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EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES ON BIOSORPTION OF CHROMIUM(VI) USING MORINDA TINCTORIA LEAF POWDER

Engineering

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ABSTRACT

Biosorption studies were carried out for the removal of chromium(VI) from aqueous solution using morinda tinctoria leaf powder in batch mode. The effects of agitation time, size and dosage of adsorbent, pH, initial chromium concentration and temperature of aqueous solution were studied. The maximum biosorption of chromium is attained at an equilibrium time of 240 min. The optimum dosage and pH are 20 g/L and 4 respectively at an initial concentration of 20 mg/L at 3030 K. The experimental values of % biosorption are in good agreement with the predicted values (RSM). The monolayer uptake capacity is 4.469 mg/g. The experimental data are well fitted in Langmuir, Freundlich isotherm models and second order kinetics. The process is irreversible, exothermic and spontaneous.

KEYWORDS

Biosorption, chromium, Morinda tinctoria leaf powder, Response Surface Methodology.

1.INTRODUCTION

Discharge of heavy metals into water bodies directly or indirectly through waste water causes water pollution. These metals are highly toxic even at low concentrations. They also contaminate the soil [1, 2]. Major industries that discharge chromium include textile, leather tanning, electro-plating, metal finishing etc. The hexavalent chromium is the most toxic than trivalent chromium. The major health problems caused due to intake of chromium are skin dermatitis, nasal membrane inflammation, ulceration, liver damage, pulmonary congestion and edema.

The treatment of waste water from different industries using low cost techniques is one of the challenging tasks in front of researchers [3]. Of the many conventional methods, adsorption is more effective and economically feasible for metal removal from effluents. Many researchers carried experiments for removal of heavy metal adsorption using low cost abundantly available agro-based materials that include sugar cane bagasse [4], pine needles [5], raw rice bran [6], tamarind hull and seeds [7, 8], tea and coffee powder [9], jack fruit leaf powder [10], water hyacinth root powder [11] and palm kernel fibre [12] etc. The main objectives of the present work deals with biosorption studies of Cr(VI) using morinda tinctoria powder, optimization of batch process variables using Central Composite Design (CCD) of Response Surface Methodology (RSM), biosorption kinetics, isotherms and thermodynamic parameters.

2.MATERIALS AND METHODS

Morinda tinctoria leaves are collected from premises of Andhra University College of Engineering in Visakhapatnam, Andhra Pradesh, India. These leaves are washed repeatedly with distilled water to remove dust and impurities and are allowed to dry in sunlight until they become crispy and colorless. The dried leaves are converted into fine powder in a mechanical grinder and the powder was sieved using Rotap sieve shaker. In the present study, 44, 72 and 104 µm size leaf powder is used as biosorbent.

2.828 g of 99.9 % analytical grade $K_2Cr_2O_7$ is dissolved in 1L of distilled water to prepare 1000 mg/L of chromium stock solution. 50 mg/L of chromium solution is prepared by proper dilutions. The pH of the aqueous solution is altered by adding required amounts of 0.1N HCL or 1N NaOH. 50 mL of aqueous solution (C_0 = 50 mg/L) is taken in each of 250 ml conical flasks. 20 g/L of biosorbent having 44 µm size is added in each of the flasks. The conical flasks are shaken on an orbital shaker for 240 min. The settled particles are filtered and the filtrates are analyzed in AAS (Perkin Elmer–3100 model with a wave length of 357.8 nm) to identify the concentrations of chromium. The experiments are repeated to cover the variables shown in Table – 1.

Table – 1: Experimental conditions for biosorption of chromium

Parameter	Values Investigated
Agitation time, t, min	1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 180, 240 and 300
Biosorbent size, dp, µm	44. 72, 104
Biosorbent dosage, w, g/L	10, 15, 20, 25 and 30
pH of the aqueous solution	1,2, 3, 4,5,6,7,8,9 &10
Initial metal concentration, Co, mg/L	5, 10, 20, 30, 40, 50, 75, 100, 125 & 150
Temperature, 0K	283, 293, 303, 313 and 323

3.RESULTS AND DISCUSSIONS

From agitation time studies for the biosorption of chromium from the aqueous solution on *orinda tinctoria* leaf powder the experiments gave the maximum sorption of Cr (VI) obtained at 240 min. From figure.1 it is clear that the removal rate is increased with a decrease in article size (104 to 44 µm). The relatively higher biosorption with smaller biosorbent particle may be attained to the fact that smaller particles have large surface areas [13]. The percentage of chromium increases (63.65 to 68.42 %) with increasing biosorbent dosage (10 to 30 g/L) due to the greater availability of sites for the ions, but the metal uptake per gram of biosorbent decreases (3.182 to 1.14 mg/g). The available sites are more and metal ions are insufficient , that lead to low metal uptake [14].

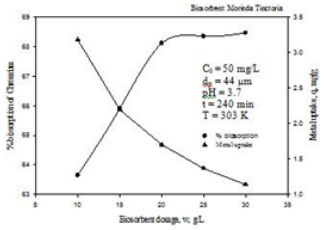

Fig. 1: Effect of biosorbent dosage on % biosorption

It is observed from fig. 2 that as the pH is increased from 1.0 to 4.0, the biosorption of chromium is increased from 58.62 to 70.49% and further increase in pH beyond 4 results in decrease in biosorption of chromium to 50.47%. The increased biosorption at pH 4.0 may be due to more negatively charged groups in biomass surface capable of binding positively charged metal ions**[15, 16].** The formation of soluble hydroxylated complexes of metal ions and their competition with the active sites results in the decrease in biosorption at higher pH (pH >4.0)**.**

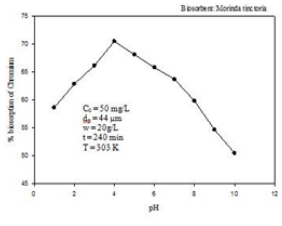

Fig. 2: Effect of pH of biosorbate

Fig. 3 shows the effect of initial biosorbate concentration on the % biosorption of chromium. The biosorption percentage is decreased with an increase of biosorbate concentration whereas metal uptake increased with biosorbate concentration. This may be due to the fact that at a fixed biosorbent dosage, the number of active biosorption sites to hold the biosorbate ion remains unchanged while with higher biosorbate concentrations, the biosorbate ions to be accommodated may be increased.

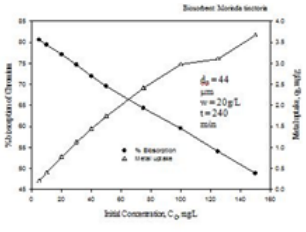

Fig. 3: Influence of initial concentration on % biosorption of chromium

3.1 Optimization of the parameters using CCD

The four parameters [pH (x_1), initial chromium concentration (x_2), biosorbent dosage (x_3) and temperature (x_4)] have been identified as the potential parameters for the percentage biosorption of chromium. The multiple regression analysis of the experimental data results in the following equation

$$Y = -431.695 + 17.548 X_1 - 0.763 X_2 + 2.379 X_3 + 2.929 X_4 - 1.638 X_1^2 - 0.076 X_2^2 - 0.062 X_3^2 - 0.005 X_4^2 + 0.170 X_1X_2 + 0.009 X_1X_3 - 0.028 X_1X_4 + 0.01 X_2X_3 + 0.004 X_2X_4 \quad \text{-----} \quad (1)$$

The response surface contour plots of percentage biosorption of chromium versus the interactive initial chromium concentration, biosorbent dosage and temperature are shown in figs. 4(a) - 4(f).

Each contour plot represents a number of combinations of two test parameters with the other parameter maintained at zero levels. The maximum percentage biosorption of chromium is indicated by the surface confined in the smallest curve (circular or elliptical) of the contour plot.

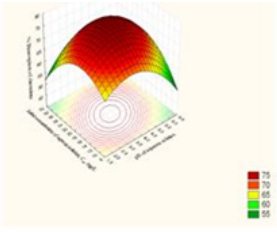

Fig. 4(a): Effect of pH and Initial Cr concentration

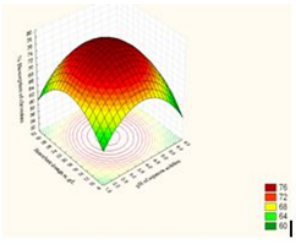

Fig. 4(b): Effect of pH and biosorbent dosage

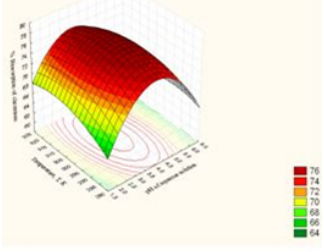

Fig. 4(c): Effect of pH and temperature

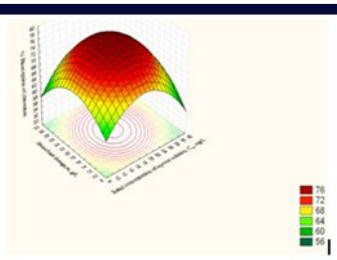

Fig. 4(d): Effect of initial Cr concentration and biosorbent dosage

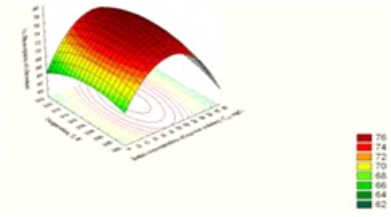

Fig. 4(e): Effect of Initial Cr concentration and temperature

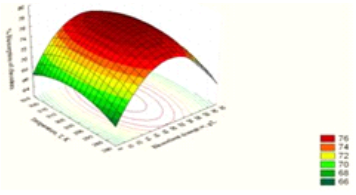

Fig. 4(f): Effect of biosorbent dosage and temperature

The optimal set of conditions for maximum percentage biosorption of chromium is at pH = 3.788, Initial chromium concentration= 19.34 mg/L, Biosorbent dosage = 19.95 g/L, Temperature = 303.83 K. And the extent of biosorption of chromium obtained was 77.65 %. The experimental values of % biosorption are in close agreement with that of predicted values. Experiments are conducted with the above predicted optimal set of conditions and the % biosorption of chromium is 77.17 %, which is closer to the predicted % biosorption.

Kinetic studies

Lagergren-first-order **[17]** and pseudo-second-order kinetic models **[18]** are used to investigate the kinetics of Cr(VI) biosorption by *morinda tinctoria* leaf powder and the potential rate-controlling steps,

The pseudo-first-order equation is given as follows

$$(dq_t/dt) = K_1 (q_e - q_t) \quad \text{----} \quad (2)$$

The plot (not shown) is found to be inadequate to explain the first order kinetics.

The pseudo second order kinetic equation is

$$(t/q_t) = (1/K_2 q_e^2) + (1/q_e)t. \quad \text{----} \quad (3)$$

A plot t/q_t versus t is shown in fig. 5 ($R^2 = 0.99$). q_e and K_2 are found to be 3.182 mg/g and 4.699 respectively. The theoretical (q_e = 3.257) value is closer to the experimental value. It is observed that pseudo-second-order model fits the experimental data.

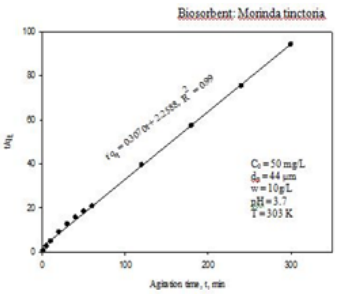

Fig. 5: Second order kinetics for biosorption of chromium

3.2 Isotherm model

Langmuir, Freundlich and Redlich-Peterson isotherms (fig. 6 to fig. 8) are drawn for modeling of experimental data. From Freundlich isotherm, the isotherm constants 'K_f' and 'n' are found to be 0.265 and 0.6445 respectively. A favorable adsorption tends to have Freundlich constant 'n' between 1 and 10. The adsorption affinity constant (b) and maximum capacity (q_m) of the chromium to form a complete monolayer on to the surface of the m*orinda tinctoria* leaf powder was found to be 0.045 L/mg and 4.464 mg/g respectively from Langmuir isotherm. The separation factor $R_L = 0.6$ indicate favorable isotherm ($0 < R_L < 1$) for biosorption of chromium ions. The Redlich-Peterson equation produced correlation coefficient of 0.93 indicating favorable conditions for biosorption. Redlich-Peterson isotherm constants obtained are B = 2.986 L/mg and g = 0.4002 ($0<g< 1$) for favorable biosorption.

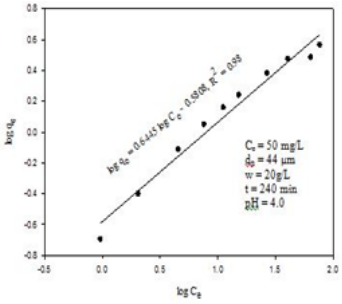

Fig. 6: Freundlich isotherm

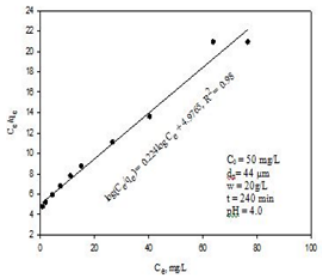

Fig. 7: Langmuir isotherm

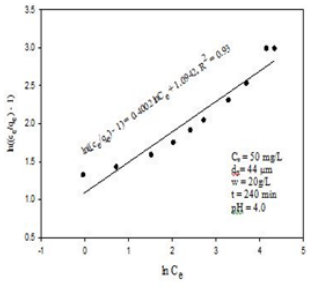

Fig. 8: Redlich - Peterson isotherm

Thermodynamic Parameters

The % biosorption is increased (72.15 % to 83.43 %) with increase in temperature of the system. (283^0 K to 323^0 K). The changes taking place during biosorption can be explained by the three main important thermodynamic parameters i.e., enthalpy change, entropy change and Gibbs free energy change . The Van't Hoff's equation relates ΔH and ΔS as

$$\log (qe/Ce) = -\Delta H/(2.303RT) + \Delta S/(2.303R)$$

The trend is shown in fig. 9, yields a straight line. Positive value of ΔH indicates the endothermic nature of adsorbent. ΔG is negative and decreases with increase in temperature indicating adsorption of Cr (VI) on *morinda tinctoria* leaf powder is spontaneous. Positive value of ΔS suggests randomness at the solid-solution interface during adsorption **[19,20,21].**

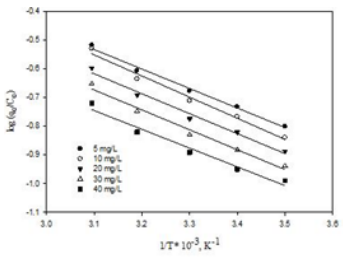

Fig. 9: Van't Hoff's plot

3.3Characterization of morinda tinctoria leaf powder

3.3.1FTIR spectrum of untreated and treated morinda tinctoria leaf powder

FTIR spectrum for untreated and treated powder is shown in figs. 10(a) and 10(b). A broad band at 3421.83 cm^{-1} suggests the presence of hydroxyl

(-OH) stretching or amine (-NH_2) stretching. The band at 2922.25 cm^{-1} is characteristic of stretching vibration of CH_2. The band at 2345.52 cm^{-1} due to the presence of isocyanate group (-NCO). The band at 1624.12 cm^{-1}indicates the presence of carboxyl group (CO). The band at 1545.03 cm^{-1} is due to the presence of amino group. The band at 1317.43 cm^{-1} denotes the presence of -CH_2 bending vibrations. The band at 1246.06 cm^{-1} suggests the presence of -SO_3 group. The band at 1155.40 cm^{-1} is characteristics of –C-O stretching. The band at 1053.17 cm^{-1} indicates the presence of stretching vibration of C-OH. The band at 1033.88 cm^{-1} is attributed to the stretching vibration of P – OH. The band at 781.20 cm^{-1}suggests the presence of characteristic of substituted benzene. The band at 518.87 cm^{-1} is due to the presence of C-Br stretching. The space lattices are measured with D-5000 Siemens XRD for Cr(VI) biosorption studies are shown in fig.11(a) and fig.11(b).

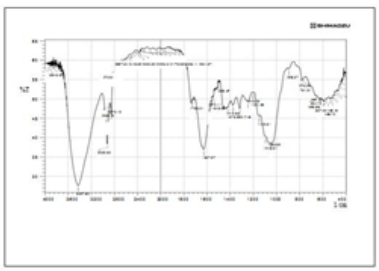

Fig. 10(a): FTIR spectrum of untreated *morinda tinctoria* leaf powder

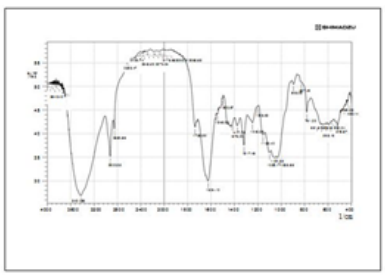

Fig. 10 (b): FTIR spectrum of treated *morinda tinctoria* leaf powder

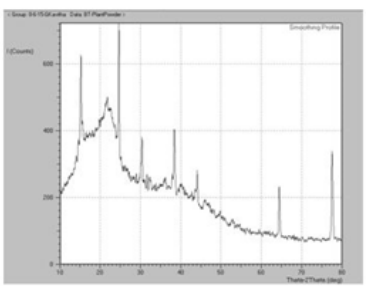

Fig. 11(a): XRD spectrum of untreated *morinda tinctoria* leaf powder

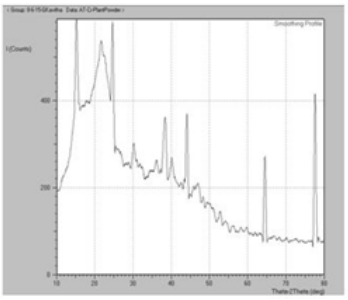

Fig. 11(b): XRD spectrum of treated *morinda tinctoria* leaf powder

3.4 SEM spectrum of untreated and treated morinda tinctoria leaf powder

The SEM spectrum of untreated and treated *morinda tinctoria* leaf powder are shown in fig. 12(a) and 12(b). The micrographs of treated biomass show that the surface has irregular texture with globular, elongated grains and shiny particles over the surface of treated biomass which are absent in the untreated biomass. These elongated grains show that the metal particles are adhered onto the surface of biosorbent. The clustered grains on treated biosorbent denote increased active surface area. The SEM of m*orinda tinctoria leaf powder* shows heterogeneous and porous surface. FTIR spectra of untreated and treated morinda tinctoria leaf powder showed bands corresponding to the presence of -OH, -CH, C=CH, C=O, COO^- and NCO. The significant changes in the wave number suggest that bromide, hydroxyl and C=O, C-O groups could be involved during biosorption.

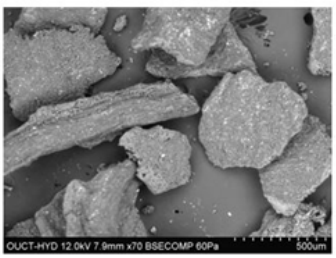

Fig. 12(a): SEM spectrum of untreated *morinda tinctoria* leaf powder

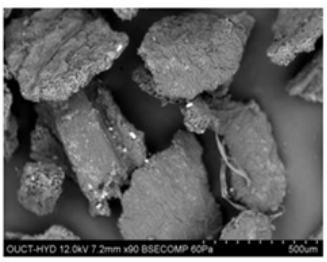

Fig. 12(b): SEM spectrum of treated *morinda tinctoria* leaf powder

CONCLUSIONS

The theoretical results obtained using Central Composite Method are close agreement with experimental values. The equilibrium data fitted well in second-order kinetic model and Langmuir and Freundlich isotherm models. The uptake capacity of the biosorbent is estimated to be 4.464 mg g^{-1}. Biosorption is exothermic and spontaneous.

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