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**OPTIMIZATION OF CHROMIUM BIOSORPTION BY AGERATUM CONYZOIDES
LEAF POWDER FROM AQUEOUS SOLUTIONS: EQUILIBRIUM KINETICS AND
THERMODYNAMICS**

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ABSTRACT

The study on low-cost adsorbent such as *Ageratum conyzoides* leaf powder was used to remove chromium from aqueous solutions. Experiments were conducted in batch mode to observe the influence of various parameters such as effect of contact time (1-180 min.), pH (2-8), biosorbent dosage (5-60g/L), effect of temperature (283- 323 K), biosorbent size (53-152), initial metal concentration (20- 200 mg/L), the equilibrium agitation time for chromium biosorption was found to be 50 minutes. The % removal of Cr increased significantly with increase in pH (6), biosorption dosage (35g/L) and temperature (303K). The percentage removal of chromium decreased by increasing the initial concentration of chromium and absorption size. The experimental biosorption data were modeled using Langmuir, Freundlich and Temkin isotherms. Based on R² values, the Freundlich (R² = 0.9967) model fitted the equilibrium biosorption data best, confirming monolayer adsorption of chromium on to the biosorbent surface followed by Langmuir (R² = 0.987) and Temkin (R² = 0.9535). The biosorption kinetics of chromium was best described by pseudo-second order (R² = 0.9890) kinetics since at all concentrations, the R² values were higher than the corresponding pseudo-first order (R² = 0.9534) values. Based on thermodynamic parameters the biosorption of Cr by *A. conyzoides* leaf powder was found to be spontaneous, endothermic and feasible under given conditions.

KEYWORDS: Plant, *Ageratum conyzoides* leaf powder, Absorption, Isotherms, Kinetics, Thermodynamics.

INTRODUCTION

The heavy metal contaminants in aqueous streams are continuously disposed without any treatment by various industries such as Mining, Mineral processing, Metallurgical operations, Electroplating, Painting, Dying and many other industrial effluents contain undesirable amounts of Cr (VI) ions in the water bodies removal of chromium is one of the most important issues throughout the world [1]. Their presence in ecosystem causes harmful effects to living organisms [2]. Metal ions are reported are priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [3], these metal ions gets accumulated in living tissues and cause various diseases and disorders [4]. In aqueous phase chromium mostly exists in two oxidation states, namely trivalent chromium (Cr⁺³), and hexavalent chromium (Cr⁺⁶). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic [5]. For example, it was reported that high levels of Cr (VI) leads to liver damage, pulmonary congestion and edema [6, 7]. The maximum permissible limit of Cr (VI) for industrial waste waters varies from 0.05 to 0.1 mg/L and total chromium containing Cr (III), Cr (VI) and other species of chromium should be below 2 mg/L [8]. Various methods have been reported for the removal of chromium such as chemical precipitation [9] Electrochemical precipitation [10] etc. However these technologies have many disadvantages like ineffective or expensive when heavy metals are present in the wastewater at low concentrations. The use of biosorption technology for the treatment of heavy metal contaminants in wastewater has become a useful method to conventional treatment. Several studies related to

chromium removal were carried out using biomaterial such as *Carum copticum* stem waste [11], wall nut hull [12], *Gracilaria corticata* var *cartecala* and *Grateloupia lithophila* [13] and saw dust [14]. Mangrove leaf powder [15].

Ageratum conyzoides is a tropical plant, which is annual and herbaceous with white flower and brown fruits with a penetrating smell of thymol that grows in Africa, Australia, USA, Southeast Asia and India. The leaf powder of *A. conyzoides* can be used as biosorbent for the removal of chromium from aqueous solutions. The aim of the present study was to investigate the chromium removal efficiency from aqueous solutions by using *A. conyzoides* leaf powder as biosorbent, which is a novel sorbent. The experiments were carried out by batch method and the effects of different parameters on biosorption of chromium were studied. Equilibrium isotherms and kinetic studies were also investigated.

MATERIALS AND METHODS

Preparation of biosorbent material

The plant weeds *Ageratum conyzoides* were collected from Selaqui area of Dehradun district, Uttarakhand, India. Weeds were packed in sterile polythene bags before transferring to the laboratory. The leaves of the plant were separated and washed with deionized water for 5 minutes to remove dirt, and unwanted materials present in it. After washing, the leaves were subjected to shade drying for 2 weeks. The dried leaves were grounded by using a domestic mixer grinder and sieved to the pore size of 53 μ m - 152 μ m using BSS sieves.

Preparation of stock solution

Aqueous chromium solution of concentration 1000 mgL⁻¹ was prepared by dissolving 2.828 g Potassium dichromate (Merck, India) salt in 1000 ml distilled water. Further various concentrations ranging from 20-200 mgL⁻¹ was prepared by serial dilution using distilled water.

Batch biosorption procedure

Various optimization process parameters like effect of pH (2-8), contact time (1, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 minutes), biosorbent size (53, 75, 105, 125 & 152 μ m), biosorbent dosage (5- 60 gL⁻¹), initial metal concentration (20, 50, 100, 150 & 200 mgL⁻¹), effect of temperature (283, 293, 303, 313 & 323 K) were studied. Experiments were carried out in 250 ml Erlenmeyer flask, using 50ml of aqueous solution, initially 20 gL⁻¹ Cr and 10 gL⁻¹ *A. conyzoides* leaf powder as biosorbent was taken and further all parameters were optimized as stated at the above range. The experimental flasks were kept in orbital shaker to provide continuous agitation and to facilitate the contact between the sorbent and the sorbate. After particular time the mixtures obtained were filtered using whatman No.2 filter paper and the filtrates were analyzed using atomic absorption spectroscopy (Perkin Elmer A Analyst 200 model) for residual chromium concentration in the solutions [16]. Langmuir, Freundlich and Temkin isotherms were studied for varying concentrations of the metal ions at constant temperature.

RESULTS AND DISCUSSION

Effect of agitation time

Effect of contact time using *A. conyzoides* leaf powder on % chromium removal was plotted in Fig.1. With the interaction time intervals of 1 to 180 minutes, in the first 5 minutes of contact time less amount of chromium is biosorbed. Then % biosorption increased rapidly up to 50 minutes. Thereafter, the % biosorption is constant indicating the attainment of equilibrium conditions. The rate of biosorption is fast in the first 50 minutes due to adequate surface area of the biosorbent available for the biosorption. Whereas at later stages, the biosorbent trends to become saturated with the metal ions due to Vander Waal's forces of attraction and results in decreased available surface area [17]. At 50 minutes of contact time equilibrium concentration was achieved indicating that all the binding sites have saturated completely [18]. The adsorbate normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted [19].

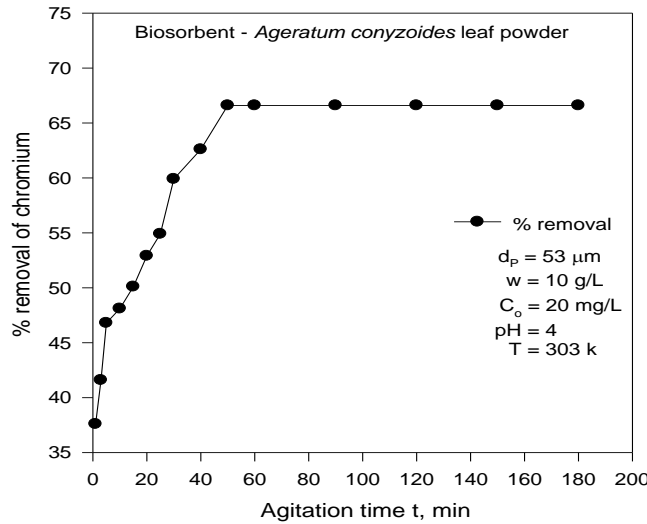


Figure 1. Effect of agitation time on % removal of chromium (biosorbent particle size = 53 μ m; dosage = 10g/L; chromium concentration = 20 mgL⁻¹; pH = 4; temperature = 303K)

Effect of biosorbent size

The effect of biosorbent size on % chromium removal is plotted in Fig. 2. Maximum percentage removal of chromium was observed at 53 μ m, with a decrease in biosorbent size, surface area of the biosorbent increases and the numbers of active sites on the biosorbent are better exposed to the biosorbate [20]. Beyond 53 μ m percentage removal of chromium decreased due to exposure to less number of active sites [21, 22].

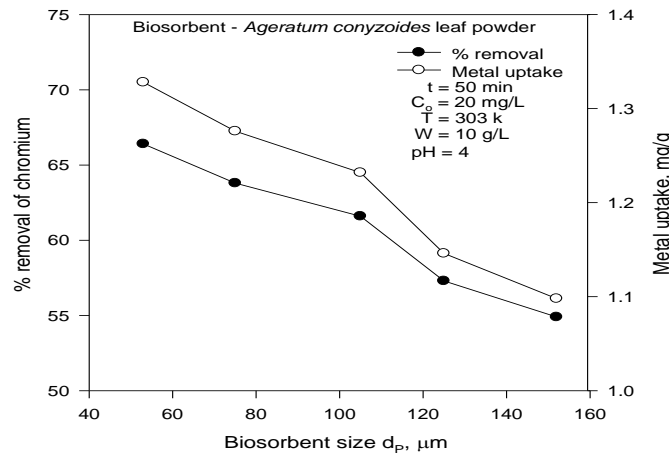


Figure 2. Effect of biosorbent size on % removal of chromium (contact time = 50 min.; chromium concentration = 20 mgL⁻¹; temperature = 303K; pH = 4)

Effect of pH

The effect of pH influences the surface charge of the adsorbent, in biosorption as plotted in Fig.3. pH affects the availability of adsorption sites on the adsorbent and also the solubility of the metal ions in the solution [23]. The % removal of chromium increased from pH value of 2 to 6 and then decreased, beyond pH value of 6. Low pH depresses biosorption of chromium, which may be due to competition with H⁺ ions for appropriate sites on the adsorbent surface [24]. However, with increasing pH, this competition weakens and chromium ions replace H⁺ ions bound to the adsorbent or forming part of the surface functional groups such as OH, COOH, etc. [25, 26].

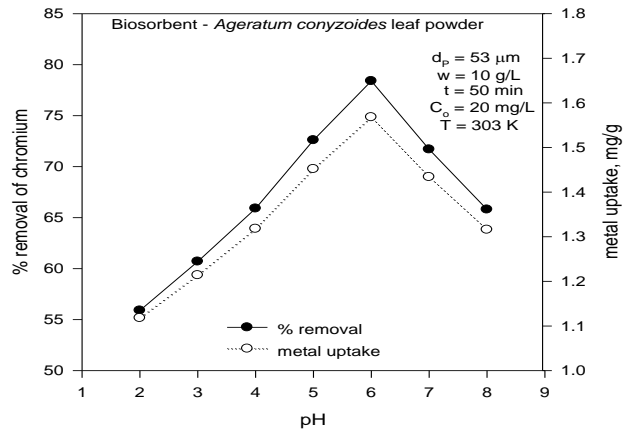


Figure 3. Effect of pH on % removal of chromium (biosorbent particle size = 53µm; dosage = 10gL⁻¹; contact time = 50 min.; chromium concentration = 20 mgL⁻¹; temperature = 303K)

Effect of initial chromium concentration

The effect of initial concentration of chromium using *A. conyzoides* leaf powder on the percentage removal of chromium is shown in Fig.4. The percentage removal of chromium ion decreased with an increase in chromium concentration from 20 mgL⁻¹ to 200 mgL⁻¹. On increasing chromium ion concentration, the available adsorption sites are already occupied and consequent adsorption is not as efficient as in the beginning [27, 28]. The percentage removal decreased as the concentration of chromium increased and it is due to lack of active sites. [29].

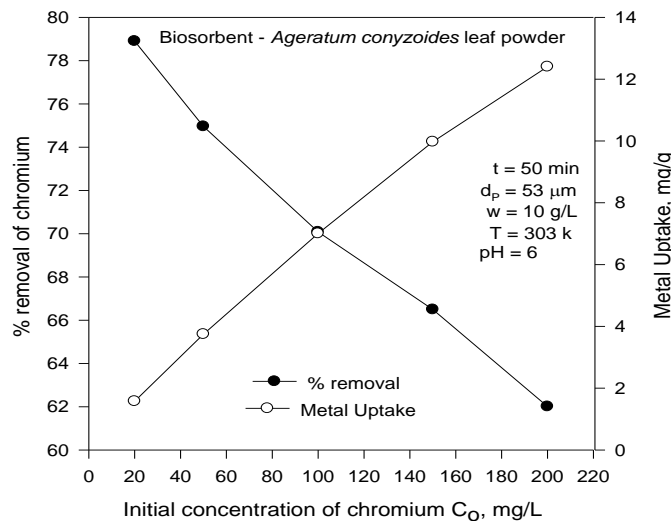


Figure 4. Effect of initial concentration on % removal of chromium (contact time = 50 min.; biosorbent particle size = 53µm; dosage = 10gL⁻¹; temperature = 303K; pH = 6)

Effect of Biosorbent dosage

The effect of biosorbent dosage on biosorption of chromium has been studied in Fig.5. The maximum biosorption of chromium was observed at biosorbent dosage of 35gL⁻¹. And the removal of chromium increased with an increase in biosorbent dosage from 5 to 35 gL⁻¹. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for chromium removal would be more. [30, 31].

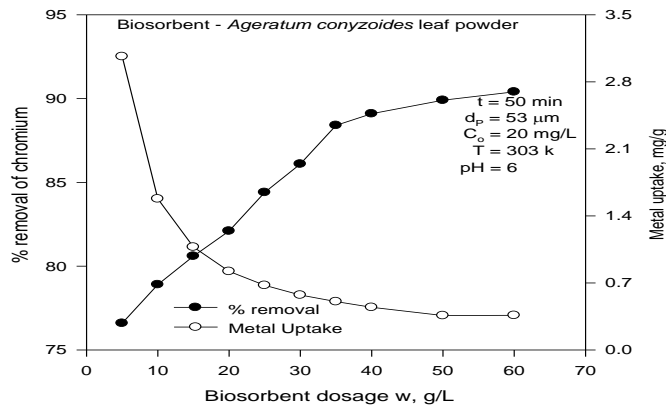


Figure 5. Effect of biosorbent dosage on % removal of chromium (contact time = 50 min.; biosorbent particle size = 53μm; chromium concentration = 20mgL⁻¹; temperature =303K; pH =6)

Effect of temperature

The effect of temperature on the equilibrium metal uptake was significant. The effect of temperature on the chromium uptake is shown in Fig.6. When temperature was lower than 303 K, chromium uptake increased with increasing temperature, but when temperature was over 303 K, the increase in chromium uptake is very minute. [32]

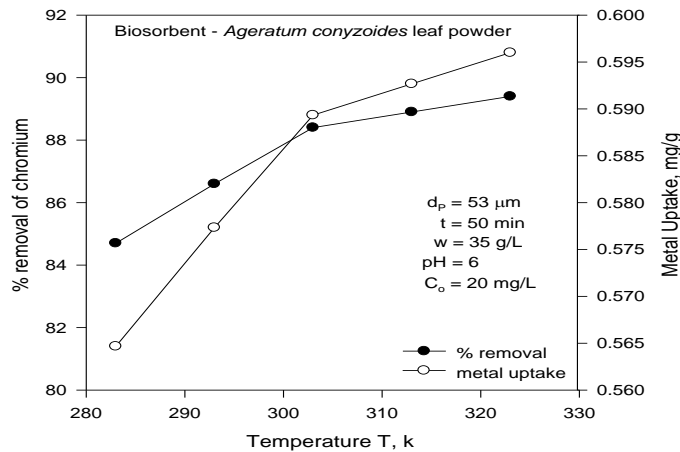


Figure 6. Effect of temperature on % removal of chromium (biosorbent particle size = 53μm; contact time = 50 min.; dosage =10gL⁻¹; pH =6; chromium concentration = 20mgL⁻¹)

This response suggested a different interaction between the ligands on the cell wall and the metal. Below 303 K, chemical biosorption mechanisms played a dominant role in the whole biosorption process, biosorption was expected to increase by increasing the temperature while at higher temperature, and the increase is marginal.

Isotherms for biosorption of chromium

The equilibrium data for removal of the chromium using *A. conyzoides* leaf powder using the Langmuir, Freundlich and Temkin isotherm adsorption models. Langmuir isotherm [33]. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete mono layer coverage on the adsorbent surface. Langmuir equation was used to correlate the equilibrium data by using the given equation.

$$C_e/q_e = 1/bq_m + C_e/q_m \quad \text{--- (1)}$$

Where C_e= Equilibrium adsorption concentration of metal, mgL⁻¹

q_e = Mass of solute adsorbed per mass of biosorbent at equilibrium, mg/g

b (1/mg) is the Langmuir constant

q_m (mg/g) is the maximum amount of metal ion per unit weight of biosorbent.

From the plots between (C_e/q_e) and C_e , the slope $(1/q_m)$ and the intercept $(1/b)$ are calculated. Further analysis of Langmuir equation is made on the basis of separation factor (R_L), defined as

$$R_L = 1 / (1 + bC_e) \quad \text{--- (2)}$$

The regression correlation coefficients (R^2) generated was 0.987 for initial Cr concentration of 10 mgL^{-1} , as shown in Fig.7. Langmuir isotherm has good linearity (correlation coefficient, $R^2=0.987$) indicating strong binding of chromium ions to the surface of *Ageratum conyzoides* leaf powder. The separation factor obtained is 0.9317, shows favorable adsorption ($0 < R_L < 1$).

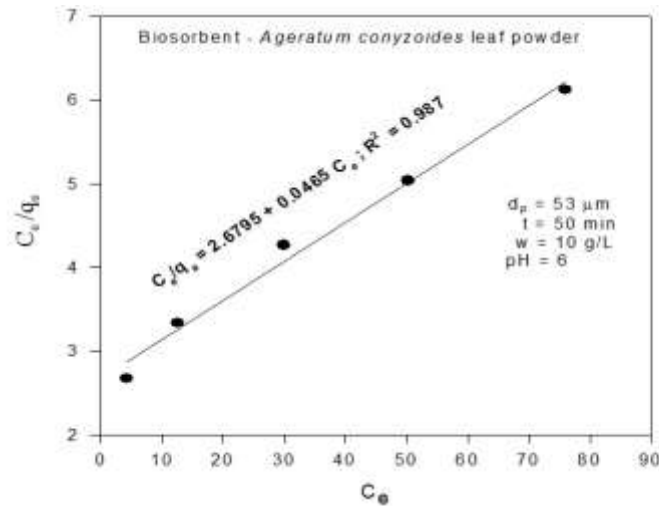


Figure 7. Langmuir isotherm for biosorption of chromium (biosorbent particle size = 53um; contact time = 50 min.; dosage = 10g/L⁻¹; pH =6)

Freundlich isotherm

Freundlich isotherm is the equilibrium relationship between the concentration of the metal in the fluid phase and its concentration in the adsorbent at a given temperature. Freundlich [34] presented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges.

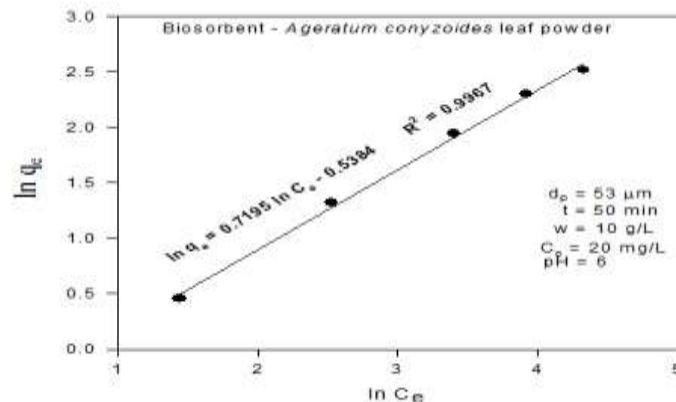


Figure 8. Freundlich isotherm for biosorption of chromium (biosorbent particle size = 53um; contact time = 50 min.; dosage

$$=10\text{gL}^{-1}; \text{chromium concentration} = 20\text{mgL}^{-1}; \text{pH} = 6$$

The equation is $\ln q_e = \ln K_f + n \ln C_e$ ---- (3)

Where

(K_f) and (n) are the Freundlich constants.

C_e = Equilibrium adsorption concentration of metal, mgL^{-1}

q_e = Mass of solute adsorbed per mass of biosorbent at equilibrium, mg/g

Freundlich isotherm is drawn between $\ln C_e$ and $\ln q_e$ in Fig.8. The resulting line has the correlation coefficient of 0.9967. The resulting equation is $\ln q_e = 0.7195 \ln C_e - 0.5384$. The 'n' value (0.7195) in the above equation satisfies the condition of $0 < n < 1$ indicating favorable biosorption.

Temkin isotherm

The Temkin [35] isotherm equation describes the behavior of many biosorption systems on the heterogeneous surface and it is based on the equation

$$q_e = RT \ln(A_T C_e) / b_T \quad \text{--- (4)}$$

Where

R = the universal gas constant

T = the absolute temperature in Kelvin

A = the equilibrium binding constant

The linear form of Temkin isotherm can be expressed as

$$q_e = (RT / b_T) \ln(A_T) + (RT / b_T) \ln(C_e)$$

Where

$$A_T = \exp [b(0) \times b(1) / RT]$$

$b(1) = RT / b_T$ is the slope

$b(0) = (RT / b_T) \ln(A_T)$ is the intercept

The obtained A_T and b_T values are 0.2836 and 675.88.

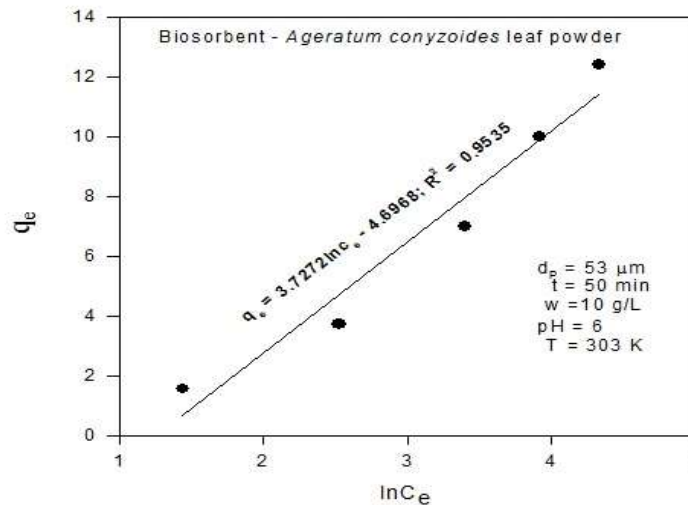


Figure 9. Temkin isotherm for biosorption of chromium (biosorbent particle size = 53μm; contact time = 50 min.; dosage = 10gL⁻¹; pH =6; temperature = 303K)

The present data are analyzed according to the linear form of Temkin isotherm and the linear plot is shown in Fig.9. The equation obtained for chromium biosorption is $q_e = 3.7272 \ln C_e - 4.6968$ with a correlation coefficient of 0.9535. The best fit model is determined based on the linear regression correlation coefficient (R). From the Fig's. 7, 8, 9, it was found that biosorption data are well represented by Freundlich isotherm with higher correlation coefficient of 0.9967 followed by Langmuir and Temkin isotherms with correlation coefficients of 0.987 and 0.9535 respectively. Table 1 indicates isotherm constants as given below

Table-1 Isotherm constants (linear method)

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
qm = 21.505 mg/g	Kf = 9.4616 mg/g	AT = 0.2836 L/mg
b = 0.0173	n = 0.7195	bT = 675.88
R2 = 0.987	R2 = 0.9967	R2 = 0.9535

Kinetics of biosorption

The kinetics of biosorption describes the order of the reaction. Most of the adsorption systems using different adsorbents for metal removal preceded by diffusion through a boundary are found to satisfy Lagergren’s first order model [36].

$$(dq/dt) = K_{ad} (q_e - q_t) \quad \text{--- (5)}$$

Where

K_{ad} is the pseudo first order adsorption rate coefficient

q_e & q_t are the values of amount adsorbed per unit mass at equilibrium at any time t .

After applying the initial condition $q_t = 0$ at $t = 0$, we get

$$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303) t \quad \text{--- (6)}$$

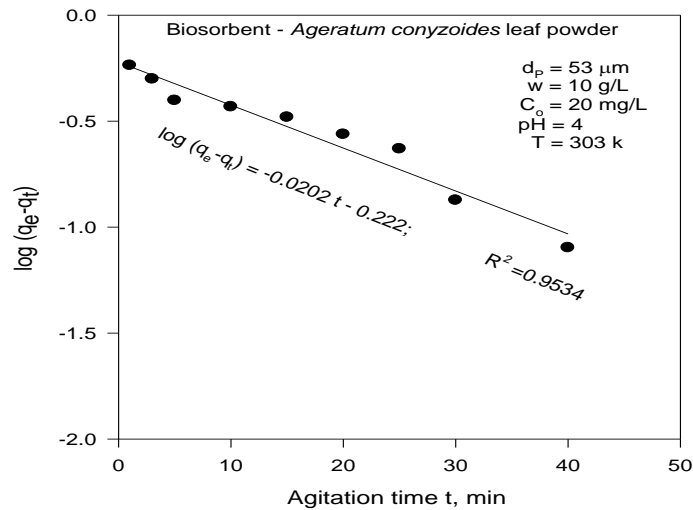


Figure 10. Pseudo first order kinetics for biosorption of chromium (biosorbent particle size = 53um; dosage =10g/L⁻¹; chromium concentration = 20mgL⁻¹; pH =6; temperature = 303K)

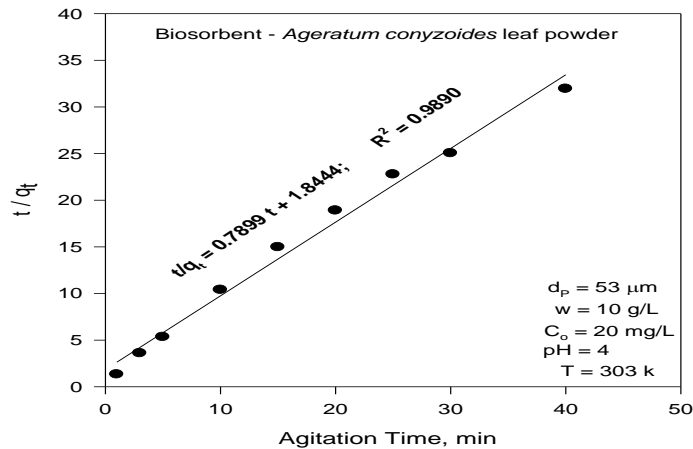


Figure 11. Pseudo Second order kinetics for biosorption of chromium (biosorbent particle size = 53um; dosage =10g/L⁻¹; chromium concentration = 20mgL⁻¹; pH =4; temperature = 303K)

If the plot of $\log (q_e - q_t)$ vs. 't' gives a straight line, it indicates that the first order kinetics better describes the biosorption. Then the biosorption rate constant (slope), K_{ad} can be calculated from equation (6). If the experimental results do not follow equation (6), the pseudo second order kinetics is applied to describe these interactions in certain specific cases. The pseudo second order kinetics [37] considers the rate limiting step as the formation of physicosorption bond involving sharing or exchange of electrons between the adsorbate and adsorbent. The second order rate equation is given by:

$$(T/qt) = (1/ K q_e^2) + (1/q_e) t \quad \text{--- (7)}$$

If the plot yields a straight line, the biosorption is described by the second order kinetics and q_e and K are calculated. In the present study, the kinetics are investigated with 50 mL of aqueous solution ($C_o = 20 \text{ mgL}^{-1}$) with biosorbent dosage of 10 gL^{-1} and the interaction time intervals of 1 to 180 min. Lagergren plot of $\log (q_e - q_t)$ versus agitation time (t) for biosorption of chromium by *Ageratum conyzoides* leaf powder is drawn in Fig.10. Pseudo second order plot was drawn between agitation time, t and t/qt and is shown in fig.11. The results show that the data are well fitted with second order equations with high correlation coefficients than the first order rate equations of Lagergren as shown in Table: 2

Table-2 Equations and rate constants

Order	Equation	Rate constants	R ²
Lagergren first order	$\log (q_e - q_t) = -0.0202 t - 0.222$	0.0465 min^{-1}	0.9534
Pseudo second order	$t/qt = 0.7899 t + 1.8444$	$0.1834 \text{ g}/(\text{mg} \cdot \text{min})$	0.9890

Thermodynamics of chromium biosorption:

Biosorption is associated with the three thermodynamic parameters namely change in enthalpy of biosorption (ΔH), change in entropy of biosorption (ΔS) and change in Gibbs free energy (ΔG). Van't Hoff expressed an equation that relates the change in biosorption affinity with change in temperature. The Van't Hoff's equation is

$$\text{Log } (q_e/C_e) = - (\Delta H/2.303RT) + (\Delta S/ 2.303 R) \quad \text{----- (8)}$$

Where

(q_e/C_e) is called the adsorption affinity.

ΔH = change in enthalpy of biosorption

ΔS =change in entropy of biosorption

From the plots between $\log (q_e/C_e)$ and $(1/T)$, slope $(-\Delta H/2.303R)$ and intercept $(\Delta S/ 2.303R)$ are determined and ΔH and ΔS values are calculated. Change in Gibbs free energy (ΔG) is related to change in enthalpy (ΔH) and change in entropy (ΔS) as

$$\Delta G = \Delta H - T (\Delta S) \quad \text{----- (9)}$$

The positive value of ΔH indicates endothermic nature and negative value of ΔH indicates exothermic nature. If the value of ΔS is less than zero, it indicates that the process is highly reversible. If ΔS is more than or equal to zero, it indicates the irreversibility of the process. The negative value for (ΔG) indicates the spontaneity of biosorption. The experiments were conducted to understand the biosorption behavior of varying temperature from 283 to 323 K. The Van't Hoff plot for the biosorption data obtained is shown in fig.12.

The equations obtained is $\log (q_e/C_e) = -0.42307 (1/T) + 0.77529$

The values obtained after calculation are $\Delta G = -4489.783$, $\Delta H = 8.1005$ and $\Delta S = 14.8445$.

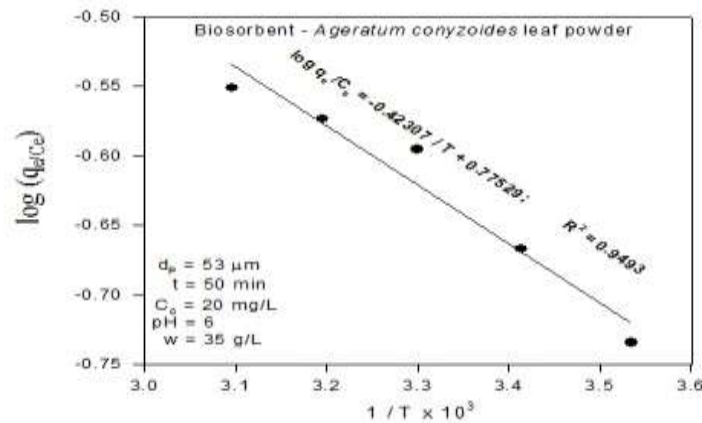


Figure 12. Van'tHoff's plot for biosorption of chromium (biosorbent particle size = 53 μm ; contact time = 50 min; chromium concentration = 20 mgL^{-1} ; pH =6; dosage = 10 gL^{-1} ;)

CONCLUSION

The *Ageratum conyzoides* leaf powder was used as an effective low cost biosorbent for the removal of chromium. Effect of contact time, pH, biosorbent dosage, effect of temperature, biosorbent size, initial metal concentration, the equilibrium agitation time on biosorption of chromium were studied. The isotherms and kinetics of the biosorption process were further investigated. The percentage removal of chromium increased significantly with increase in biosorbent dosage from 5 to 35 gL^{-1} at pH 6. The maximum uptake capacity of 21.505 mg/g is obtained at 303K and absorption size of 53 μm . The percentage removal of chromium decreased by increasing the initial concentration from 20 mgL^{-1} to 200 mgL^{-1} . Langmuir biosorption model adequately described the biosorption of chromium by the *Ageratum conyzoides*. Kinetics results were well described by pseudo-second order model. Thermodynamic studies show negative values of ΔG indicating that the absorption is spontaneous and endothermic in nature. It can be concluded from the present study that *Ageratum conyzoides* leaf powder could be employed as a cost effective and eco-friendly biosorbent in the treatment of waste water.

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