

TEMPERATURE AND PH KINETICS FOR ENHANCED BIOSORPTION OF CR (VI) BY HIGHLY CHROMIUM RESISTANT FUNGI *GLIOCLADIUM* SPP. ZIC₂₀₆₃

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Abstract

This study investigates the kinetics of Cr (VI) biosorption by locally isolated high Cr tolerant fungus *Gliocladium* sp. ZIC₂₀₆₃. The effect of two most important variables pH and temperature was investigated for enhanced Cr (VI) biosorption. The applicability of the Langmuir and Freundlich models for the different parameters was tested. The result showed that the most suitable sorption temperature was 30°C with maximum biosorption rate of 185.69 mg/l. The data showed that the sorption process is spontaneous and exothermic in nature and that lower solution temperatures favors metal ion removal by the biomass. Similarly Cr (VI) uptake by *Gliocladium* sp. ZIC₂₀₆₃ was maximum at optimum pH of 3.5. The findings of this investigation suggest that pH and temperature plays a significant role in enhancing the biosorption rate. The coefficient of determination (R²) of both models were mostly greater than 0.9. This indicates that biosorption data is best fitted in both models.

Key words: Langmuir and Freundlich models, pH, Temperature.

Introduction

Microbial biomass such as bacteria, fungi and algae have been used as biosorbents (Volesky, 1990). Biosorption of metal ions by biosorbent occurs by one or a combination of metal-binding mechanisms such as complexation, coordination, chelation, ion exchange, adsorption and inorganic microprecipitation. The fungal cell walls and their components play a major role in the biosorption. Fungal biomasses are used in the biosorption of various metal ions (Mashitah *et al.*, 2008). Biosorption is particularly useful for the removal of trace levels of contaminants from industrial effluents (Amna *et al.*, 2011).

The present research work is based on the investigations that several environmental conditions such as metal ion concentration, temperature, pH and the amount of biosorbents affect biosorption of heavy metal ions onto fungal biomass. Earlier studies have shown that the most critical parameter in the treatment of heavy metals by biosorbents is the pH and temperature of the biosorption medium. Temperature is a crucial parameter in adsorption reactions. Temperature influences the biosorption by affecting the configuration and stability of fungal cell wall. Biosorption process is usually not operated at high temperature because it will increase the operational cost (wang, 2001). The tests are usually performed at approximately 25-30°C. pH seems to be the most important factor in the biosorption process. Fungal surfaces are negatively charged in the pH range of 2-6 (Mala, 2006; Shankar *et al.*, 2007), thereby contributing to metal binding. pH affects the solution chemistry of the metals, ionization state of the functional groups on microbial surfaces, and the competition of metallic ions (Shankar *et al.*, 2007; Munagapati & Yeoung, 2013). Langmuir and Freundlich adsorption isotherms (especially Langmuir isotherm) were applied to analyze adsorption data. The Langmuir model described the surface phenomenon of binding sites and Cr (VI) metal ions concentration in biosorption medium. Freundlich

isotherm was used to describe that the metal binding energy to any adsorption site is independent of its availability. The present research work is first report on the pH and Temperature biosorption kinetics of *Gliocladium* sp. ZIC₂₀₆₃ for Cr removal. Biosorption capacity of locally isolated fungal species *Gliocladium* sp. ZIC₂₀₆₃ was enhanced to a great extent after optimization of pH and incubation temperature.

Material and Method

Organism: *Gliocladium* sp. ZIC₂₀₆₃ previously isolated was used to evaluate the effect of pH and temperature on the biosorption of Cr (VI). For the preparation of fungal pellets 7 days old spore inoculum (10%v/v) was inoculated into sterile 50 ml Potato Dextrose Broth in a 250ml conical flask and incubated at 30°C in shaker incubator at 122 rpm for 96 hour. Propagated mycelial pellets were filtered by cheesecloth. These fungal pellets (2g wet weight) were added into 10% diluted effluent (pH 3.0) in 250ml conical flask and incubated at 30°C for 24 h at 122 rpm.

Batch studies on biosorption kinetics of chromium

(VI): To study biosorption kinetics of Cr (VI) from Spent Chrome Liquor different concentrations of Cr₄ (SO₄)₃ (OH)₂ were prepared. The influence of initial pH on the biosorption rate (%) was investigated in range of 2.0-6.0. The influence of incubation temperature was checked in the range of 20-40°C. The samples were withdrawn after every 5min interval for first 1 h biosorption.

Analytical method for chromium (VI): Samples (almost 5 ml each) of first 1h biosorption kinetics taken at predetermined interval were centrifuged and filtered. The supernatant were analyzed for Cr (VI) concentration using Polarized Zeeman Atomic Absorption Spectrophotometer Z-5000 (Perkin Elmer Analyst 300 Hitachi, Japan).

Application of biosorption isotherms: Langmuir and Freundlich adsorption isotherms were applied on the data to analyze its applicability for wastewater treatment bioreactors. The chromium biosorption coefficient (q) the construction of sorption isotherms was calculated from the initial concentration (C_i) and the final or equilibrium concentration (C_f) in every flask, as follows:

$$q = [V(C_i - C_f) / M]$$

where, V is the volume of the chromium solution in the flask and M is the dry mass of biosorbent (Cossich *et al.*, 2009). The Langmuir sorption model was chosen for the estimation of maximum metal biosorption by the biosorbent. The Langmuir isotherm can be expressed as:

$$q = [q_{max} b C_f / 1 + b C_f]$$

where b is a constant related to adsorption/desorption energy, and q_{max} is the maximum biosorption upon complete saturation of the surface (Cossich *et al.*, 2002). The linearized equation for the Langmuir's isotherm is:

$$1/q = [1/q_{max} + 1/b q_{max} \times 1/C_f]$$

The Langmuir's constant b was calculated from the initial slope of the linear plot of $1/q$ vs. $1/C_f$ using SPSS version 12.0 (SPSS Inc., Chicago, USA). The Freundlich model is represented by the Equation.

$$q = K C_f^{(1/n)}$$

where k and n are constants (Cossich *et al.*, 2002). The plot of $\log C_f$ versus $\log q$ was employed to generate the intercept value of K and the slope of n using SPSS version 12.0 (SPSS Inc., Chicago, USA).

Results and Discussion

Biosorption kinetics at various initial pH: pH is the most important single parameter influencing the sorption capacity of biomass. The heavy metal removal capacity increased very sharply with increase in pH. The pH of solution affects not only the site dissociation of the

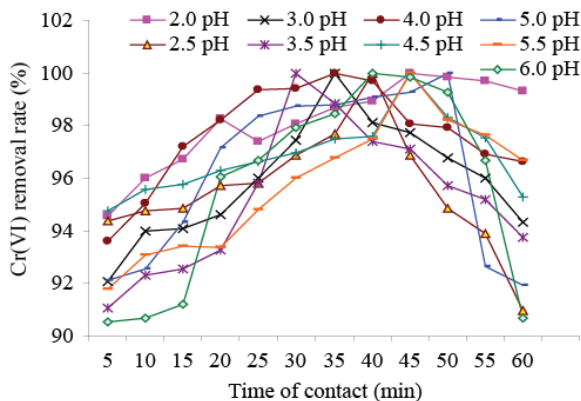


Fig.1. Biosorption kinetics of Cr (VI) at various initial pH Cr (VI) conc. 200 mg/l, Temperature 30°C, Biosorbent 2 g (wet weight), agitation 122 rpm, volume of Cr (VI) solution 50 ml in 250 ml conical flask.

biomass surface, but also the solution chemistry of the heavy metals (Wang, 2001). To avoid possible OH precipitation, in the adsorption medium biosorption experiments could not be performed at PH >5.0 (Li *et al.*, 2008). It was revealed from the data that maximum Cr (VI) removal rate (78.39%) was obtained at pH 3.5 (Fig. 1). After 30 min 156.79 mg/l Cr (VI) was removed. The removal rate suddenly increased above pH 4.5 which was 87.24%, 93.475 and 99.41% at pH 5.0, 5.5 and 6.0 respectively. Cr (VI) ions precipitation started at pH 5.0. At pH 3.5 biosorption co-efficient of 3919.75 mg/g was recorded (Fig. 2). The highest chromium removal by *Gliocladium viride* ZIC₂₀₆₃ was observed at pH 3.5. A similar trend has been reported by researcher with variety of biosorbents (Bai & Abraham, 2001; Niu & Volesky, 2003; Bingol *et al.*, 2004; Tunali *et al.*, 2005). At low pH the overall surface charge on the fungal biomass become positive or less negative, which will promote a stronger attraction towards negatively charged Cr (VI) complex ions in the solution. Hence, biosorption increases with an increase in the acidity of the solution. But as the pH rises, the concentration of OH⁻ ions increases and overall charge on the biomass surface becomes negative. This causes a hindrance to the biosorption of negatively charged Cr (VI) ions such resulting in a decrease of biosorption of chromium at higher pH levels ((Niu & Volesky, 2003; Mungasavalli *et al.*, 2007).

The data of Cr (VI) ions adsorption by *Gliocladium viride* obtained at different pH was applied to Langmuir and Freundlich models. The relative parameters and correlation (R^2) were listed in Table 1. Data was evaluated for sorption isotherms at different pH values (Figs. 3-20). It was found that both the isotherm models fit very well when the R^2 values are compared ($R^2 > 0.09$) except at pH 5.5 and 6.0. However the Freundlich isotherm model best fitted the data since it presents higher R^2 values. The values of q_{max} and b are 3412.75 and -0.088 for pH 2.0, 3545 and -0.010 for pH 2.5, 3824 and -0.004 for pH 3.0, 3919.75 and -0.004 for pH 3.5, 3773.5 and -0.005 for pH 4.0, 3426 and -0.010 for pH 4.5, 4360.25 and -0.001 for pH 5.0, 4673.75 and -0.000 for pH 5.5 and 4970.75 and -0.000 for pH 6.0 respectively. Higher values of q_{max} and lower values of constant b indicate the high affinity of the biosorption of Cr (VI) with *Gliocladium viride*.

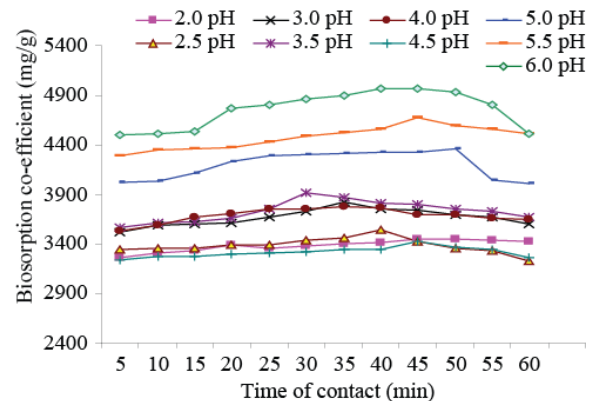


Fig. 2. Biosorption co-efficients rate at different Initial pH range Cr (VI) conc. 200 mg/l, Temperature 30°C, Biosorbent 2 g (wet weight), agitation 122 rpm, volume of Cr (VI) solution 50 ml in 250 ml conical flask.

Table 1. Comparison of Langmuir and Freundlich isotherms constants along with correlation co-efficient (r^2) at different initial pH of biosorption medium.

Initial pH of biosorption medium	Langmuir isotherm constants		correlation co-efficient (r^2)	Freundlich isotherm constants		correlation co-efficient (r^2)
	q_{max}	b		k	n	
2.0	3412.75	-0.088	0.949	4.375	-0.467	0.974
2.5	3545	-0.010	0.819	4.386	-0.473	0.998
3.0	3824	-0.004	0.748	4.187	-0.361	0.998
3.5	3919.75	-0.004	0.987	4.140	-0.334	0.997
4.0	3773.5	-0.005	0.988	4.194	-0.365	0.999
4.5	3426	-0.010	0.993	4.431	0.498	0.999
5.0	4360.25	-0.001	0.986	3.914	0.194	0.998
5.5	4673.75	-0.000	0.714	3.798	-0.112	0.984
6.0	4970.75	-0.000	0.537	3.707	-0.037	0.967

Both Langmuir and Freundlich adsorption isotherms on data of biosorption kinetics for parameter of initial pH showed liner regressions. At all pH correlation co-efficient (r^2) is almost 1.

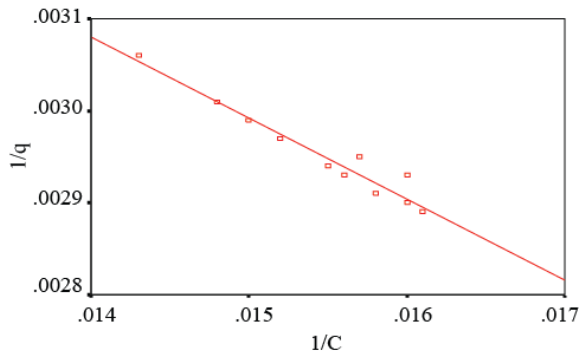


Fig. 3. Langmuir isotherm plots for biosorption of Cr (VI) at 2.0 pH.

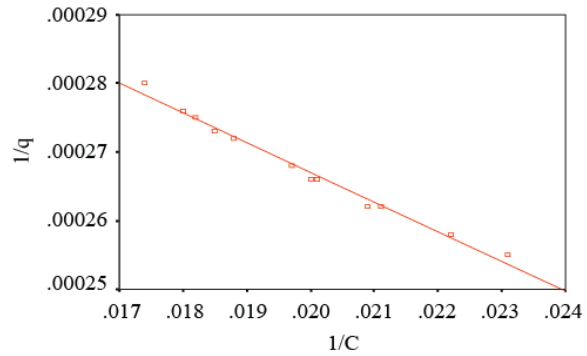


Fig. 6. Langmuir isotherm plots for biosorption of Cr (VI) at 3.5 pH.

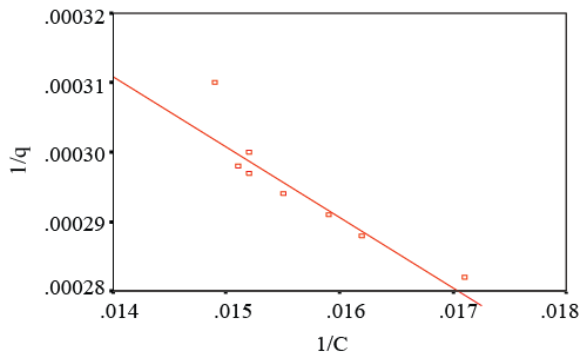


Fig. 4. Langmuir isotherm plots for biosorption of Cr (VI) at 2.5 pH.

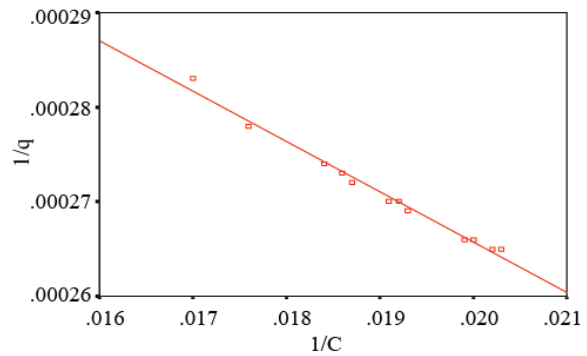


Fig. 7. Langmuir isotherm plots for biosorption of Cr (VI) at 4.0 pH.

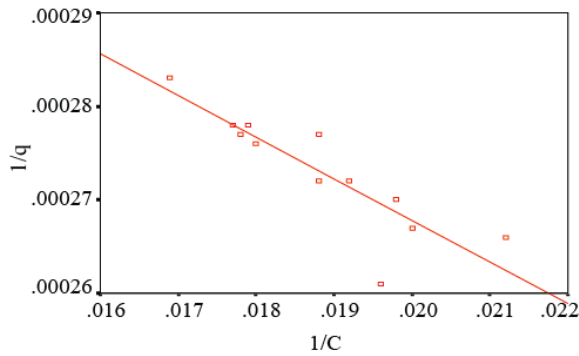


Fig. 5. Langmuir isotherm plots for biosorption of Cr (VI) at 3.0 pH.

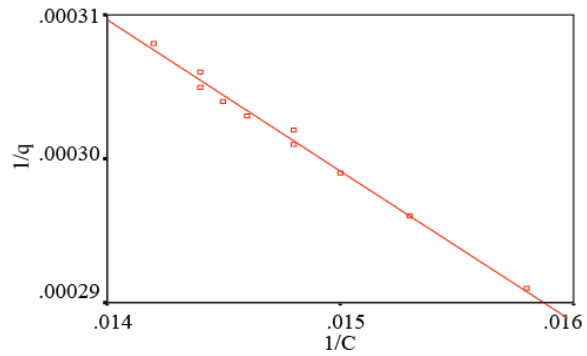


Fig. 8. Langmuir isotherm plots for biosorption of Cr (VI) at 4.5 pH.

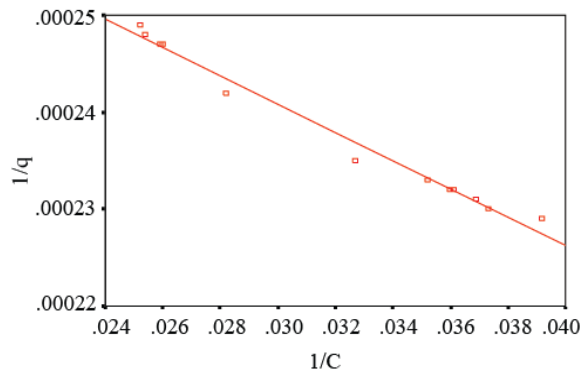


Fig. 9. Langmuir isotherm plots for biosorption of Cr (VI) at 5.0 pH.

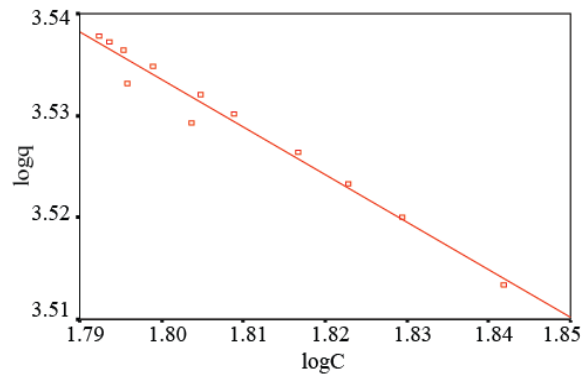


Fig. 13. Freundlich isotherm plots for biosorption of Cr (VI) at 2.5 pH.

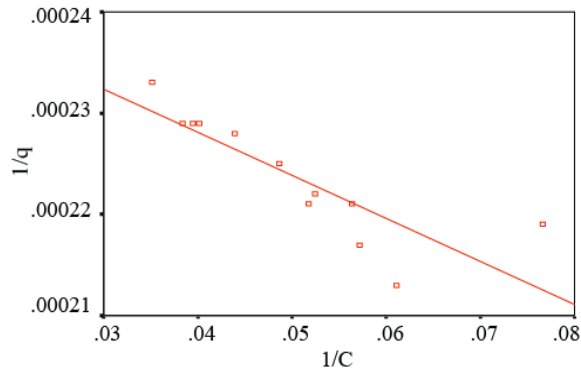


Fig. 10. Langmuir isotherm plots for biosorption of Cr (VI) at 5.5 pH.

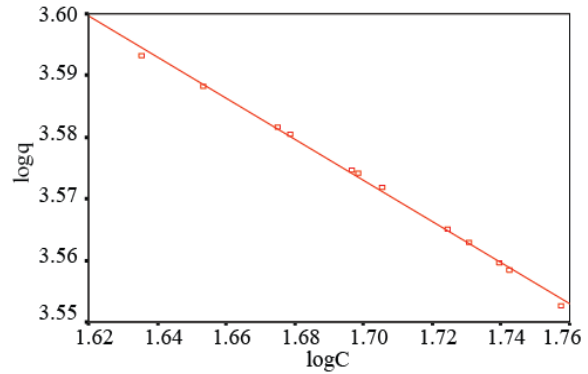


Fig. 14. Freundlich isotherm plots for biosorption of Cr (VI) at 3.0 pH.

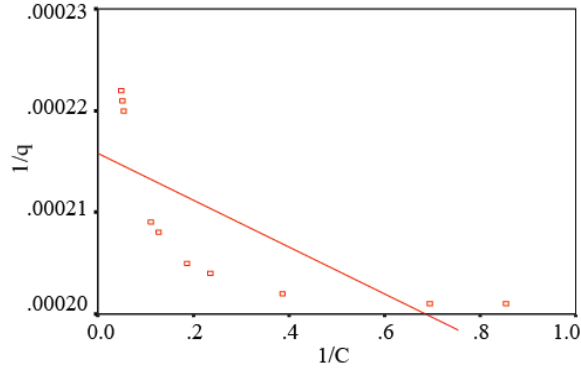


Fig. 11. Langmuir isotherm plots for biosorption of Cr (VI) at 6.0 pH.

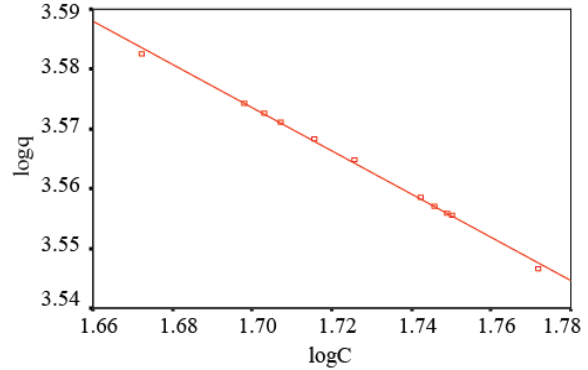


Fig. 15. Freundlich isotherm plots for biosorption of Cr (VI) at 3.5 pH.

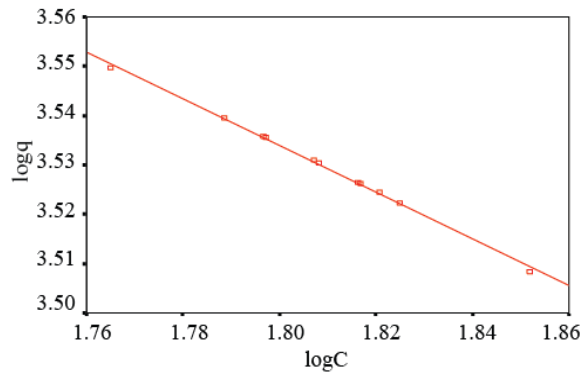


Fig. 12. Freundlich isotherm plots for of Cr (VI) at 2.0 pH.

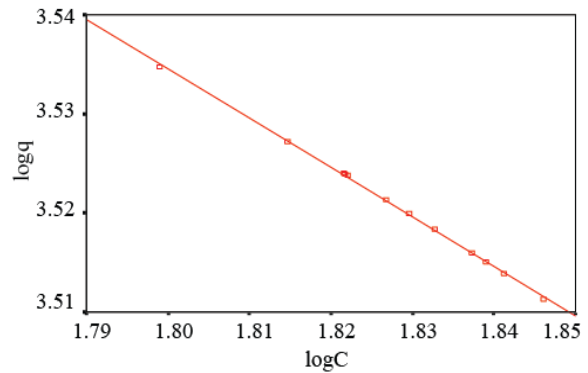


Fig. 16. Freundlich isotherm plots for biosorption of Cr (VI) at 4.0 pH.

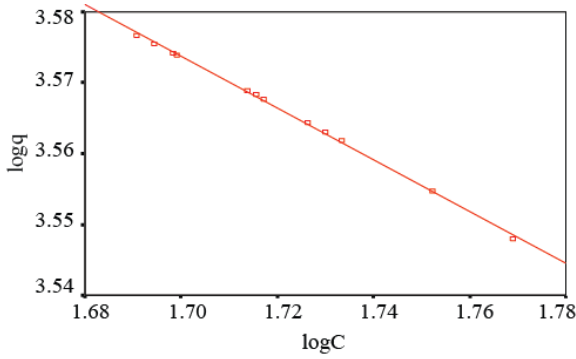


Fig. 17. Freundlich isotherm plots for biosorption of Cr (VI) at 4.5 pH.

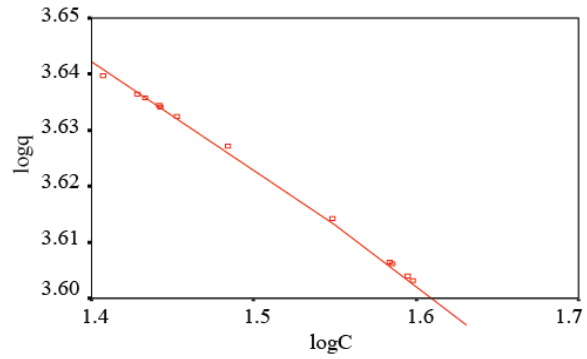


Fig. 19. Freundlich isotherm plots for biosorption of Cr (VI) at 5.5 pH.

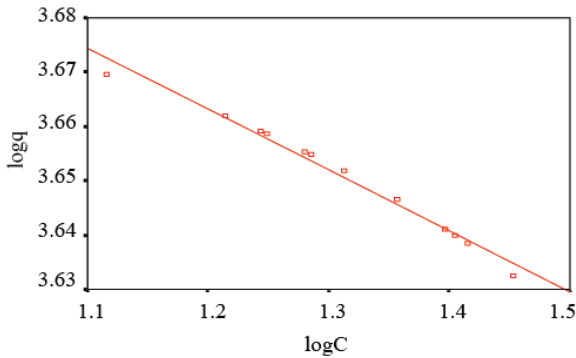


Fig. 18. Freundlich isotherm plots for biosorption of Cr (VI) at 5.0 pH.

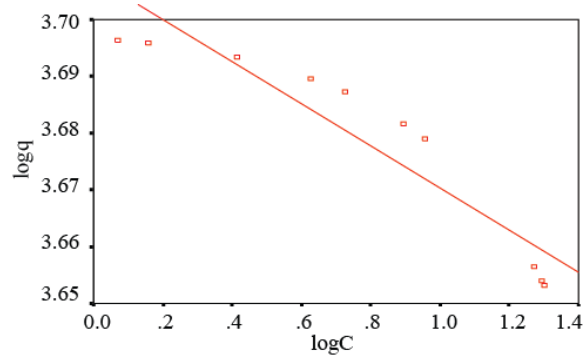


Fig. 20. Freundlich isotherm plots for biosorption of Cr (VI) at 6.0 pH.

The values of K and n were found to be 4.375 and -0.467 for pH 2.0, 4.386 and -0.473 for pH 2.5, 4.187 and -0.361 for pH 3.0, 4.140 and -0.334 for pH 3.5, 4.194 and -0.365 for pH 4.0, 4.431 and 0.498 for pH 4.5, 3.914 and 0.194 for pH 5.0, 3.798 and -0.112 for pH 5.5, 3.707 and -0.037 for pH 6.0 respectively. K is a measure of the capacity of the adsorbent (mass adsorbate/ mass adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. Values of n>1 indicate that affinities decrease with increasing adsorption density.

Biosorption kinetics at various incubation temperatures: Biosorption process is usually not operated at high temperatures because it increase the operational cost (Wang, 2002).The decrease of biosorption capacity at high temperature may be due to damage of active binding sites in the biomass (Ozer & Ozer, 2003). Due to exothermic nature of some adsorption processes, an increase in temperature has been found to reduce the biosorption capacities of the biomass. The biosorption of Cr (VI) by the *Gliocladium viride* ZIC₂₀₆₃ appeared to be temperature dependent over the temperature range (20-40°C) (Fig. 21). The highest Cr (VI)

removal rate (92.84%) was attained at 30°C with saturation of 15 min. At 30°C 185.69 mg/l Cr (VI) was removed from 200mg/l solution. Biosorption co-efficients of 3094.83 mg/g was reported at 30°C (Fig. 22). Temperature can affects the stability of cell wall, its configuration and can also cause ionization of chemical moieties. These factors may simultaneously affect the binding sites of fungal biomass and causing reduction in Cr (VI) removal (Congeevaram *et al.*, 2007; Gulay *et al.*, 2003). Maximum Cr (VI) removal rate (92.84%) was achieved at 30°C and further increase in temperature decreased the biosorption capacity. These results are in agreement with other researchers (Srivastava & thakur, 2006). Meena *et al.*, 2005 reported that with increase in adsorption temperature the number of active surface sites on fungal cell wall increased. But at high temperature (above 30°C) these active sites are deactivated or destroyed due to bond rupturing. Similarly on biosorption experiment data of incubation temperature 20, 25, 30, 35 and 40°C. Only Langmuir adsorption isotherm was found linearly fitted (Figs. 23-32). Langmuir and freundlich isotherms constants were also compared (Table 2).The results showed that Langmuir and freundlich isotherms fit well with experimental data.

Table 2. Comparison of Langmuir and Freundlich isotherms constants along with correlation co-efficient (r²) at different incubation temperature (°C).

incubation temperature (°C)	Langmuir isotherm constants		correlation co-efficient (r ²)	Freundlich isotherm constants		correlation co-efficient (r ²)
	q _{max}	b		k	n	
20	2541.16	-0.002	.983	4.400	-0.309	.999
25	2779.66	-0.002	.993	3.937	-0.208	.999
30	3094.83	-0.001	.979	3.451	-0.019	.001
35	3032.83	-0.001	.991	3.505	-0.118	.999
40	2909.5	-0.002	.986	3.437	-0.139	.985

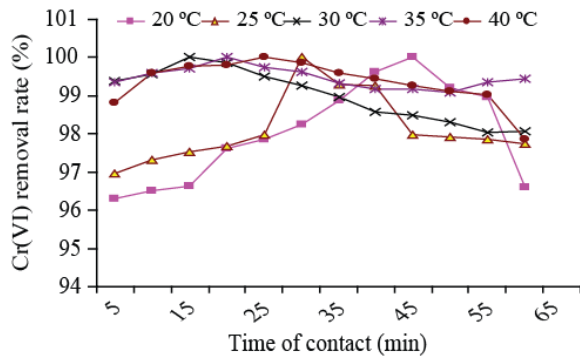


Fig. 21. Biosorption kinetics of Cr (VI) at various incubation temperatures (°C) Cr (VI) conc. 200 mg/l, pH 3.5, Biosorbent 3 g (wet weight), agitation 122 rpm Volume of Cr (VI) solution 50 ml in 250 ml conical flask.

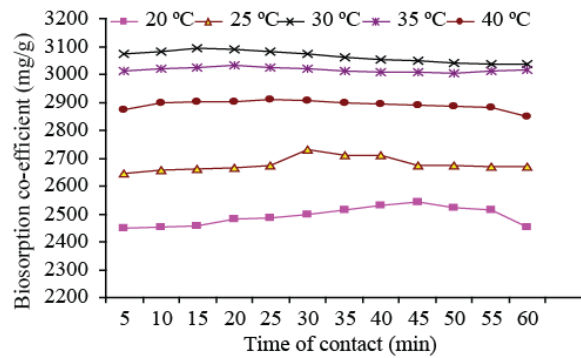


Fig. 22. Biosorption co-efficients rate at different Incubation temperature (°C) Cr (VI) conc. 200 mg/l, pH 3.5, Biosorbent 3 g (wet weight), agitation 122 rpm Volume of Cr (VI) solution 50 ml in 250 ml conical flask.

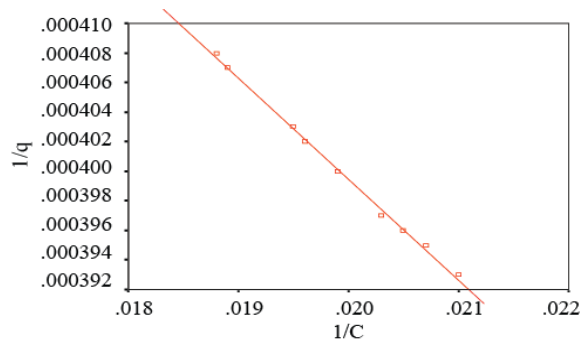


Fig. 23. Langmuir isotherm plots for biosorption of Cr (VI) at 20°C temperature.

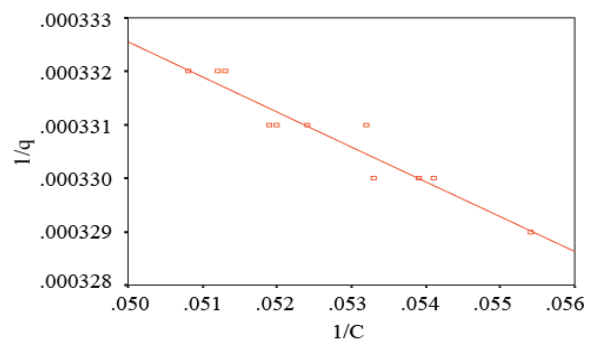


Fig. 26. Langmuir isotherm plots for biosorption of Cr (VI) at 35°C temperature.

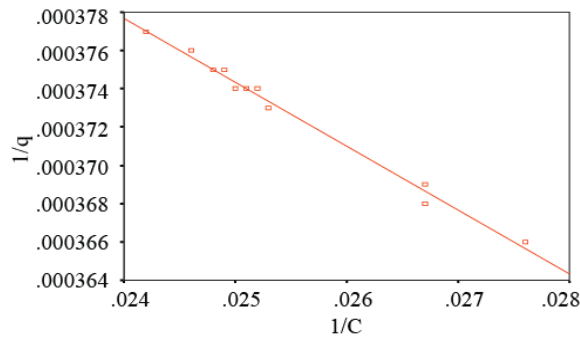


Fig. 24. Langmuir isotherm plots for biosorption of Cr (VI) at 25°C temperature.

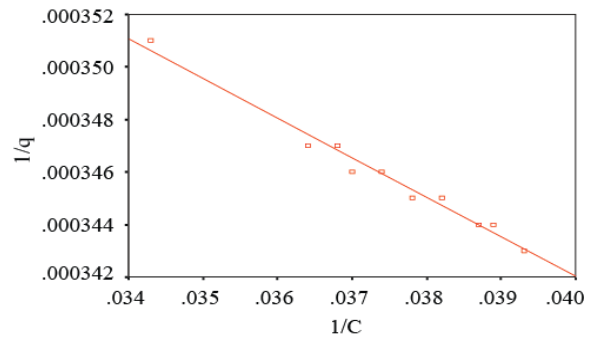


Fig. 27. Langmuir isotherm plots for biosorption of Cr (VI) at 40°C temperature.

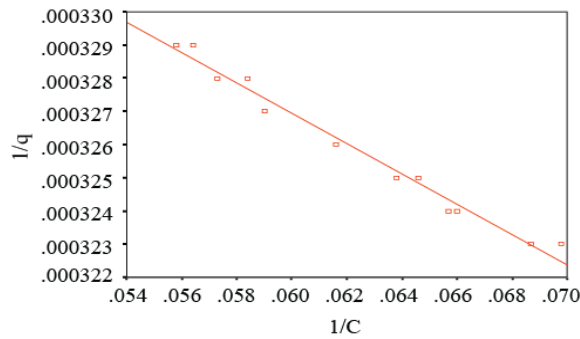


Fig. 25. Langmuir isotherm plots for biosorption of Cr (VI) at 30°C temperature.

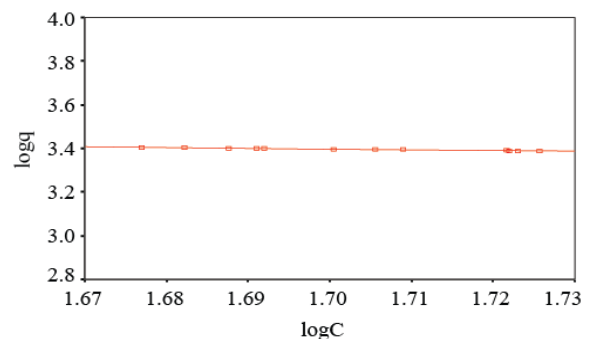


Fig. 28. Freundlich isotherm plots for biosorption of Cr (VI) at 20°C temperature.

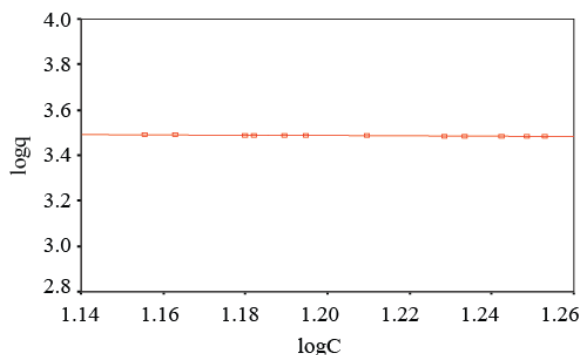


Fig. 29. Freundlich isotherm plots for biosorption of Cr (VI) at 25°C temperature.

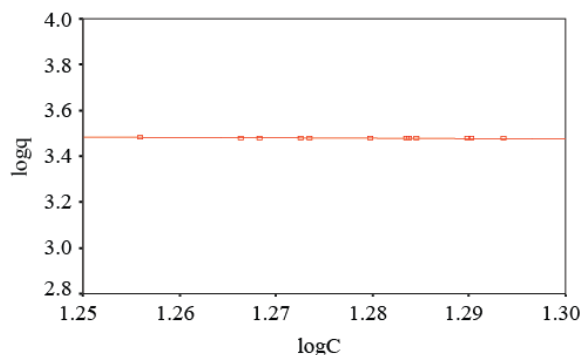


Fig. 31. Freundlich isotherm plots for biosorption of Cr (VI) at 35°C temperature.

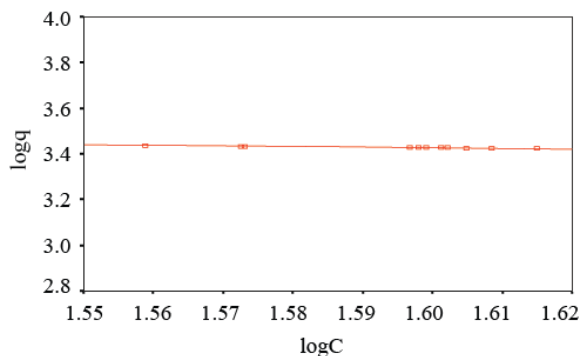


Fig. 30. Freundlich isotherm plots for biosorption of Cr (VI) at 30°C temperature.

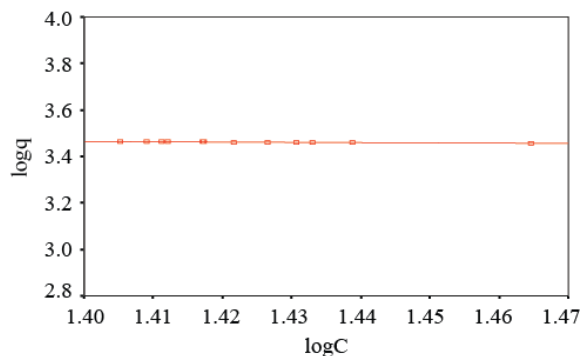


Fig. 32. Freundlich isotherm plots for biosorption of Cr (VI) at 40°C temperature.

Conclusion

Studies pertaining to the assessment of the best adsorption parameters and quantitative analysis of Cr (VI) uptake by *Gliocladium viride* revealed that the optimum pH for biosorption of Cr (VI) was 3.5. High values of correlation co-efficient ($R^2 > 0.90$) indicates the adsorption data best fitted in both Freundlich and Langmuir isotherms model. The results showed that *Gliocladium viride* is an efficient biosorbent for removal of Cr (VI) ions from aqueous solutions. The result showed that the most suitable sorption temperature was 30°C with maximum biosorption rate of 185.69 mg/l.

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