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Removal of Chromium (III) from Tannery Wastewater by Bioaccumulation Method Using *Vallisneria sp.* River-weed

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Abstract

The presence of chromium (III) in the wastewater is one of the major concerns for the tannery industry in Bangladesh. In this study the removal of chromium (III) from tannery effluent has been carried out by bioaccumulation method using abundantly available *Vallisneria sp.* river-weed in river all over Bangladesh. Various factors influencing the uptake of chromium, viz., quantity of river-weed, concentration of chromium (III), pH of the solution and duration of treatment have been optimized. Chemical modifications of the river-weed through pretreatment with H_2SO_4, $CaCl_2$ and $MgCl_2$ showed improved removal efficiency of chromium (III). Langmuir isotherm has been fitted for 0.5 g of river-weed. The dynamic method of treatment of protonated river-weed with a chromium (III) solution at a pH of 3.2 for duration of 4 days gave the maximum uptake of about 81%. A similar uptake has been established for commercial chrome tanning wastewater. In addition, the potential reuse of chromium-containing river-weed for the preparation of basic chromium sulfate (tanning agent) has been demonstrated.

Key words: Chromium (III), Bioaccumulation, *Vallisneria sp.*, River-weed, tannery Wastewater.

I. Introduction

In Bangladesh there are about 170 tannery units located at Hazaribagh of Dhaka city in only 50 acres of land, popularly known as tannery estate, beside the river Buriganga [1]. These industries use tanning agent (basic chromium sulfate) for leather processes and release chromium containing wastewater in the river Buriganga. Therefore, these industries have gained negative image in society with respect to its pollution potential and therefore facing a severe challenge. Chromium has low, acute and chronic toxicity to humans at high doses. Chromium in its trivalent form is an essential trace element when present in micro level [2], whereas the same element when present in excess is proven to be a potential soil, surface water, groundwater, and air contaminant under specific conditions [3]. Although the oxidation state of chromium in the basic chrome sulfate is only trivalent, discharge norms do not specify the redox states, because of concerns about the possible conversion of the trivalent state to the more toxic hexavalent form [4, 5].

There are many chromium removal methods have been developed by many researchers. These methods include precipitation[6-8], ion exchange [9-12], membrane technologies [13-15], and adsorption by several types of adsorbent [16-20], such as activated charcoal, bone charcoal, and waste activated sludge [21,22]. Most of these materials and methods suffer from drawbacks such as high capital or operational cost. Therefore, there is a need for the development of a methodology with low cost, easily available material by which chromium can economically be removed from tannery wastewaters. The use of natural resources for the removal of chromium is being looked upon by researchers in presence to the other conventional methods. The application of water hyacinth weeds, treated sawdust, brown seaweed biomass, seaweed, and coconut shell as adsorbents for the removal of chromium from wastewaters was reported earlier [22-24]. The potency for accumulating metal ions by certain types of dead biomass was well established over the last two decades. Biological materials, both living and dead, are capable of removing heavy metal ions from solutions through a process involving number of diverse mechanisms collectively known as biosorption [25].

This work aims at the removal of chromium (III) from the tannery wastewater by abundantly available river-weed, *Vallisneria s*. The present study also aims to develop a suitable methodology to maximize the removal efficiency of chromium by the river-weed from the wastewater and to find a suitable means to recovery of chromium from river-weed.

II. Experimental

River-weed *Vallisneria sp.* was collected from Kumar River, Muksudpur, Gopalganj as shown in Fig. 1. Then the river-weed was washed with distilled water thoroughly to remove dirt and other debris materials. The washed river-weed was then shade-dried and stored in an air tight pack to prevent moisture absorption. The moisture content of the dried river-weed was estimated and was found to be 7±1%. Deionized water was used throughout the work. The industrial wastewater samples were collected from Apex Tannery Dhaka, Bangladesh.

Preparation of synthetic Chrome tanning solution

A stock solution containing 1000 mg/L of river-weed was prepared using commercial basic chromium sulfate, $Cr_2(SO_4)_3$. $12H_2O$. The pH was adjusted to be 3.0-3.5, and the solution was aged for 12 h and stored in a refrigerator (4 °C) temperature. For further experiments, the requisite quantity was taken from the stock solution and made up to the required volume. The pH of the synthetic chromium (III) solution was adjusted accordingly by using either 0.05M H_2SO_4 or 0.05 M NaOH solution.

Pretreatment of Vallisneria sp river-weeds

The river-weeds were pretreated with various chemicals before contacting them with synthetic chromium (III) solution in attempts to increase their uptake efficiency. The air dried river-weed was treated with 0.2 M H_2SO_4, a 0.25 M solution of $CaCl_2$, and a 0.25 M solution of $MgCl_2$ for a period of 10 min under stirring [26]. The acid, calcium ion, and magnesium ion treated river-weed was then washed

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twice with deionized water. Finally, the washed materials were air dried and kept in an airtight pack for further experiments.

Fig. 1. River-weed **(***Vallisneria sp.).*

Adsorption procedure

To optimize the maximum uptake conditions for chromium, five trial experiments were carried out for each pretreated sample at varying time intervals. A 50 mL aliquot of 150 mg/L chromium (III) was taken in a 100 mL conical falsk for each trial. Pretreated river-weed was added to each flask and agited in a mechanical shaker. The amount of chromium (III) remaining in the solution was determined using an Atomic Absorption Spectroscopy (Analyst 800, Perkin Elemer, USA).

Equilibrium Studies

Langmuir adsorption isotherms have been tested for the validity of the chromium (III) uptake behavior of the river-weed. Adsorption isotherms were determined by the treatment of 0.25, 0.5 and 1.0 g of protonated river-weed with 50 mL of 100 mg/L chromium (III) for a contact time of 4 days in a mechanical agitator, respectively. After agitation, the contentents of the flasks were decanted. The concentration of chromium (III) remaining in the solution was determined by Atomic Absorption Spectroscopy

III. Results and discussion

Influence of pH in the uptake of chromium (III)

The removal of chromium (III) with *Vallisneria sp.* river-weed is highly dependent on the pH of the solution which affects the uptake capacity of river-weed. The pH can significantly influence the bio-removal behavior of heavy metals, and there will be an optimum pH for maximum uptake, below or above which decrease in uptake could occur. Therefore, experiments have been carried out to study the uptake of chromium (III) by *Vallisneria sp.* river-weed at varying pH of chromium (III) solution at constant chromium (III) concentration (150 mg/L). The uptake of chromium (III) by *Vallisneria sp.* river-weed at different pH is shown in Fig.2.

It was found that the chromium uptake capacity by river-weed was low at a pH of 2.0. The isoelectric point (i.e. where the overall charge of the surface is neutral) of the river-weed is 3.0.[27] A maximum chromium (III) uptake of 0.116 mg/g of *Vallisneria sp.* occurred at a pH of 3.2. With a further increase in pH to 6, the chromium uptake of river-weed decreases to 0.108 mg/g.

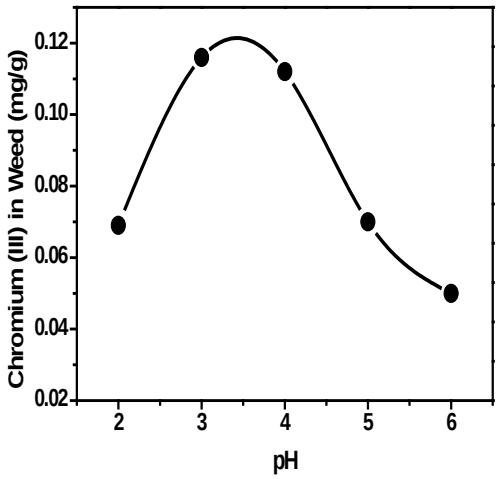

Fig.2. Uptake of chromium (III) from synthetic chromium (III) solution by *Vallisneria sp.* river-weed; Initial concentration of chromium (III): 150 mg/L; Contact time: 4 days.

The bio-removal of chromium from aqueous solution by river-weed was more efficient at a pH around 3.1-3.4. The efficiency of uptake decreased as the pH is shifted above or below this value. The investigation at pH values above pH 6.0 was not possible since chromium precipitation [$Cr(OH)_3$] was occurred. Thus, a pH of 3.2 was maintained in a subsequent-experiment.

Effect of pre-treatment of river-weeds in the uptake efficiency

River-weed is negatively charged and mainly contains carboxylic functional groups [26]. Treatment with sulfuric acid solution not only protonates the charged sites but also replaces the natural mix of ionic species present in the biomass with protons. Volesky has shown that pre-treatment of the brown sea weeds with sulfuric acid and calcium ions resulted in the increase of chromium uptake [27]. This was due to increase of ion exchange, diffusion capability and additional bonding of chromium (III) with pectins, carboxyls of uronic acids, sulfates of carrageenans, xylans, galactans of treated sea weeds. Hence, the present study, river-weed was pre-treated with sulfuric acid, calcium chloride and magnesium chloride respectively before treatment with chromium (III) solution in order to improve chromium (III) uptake.

Experiments with pretreated river-weed

Influence of the quantity of river-weed on the uptake of chromium

The effect of the amount of riverweed on the percentage uptake of chromium for the pretreated river-weed is shown in Fig. 3. The amount of weed used for the treatment studies

is an important parameter as it determines the potential of the material to accumulate chromium for a given initial concentration of the solution.

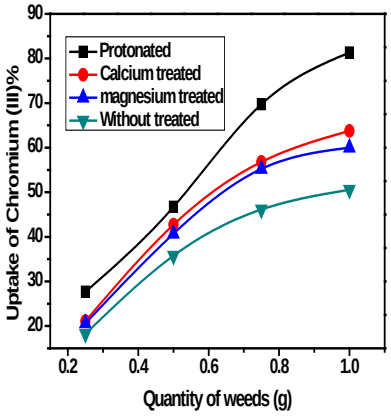

Fig. 3. Percentage uptake of chromium (III) with amounts of *Vallisneria sp.* river-weed; pH: 3.2; Initial concentration of chromium (III): 100 mg/L; Contact time: 4 days

The chromium solution containing effective 150 mg/L in 50 mL was treated with varying quantities of river-weed (0.25-1.0 g). The results as seen from Fig. 3 demonstrated that an increase in the amount of weeds increased the percentage of uptake of chromium. When the quantity of protonated *Vallisneria sp.* river-weed was increased from 0.25 to 0.5g, the uptake increased from 28% to 47%. With a further increase in the quantity of protonated weed, the corresponding increase in the observed uptake of chromium dropped off, leaving off at a maximum of 81% uptake with 1.0 g of protonated river-weed. Calcium and magnesium treated weed revealed a trend similar to that of the protonated weed. However, they showed a lower percentage uptake of chromium of 64 and 60% for calcium and magnesium-treated river-weed, respectively. The uptake of chromium by protonated *Vallisneria sp.* river-weed was generally greater than that for other pretreated weed. Therefore, river-weed pretreated with sulfuric acid (protonated) were selected for adsorption isotherm studies.

Influence of time on the uptake of chromium

The effect of contact time on percentage uptake of chromium by protonated *Vallisneria sp.* samples with chromium solution, with agitation is shown in Fig. 4.

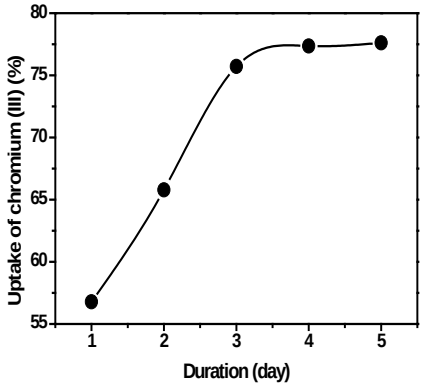

Fig. 4. Effect of time of treatment on the percentage uptake of chromium (III) by *Vallisneria sp.* river-weed; pH: 3.2; Initial concentration of chromium: 100 mg/L; Amount of weed: 1.0 g.

It is clearly observed that uptake of chromium by *Vallisneria sp.* is saturated after 5 days. The maximum percentage of uptake for protonated *Vallisneria sp.* river-weed is found 78%. Fig. 5 shows that, after 5 days treatment, 0.078 mg of chromium is taken up per gram of protonated river-weed.

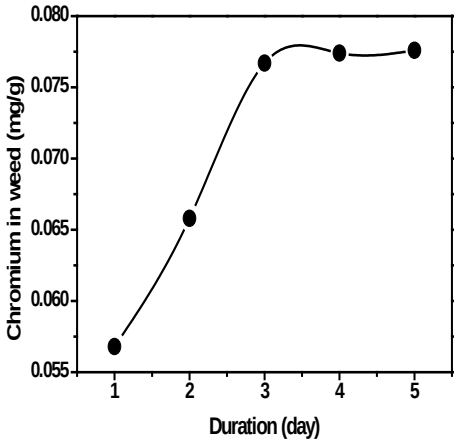

Fig. 5. Effect of time of treatment on the maximum uptake capacity of protonated river-weed; pH: 3.2; Initial concentration of chromium (III): 100 mg/L; Amount of weed: 1.0 g.

Influence of initial concentration of chromium (III) versus uptake

The effect of the initial concentration of chromium on the maximum uptake capacity of river-weed is shown in Fig. 6. Maximum uptake in terms of percentage removal of chromium has been found to be higher at a lower concentration of the solution. However, about 68% uptake efficiency was achieved when the concentration was 10 mg/L. As the concentration was increased, the percentage uptake capacity of river-weed was decreased. The effective amount of chromium (III) taken up by the river-weed in terms of milligram of chromium per gram of river-weed increase with increasing initial concentration of chromium, which is shown in Fig. 7.

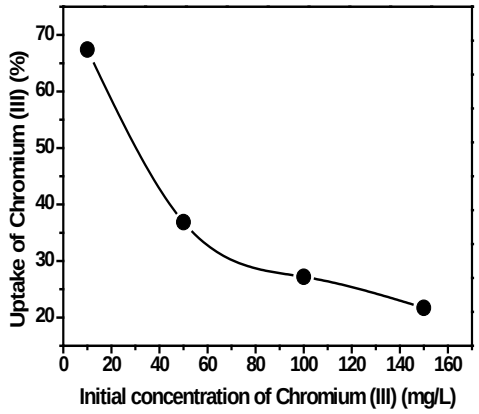

Fig.6. Effect of initial concentration of chromium(III) on the maximum uptake capacity of protonated river-weed; pH: 3.2; Duration: 4 days; Amount of weed: 1.0 g.

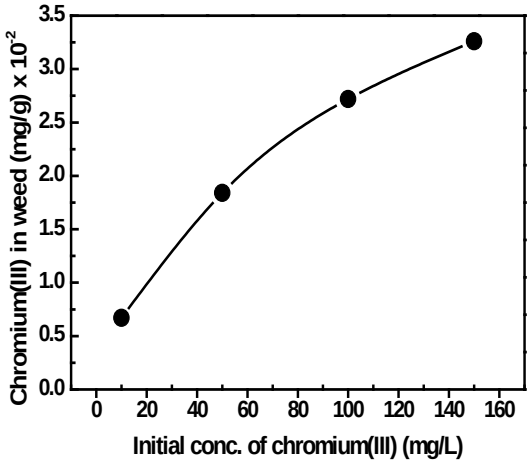

Fig.7. Effect of the initial concentration of chromium (III) in solution on the maximum uptake of chromium for protonated *Vallisneria sp.* river-weed; pH: 3.2; Volume of solution: 50 mL; Amount of weed: 1.0 g.

For an initial concentration of 150 mg/L, the maximum uptake capacity of river-weed is 3.26 x 10^{-2} mg/g by protonated *Vallisneria sp.* river-weed. This clearly indicates that the accumulation of chromium (III) by the river-weed is driven by the concentration of chromium solution.

Equilibrium Studies

The Langmuir adsorption isotherm model assumes that the adsorbed layer will be only one molecule thick. All sides of the adsorbent will have equal affinities for molecules. Thus, the presence of adsorbed molecules at one side will not affect the adsorption of molecules at an adjacent side[26].

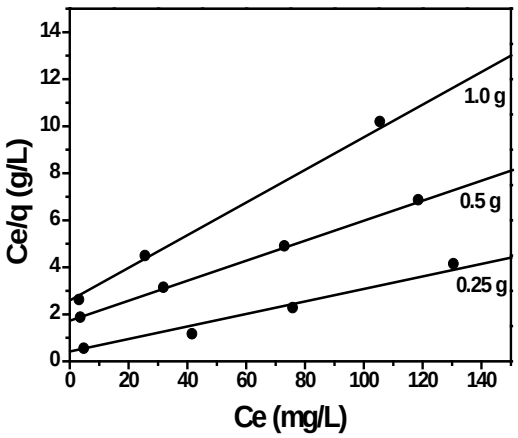

Fig. 8. Effect of the quantity of protonated river-weed used on Langmuir adsorption isotherms (25°C).

Langmuir constants q_0 and b can be determined from the linear plot of C_e/q versus C_e , which has a slop of 1/ q_0 and an intercept of 1/ q_0 b. The linear form of the Langmuir plot is given as

$$C_e/q = 1/ q_0 b + 1/ q_0 \quad (1)$$

The constant q_0 signifies the adsorption capacity (mg/g), and b signifies the energy of adsorption. C_e is the equilibrium concentration of the chromium (III) ion. The values q_0 and b along with the correlation coefficient (R^2) are given in Table 1. Fig. 8 shows the Langmuir plots for protonated *Vallisneria sp.* Species. A linear relation is observed among the plotted parameters, which indicates the applicability of the Langmuir model. From the Table, the sorption capacity (q_0) value of river-weed is 82.2 mg/g when 0.25 g of river-weed was used. The values decrease as the dosage of river-weed increases to 0.5 and 1.0g. A higher value of b implies a strong binding of chromium (III) ions with river-weed.

Table 1. Langmuir constants for chromium (III) adsorption onto protonated river-weed.

Quantity (g)	q_0 (mg/g)	b(L/mg)	Correlation coefficient (R^2)	R_L
0.25	82.2	0.025	0.983	0.211
0.5	38.5	0.065	0.999	0.096
1.0	21.4	0.110	0.990	0.063

The essential features of the Langmuir isotherm can be expressed in terms of a dimentionless constant, separation factor or equilibrium parameter R_L, which is defined as

$$R_L = 1/(1+bC_0) \quad (2)$$

Where b is the Langmuir constant (L/mg) and C_0 is the initial concentration of chromium (III) ion (mg/L). R_L values between 0 and 1 indicate favorable adsorption of the chromium (III) ion on to river-weed. The R_L values obtained in Table 1 indicate that the uptake of chromium (III) by protonated river-weed is a favorable process.

Application of the optimized method for the removal of commercial chromium containing wastewater

Chromium (III) containing wastewater was collected from a tannery (Hazaribagh). The chrome content in the wastewater was found to be 778.0 mg/L, and the pH was ~3.4. Since the chromium (III) concentration of this commercial tannery wastewater is high, chromium removal by river-weed was carried out in five stages (Stage: I-V). Stage-I: In this case, 1.0 g of protonated *Vallisneria sp.* river-weed was added to 100 mL of commercial tannery wastewater. It was agited for a period of 4 days. After 4 days, the river-weed was separated by filtration and the chrome content in the river-weed was measured. Stage-II: The treated liquor was taken to the next stage where the same procedure was followed with a fresh batch of river-weed (1.0 g) and the effluent pH was adjusted to 3.2. Similar treatment procedure was followed up to five stages with new river-weed (1.0 g) (Stage-III-V). In total, five stages of treatments were employed to reduce the concentration of chromium in the wastewater to the stipulated value of 19 mg/L. The concentration of chromium (III) in the treated wastewater after each stage of treatment is shown in Table 2.

Table 2. Concentration of chromium after different stages of treatment and the corresponding removal.

Stages	Chromium concentration		Removal (%)
	Before treatment (mg/L)	After treatment (mg/L)	
1	778	552	29
2	552	287	48
3	287	142	50
4	152	95	37
5	95	19	80

Volume of wastewater; 100 mL; Adjusted pH: 3.2; Amount of adsorbent: 1.0 g; Duration of each stage: 4. 0 days

At an initial concentration the chromium (III) in the wastewater was around 778.0 mg/L, the removal was around 29%. As the stages were increased, the concentration of chromium (III) in the effluent decreased, and as a result the percentage of uptake increased. An uptake of 80% was attained at stage 5, whereby the chromium concentration in the effluent was reduced to 19 mg/L.

Table 3. Desorption of chromium from chromium (III) loaded river-weed.

Conc. of H_2SO_4 (M)	Chromium concentration		Desorption (%)
	Before treatment (mg/L)	After treatment (mg/L)	
1	3.3	3.0	9
2	3.3	2.9	12
3	3.3	2.7	18
4	3.3	2.4	27
5	3.3	1.9	42

Duration of treatment with H_2SO_4: 5. 0 hours

Utilization/disposal of chromium loaded river-weed

A suitable way of disposing of the chrome-bearing river-weed is an important aspect because accumulation the wastewater. The chromium from the river-weed needs to be removed for disposal of river-weed. The removal of chromium (III) from biomass has been carried out with various concentrations of sulfuric acid. The quantity of chromium in *Vallisneria sp.* after acid treatment is shown in Table 3. From the Table, it is clearly seen that 5M H_2SO_4 is more effective compared to the lower concentrations. However, only 42% of the chromium is removed after 5 hours of treatment from *Vallisneria sp.* species.

Possible mechanism of chromium removal by river-weed

The chromium in the wastewater solution exists as highly cationic species [28]. These cationic species of chromium are ionically exchanged for the cationic alkaline earth metal ions present in the river-weed [26]. In addition, there is a

possibility of interaction with chromium at carboxylic functional sites of the river-weed.

IV. Conclusion

The present study clearly indicates the possibility of using *Vallisneria sp.* river-weed as a suitable alternative for the removal of chromium from tannery wastewater. The strategy of using *Vallisneria sp.* river-weed for the removal of chromium from chrome bearing wastewater not only gives a low cost treatment option but also save the aquatic environment from this unabated plants which grow and complete their life cycle in water and cause harm to aquatic environment.

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