

**INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH
TECHNOLOGY****HEAVY METAL REMOVAL FROM ELECTROPLATING EFFLUENT BY
SPIROGYRA SP.****Jaipal*, Asha Gupta, Jitender saini***Deptt of Environmental Science and Engineering Guru Jambheshwar University of Science and
Technology, Hissar, Haryana**ABSTRACT**

The biosorption potential of algal biomass of *Spirogyra* sp. for removal of Hexavalent Chromium was assessed in batch mode in different pH, contact time, biosorbent dose, temperature and initial metal ion concentration. The maximum Chromium was removed by 0.6 gm/50 ml dose of algal biosorbent in 30 ppm initial metal ion concentration at pH-2, contact time-60 minutes, temp.-35 °C and 150 rpm agitation speed. The biosorption data fitted to Freundlich and Langmuir isotherm models. Therefore *Spirogyra* sp. is capable to remove the Hexavalent Chromium from diluted electroplating effluent.

KEYWORDS: Electroplating effluent, *Spirogyra* sp., biosorption, Hexavalent Chromium, Freundlich model.**INTRODUCTION**

Large amount of Cr (VI) in the form of effluents from leather, tanning, paint & pigment, glass, electroplating, ceramic, photography and textile/ dyeing industries is discharged into natural aquatic bodies and on land (Raji and Anirudhan, 1997). Chromium is one of the toxic heavy metals which exists in two stable oxidation states (Cr (III) and Cr (VI)) in which Cr (VI) state is of particular concern because of its toxicity. As Per Indian standards its recommended limit in potable water is 0.05 mg/l and for discharge of industrial effluents to surface water is 0.1 mg/l. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/l. On contact, it causes irritation of respiratory tract & the disease, lungs carcinoma (Hayes, 1982) and on ingestion, it causes epigastric pain, nausea, vomiting and severe diarrhoea (Selvaraj et al., 1997). Thus, it becomes essential to remove chromium from industrial waste water before discharging them into water bodies or onto land. Various methods such as chemical precipitation, reverse osmosis, evaporation, ion exchange and adsorption (Rawat and Singh, 1992) were used by the researchers for removal of chromium ions from waste water. These methods are encountered due to certain major disadvantages, such as incomplete metal removal, high capital investment, high energy requirements and generation of large quantity of toxic waste sludge (Peters et al, 1985 and Brierlay et al, 1986).

The use of microbial biosorbents for removal of toxic heavy metals from waste stream has emerged as an alternate to the existing method as a result of search for low cost innovative methods. Biosorption technology based on utilization of dead biomass offers certain major advantages over living biomass such as lack of toxicity constraints, non-requirement of nutrient supply and recovery of bound metal species by an appropriate desorption method (Gadd, 1990). In the present study a freshwater alga namely *Spirogyra* sp. was used as biosorbent for removal of hexavalent chromium from electroplating effluent as its biomass is easily available.

MATERIALS AND METHODS**Collection of algal biomass and waste water samples:**

Biomass of fresh water alga namely *Spirogyra* was collected from ponds of Rohtak, Haryana and the waste water sample was collected from electroplating unit of Laxmi Precision Screw, Rohtak, Haryana.

Preparation of algal biosorbents

After collection for removal of dirt and unwanted materials, it was washed several times with tap and distilled water. Then it was soaked in distilled water for 24 hours to remove salt and metal ions present in this algae. It was air dried for 4-5 days and oven dried at 60°C for 12 hours. Dried biomass was ground and sieved through standard sieve (Sonar, GSMS, Mumbai) to obtain particles of size up to 0.3 mm. Then it was treated with 1% formaldehyde

in the ratio of 1: 5 (biomass: formaldehyde, w/v) at 50°C for 6 hours to immobilize the color and water soluble substances.

Characterization of waste water sample

The different physico-chemical parameters were analysed by APHA, 1995 standards methods.

Preparation of Cr (VI) solution

A stock solution of Cr (VI) having concentration 1000 mg/l was prepared using $K_2Cr_2O_7$ and double distilled water. Solutions of the desired concentrations were obtained by successive dilutions.

Batch biosorption experiments

Batch biosorption experiments were conducted in round bottomed flask having 250 ml capacity on rotatory shaker at 150 r.p.m. speed for the impact assessment of pH, biosorbent dose, contact time, temperature and initial metal concentration on the Cr (VI) biosorption potential of *Spirogyra sp.* from synthetic solution. After desired contact period flask were removed and allowed to stand for two minutes. The solution were filtered through Whatman filter paper 41 and filtrate was analyzed for Cr (VI) concentration spectrophotometrically at 540 nm wavelength using the 1,5-diphenyl-carbazide (complexing agent) in acid medium according to the standard methods (APHA, 1995). The optimized conditions are applied for assessment of hexavalent chromium biosorption potential of *Spirogyra sp.* from electroplating waste water.

RESULTS AND DISCUSSION

Characterization of electroplating effluent

The result of different physico-chemical parameters of are presented in Table-1

Table 1. Characterization of electroplating effluent

SR. NO.	PARAMETERS	CHARACTERISTICS
1.	Colour	Dark green
2.	pH	1.8
3.	Sulphate	490 mg/l
4.	Phosphate	0.16 mg/l
5.	Chromium	172.02 mg/l
6.	Iron	8.55 mg/l
7.	Zinc	236 mg/l
8.	Copper	0.80 mg/l
9.	Cyanide	152 mg/l
10.	COD	590 mg/l
11.	BOD	205 mg/l
12.	Oil and grease	18 mg/l
13.	TDS	27633 mg/l

Effect of pH on Cr (VI) removal

The impact of pH on the biosorption of Cr (VI) by *Spirogyra* biosorbent is presented in Table 2. As evident from the results, progressive decrease in Cr (VI) biosorption was observed with increase in pH (2-8) and maximum 82.5 % biosorption was observed at pH 2. The high biosorption of Cr (VI) at low pH is due to the greater electrostatic force of attraction between Cr (VI) species ($Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}) and biosorbent surface as under acidic condition, the surface of biosorbent becomes protonated and attracts anionic species of Cr (VI). (Selveraj et al., 1997). Similar results were reported by Nair and Krishnamurthi (1991).

Table2. Effect of pH on Cr (VI) removal by Spirogyra biosorbents

PH	HEXAVALENT CHROMIUM REMOVAL (%)
2	82.5
3	78.5
4	71.5
5	69.0
6	65.0
7	63.0

8	58.5
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Initial Cr (VI) concentration = 30 ppm, Dose = 0.8 gm/50 ml, Temperature = 25°C, Contact time = 1 hr, Agitation speed = 150 rpm.

Effect of biosorbent dose

Results of Cr (VI) removal at different biosorbent doses (0.2-1.4 g/50 ml) are given in Table 3. It was observed from the results that the maximum 79.0% chromium was removed with 0.6 gm/50 ml biosorbent dose. The percentage removal of Cr (VI) increases with increase in biosorbent dose upto some extent, thereafter with further increase in biosorbent dose, there was no appreciable increase in percentage removal which may be explained as with increase in adsorbent dose, more and more binding sites becomes available for the complexation of Cr (VI) ions and this increased the rate of biosorption. However very slow increase in removal beyond an optimum dose may be attributed due to the binding of almost all the ions to biosorbent and establishment of equilibrium between adsorbate and biosorbent at the existing operating conditions (Bai and Abraham, 2001; Rai and Kumar, 1999).

Table3. Effect of dose on Cr (VI) removal by Spirogyra biosorbents

DOSE (GM)	HEXAVALENT CHROMIUM REMOVAL (%)
0.2	50.16
0.4	63.5
0.6	79.0
0.8	82.8
1.0	85.2
1.2	86.0
1.4	86.5

Initial concentration = 30 ppm, Temperature = 25°C, Contact time = 1 hr, Agitation speed = 150 rpm, pH = 2

Effect of contact time

Cr (VI) removal by algal biosorbent as a function of contact time is presented in Table 3. From the results optimum time was observed 60 minutes with 79.0 % removal. After optimum time there was no appreciable increase in percent of Cr (VI) removal which may be explained as initially biosorbent showed the fast biosorption which gets slowed down later on, because initially large number of vacant surface site may be available for biosorption and after some time the remaining vacant surface sites may be exhausted due to repulsive forces between the soluble molecules of solid and bulk phase (Chand, 1999 and Vishwanathan et al., 2000).

Table4. Effect of time on Cr (VI) removal by Spirogyra biosorbents

TIME (MINUTES)	HEXAVALENT CHROMIUM REMOVAL (%)
20	58.0
40	64.0
60	78.9
80	79.2
100	79.3
120	79.6
150	79.6

Initial concentration = 30 ppm, pH = 2, Dose = 0.6 gm/50 ml, Temperature = 25°C, Agitation speed = 150 rpm.

Effect of temperature

Effect of temperature on chromium (VI) removal is shown in Table 4. The optimum temperature for was 35°C with 82 % removal and it was reduced to 47.2 % with rise in temperature from 35°C to 75°C. The amount of Cr (VI) adsorbed was found to be decreased with rise in temperature indicating the process to be exothermic (Bai and Abraham, 2001).

Table5. Effect of temperature on Cr (VI) removal by Spirogyra biosorbents

TEMPERATURE (°C)	HEXAVALENT CHROMIUM REMOVAL (%)
25	79.6
35	82.0
45	68.2

55	57.5
65	49.3
75	47.2

Initial concentration = 30 ppm, pH = 2, Dose = 0.6 gm/50 ml, Contact time=60 minutes, Agitation speed = 150 rpm.

Effect of initial Cr (VI) concentration

The results of Cr (VI) removal at different concentrations of chromium are shown in Table 5. It was observed from results that percentage biosorption of Cr (VI) ions decreased as initial concentration of metal ions increased (5 to 60 ppm). This was due to number of ions competing for available binding sites in the biomass and also due to lack of binding sites for complexation of higher concentration levels. At lower concentration almost all the metal ions present in the solution could interact with binding sites and thus facilitating maximum biosorption at 5 ppm concentration i.e. 92.2%. However biosorption was found to be effective upto 30 ppm concentrations (82.0). At higher concentrations more chromium ions are left unadsorbed in the solution due to saturation of adsorption sites (Bai and Abraham, 2003).

Table 6. Effect of concentration on Cr (VI) removal by *Spirogyra* biosorbents

Concentration (ppm)	Hexavalent chromium Removal (%)
5	92.2
10	83.2
30	82.0
40	76.4
50	65.2
60	67.3

Dose = 0.6 gm/50 ml, pH = 2, Contact time= 60 minutes, Temperature = 35°C, Agitation speed = 150 rpm.

Removal of Cr (VI) from electroplating effluent

The electroplating effluent was diluted to 30 ppm concentration and the percentage removal was observed at synthetic solution optimized condition (pH-2, dose-0.6 gm/50ml, contact time-60 minutes, temp.-35 °C and 150 rpm agitation speed). The biosorbent of *Spirogyra sp.* was removed 71.0 % chromium from the electroplating effluent.

Adsorption isotherms

The adsorption isotherm study is helpful in determining the adsorption capacities of various adsorbents for removal of Cr (VI) at certain temperatures.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/gm), Q_0 and b are Langmuir constants indicating the sorption capacity and energy, respectively and are determined from slope and intercept of the plot. The linear plots of C_e/q_e Vs C_e at different temperature for different biosorbents (Fig. 1) demonstrate the applicability of Langmuir model of sorption. The values of Q_0 and b are represented in table 7. The essential features of Langmuir isotherm can be expressed in terms of dimensionless "separation factor or equilibrium constant R_L ".

$$R_L = 1 / (1 + Q_0 C_i)$$

Where C_i is the initial concentration and Q_0 is the Langmuir constant indicating the nature of adsorption. Separation factor (R_L) indicates the isotherm shape as).

If, $R_L > 1$ Unfavourable
 $R_L = 1$ Linear
 $0 < R_L < 1$ Irreversible

So R_L was determined and the values are between 0 and 1 (Table 7). This indicates favourable sorption by all the biosorbents.

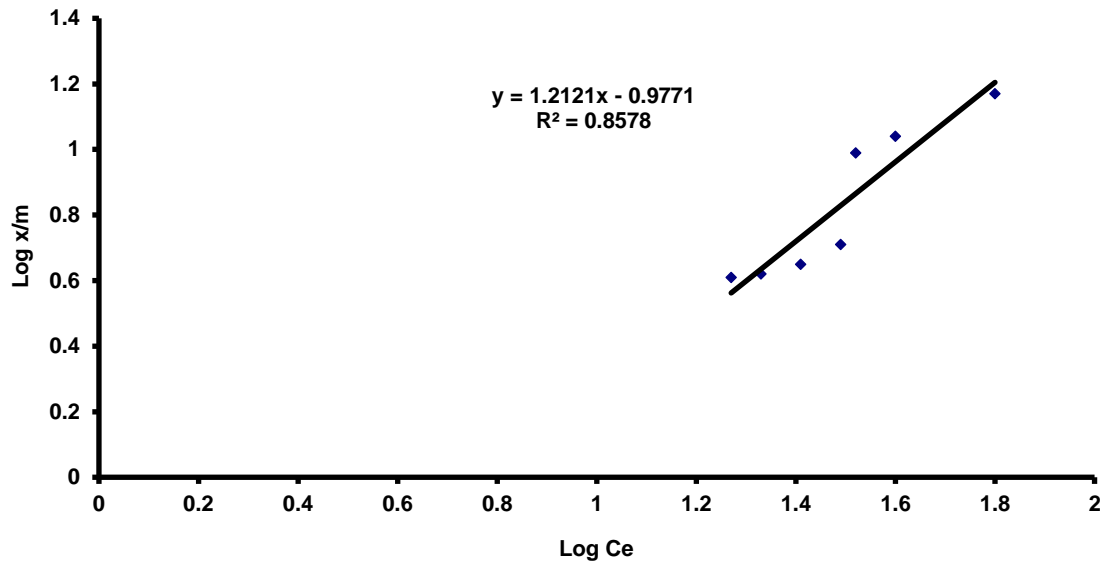


Fig. 1. Freundlich isotherm for the biosorption of Cr (VI) by Spirogyra treated

Table 7. Isotherm model constants and correlation coefficient for biosorption of Cr (VI)

BIOSORBENT MATERIALS	LANGMUIR CONSTANT (mg/g)				FREUNDLICH CONSTANT (mg/g or L/mg)			
	Q ₀	B	R _L	r	K	1/n	N	r
Spirogyra	14.81	0.28	0.002293	0.9824	2.63	1.2121	0.82	0.8575

r = correlation coefficient, R_L separation factor or equilibrium constant The applicability of Freundlich isotherm was also tested using following general equation. $\text{Log } x/m = \text{log } K + 1/n \text{ log } C_e$ K and n are constant representing the adsorption capacity and intensity of adsorption respectively. Plot between log x/m and log C_e yields a linear Freundlich isotherm (Fig. 2) values of K and 1/n are represented in Table -7. Higher the value of K, higher will be the biosorption capacity.

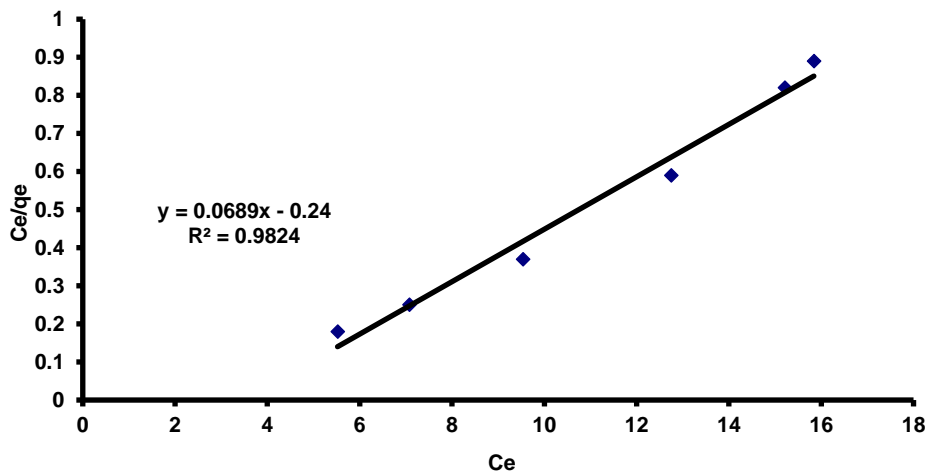


Fig. 2 Langmuir plot for the biosorption of Cr (VI) by Spirogyra treated

CONCLUSION

From the results, it can be concluded that the hexavalent chromium biosorption potential of *Spirogyra sp.* was affected by varying pH, biosorbent dose, contact time, temperature and initial metal ion concentration. The algal biosorbent can remove 82.0 % chromium (VI) from its synthetic solution of 30 ppm concentration and 71.0% from diluted waste water of electroplating industry at optimized conditions (pH 2, biosorbent dose 0.6 g/50 ml, contact time 60 minutes, temperature 35°C and at 150 rpm agitation speed).

Spirogyra sp. was found suitable biosorbent for the biosorption Cr (VI) from electroplating effluent due to its good biosorption potential and easy availability.

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