

Unleashing the Power of *Colchicum luteum* Leaf Powder for Hexavalent Chromium [Cr(VI)] Removal in Water - A Kinetic Study

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Abstract

This research paper investigates the efficacy of a biosorbent derived from leaf powder of *Colchicum luteum* for the mitigation of hexavalent chromium Cr(VI) from aqueous solution. The study aims to explore the potential of utilizing natural materials as a cost-effective and eco-friendly approach for heavy metal remediation. The biosorbent was prepared by processing the dried leaves of *C. luteum* into a fine powder. Batch experiments were conducted to evaluate the biosorption capacity of the prepared biosorbent for Cr(VI) removal. The effects of various parameters, including initial Cr(VI) concentration, contact time, temperature, concentration of solution and biosorbent dosage, were investigated to understand their influence on the biosorption process. The results of the study indicated that the biosorption of Cr(VI) onto *C. luteum* leaf powder followed the Freundlich, Langmuir, and Elovich isotherm models. The biosorption capacity varied with the initial concentration of Cr(VI) and the amount of biosorbent used. The study also revealed that the biosorption efficiency decreased with increasing biosorbent dose, suggesting the involvement of intraparticle diffusion. Further, the contact time and initial ion concentration influenced the biosorption process, with the maximum biosorption observed at 3 ppm Cr(VI) concentration.

Keywords: *Colchicum luteum*, Hexavalent chromium [Cr(VI)], Biosorption, Isotherm models.

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1. Introduction

Sura-ranjan (*Colchicum leuteum*) has various uses in Ayurvedic medicine such as liver disorder, spleen and skin problems, gout rheumatic disorder and leukaemia [1-2]. The chemical constituents are colchicine, demecolcine, colchifoline, N-formyl colchicine and corregerine are important Phytochemicals present in different species [3]. Medicinal plants have gained importance all over the world because of its long term relief against many diseases and lesser side effect [4]. But use of raw medicinal plants growing on a soil containing heavy metals can cause adverse health effects [5]. Generally, Pb, Cd, Cr are accumulated by the medicinal plants [6-8]. Detailed information on the medicinal properties, phytoremediation of Cr(VI), and specific information on *C. luteum* has been reported [9]. In view of these problems, the heavy metal uptake such as Cr(VI) by *Colchicum Leuteum* was studied and the data analysed for different isotherm [9-11]. Due to rapid industrialization and urbanization, aquatic environments are under imminent danger and facing a catastrophe. Hexavalent chromium Cr(VI), excessively released from various industries, has become a global concern [12]. Cr(VI) receives significant attention due to its widespread industrial applications and stability in the natural environment [13]. In some areas of the Gangetic basin in India, Cr(VI) naturally occurs in groundwater aquifers, leading to groundwater contamination.

The World Health Organization (WHO) has set a permissible concentration of Cr(VI) in water bodies at 0.05 ppm. Therefore, it is essential to decontaminate Cr(VI) from industrial wastewater before disposal and its return to the natural environment [14-15]. Numerous conventional methods have been developed and successfully implemented for Cr(VI) mitigation in water bodies. However, these methods are often cost-effective and technologically complicated, making them impractical for remote villages and distant locations. In recent years, several methods utilizing plant-based bio-sorbents have been developed for the treatment of heavy metals. Plant materials are advantageous as they are inexpensive, readily available, and can be applied without the need for external energy sources [16]. Various medicinal plants and herbs have been identified as effective agents for decontaminating Cr(VI) from aqueous solutions [17-18]. After extracting the medicinally important bioactive compounds, the waste parts of medicinal plants can be utilized as biosorbents for Cr(VI) mitigation [19]. One such plant of interest is *C. luteum*, also known as Suranjan. The objective of this work is to evaluate the biosorption capacities and kinetics of Cr(VI) using Langmuir, Freundlich, and Elovich isotherms.

2. Material and methods

2.1. Preparation of biosorbent from leaf biomass of *C. luteum*.

Healthy and green leaves of *C. luteum* were selected for biosorption studies of Cr(VI). Green leaves were cut into small pieces and also washed five times with running tap water and again thrice with distilled water. After that, the sample was air dried and cut into more small pieces again, put in an oven at 60 °C for 8 h (hour). After that, leave biomass was crushed in a grinder up to 200 mesh and again dried for 4 h at 60°C. Now biosorbent was prepared for batch operations.

2.2. Preparation of reagents

2.828 g of potassium dichromate (K₂Cr₂O₇) is dissolved in 1000 ml deionized water to get 1000 ppm Cr(VI) solution. The working solutions were obtained by serial dilution of the stock solution to the appropriate volume and 1, 2, and 3 ppm solutions were prepared. Murasige and Skooge basal salt solution (Himedia) was also added to the solution for nutrient support to plants.

2.3. Batch biosorption experiment of Cr(VI) by leaf biomass of *C. luteum*

The biosorbent properties of leaf biomass of *C. luteum* on Cr(VI) ions were investigated in batch operation at room temperature (300 K). Cr(VI) removal treatment was carried out in a series of conical flasks (250 mL) for a known concentration of Cr(VI) i.e. 1, 2, and 3 ppm of 100 ml aqueous solution, taken separately in 250 mL stoppered conical flask. Initial pH was adjusted by 1N NaOH and HCl at 6.5 – 7.0 (Tab. 1-3). Different masses of biosorbent dose were added separately for all above-mentioned concentrations for different time intervals i.e. 1g biomass for 1, 2, and 3 h separately as well as different weights of biomass (1, 2, 3, and 4 g) biomass doses for 1 h time period separately. Apart from these blank, aqueous solutions were also measured (without biomass) as control. After completion of treatment time, biosorbent was separated by filter paper and the residual solution of Cr(VI) was analyzed by UV double beam spectrophotometer (Pharo300) (Tab. 1-3). Cr(VI) was estimated by Spectroquant Chromate test kit (Merck). Total Cr(VI) present in the sample was determined after pretreatment of the sample by using this kit. In this procedure dry test tube is taken and 1 level microspoon (assembled in the cap of the bottle) Cr-1 reagent is added then 6 drop of reagent Cr-2 is added, provided in the kit. After that it is shaken properly until the reagent is completely dissolved then add 5 mL residual sample. It is left for 1 min at room temperature and measured in the spectrophotometer by balancing bar code for set up wave length. The concentration of Cr(VI) was also estimated by diphenyl carbazide method from UV double beam spectrophotometer systronics 2203 model. The values of concentration are in agreement with each other. The amount of Cr(VI) sorbed per unit mass adsorbent was evaluated by using mass balance equation (I) and the removal percentage was also determined according to the given equations (II). The adsorption amount per unit mass of adsorbent has been calculated by the equation given below.

$$q_t = (C_0 - C_t) V/W \quad (I)$$

where,

q_t is (mg/g) the amount of As (III) and Cr(VI) absorbed after time t in minutes. C_0 represents the initial concentration and C_t final concentration. V is the volume of As (III) and Cr(VI) solution (mL) and W is the weight of bio sorbent (g). The removal percentage (%) of Cr(VI) ions from the aqueous solution after biosorption was calculated by applying the following equation.

$$\text{Removal (\%)} = (C_0 - C_t)/C_t \times 100 \quad (II)$$

where,

C_0 and C_t were the initial and final concentrations respectively for Cr(VI) solution after the biosorption process.

2.4. Sorption isotherm models

Modelling of sorption isotherm data is important for predicting and comparing the sorption performance of the biosorbent. Therefore, the equilibrium data fitted using different isotherm models, namely Langmuir, Freundlich and Elovich. Sorption isotherms were performed by leave biomass of *C. luteum* in above mentioned batch condition and isotherm models were validated by their respective linear regression coefficient (R^2) as given in Fig 1- 10. To estimate the type of interaction involved, adsorption mechanism is derived by adsorption isotherms. Analysis of equilibrium sorption data of Cr(VI) onto biosorbent of *C. luteum* fitted to *Freundlich isotherm*, *Langmuir isotherm* and *Elovich isotherm* models, whose linear equations are given (III), (IV) and (V), respectively.

$$\log q_t = \log K_F + \frac{1}{n} \log C_t \quad (III)$$

$$\frac{1}{q_t} = \frac{1}{K_L q_m} \left(\frac{1}{C_t} \right) + \frac{1}{q_m} \quad (IV)$$

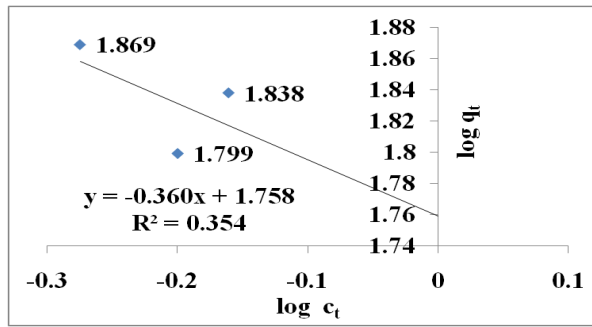
$$\ln \left(\frac{q_t}{C_t} \right) = \ln K_e q_m - \frac{q_t}{q_m} \quad (V)$$

In the above equations q_e = amount of adsorbate (mg) adsorbed per unit mass (g) of adsorbent, C_e = the equilibrium concentration (mgL⁻¹) of the adsorbate in the solutions. The applicability of Freundlich, Langmuir and Elovich isotherm analysis were determined by linear regression coefficient (R^2 Value) using Freundlich plot ($\log q_t$ versus $\log C_t$), Langmuir plot ($\frac{1}{q_t}$ versus $\frac{1}{C_t}$) and Elovich plot ($\ln \left(\frac{q_t}{C_t} \right)$ versus q_t) applied on batch equilibrium data at room temperature 308 K.

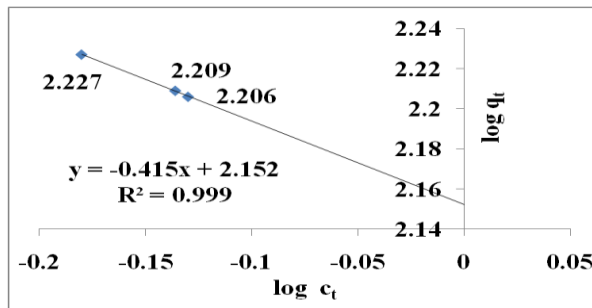
3. Results and discussion

3.1. Isotherm analysis of biosorption by leave biomass

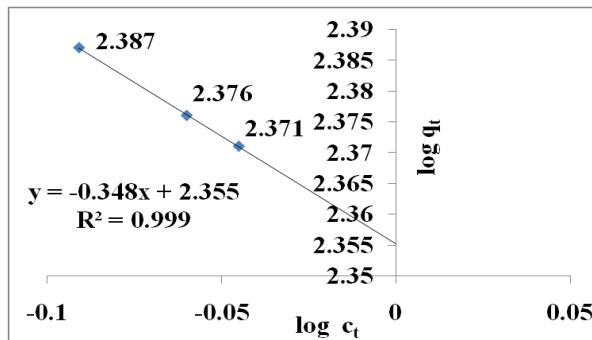
The type of adsorption mechanism involved in biosorption processes is determined by the adsorption isotherm model. Analysis of equilibrium sorption data of Cr(VI) on biosorbent dose of *C. luteum* fitted to Freundlich isotherm. Batch experiments for removal of Cr(VI) by leaf biomass of *C. luteum* from fixed weight (1g) of biosorbent dose with 1, 2 and 3 h time treatment separately, plots show linear regression coefficient (R^2) of Freundlich isotherm as 0.354, 0.999 and 0.999 (Fig. 1) for 1, 2 and 3 ppm initial concentration dose respectively. These results confirm that 1 ppm initial concentration does not obey the Freundlich model while the other two initial ion batches i.e. 2 ppm and 3 ppm exactly fitted on Freundlich model. In further studies, different weights of powdered biomass (1g, 2g, 3g, and 4 g) for fixed time intervals (1 h) were taken separately.



A



B



C

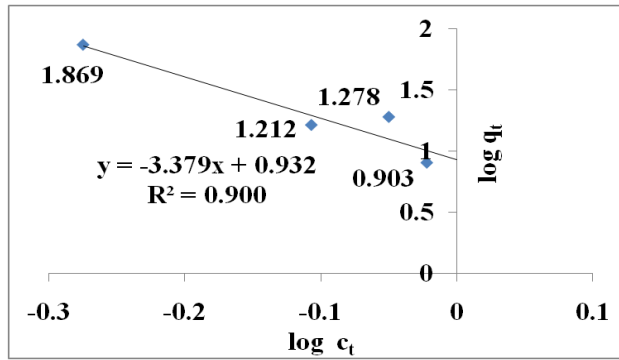
Figure 1: Plot of Freundlich isotherm of Cr(VI) biosorption by fixed weight biomass of *C. luteum* (1g) with different time interval (1h, 2h and 3h). Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).

Table 1: Langmuir, Freundlich and Elovich isotherm parameters for adsorption of Cr(VI) onto leave surface of *C. luteum* at room temperature and 1 ppm initial concentration

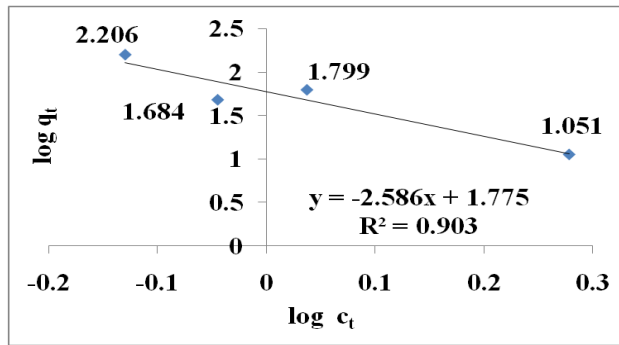
Biomass (g) with time interval (h)	C ₀	1 ppm Cr(VI) initial ion concentration									
		C _t	q _t	log C _t	log q _t	R ² (Freundlich)	1/C _t	1/q _t	R ² (Langmuir)	ln (q _t /C _t)	R ² (Elovich)
1g for 1h	1.27	0.53	74	-0.275	1.869	0.354	1.886	0.013	1.0	4.864	0.817
1g for 2h		0.64	63	-0.200	1.799		1.562	0.015		2.286	
1g for 3h		0.58	69	-0.161	1.838		1.724	0.014		4.778	
1g for 1h	2.35	0.53	74	-0.275	1.869	0.900	1.886	0.013	0.652	4.864	0.944
2g for 1h		0.89	19	-0.050	1.278		1.123	0.052		3.060	
3g for 1h		0.78	16.33	-0.107	1.212		1.282	0.061		3.0411	
4g for 1h		0.95	8	-0.022	0.903		1.052	0.125		2.130	

Table 2: Langmuir, Freundlich and Elovich isotherm parameters for adsorption of Cr(VI) onto leave surface of *C. luteum* at room temperature and 2 ppm initial concentration

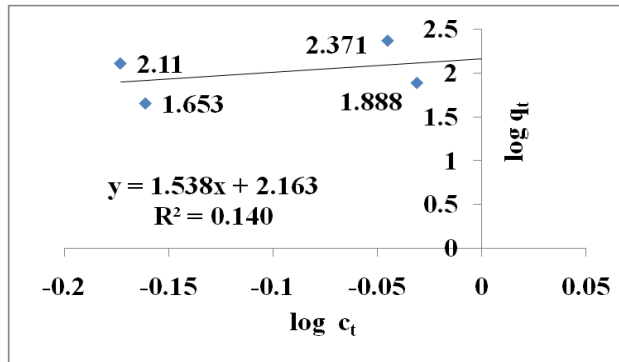
Biomass (g) with time interval (h)	C ₀	2 ppm Cr(VI) initial ion concentration									
		C _t	q _t	log C _t	log q _t	R ² (Freundlich)	1/C _t	1/q _t	R ² (Langmuir)	ln (q _t /C _t)	R ² (Elovich)
1g for 1h	2.35	0.74	161	-0.130	2.206	0.999	1.351	0.0062	0.995	5.382	1.0
1g for 2h		0.66	169	-0.180	2.227		1.515	0.0059		5.545	
1g for 3h		0.73	162	-0.136	2.209		1.396	0.0061		5.402	
1g for 1h	2.35	0.74	161	-0.130	2.206	0.903	1.351	0.0062	0.823	5.382	0.805
2g for 1h		1.09	63	0.037	1.799		0.917	0.0161		4.056	
3g for 1h		0.90	48.33	-0.045	1.684		1.111	0.0206		3.983	
4g for 1h		1.90	11.25	-0.278	1.051		0.526	0.0888		1.77	



(A)

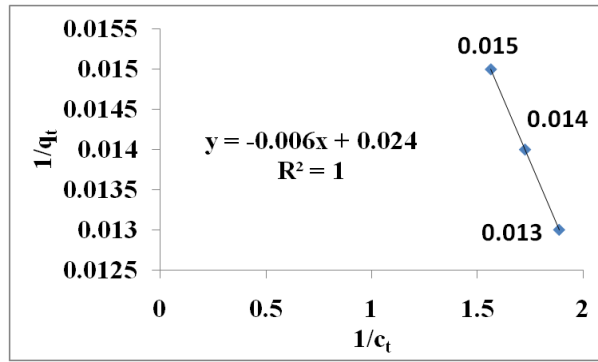


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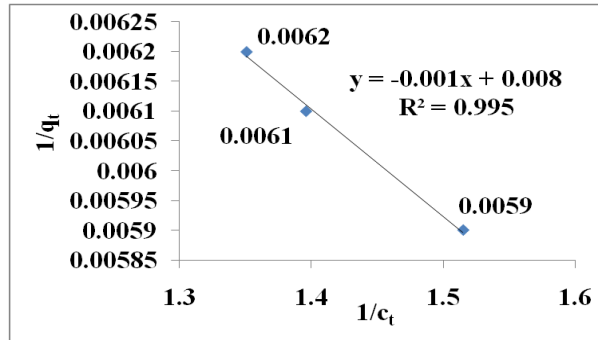


(C)

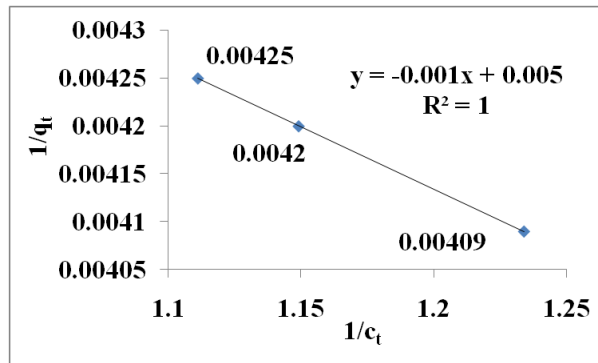
Figure 2: Plot of Freundlich isotherm of Cr(VI) biosorption by different weight biomass of *C. luteum* (1g, 2g, 3g and 4g) with uniform time interval (1h). Initial Cr(VI) concentration of 1 ppm (A), Initial Cr(VI) concentration of 2 ppm (B) and initial Cr(VI) concentration of 3 ppm (C),



(A)

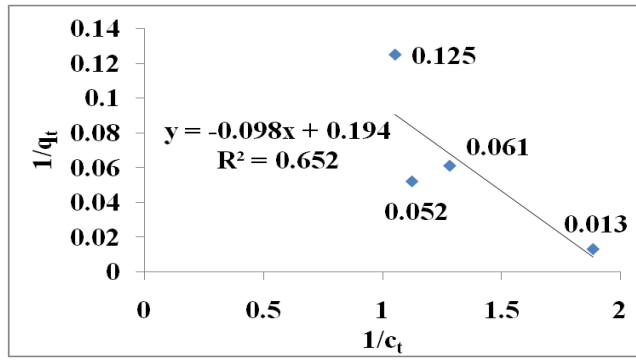


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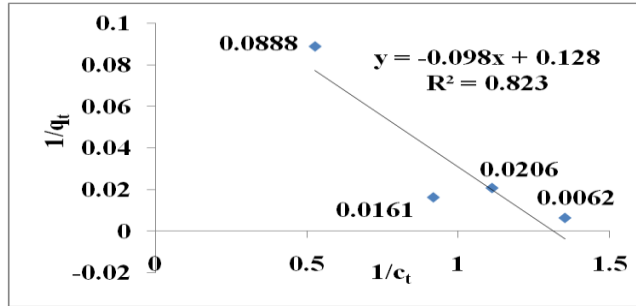


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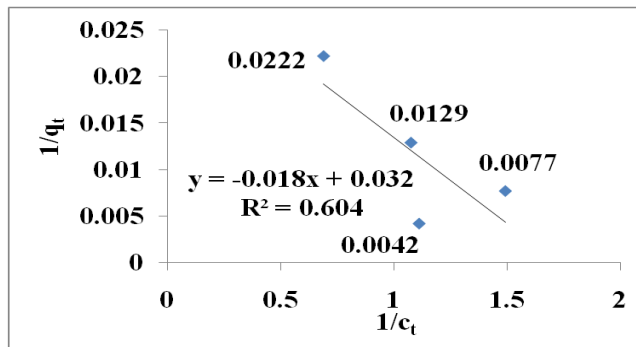
Figure 3: Plot of Langmuir isotherm of Cr(VI) biosorption by fixed weight biomass of *C. luteum* (1g) with different time interval (1h, 2h and 3h). Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)

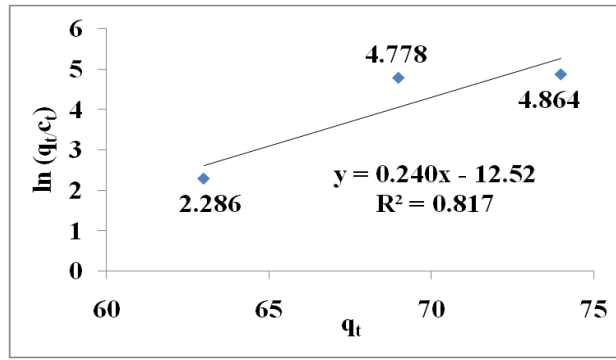


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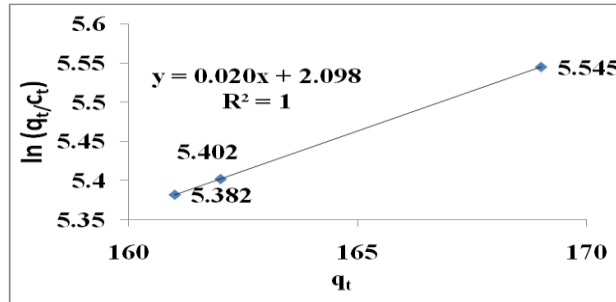


(C)

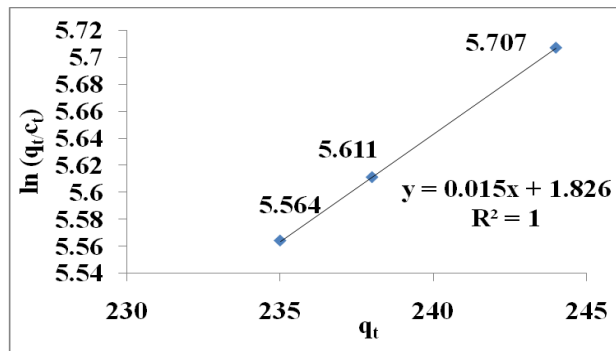
Figure 4: Plot of Langmuir isotherm of Cr(VI) biosorption by different weight biomass of *C. luteum* (1g, 2g, 3g and 4g) with uniform time interval (1h). Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)

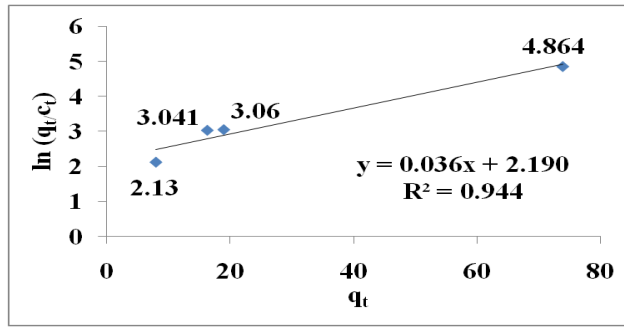


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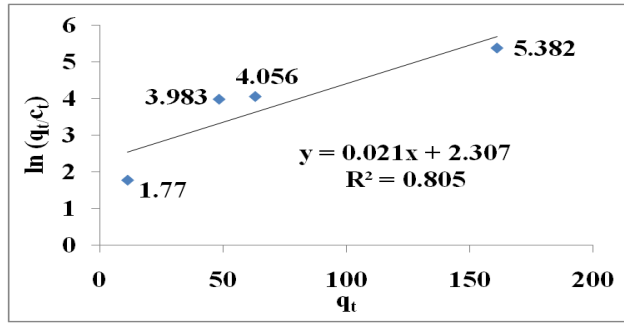


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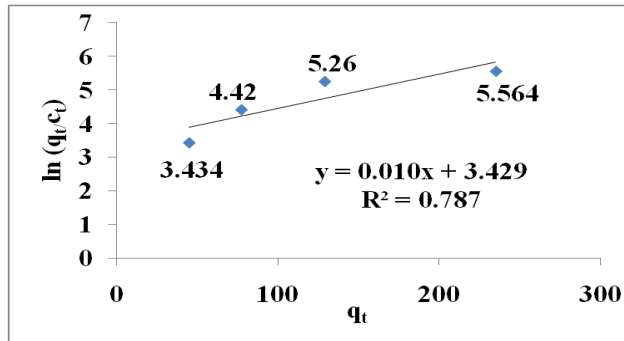
Figure 5: Plot of Elovich isotherm of Cr(VI) biosorption by fixed weight biomass of *C. luteum* (1g) with different time interval (1h, 2h and 3h). Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)

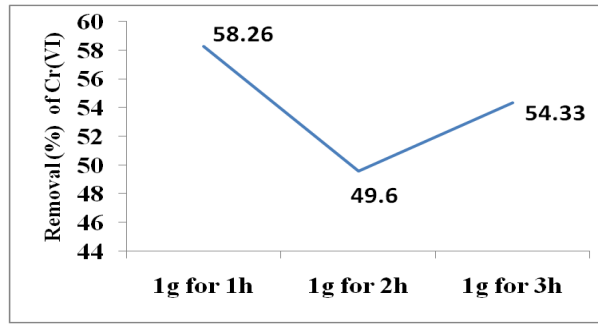


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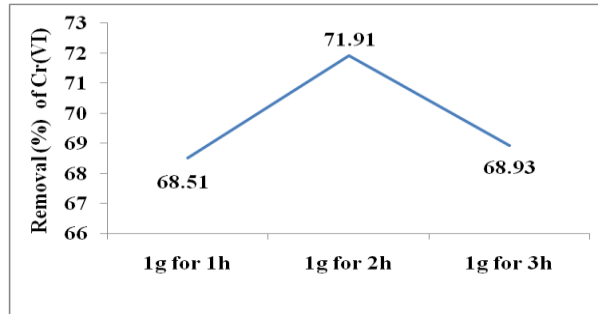


(C)

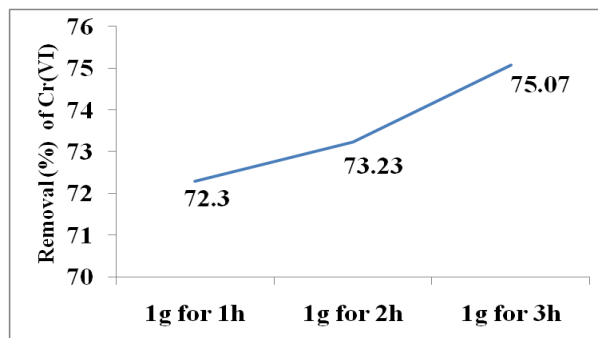
Figure 6: Plots of Elovich isotherm of Cr(VI) biosorption by different weight biomass of *C. luteum* (1g, 2g, 3g and 4g) with uniform time interval (1h). Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)

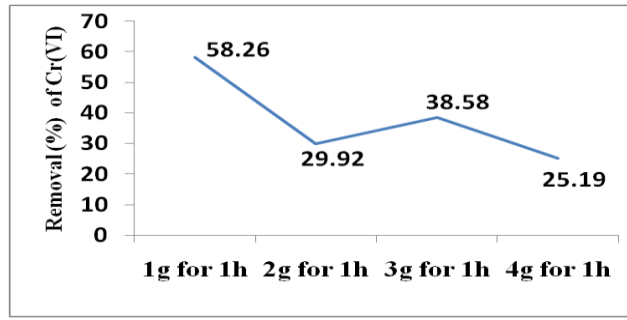


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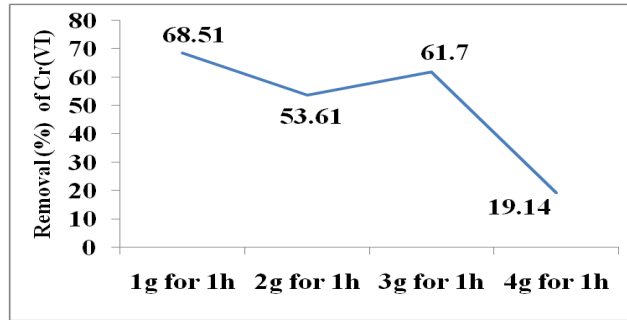


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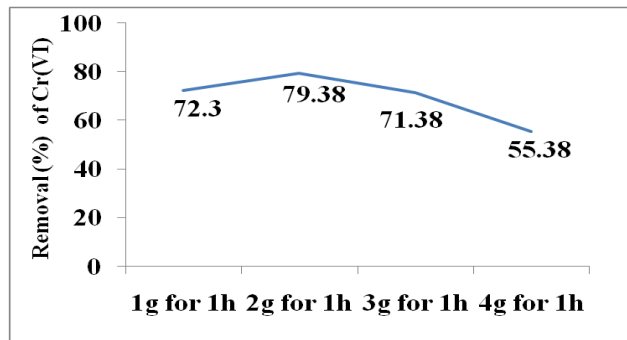
Figure 7: Graphs show removal percentage (%) of Cr(VI) after biosorption by fixed biomass of *C. luteum* (1g) of sorbent dose with different time interval (1h, 2h and 3h) at different initial As(III) and Cr(VI) concentration. Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)

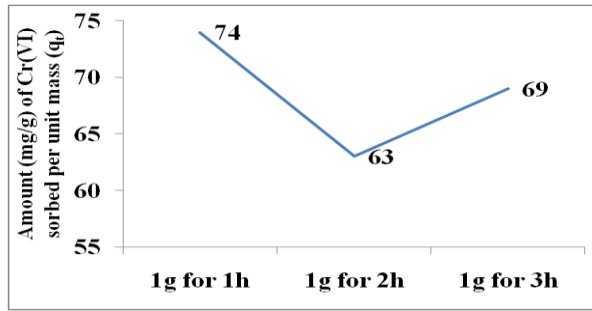


(B)

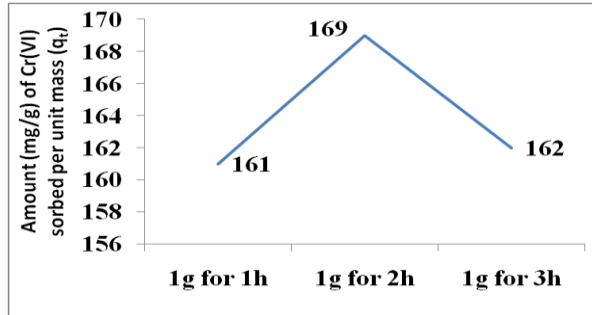


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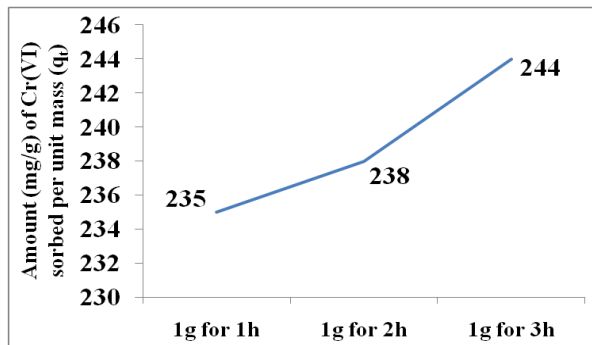
Figure 8: Graphs show removal percentage (%) of Cr(VI) after biosorption by Different biomass (*C. luteum*) (1g, 2g, 3g and 4g) of sorbent dose with fixed time (1h) interval at different Initial Cr(VI) concentration. Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)

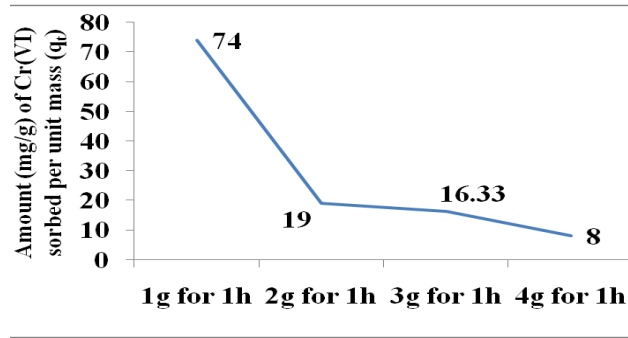


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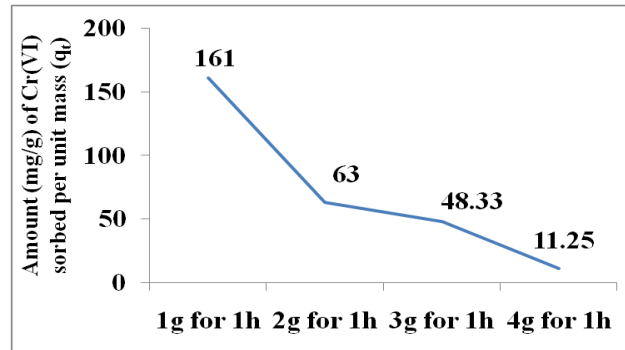


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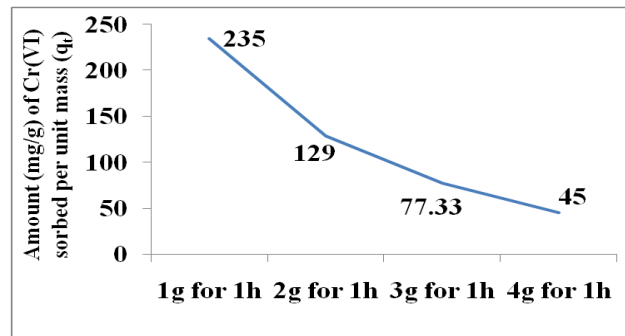
Figure 9: Amount of Cr(VI) sorbed per unit mass (q_t) by fixed biomass (*C. luteum*) (1g) of sorbent dose with different time interval (1h, 2h and 3h) at different initial Cr(VI) concentration. Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B), and initial Cr(VI) concentration of 3 ppm (C).



(A)



(B)



(C)

Figure 10: Amount of Cr(VI) sorbed per unit mass (q_i) by different biomass (*C. luteum*) (1g, 2g, 3g and 4g) of sorbent dose with uniform time interval (1h) at different initial Cr(VI) concentration. Initial Cr(VI) concentration of 1 ppm (A), initial Cr(VI) concentration of 2 ppm (B) and initial Cr(VI) concentration of 3 ppm (C).

Table 3: Langmuir, Freundlich and Elovich isotherm parameters for adsorption of Cr(VI) onto leave surface of *C. luteum* at room temperature and 3 ppm initial concentration.

Biomass (g) with time interval (h)	C ₀	3 ppm Cr(VI) initial ion concentration									
		C _t	q _t	log C _t	log q _t	R ² (Freundlich)	1/C _t	1/q _t	R ² (Langmuir)	ln (q _t /C _t)	R ² (Elovich)
1g for 1h	3.25	0.90	235	-0.045	2.371	0.999	1.111	0.00425	1.0	5.564	1.0
1g for 2h		0.87	238	-0.060	2.376		1.149	0.00420		5.611	
1g for 3h		0.81	244	-0.091	2.387		1.234	0.00409		5.707	
1g for 1h		0.90	235	-0.045	2.371	0.140	1.111	0.00425	0.604	5.564	0.787
2g for 1h		0.67	129	-0.173	2.110		1.492	0.0077		5.260	
3g for 1h		0.93	77.33	-0.031	1.888		1.075	0.0129		4.420	
4g for 1h		1.45	45	-0.161	1.653		1.689	0.0222		3.434	

R² values of Freundlich isotherm were 0.900, 0.903, and 0.140 (Fig. 2) for 1, 2 and 3 ppm respectively. These data were perfect for 1 and 2 ppm concentrations in Freundlich plots whereas at 3 ppm it does not apply. Langmuir isotherm application for estimation of biosorption mechanism in all three initial ion concentrations of Cr(VI) was studied. The biosorption of Cr(VI) in the batch operation of fixed biomass (1 g) for different time intervals i.e. 1 h, 2 h, and 3 h was studied. Langmuir plots illustrated that R² values are 1.0, 0.995, and 1 for 1,2 and 3 ppm ion concentration respectively (Fig. 3). These plots show that Langmuir isotherm is the best fit. In another set where, different weights of biomass (1 g, 2 g, 3 g, and 4 g) were treated for the same time duration (1 h) separately, their Langmuir plots showed that their R² values were 0.652, 0.823 and 0.604 for 1 ppm, 2 ppm and 3 ppm respectively (Fig. 4). This analysis states that Langmuir model is the best fit on the biosorption studies when treatment time varied with a fixed weight of biomass. An illustration of the Elovich model is also applied to this study. In batch experiments of fixed biomass (1 g) with ascending time treatment (1h, 2 h and 3 h), plots show 0.817, 1.0 and 1.0 (Fig. 5) R² data respectively for 1 ppm, 2 ppm and 3 ppm ion concentrations. At batch of 1 ppm Elovich model is overall a good fit while at 2 ppm and 3 ppm it shows maximum R² value i.e. a fit of this model. These results established that Cr(VI) adsorption implies multilayer sorption and adsorption sites increase during biosorption. Another set with different ranges of biosorption dose (1 g, 2 g, 3 g and 4 g) with fixed time treatment (1h) shows 0.994, 0.805 and 0.787 (Fig. 6) for R² data of 1 ppm, 2 ppm and 3 ppm respectively, show overall a good fit. Elovich model is completely suitable for all sets of these experiments.

3.2. Effect of adsorbent dose in biosorption

The batch sorption experiment was carried out by four doses (1, 2, 3 and 4 g) in 100 ml Cr(VI) containing medium for 1 h treatment with initial ion concentrations of 1, 2 and 3 ppm (Tab. 1-3). Biosorption of Cr(VI) decreased when the adsorption dose is increased up to 4 g (Fig. 8). This trend may be due to intraparticle diffusion whereas the amount of Cr(VI) sorbed per unit biomass also show decreasing trend (Fig. 10) in all three ion concentrations. Further, fixed biomass (1 g) was treated for 1 h, 2 h and 3 h treatment, Cr(VI) ion sorbed per unit mass only showed an increase with 3 ppm (Fig. 9). Amount of sorbed ion on per unit mass was illustrated (Fig. 9, 10). Biosorption experiment with 1 g biomass for 1 h, 2 h and 3 h at 1 ppm, 2 ppm and 3 ppm initial Cr(VI) concentration respectively shows decreasing trends with respect to increasing time (Fig. 10) whereas, further study with different weight of biomass (1 g, 2 g, 3 g and 4 g) for 1h with 1 ppm, 2 ppm and 3 ppm initial Cr(VI) concentration. At 1 ppm and 2 ppm set, it also follows the decreasing rate of q_t while at 3 ppm only shows increasing trends (Fig. 9).

Effect of contact time and ion concentration on biosorption

It was observed that the maximum biosorption took place in 3 ppm (Fig. 7, 8) ion concentration.

In different biosorbent doses (1, 2, 3 and 4 g) at 1 h time treatment for three different Cr(VI) concentration of 1 ppm, 2 ppm and 3 ppm, samples started showing desorption of Cr(VI) with almost every biosorption (Fig. 8). Further, 1 g biomass separately in 100 ml aqueous medium at 1 h, 2 h and 3 h time treatment, it was observed that effect of intraparticle diffusion had been found in 1 ppm and 2 ppm Cr(VI) ion

concentration whereas in 3 ppm ion concentration rate of biosorption increased with their contact time (Fig. 7).

The uptake of Cr(VI) by *Colchium leuteum* takes place either through bonding of ions to the surface complexation and electrostatic interaction [20-24].

4. Conclusions

Freundlich isotherm was best fitted on fixed leave biomass (1 g) experiment with 2 ppm and 3 ppm initial Cr(VI) concentration. On other hand Langmuir isotherm was completely fitted on all initial concentration of batches of fixed biomass set. Elovich isotherm was a fit for 1 ppm and 2 ppm batch of fixed biomass set whereas it only fitted on 1 ppm initial ion concentration from different weight of biomass set. In biosorption experiment of Cr(VI) by leave biomass of *C. luteum*, a maximum removal percent of 79.38 was observed. Thus the biosorption capacity varied with the initial concentration of Cr(VI) and the amount of biosorbent used. It was observed that the biosorption efficiency decreased with increasing biosorbent dose. The maximum biosorption was achieved at 3 ppm Cr(VI) concentration. Plant-based biosorbents offer a cost-effective and environmentally friendly alternative for heavy metal remediation. The uptake of Cr(VI) by *Colchium leutium* revealed that analysis of heavy metals should be done before consumption and contamination soil sites must be excluded for growing medicinal plants and drug preparation

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