | $CW_{C2}$ Removal ( % ) | $CW_{C0}$ Mean (mg/L) | $CW_{C0}$ Removal ( % ) | $CW_{Control}$ Mean (mg/L) | $CW_{Control}$ Removal ( % ) |
|---|---|---|---|---|---|---|---|---|
| TN | 6.99 | 69±9 | 5.13 | 77±7 | 4.76 | 79±8 | 11.09 | 45±5 |
| TKN | 6.63 | 70±10 | 4.85 | 77±7 | 3.88 | 79±8 | 10.63 | 45±5 |
| $NH_4$-N | 3.97 | 73±11 | 3.06 | 79±9 | 2.33 | 82±9 | 6.71 | 51±7 |
| Organic-N | 2.66 | 58±9 | 1.77 | 69±10 | 1.55 | 69±8 | 3.92 | 30±5 |
| $NO_3$-N | 0.22 | 50±10 | 0.19 | 55±11 | 0.12 | 71±9 | 0.22 | 48±11 |
| $NO_2$-N | 0.06 | 67±8 | 0.04 | 74±06 | 0.03 | 80±5 | 0.06 | 58±14 |

**Table 2- Plant uptake rate of Nitrogen**

| Consortium | Initial period ( Before spiked chromium) | | | 4- months after | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $CW_{C1}$ | | | $CW_{C2}$ | | | $CW_{C3}$ | | |
| | leaves | root | total | leaves | root | total | leaves | root | total | leaves | root | total |
| Dry biomass ( ton/ha) | 6 | 4 | 11 | 37 | 12 | 49 | 49 | 10 | 59 | 52 | 12 | 64 |
| N content (kg/ton) | 5 | 3 | - | 5 | 4 | - | 4 | 4 | - | 3 | 3 | - |
| N storage ( kg/ ha) | 33 | 14 | 48 | 172 | 45 | 217 | 200 | 37 | 236 | 177 | 42 | 220 |
| N plant uptake rate (kg/ha.4month) | | | | 139 | 30 | 169 | 167 | 22 | 189 | 144 | 28 | 172 |
| N plant uptake rate ( kg/(ha. day) | | | | 1.16 | 0.25 | 1.41 | 1.39 | 0.19 | 1.57 | 1.20 | 0.23 | 1.44 |
| % of TN input | | | | 8.72 | 1.92 | 10.63 | 10.48 | 1.40 | 11.88 | 9.08 | 1.76 | 10.84 |

Average
TN input = 13.25 kg/ha.day

$NH_4$-N removal efficiency was observed to be deteriorated rapidly with increasing Cr concentration in planted CW units. Among these three units, one with the highest charcoal in the wetland bed ($CW_{C2}$) gave less deterioration compared to other two. In contrast, gradient of the $NH_4$-N with Cr concentration in unplanted CW unit ($CW_{Control}$) was not considerable compared to other three. Thus from the above observations it can be concluded that there is a significant effect on Cr to plant uptake of $NH_4$-N while increasing the Cr concentration.

Lim et al [4] reported that the efficiency of $NH_4$-N removal in both horizontal free water surface and subsurface flow CW systems deteriorated with increasing Cu loading, whereas the removal efficiency of COD was particularly unaffected. Recently, Lim et al [3] experienced the same results with four lab scale subsurface flow CW units for Zn, Pb and Cd as well. There the range of metal concentration considered was up to10 mg/L and flow rate was limited to 25ml/min

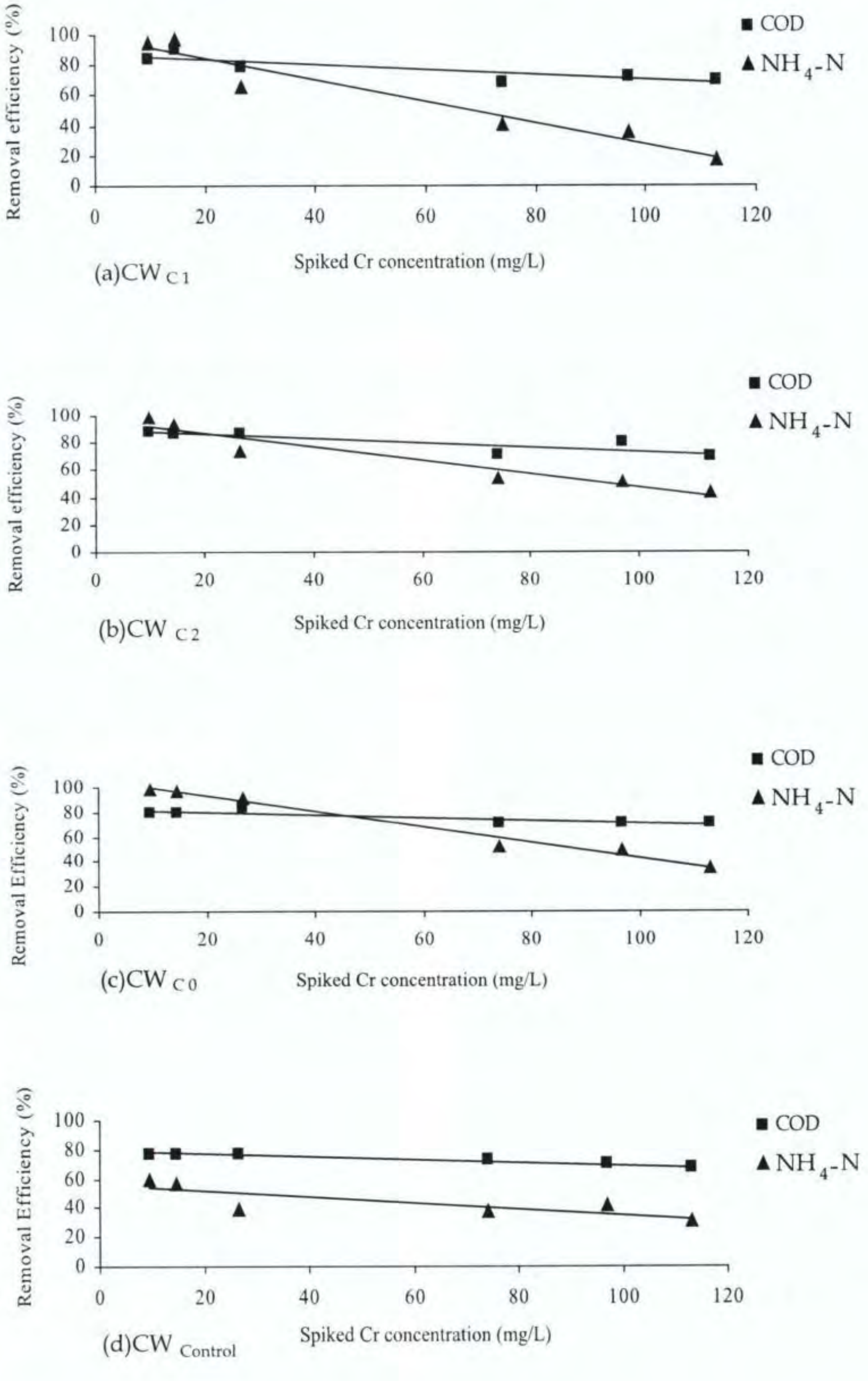


**Figure 4 - Variation of $NH_4$-N and COD removal efficiencies Vs Spiked Cr**

## 4. Conclusions

Based on the findings of this study, following conclusions can be drawn:

- CW units which consisted of charcoal layers as wetland bed material, perform differently in treating COD. Further both CW units with thick and thin charcoal layers in the bed media gave the higher mean COD mass removal efficiencies, 91.7% and 90.3% respectively during the experimental period.

- The total nitrogen removal efficiency deteriorated rapidly with increasing Cr. In contrast, there was essentially no observed effect on the COD removal efficiency within the range of the metal loading applied.

- All CW units met Cr effluent standard of 2mg/L when the influent concentration was about 30mg/L. However among the planted CW units, the one with thick charcoal layer was tally with effluent standard of 2 mg/L even for influent Cr concentration was 100mg/L .

- Vertical flow constructed wetland is one of the best option in treating industrial wastewater containing Cr (Tannery, Electroplating etc.. as a secondary treatment process.

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