

## BIOREMEDIATION OF HEXAVALENT CHROMIUM BY USING CYANOBACTERIA AND ITS APPLICATION OF THE BEST ISOTHERMS

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### ABSTRACT

The present study aimed to evaluate the efficiency of hexavalent chromium Cr(VI) removal from synthetic waters using locally available Cyanobacteria is also called blue-green algae are commonly found in lakes, rivers, and ponds. Various sorption factors like optimum pH, period of exposure, biomass dose, and primary chromium concentrations were investigated to originate their impacts on the sorption of Cr(VI). FTIR (Fourier-transform infrared spectroscopy) and SEM (Scanning electron microscopy) were used to examine the biosorption mechanisms of Cr(VI) ions onto blue-green algal biomass. The Langmuir and Freundlich isotherm models accurately illustrate the equilibrium experimental results. The Results indicated that the biosorption of blue-green algal biomass was shown to be biomass and pH-dependent. The hexavalent chromium removal efficiency was found to be 97.6% for an initial chromium concentration of 500 mg/L within 60 minutes at pH 2, 250 rpm, and a 10g/L blue-green algal biomass dose. According to the Langmuir isotherm, the highest biosorption ability was about 396 mg/g of dry biomass, and the Freundlich constants Kf and n were 0.514 [mg/g (1/mg)<sup>n</sup>] and 32.73, respectively. At the outset, the study of "blue-green algae" can be well-advised as a propitious and precious universal adsorbent to treat the waters contaminated with toxic Cr(VI) ions.

**Keywords:** Biosorption, Blue-green algae, Hexavalent chromium, Heavy metal pollution, Isotherm models, Water pollution.

### Introduction

Water contamination is the world's most vulnerable issue. Major research and the state of art technologies are coming to treat the wastewater and to remove the pollutants from the wastewater. Pollution of the water mainly due to toxic heavy metals containing effluents from textile, paint, leather tanning, etc. is discharging the wastewater into the water bodies. Currently, this is one of all the major environmental concerns within the world.

In heavy metals Chromium, being one of the most hazardous and carcinogenic metals has drawn a lot of interest from researchers. Only two of the chemical forms of chromium (Cr (III) and Cr(VI)), are stable and found in nature. Electroplating, chromate production, alloy manufacturing companies, metal purification and handling, leather processing, and

wood maintenance are just a few of the industrial sources that employ this metal and its derivatives. Because of its significant adverse health properties, Cr (VI) should be effectively removed before disposal. Ramsenthil (2018).

Many researchers reported that the different treatment technologies for removal of chromium like membrane separation, ion exchange, chemical reduction/precipitation, and adsorption. However, these methods are not economically facing able, which, need a very huge amount of chemical reagents and a lot of energy, to overcome these problems researchers proposed biosorption to adsorb pollutants through biological sources as a potential alternative.

Innovative ways of using various biological sources, rockweed, amphibious plants, and plant-based sorbents as economical and effective absorbents are being developed. Because of its environmentally benign character, even wastewaters with metal pollution may be remedied with this high-performance, low-cost domestic approach, biosorption has become an essential and state-of-the-art technology in recent years. M. Costa (2003), G. Donmez (2002), Chi-ChuanKan (2017), WC Leung, (2001), R Majumder (2017), S.K Das (2007), D. Park (2005), Parul Sharma (2007), S Basha (2008), P Suksabye (2007), H Gao et al (2008).

Studies have shown that, the short-term accumulation of chromium (VI) by contacts with Cyanobacteria using their capability to seize chromium. D Shukla (2002). Aksu & Balibek (2007) studied the impact of salt addition on the adsorption of Cr (VI) by dried *Rhizopusarrhizus*. Arica et al. (2005) investigated the kinetics of Cr (VI) adsorption from synthetic waters expending free and restrained biomass produced from *Lentinussajorcaju*. Arica (2015). As a result, fungal species may remove chromium ions as well. The biosorption of Cr (VI) ions on the cell surface of trichoderma fungus under aerobic conditions at pH 5.5 was found to be 97.39 percent Vankar et al (2008). *Chlamydomonas reinhardtii*, natural, heat-treated, and acid-treated microalgae, was used for chromium (VI) ion biosorption.

The purpose of this research is to study the effect of several factors on the removal efficiency of chromium ions, such as adsorbent dosage, initial pH, time duration, and optimum Cr (VI) levels, on the adsorption of hexavalent chromium from synthetic chromium solutions using blue-green algae as an absorbent. To describe the experimental data, adsorption isotherms were used.

## **Materials and methods:**

### **Biomass preparations:**

A blue-green alga sample was taken from a small water body near Rajendra Nagar in Hyderabad, India. To eliminate contaminants and other undesirable components like sand and soil particles, the biomass was thoroughly washed in running tap water, then three to four times in Millipore water. The collected biomass was allowed to air dry before

being dried in a 60°C oven. Dry biomass was mashed in a marble crusher blender and mesh sieve to achieve the desired particle size (0.5mm).

### Preparation and analysis of metal solution

The Chromium primary solution was made by dissolving 2.827g potassium dichromate ( $K_2Cr_2O_7$ ) in Milli-Q water. It was then diluted with ultra-pure ultra-distilled water to make solutions with concentrations of 500 to 1500 mg/L. The complete study was conducted in batches at  $28\pm 2^\circ C$ . The hexavalent chromium concentration was determined by a UV-Spectrophotometer method based on red-violet colored complex production of chromate ions by the interaction of DPC (1,5-diphenylcarbazide) in an acidic solution. Gilcreas et al (1965). The Systronic-2205UV-Vis spectrophotometer was used to detect absorbance across a wavelength of 540 nm after 15 minutes. The pH was adjusted using Systronic pH system-361, well-calibrated with NIST traceable pH buffers. Remi manufactured a mechanical shaker used for adsorption and kinetic studies.

### Hexavalent chromium adsorption studies:

250 ml conical flasks were swirled at 250 rpm on a stirrer at ambient temperature ( $28\pm 2^\circ C$ ) for batch biosorption studies. The impact of pH solutions ranging from 1.0 to 10.0, exposure time (060 minutes), and optimal Cr(VI) ions concentration (500 to 1500 ppm with 10g biomass dosage) on the biosorption rate and efficiency were investigated To explore the adsorption efficiency of Cr(VI) and blue-green algal biomass, 10g/L biomass was soaked in Cr (VI) synthetic water of various concentrations ranging from 500 - 1500 ppm to evaluate biosorption isotherms. The samples were obtained at various periods (0 to 60 mins). The supernatant was tested for residual chromium metal ion concentration after centrifugation at 4500 rpm for 15 minutes. The following equation was used to calculate the quantity of Cr (VI) ions adsorption efficiency per unit biomass of the adsorbent under equilibrium conditions  $Q_e$  (mg/g).

$$Q_e = (C_0 - C_e)V \div m \quad \text{Equation-1}$$

Where,  $C_0$  and  $C_e$  (mg/L) are initial & equilibrium concentrations of chromium solution respectively,  $V$  is the volume of solution (L), and  $m$  is Blue-green algal biomass (g).

The efficiency of biosorption (%) was determined using the following equation:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{Equation-2}$$

### Characterization of adsorbent

The studies were conducted using a Perkin Elmer Model Spectrum BXI FTIR spectrophotometer (FTIR) on KBr discs with a finely powdered 1% sample. In the

wavenumber varies from 650-4000 $\text{cm}^{-1}$ , spectral data with a resolution of 4  $\text{cm}^{-1}$  was analyzed using spectrum software. The biomass was evaluated after and before the chromium ion interaction. The surface structure and metal adsorption on biosorbent were studied using a scanning electron microscope (SEM).

### **Equilibrium Isotherms analysis:**

The biosorption data were applied to several sorption isotherms, notably the Freundlich and Langmuir, to quantitatively explain chromium metal sorption by the blue-green algal biomass. The nonlinear regression method was used to determine  $q_e$  and  $b$  in this investigation. The findings of the correlation coefficient ( $R^2$ ) were used to determine which of the two models described above was the most well-fitting.

The Freundlich isotherm is an empirical equation that defines adsorption on a heterogeneous surface with non-uniform energy distribution. The biosorption studies were conducted out with a predetermined initial adsorbent dosage (10g) and various initial adsorbate levels (500, 750, 1000, 1250, and 1500 mg/L) solutions, with the data's relevance to the Langmuir adsorption isotherm being evaluated. The tests were performed for sufficient time to achieve equilibrium at the original pH of 2. The Langmuir model was used to deal with uncertainties.

### **Results and Discussion:**

Cr (VI) adsorption by blue-green algae is optimum when the pH is 2 and the biomass dose is 10g. According to the findings of this study, the highest adsorption capacity of blue-green algal biomass is 396 mg/g, and the optimum agitation rate of 250 rpm is continued during the 60-minute preset time. The current results of blue-green algae's maximal adsorption capacity are compared to similar research on Cr (VI) adsorption utilizing various sorbents. The highest adsorption rate using activated charcoal (made from wood apple shell) employed to absorb chromium from water with a concentration of 1250 mg/g was reported to be 151.51 mg/g at a pH of 1.8. Their substance is shown to be more effective at low pH, and their  $q_{\text{max}}$  was lower than this research Doke & Khan(2017).

At pH 2 and 0.2g of dosage, a magnetic natural zeolite Chitosan composite was used as an absorber to absorb Cr (VI) from a 200 mg/L aqueous solution, with a removal efficiency of 98% Gaffer et al (2017). The chemically-treated banana peels were used as an adsorbent in 400 mg/L chromium synthetic water and revealed that the maximum removal efficiency was 6.178 mg/g within 120 minutes of contact time with 4 g/L dosages at pH 3 Ali et al (2016).

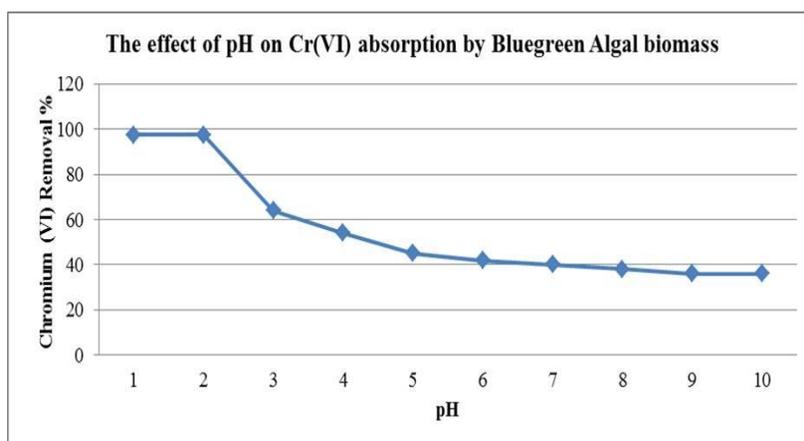
### **pH Impact on adsorption:**

The objective of this study was to determine the ideal pH for removing chromium ions from aqueous solutions. Experiments were performed in batches with various concentrations of chromium solution by ranging the pH levels from 1 to 10 and results

were evaluated (Figure 1). In aqueous solutions, chromium is known to have pH-dependent equilibria. When the pH varies, the equilibrium shifts. The  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions were in equilibrium in the pH range of 1 to 10. On the other hand, at pH 2.0,  $\text{Cr}_3\text{O}^{10-}$  and  $\text{Cr}_4\text{O}_{13}^{2-}$  species are released. The optimal initial pH for Cr (VI) bioremediation using this biosorbent was found to be pH 2.0, suggesting that lower pH causes more polymerized chromium oxide molecules to be produced. The decreased chromium removal effectiveness at higher pH is thought to be owing to ions being repelled by anions on the surface of the adsorbent. The removal efficiency rose as the pH was reduced, reaching 97.6% at 500 mg/L Cr (VI) concentrations, according to the findings. Some of the organic carbons in the biomass were transformed to inorganic carbon during Cr (VI) reduction ( $\text{HCO}_3^-$  and  $\text{CO}_2$ ). Protons were consumed during absorption when pH decreased.

### Effect of Contact Time

The amount of Cr (VI) absorbed varies depending on the starting concentration, which ranges from 500 to 1500 mg/L at pH 2. (Table 1). Since the pH affects the system's sorbent equilibrium, the combination of chromium levels and adsorbent is an important factor to consider for successful biosorption. The time it took for the system to reach equilibrium was less than 60 minutes. Metal uptake was affected by variables disrupting mass flow from the bulk solution to binding sites Mohanty et al (2018).



**Figure 1. The effect of pH on the removal efficiency of hexavalent chromium.**

However, even though sorption equilibrium was achieved at the same time, chromium ion biosorption declined with time. It is explained as a result of a rise in the number of ions vying for accessible binding sites in biomass, as well as a scarcity of binding sites. Because binding sites are saturated at greater concentrations, more Chromium ions are left in the solution.

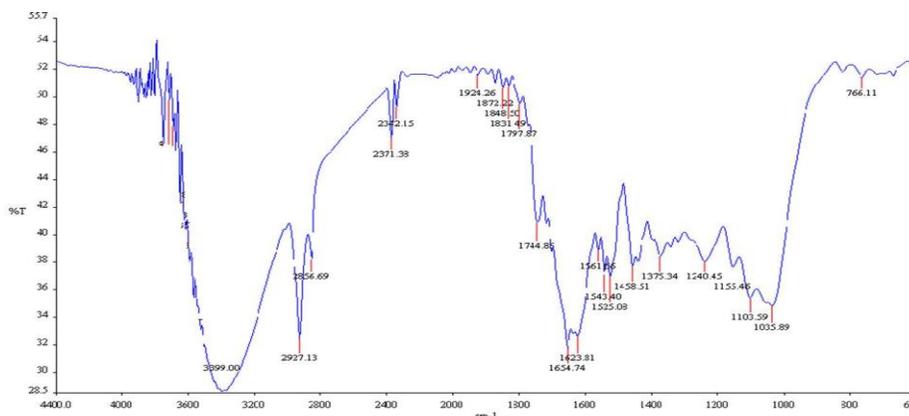
**Table 1: Chromium (VI) removal percentage at a different contacting time using blue-green algae**

Removal Percentage of chromium VI by using blue-green algal biomass						
Concentration (ppm)	10 min	20 min	30 min	40 min	50 min	60 min
500	40	56	68	74	89	98
750	36	48	52	68	72	96
1000	32	54	58	76	84	92
1250	28	59	66	80	88	88
1500	16	28	43	56	66	72

**FTIR Spectra Analysis:**

An unreacted, chromium-treated blue-green algae sample was prepared and scanned using FTIR, with percentage transmission for various wavenumbers shown. The attribution of corresponding functional groups to absorption bands identified using acquired spectra is explained.

The existence of OH groups on the biosorbent surface was indicated by wavenumbers of 3,000 and 3,399  $\text{cm}^{-1}$  for blue-green algae. The existence of C-H groups is indicated by the dip seen at 2,927  $\text{cm}^{-1}$  and 893  $\text{cm}^{-1}$ . The presence of an amide band is shown by the 1,649  $\text{cm}^{-1}$  band, which is the consequence of CO stretching mode coupled to NH deformation mode. The dip at 1,154  $\text{cm}^{-1}$  is caused by CO or CN groups, which proves the existence of numerous efficient ions on the surface of blue-green algae that bind Cr(VI) ions. (Figure 2).



**Figure 2. FTIR Spectrum for blue green algae biomass.**

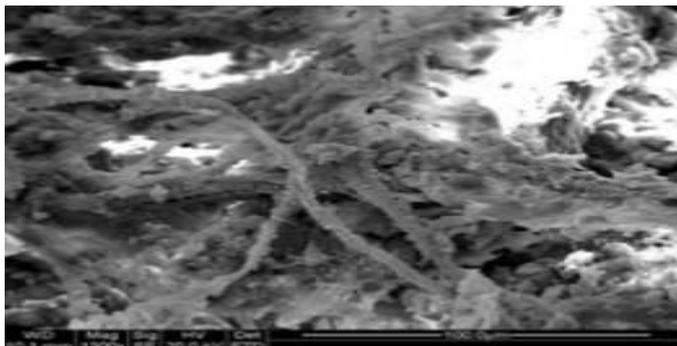
Scanning Electron Microscope (SEM) combined with Energy Dispersive X-ray (EDX) spectroscopy was used to explore the Cr (VI) adsorption and surface structure of the blue-green algal biomass sample. EDX spectroscopic experiment found the percent quantity of Cr (VI) in the biomass after biosorption, which was used to determine the percentage of elements.

The blue-green algal biomass sample was tested against 500 mg/L hexavalent chromium, and the biomass removed 97.6% of the Cr (VI) ion using 10 g of biomass at pH 2. This indicates that the biomass's surface area is acting as a biosorption agent. The morphology of biomass was explained by SEM micrographs, as illustrated in Figs. 3 and 4, respectively.

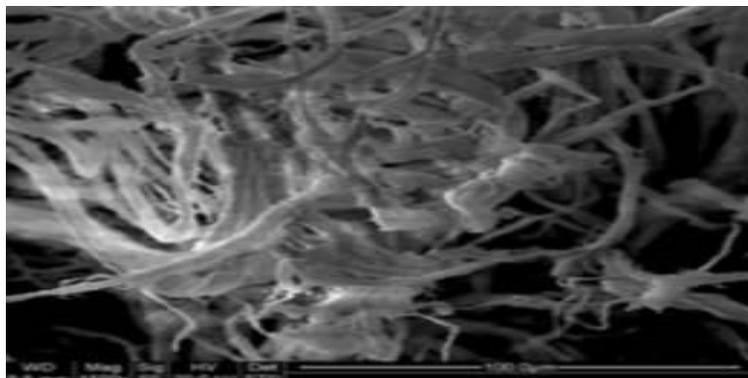
### **Biosorption equilibrium studies:**

Experiments were conducted through adsorbent doses of 10 g/L and various adsorbate contents (500-1500 mg/L) solutions, the results were examined by Langmuir adsorption isotherm. The tests were performed for sufficient time to achieve equilibrium at the original pH of 2. The findings were familiar to the Langmuir model that can be articulated by using the equation.

$$q_e = \frac{bq_{\max}C_e}{1+bC_e} \quad \text{Equation – 3}$$



**Fig. 3. SEM of blue-green algae biomass before biosorption.**



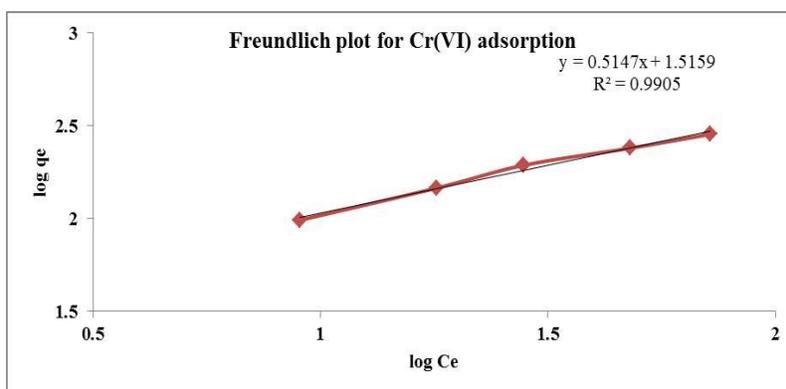
**Fig. 4. SEM of Bluegreen algae biomass after biosorption**

Where  $q_e$  is the metal uptake (mg/g) at equilibrium;  $q_{max}$  is the maximum Langmuir uptake (mg/g);  $C_e$  is the final metal concentration at equilibrium (mg/L);  $b$  is the Langmuir affinity constant (L/mg of the metal). The Langmuir affinity constant was found to be highly linked with the similarity between biomass and Cr (VI), with a higher value indicating a high affinity. Using a linear representation of the Langmuir model ( $C_e/q_e$  vs  $C_e$ ), these adsorption variables may be derived from the isotherm:

$$\frac{C_e}{q_e} = \frac{C_2}{q_{max}} + \frac{1}{bq_{max}} \quad \text{Equation -4}$$

These assumptions underpin the Langmuir isotherm. Langmuir (1916). Metal ions are adsorbed chemically at a finite number of well-defined sites, each of which can only hold one ion at a time. The ions do not interact, and all sites are energetically equivalent.

The linear plot of  $C_{eq}/q$  vs  $C_{eq}$  shows the adsorption follows the Langmuir adsorption model (Figure 5). 0.99 was the correlation coefficient. The slope and intercept of the figure were used to determine  $b$  and  $q_{max}$ , which were 0.06 L/mg and 396 mg/g, respectively.



**Figure 5. Freundlich plot for hexavalent chromium adsorption efficiency.**

### Separation factor - $R_L$

The main characteristics of the Langmuir isotherms may be represented as dimensionless constant separation factors or equilibrium parameters.  $R_L$ , which is well-defined as:

$$R_L = \frac{1}{1+bC_o} \quad \text{Equation -5}$$

Where  $C_o$ =initial concentration in mg/L;  $b$ =Langmuir constant

$R_L$  values define the isotherm categories; if the  $R_L$  value is greater than one, the isotherm is unfavorable and linear; if the  $R_L$  value is less than one, the isotherm is favorable; For Cr (VI) adsorption, the  $R_L$  values obtained are smaller than one (Table 2).  $R_L$  values between 0 and 1 recommend good adsorption Mcka et al (1982).

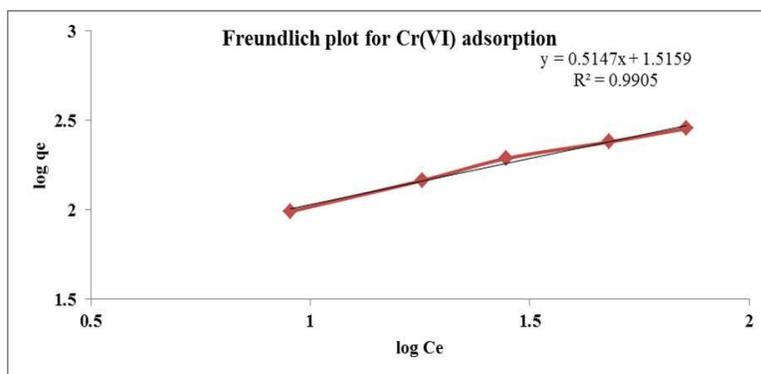
**Table 2. The values of Separation factor**

$C_o$	$R_L$
500	0.032209
750	0.021705
1000	0.016368
1250	0.013137
1500	0.010972

The adsorption of chromium (VI) on a blue-green algal biomass was also investigated using the Freundlich isotherm, which was assessed using the equation below Freundlich (1906).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Equation-6}$$

Where  $K_f$  is a constant proportional to the Freundlich biosorption capability (L/mg), and the  $\log$  is an experimental measure indicating sorption efficiency, which differs with substance variability. Freundlich isotherms derived by applying equilibrium data to equation 6 are shown in Figure 6.



**Figure 6. Freundlich plot for hexavalent chromium adsorption efficiency.**

Kf and  $1/n$  were found to have values of 32.74 and 0.541, respectively. The  $1/n$  results falling well under the specified values (0- 1), which denotes chromium ion adsorption was satisfactory under these conditions. Magnitudes of Kf and n reveal a strong adsorption capability and removal efficiency of hexavalent chromium from contaminated waters. Ozel Uzun et al (2002).

### Conclusion

According to the results of this study, blue-green algae is a viable substitute for absorbing Cr (VI) from the waters. In biosorption, the results of FTIR bands related to its functional groups made a crucial impact. The optimum hexavalent chromium removal percentage was optimum at pH.2, and raising the pH from acidic to alkaline resulted in a decrease in chromium removal percentage. The maximal chromium VI ion removal was determined to be 97.6% in 60 minutes at pH 2 with 250 rpm agitation and 10 g/L blue-green algae biomass. Studies of equilibrium isotherms indicated that they were significant and fit well within the allowable limits. Cr(VI) ion biosorption on blue-green algae eventually reached a maximum capacity of 396 mg/g biomass. Blue-green algae is an inexpensive and easily available biosorbent, making it a viable choice for removing chromium ions from contaminated wastewaters.

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### Declaration of Competing Interest

All the authors confidently declare that there is no conflict of interest, and all authors for publication approve the paper.

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