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STUDIES OF REMOVAL OF CHROMIUM BY MODEL CONSTRUCTED WETLAND

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Abstract - Chromium is a pollutant present in tannery wastewater, its removal is necessary for protection of the environment. *Penisetum purpureum*, *Brancharia decumbens* and *Phragmites australis* were grown hydroponically in experimental gravel beds to determine their potential for the phytoremediation of solutions containing 10 and 20 mg Cr dm^{-3}. These concentrations, similar to tannery wastewater after initial physico-chemical treatment were used with the aim of developing an economic secondary treatment to protect the environment. All the systems achieved removal efficiencies of 97 – 99.6% within 24 hours. *P. purpureum* and *B. decumbens* removed 78.1% and 68.5% respectively within the first hour. Both *P. purpureum* and *B. decumbens* were tolerant of the concentrations of chromium applied, but *P. purpureum* showed the greatest potential because its faster growth and larger biomass achieved a much greater chromium removal over the whole length of time of the experiment.
Keywords: Chromium; Constructed wetland; Phytoremeditation; *Penisetum purpureum*; *Branchiaria decumben*; Tannery wastewater.

INTRODUCTION

Brazil is one of the five biggest producers of leather in the world, Rio Grande do Sul, in the south of Brazil is the principal state with 185 factories producing fourteen million skins per year, which results in approximately 14 million cubic metres of tannery wastewater per year (Koetz et al., 1995). Tannery wastewaters are characterized by being strongly alkaline with a high oxygen demand and a high salt content, one of which is chromium (Bajza and Vrcek, 2001). Nowadays chrome tanning is favoured by the majority of the leather industry because of the speed of processing, low cost, colour of leather and greater stability of the resulting leather (Hafez et al., 2002). However, uptake of the chromium into the leather is not complete and relatively large amounts are found in the effluent. Estimates range from 2,000 – 3,000 mg dm^{-3} (Bajza and Vrcek, 2001) to 3 – 350 mg dm^{-3} (Vlyssides and Israilides, 1997).

If these wastewaters are not treated before discharge they can cause serious environmental pollution. Treatment of these wastewaters is expensive, so many poorer countries only employ an initial treatment. Primary treatment may employ biological, oxidation or physico-chemical processes. These treatments though often still leave chromium levels in the wastewater above the legal discharge limit for surfaces waters, which in Brazil is 0.5 mg dm^{-3} (Alves et al., 1993). Therefore in the case of chromium further treatment is often required. Ion exchange resins (Kocaoba and Akcin, 2002), reverse osmosis (Hafez et al., 2002) and an electrolysis system (Vlyssides and Israilides, 1997) have all been investigated as methods of further purification. These methods however, are expensive and are often

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not considered cost effective for small sized tanneries. The phytoremediation of soils polluted with tannery effluent using trees with tolerant mycorrhizal fungi has been investigated by Khan (2001), and is thought to have potential.

This paper investigates the potential of a constructed wetland for the phytoremediation of chromium directly from the wastewater after the primary treatment. Two tropical species, *Penisetum purpureum* and *Branchiaria decumbens*, and a global species, *Phragmites australis* were tested in the system. The rate of reduction of chromium from the liquid and the tolerance of the plants to chromium were studied using small experimental units in order to assess the potential of larger constructed wetland systems for the phytoremediation of chromium from tannery wastewaters.

MATERIALS AND METHODS

Experimental Wetland

The experimental wetland systems each consisted of two 30 litre square tanks. The upper tank contained five centimetres of 25mm gravel in the base followed by 15 cm of 10mm gravel. The lower tank contained the treatment solution, which was pumped onto the gravel bed at a rate of three litres per minute in a two hours on, half an hour off regime. The upper tank had an exit pipe near the base, through which the treatment solution returned to the lower tank to achieve a continuous re-circulating system (Figure 1). Four wetland systems were constructed, one was a control, containing no plants, the other three were planted up with one of three species under investigation, *P. purpureum*, *B. decumbens* or *P. australis*. The systems were then irrigated with primary settled sewage for two months to allow the plants to establish and for a healthy biofilm to develop on the gravel and roots. The experiment was carried out in a glasshouse to achieve the tropical environment found in Brazil.

Experimental Procedure

The wetlands were irrigated with a nutrient (Long Ashton) solution at one-quarter strength, to achieve a similar strength of nutrients to that of primary settled wastewater, this was amended with chromium at 10 and 20 mg dm^{-3}. These two concentrations were chosen because in Portugal the concentration of chromium found in tannery effluents after physico-chemical treatment is between 5 and 20 mg dm^{-3} (Alves et al., 1993). A stock solution of 1,000 mg dm^{-3} chromium was prepared from $CrK(SO_4)_2 12H2O$. Chromium (III) sulphate was used in the experiment because this is the salt used in tanning. A suitable volume of this stock was then added to each tank to give 10 or 20 mg dm^{-3}.

The experiment ran for eight weeks. Each week fresh nutrient solutions were prepared. On day one of each week the nutrient solution was amended with 10 mg dm^{-3} of chromium. Samples of the effluent were then taken at regular intervals for the first six hours and then first thing the next morning, the samples were acidified with 2 cm^3 of concentrated nitric acid. On day two another 10 mg dm^{-3} of chromium was added to the tanks and samples were again taken throughout the day and acidified. For the last three weeks on the second day of each weekly experiment 20 mg dm^{-3} was added in order to subject the plants a greater toxicity and to try to attain saturation capacity of the model system.

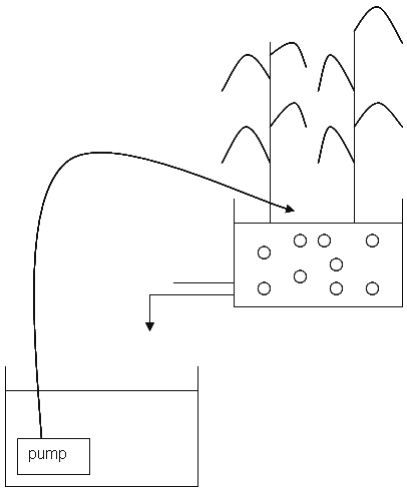

Figure 1: Diagram of the model constructed wetland system.

Analysis of Experiment

The treatment solution samples were analysed for chromium on an atomic absorption spectrophotometer (Pye Unicam SP9). At the end of the experiment the plants were harvested, dried at 105°C, samples (1g aerial parts and 0.3g for the roots) were then digested in 10 cm^3 concentrated nitric acid in a warm (60°C) water bath for two hours, filtered through a Whatman 540 filter paper, made up to volume and then analysed on the atomic absorption spectrophotometer.

The amount of chromium which had been adsorbed or absorbed to the gravel or the biofilm on the gravel was examined by digesting a sample of gravel (50g) in 50 cm^3 of 1 M HNO_3 acid in a warm (60°C) water bath for two hours, filtered, made up to volume and analysed by atomic absorption spectrophotometry.

Statistical analysis of the data was carried out using MINITAB (MINITAB Inc. USA, release 13.1). Statistical differences between treatments were determined by analysis of variance. Results were considered significant at $p<0.05$.

RESULTS

Removal of Chromium from the Treatment Solution

In both the 10 and 20 mg dm^{-3} experiments and throughout the eight weeks of experimentation the removal of chromium from the solution by each wetland system followed a similar pattern of decline. As an example Figure 2 shows the data from the 10 mg Cr dm^{-3} application on week 7. The efficiency of the different wetlands was examined firstly by studying the percentage reduction of chromium in the water phase in the first hour, and secondly by the time taken to decrease to below the environmental limit of 0.5 mg dm^{-3} (Alves et al., 1993).

Analysis of the percentage reduction in chromium after one hour in all of the 10 mg dm^{-3} experiments shows that there is no difference in the performance between *P. purpureum* (78.1%) and *B. decumbens* (68.5%), and that these two species performed significantly better than *P. australis* (56.7%) and the control (47.2%). There was no significant difference in performance in the first hour of the experiment between these latter two systems. When the systems were sampled the next day (24 hours) all had achieved removal efficiencies of 97 – 99.6%. Similar results were obtained for the 20 mg Cr dm^{-3} solutions.

The time taken for the chromium to be reduced to below the environmental limit of 0.5 mg dm^{-3} is an important factor to consider, as an increase in time would indicate that the system could be reaching its capacity to retain the metal. It is clear from the data (Table 1) that in the control and the *P. australis* systems the time taken to reach the environmental limit does increase. In the other two systems an increase in time is not readily obvious. In addition these two systems did not take any longer to reduce 20 mg dm^{-3} of chromium than they did for the 10 mg dm^{-3}.

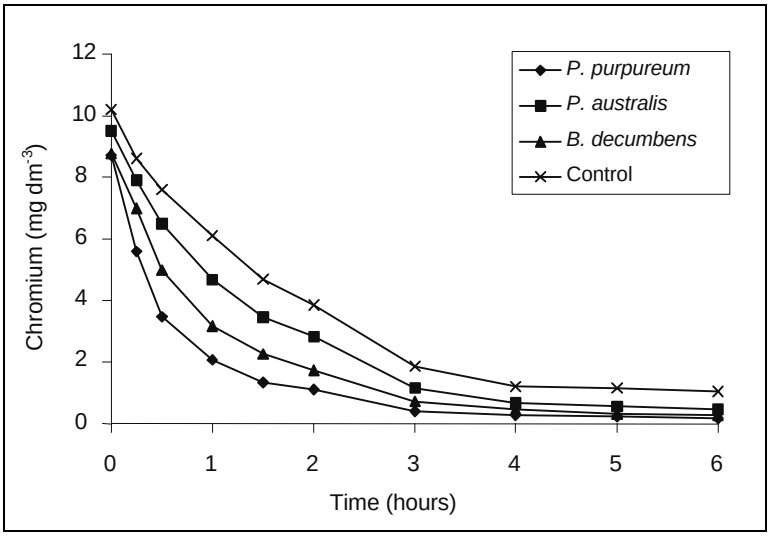

Figure 2: Reduction of chromium in the treatment solution with time. Results displayed are from the 10 mg Cr dm^{-3} experiment in the penultimate week of the experiment.

Table 1: Time taken for the concentration of chromium in the solution to reach the environmental quality standard of 0.5 mg dm^{-3}.

Weeks	Chromium solution	*P. purpureum*	*B. decumbens*	*P. australis*	Control
1	10 mg dm^{-3}	2h 40min	4h 30min	4h 40min	5h
2	10 mg dm^{-3}	1h 55min	3h	3h 30min	5h 20min
2	10 mg dm^{-3}	1h	1h 20min	5h 50min	>6h
3	10 mg dm^{-3}	2h 45min	3h 15min	4h 20min	5h 45min
4	10 mg dm^{-3}	2h 30min	3h 40min	4h	2h 50min
4	10 mg dm^{-3}	50min	3h 30min	4h	4h 40min
5	10 mg dm^{-3}	2h 50min	4h	4h 45min	4h 50min
5	10 mg dm^{-3}	1h 25min	2h 35min	>5h	>5h
6	10 mg dm^{-3}	3h 30min	5h	6h 30min	>7h
6	20 mg dm^{-3}	4h	4h	6h 15min	7h 30min
7	10 mg dm^{-3}	2h 55min	4h	6h	>6h
7	20 mg dm^{-3}	2h 55min	3h	>6h	>6h
8	10 mg dm^{-3}	3h 30min	3h 30min	6h	>6h
8	20 mg dm^{-3}	3h	3h 30min	7h	>6h

Accumulation of Chromium in the Plants

The concentration of chromium in the plants and whether they appear healthy or not can indicate the tolerance of that plant to the metal concerned, and therefore their potential for phytoremediation. *P. australis* had a significantly greater concentration of chromium in its leaves and stems than *P. purpureum* and *B. decumbens* (Table 2). *P. australis* however did not thrive in the system and although it did not exhibit the classical signs of chromium toxicity (Sharma et al., 2003) it was not healthy and did not grow well. This fact is reflected in the chromium content, the concentration multiplied by the dry weight of the plant biomass in each experimental system (Table 3). Both the leaf and stem biomass of the *P. purpureum* contained significantly more chromium than the plants in the other systems. The biomass of the aerial parts of *B. decumbens* contained significantly more chromium than that of *P. australis.* The concentration of chromium in the roots of *B. decumbens* was significantly greater than that found in the roots of *P. purpureum*. The *P. purpureum* however removed significantly more chromium because of its greater root mass.

Table 2: Concentration (µg g-1 dry weight) of chromium in the plant tissues in each of the three planted wetland systems. Values followed by the same letter within each row are not significantly differrent from each other at p<0.05. Standard errors of the means are given in brackets. (n = 3).

Plant tissues	*P. purpureum*	*B. decumbens*	*P. australis*
Leaves	6.404^{b} (0.505)	4.618^{b} (0.15)	12.863^{a} (1.83)
Stems	1.995^{b} (0.094)	5.478^{b} (0.504)	15.505^{a} (1.635)
Roots	925.0^{b} (46.87)	1694.5^{a} (44.74)	406.2^{c} (33.295)

Table 3: Content (mg) of chromium in the whole plant biomass of each of the three planted wetland systems. Values followed by the same letter within each row are not significantly differrent from each other at p<0.05. Standard errors of the means are given in brackets. (n = 3).

Plant tissues	*P. purpureum*	*B. decumbens*	*P. australis*
Leaves	1.994^{b} (0.1905)	0.782^{b} (0.025)	0.170^{a} (0.046)
Stems	1.196^{b} (0.056)	0.848^{b} (0.078)	0.380^{a} (0.04)
Roots	182.83^{a} (9.26)	55.36^{b} (1.46)	13.42^{c} (1.098)

Chromium Partitioning in the Wetland System

At the end of the experiment the amount of chromium remaining in the solutions at the end of each week (concentration x litres remaining in the tank) were summed, and the amount (concentration x mass) found on the gravel and in all the plants for each experimental system were calculated and are displayed as percentages in Table 4. Both *P. purpureum* and *B. decumbens* cleaned up the solution to a similar level. Only 0.6% and 0.7% respectively of the total chromium added over the eight-week experiment was accounted for in the water phase. In the *P. purpureum* system a greater proportion of chromium was accounted for in the plant biomass than in the *B. decumbens* system (32% and 9% respectively). In the *P. purpureum* system the gravel only contained 67.4% of the chromium compared to 90.3% in the *B. decumbens* system suggesting that there will be more capacity for chromium removal remaining in the *P. purpureum* system than in the *B. decumbens* system, therefore, it should have a longer useful lifetime.

Table 4: Partitioning of the chromium within the wetland system.

Wetland system	Plant	Gravel	Solution
P. purpureum	32%	67.4%	0.6%
B. decumbens	9%	90.3%	0.7%
P. australis	2%	96.5%	1.5%
Control	0	97.8%	2.2%

DISCUSSION

Phytoremediation by the Experimental Systems

The wetland system currently under investigation might not match ion exchange resin treatment (Kocaoba and Akcin, 2002) for speed (20 minutes) of treatment, but the *P. purpureum* and *B. decumbens* systems achieved a similar percentage removal (95%) in 3 – 4 hours, and up to 99.6% within 24 hours.

The potential of other biological systems to remove chromium from wastewaters have been investigated. Alves et al. (1993), using pine bark achieved 90% removal in 16 hours. Soltan and Rashed (2003), using water hyacinths growing hydroponically in culture solutions containing a mixture of metals at 10 mg dm^{-3} achieved removal of only 17.5% of the chromium in 24 hours. The superior removal efficiency and speed of chromium removal achieved by the two tropical grasses in the experimental constructed gravel wetlands currently under investigation is clear. This type of system may therefore have the potential to aid in the cleaning of tannery wastewaters in poorer countries.

Although this work was conducted on nutrient solutions containing chromium, in the UK constructed gravel *P. australis* beds have been used for many types of wastewater and are considered to be fairly robust. The parameters (BOD, COD, Cl^- and NH_4^+) of tannery wastewater (Vlyssides and Israilides, 1997) are broadly similar to the parameters of landfill leachate (Tyrrel et al., 2002) and it has previously been suggested (Jenssen et al., 1994) that constructed ponds and wetlands treating landfill leachate have a high treatment efficiency. Therefore, having shown that these tropical grasses can withstand the concentration of chromium expected in the tannery wastewater these systems should be healthy enough to be able to reduce the BOD and COD in this wastewater as well.

Chromium Tolerance of the Plants

97 – 98% of all the chromium taken up by the plants during the experiment remained below ground, in/on the roots. The amounts taken up into the aerial parts constitute increased concentrations compared to quoted (Allen et al., 1974) normal concentrations (0.05 – 0.5 μg g^{-1}).

Chromium toxicity is thought to be caused by the reaction of the chromium with reducing agents, such as NAD(P)H, which in turn react with H_2O_2 to generate damaging ·OH radicals as well as chromium reacting with the carboxyl and sulfhydryl groups of enzymes thereby inhibiting their activity (Cervantes et al., 2001). The ability of a plant to minimise these effects and thereby withstand greater concentrations indicates a plants tolerance to the metal. Phytotoxicity thresholds are usually quoted as a percentage of growth inhibition. Comparisons of the phytotoxicity thresholds of some other grasses with the chromium concentrations found in the grasses currently under investigation suggests that they

might exhibit an enhanced tolerance to chromium. Barley seedlings exhibited a 40% growth inhibition when grown in a solution containing 5.2 mg Cr dm^{-3} (Cervantes et al., 2001). Maize exhibited 50% growth inhibition at tissue concentrations of 5.9 mg Cr kg^{-3} (Chang et al., 1992). *P. purpureum* and *B. decumbens* exhibited similar leaf tissue concentrations (6.4 and 4.6 mg Cr dm^{-3} respectively) and were growing in a more concentrated solution of chromium, but they were still growing healthily. This suggests that these two grasses may therefore be suitable for phytoremediation of wastewaters containing chromium. The *P. australis* never looked healthy in the system, it was initially thought that it was not suited to the tropical temperatures in the greenhouse. However it is more likely that the 12.8 mg Cr dm^{-3} found in its leaves was above its phytotoxicity threshold. Therefore *P. australis* is not suitable for the phytoremediation of chromium in a tropical environment.

The ability of the plants to stay healthy and therefore continue to grow is an important factor in the choice of plants for phytoremediaton. A plant will only take up the metal to any great extent if it is growing, and it will only grow if it can tolerate the concentration of metal in the media in which it is growing. Although phytoremediaton of the solution was achieved by both tropical grasses, *P. purpureum* is favoured over *B. decumbens* for use in the system because its much greater growth rate and biomass production removed a greater amount of chromium.

CONCLUSION

Although further treatment of tannery wastewater after initial physico-chemical treatment, using methods such as ion exchange (Kocaoba and Akcin, 2002) or reverse osmosis (Hafez et al., 2002) are efficient; they are however, in terms of energy and/or chemicals used considered expensive. Therefore for small factories these treatments are often not considered to be commercially viable (Khan, 2001). This current research indicates that a biological system such as the constructed wetland under investigation, using *P. purpureum*, could achieve the same, or similar levels of clean up. Biological systems such as constructed wetlands are often very cost efficient (Jenssen et al., 1994). Therefore the development of this experimental system into a large-scale working unit offers an attractive proposition for poorer countries needing to protect their environment.

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REFERENCES

Allen, S.E., Grimshaw, H.M., Parkinson, J.A., Quarmby, C., 1974. Chemical Analysis Of Ecological Materials. Blackwell Scientific Publishing, Oxford. Pp 314.

Alves, M.M., Gonzalez Beca, C.G., Guedes De Carvalho, R., Castanheira, J.M., Sol Pereira, M.C., Vasconcelos, L.A.T., 1993. Chromium Removal In Tannery Wastewaters 'Polishing' By Pinus Sylvestris Bark. Water Research 27(8), 1333-1338.

Bajza, Z., Vrcek, I.V., 2001. Water Quality Analysis Of Mixtures Obtained From Tannery Waste Effluents. Ecotoxicology And Environmental Safety 50, 15-18.

Cervantes, C., Campos-Garcia, J., Devars, S., Gutierrez-Corona, F., Loza-Tavera, H., Torres-Guzman, J.C., Moreno-Sanchez, R., 2001. Interactions Of Chromium With Microorganisms And Plants. Microbiology Reviews 25, 335-347.

Chang, A.C., Granato, T.C., Page, A.L., 1992. A Methodology For Establishing Phytotoxicity Criteria For Chromium, Copper, Nickel And Zinc In Agricultural Land Application Of Municipal Sewage Sludges. Journal Of Environmental Quality 21(4), 521-536.

Hafez, A.I., El-Manharawy, M.S., Khedr, M.A., 2002. RO Membrane Removal Of Unreacted Chromium From Spent Tanning Effluent. A Pilot-Scale Study, Part 2. Desalination 144, 237-242.

Jenssen, P.D., Maehlum, T., Roseth, R., Braskerud, B., Syversen, N., Njos, A., Krogstad, T., 1994. The Potential Of Natural Ecosystem Self-Purifying Measures For Controlling Nutrient Inputs. Marine Pollution Bulletin 29(1-6), 420-425.

Khan, A.G., 2001. Relationships Between Chromium Biomagnification Ratio, Accumulation Factor, And Mycorrhizae In Plants Growing On Tannery Effluent-Polluted Soil. Environmental International 26, 417-423.

Kocaoba, S., Akcin, G., 2002. Removal And Recovery Of Chromium And Chromium Speciation With MINTEQA2. Talanta 57, 23-30.

Koetz, P.R., Faria, O.L.V., Nunes, W.A., 1995.

Tratamento De Efluentes Homogeneizados De Curtume Por ' IJ H-W Anaeróbia Em Reatores De Fluxo Ascedente. Review Brásil AGROCIÊNCIA 1(1), 23-29.

Sharma, D.C., Sharma, C.P., Tripathi, R.D., 2003. Phytotoxic Lesions Of Chromium In Maize. Chemosphere 51, 63–68.

Soltan, M.E., Rashed, M.N., 2003. Laboratory Study On The Survival Of Water Hyacinth Under Several Conditions Of Heavy Metal Concentrations. Advances In Environmental Research 7, 321 – 334.

Tyrrel, S.F., Leeds-Harrison, P.B., Harrison, K.S., 2002. Water Research 36(1), 291-299.

Vlyssides, A., Israilides, C.J., 1997. Detoxification Of Tannery Waste Liquors With An Electrolysis System. Environmental Pollution 97(1-2), 147-152.