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Equilibrium, Kinetics and Thermodynamic Studies for Adsorption of CR (VI) onto Natural Adsorbents

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Abstract: The study on the performance of natural adsorbents like chitosan saw dust and tea waste in the removal of chromium ion (Cr (VI)) from wastewater has been performed in batch mode. The effects of pH, adsorbent concentration, Cr (VI) concentration, contact time and shaking speed were studied on the removal of Cr (VI) from synthetic wastewater. A comparative study has been done on the adsorption capacities of the three adsorbents for Cr (VI) adsorption. The highest adsorption capacity of 99.257% has been observed with chitosan as adsorbent at optimized conditions. The equilibrium data for the batch adsorption of Cr (VI) onto natural adsorbents have been tested with Langmuir, Freundlich, BET and Dubinin-Radushkevich isotherm models. The mechanism of Cr (VI) sorption by chitosan gave good fits with the Langmuir model with a maximum adsorption capacity of 35.7 mg/g. It has been found that the kinetics of Cr (VI) adsorption onto chitosan can be explained well by the pseudo second order kinetic model. Desorption of Cr (VI) ions from the metal loaded chitosan was maximum at 0.1M of H_2SO_4 with an agitation speed of 120 rpm and a contact time of 60 minutes. A multiple response method, using the design expert software 8.0.6.1 was applied for optimization of adsorbent dosage, Cr (VI) concentration, contact time, agitation speed % adsorption and % desorption.

Key words: Cr (VI) adsorption , chitosan, isotherm, kinetics, saw dust and tea waste.

I INTRODUCTION

Water is a unique substance, because it can naturally renew and cleanse itself, by allowing pollutants to settle out or break down, or by diluting the pollutants to a point where they are not in harmful concentrations. However, this natural process takes time, and is difficult when excessive quantities of harmful contaminants are added to the water[1]. Industrial activities are responsible for the discharge of waste into the environment, most of which contain toxic and hazardous substances that are detrimental to human health. Heavy metals are major toxicants found in industrial wastewaters; they may adversely affect the quality of water[2]. Chromium is a heavy metal, whose compounds are considered to be highly toxic to humans. Cr (VI) is generally produced by industrial processes, due to its toxicity and suspected carcinogenicity, however, chromium is heavily regulated to human health and the environment [3],[4]. Conventional physico-chemical treatment methods for removing heavy metals from the waste streams include precipitation, filtration, oxidation-reduction, ion exchange and membrane separation. However, when metals are dissolved in huge volumes in relatively low concentrations, these methods become generally ineffective or expensive [5].Thus, there is a need for cheaper methods for effluent treatment.

Among the different physicochemical treatments being employed for wastewater treatment, adsorption technique has been found to be very effective to treat effluents with high loadings of contaminants at dilute concentrations typically <100 mg/L. various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the adsorbents can subsequently bind the heavy metals[6]. A variety of natural materials like agriculture waste, marine organism and micro organisms have been successfully used as adsorbents for the removal of heavy metals[6]. Biosorption is a process that utilizes biological/natural materials as adsorbents. This method has been studied by several researchers as an alternative technique to conventional methods for heavy metal removal from wastewater [7]. The binding mechanisms of heavy metals by biosorption could be explained by the physical and chemical interactions, ion exchange, complexation, coordination and micro precipitation. The diffusion of the metal from the bulk solution to the active sites of adsorbents occurs predominantly through passive transport mechanisms [8].

Chitosan displays the basic properties that impart it with unique physico-chemical characteristics. It is an excellent chelating agent for removing heavy toxic metals from sewage [9].The amino group is responsible for the polycationic character of chitosan, and for the formation of the well-known intermolecular complexes with carboxylic and polycarboxylic acids[10]. Metal adsorption is a rather complex process and affected by several other factors too [11]. The major advantages of using natural adsorbents include: low cost, high efficiency regeneration of adsorbent and the possibility of metal recovery [12-14].

One- third of the total dry matter in tea leaves should have good potential as metal scavengers from solutions and waste waters since the above constituents contain functional groups. The responsible groups in lignin, tannin or other phenolic compounds are mainly carboxylate,

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aromatic carboxylate, phenolic hydroxyl and oxyl groups [15]. The feasibility of tea waste as an adsorbent for the removal of chromium in fixed bed was studied elsewhere andindicated that the tea waste can be used as an effective and environment friendly adsorbent for the treatment of chromium in aqueous solutions [16]. Sawdust contains water-soluble compounds like tannin, which is again responsible for hydroxyl and carboxylic group on chemical treatment [17].Sawdust provides cationic active sites (i.e., amino groups) and enhances the substantively of wood cellulose for anionic metals.

The batch studies for the adsorption of Cr(VI) from synthetic wastewater are being influenced by the operating conditions such as temperature, pH, adsorbent dose ,initial metal concentrations ,contact time and agitation speed[18]. The Response surface methodology (RSM) is a collection of mathematical and statistical techniques has an important application in the process design and optimization, as well as in the improvement of the existing design[19-20].

Based on the comprehensive review of literature, the present study was undertaken with the following objectives:

1. To do experimental and theoretical investigation on adsorption of Cr (VI) from aqueous waste water solutions using naturally available adsorbents (Chitosan, Saw dust and Tea waste).
2. To identify the effective adsorbent among the three for Cr (VI) adsorption.
3. To study the isotherm, kinetics and thermodynamic effect on Cr (VI) adsorption at batch operations.
4. Non-destructive recovery of heavy metals by certain potential desorbing agents and to regenerate the adsorbent material for another cycle of application.
5. To do modeling and simulation approach to validate the experimental results using response surface methodology (RSM).

II MATERIALS AND METHODS

MATERIALS USED

All the chemicals used are of analytical grade and samples were prepared using double distilled water.

Synthetic metal solution

Synthetic wastewater containing Cr (VI) was prepared by adding 2.8287 g of potassium dichromate ($K_2Cr_2O_7$) in 1000 ml of deionized water i.e. 1000 ppm chromium solution. 1 ml of the standard solution was dissolved in 100 ml distilled water to make 10 ppm solution. This solution was further mixed in the ratio 2:8, 4:6, 6:4, 8:2 with distilled water to form 2, 4, 6, 8 ppm solutions respectively.

Adsorbents

The adsorbents used for the present experiments are saw dust, tea waste and chitosan.

Saw dust

Saw dust was taken from the carpentry workshop. It was screened through BSS 25 mesh for uniform sized particle. It was washed thoroughly using distilled water and dried in an oven at 80°C for duration of 4 hours.

Chitosan

Chitosan is obtained from the deacetylation of chitin. Chitin is one of the most abundantly available polymers after cellulose. Present experiments were carried out using pelletized form of chitosan (donated by Cochin Institute of Fisheries Technology, Cochin). CIFT has developed an efficient and economical technology to produce chitin and chitosan from this shrimp waste, process for the production involves de-proteinisation and demineralization of shrimp shell by which chitin is produced and then converted to chitosan by deacetylation.

Tea waste

Tea powder was boiled at 60 ^{0}C for 15 minutes and then filtered; the tea residue left over the whatmann no 1 filter paper was dried at 80 ^{0}C for 90 minutes and used as adsorbent.

Instrumentation

The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS),Thermo scientific AA 303.Centrifugation and filtration were done before atomic adsorption measurements to remove suspended particles and thus to avoid turbidity problems. FTIR spectra were recorded on a Thermo Nicolet Model-Avater 320 FTIR spectrophotometer. The surface morphology of adsorbents was examined using a Scanning Electron Microscope, (HITACHI SU 6600 Japan).

EXPERIMENTAL METHODS

The experiments in this work were divided into two parts. The first part of the study was aimed at investigating the effect of experimental conditions on Cr (VI) adsorption from synthetic Cr (VI) solutions using naturally available adsorbents like chitosan, saw dust and tea waste and determining the conditions that achieve the maximum amount of chromium removal. The second part of the study examined the desorption efficacy. Studies were done in detail to regenerate the adsorbent effectively for reuse. Isotherm, kinetic and thermodynamic parameters were evaluated. Modeling and optimization were done using RSM.

Batch adsorption studies: Adsorption tests of Cr (VI) on chitosan obtained from shrimp shells and other adsorbents like tea waste and saw dust were carried out at different metal concentration, biosorbent concentration, contact time, shaking speed, pH and temperature. Borosil glass conical flasks of 250 ml capacity with 50 ml of synthetic and industrial wastewater of desired concentrations and pH were used. Adsorbents were added as per dose requirements and subsequently the flasks were shaken at a constant rpm in an incubator. The flasks were taken out from the shaker at pre-determined intervals and the content was filtered using Whatman No. 1 filter paper. The filtrate containing the residual Cr (VI) was analyzed using an atomic absorption spectrophotometer [21]. The amount of Cr (VI) removed by the biosorbent was calculated using Eq (1)

$$\text{Metal Removal}(\%) = \left(\frac{C_{in} - C_o}{C_{in}}\right) \times 100 \qquad (1)$$

CHITOSAN AS ADSORBENT

Batch experiments were carried out in different sets by taking chitosan in the range of 0.2 -1.4 g/l of synthetic Cr (VI) solution for a varying initial Cr(VI) concentration (2-10 mg/l) in a series of conical flasks at a varying pH (2–10), varying shaking time (30- 240 min) and shaking speed (30 -150 rpm) in an incubator shaker. Samples were collected at different time intervals and analyzed using AAS for Cr (VI) concentration. And determined the optimum conditions that achieve the maximum amount of chromium removal.

SAW DUST AS ADSORBENT

Batch experiments were repeated in different sets by taking saw dust in the range of 0.5 -4 g in 50 ml of synthetic Cr (VI) solution of desired initial Cr (VI) concentration (6 mg/l) in a series of conical flasks at a varying pH (2–8), varying shaking time (30- 480 min) and shaking speed (30 -150 rpm) in an incubator shaker. Samples were collected at different time intervals and analyzed using AAS for Cr (VI) concentration. And determined the optimum conditions that achieve the maximum amount of chromium removal.

TEA WASTE AS ADSORBENT

Batch experiments were repeated again in different sets by taking tea waste in the range of 0.5 - 40 g/l of synthetic Cr (VI) solution of desired initial Cr (VI) concentration (6 mg/l) in a series of conical flasks at a varying pH (3–9), varying shaking time (30- 240 min) and shaking speed (30 -150 rpm) in an incubator shaker. Samples were collected at different time intervals and analyzed using AAS for Cr (VI) concentration. And determined the optimum conditions that achieve the maximum amount of chromium removal.

On comparing the Cr (VI) adsorption capability of the three adsorbents. Chitosan had the maximum adsorption capacity for Cr (VI). So the desorption experiments were conducted for metal loaded chitosan.

EQUILIBRIUM, THERMODYNAMICS AND KINETICS STUDIES FOR ADSORPTION OF Cr (VI)

Equilibrium studies were carried out to determine the conditions for maximum Cr (VI) removal onto chitosan. It was observed that adsorption capacity reaches an equilibrium value beyond which there was negligible change in the residual Cr (VI) concentration. The distribution of Cr (VI) between the liquid phase and the solid phase is a measure of the position of equilibrium in the adsorption process.

The quantity of adsorbate that can be taken up by adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. The amount of material adsorbed is determined as a function of concentration at a constant temperature; the resulting function is called an adsorption isotherm. The analysis of the isotherm data is of particular importance to develop an equation which accurately represents the results and could be used for design purpose.

In this study, the experimental data of Cr (VI) adsorption onto natural adsorbents (Chitosan, saw dust and tea waste) were fitted to the Langmuir, Freundlich, BET and Dubinin-Radushkevich isotherm models. Adsorption isotherms known as equilibrium data are the fundamental requirements for the design of adsorption systems [22-23]. The linear form of Langmuir, Freundlich, BET and Dubinin-Radushkevich isotherm equation along with their inference are illustrated in Table.1.

ADSORPTION DYNAMICS

The study of adsorption dynamics describes the solute uptake rate and evidently this controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(VI) adsorption onto natural adsorbents (chitosan, saw dust and tea waste) was analyzed using the pseudo first order, pseudo second order and Elovich and intra particle diffusion models [27]. The conformity between the experimental data and the model values has been expressed by the correlation coefficients (R^2, values closer or equal to 1). The linear form of pseudo first order, pseudo second order , Elovich and intra particle diffusion models along with their inference are illustrated in Table.2

Thermodynamic Parameters of Adsorption

The thermodynamic parameters that must be considered to determine the process, enthalpy of adsorption (ΔH), free energy change (ΔG) and entropy change (ΔS) due to transfer of unit mole of solute from solution onto the solid–liquid interface[30].

A negative enthalpy (ΔH) indicates that the adsorption process is exothermic. Decrease in adsorption with rise in temperature may be due to weakening of adsorptive forces between the active sites of adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase. A negative change in entropy (ΔS) indicates that the biosorption is stable, as there is increase in orderliness of the system, which is at the aqueous metal ion- solid biosorbent interface. In general, negative values of ΔG show the feasibility and spontaneous nature of the sorption. A positive ΔH indicates endothermic reaction. A positive change in entropy is an indication of increase in randomness at the solid-liquid interface.

Batch desorption studies: The desorption studies were carried out using the metal loaded adsorbents obtained after adsorption studies. The desorption tests were conducted in 250 ml flask with 50 ml of synthetic eluants like dilute mineral acids (H_2SO_4 and HCl), complexing agent (EDTA) and organic acids (acetic acid and citric acid) at different concentrations ranging from 0.001M to 0.1M [31]. The effect of temperature, contact time and shaking speed were studied in detail. In the tests, a given mass of metal loaded adsorbent (chitosan) was added to the solution and the resultant suspensions were shaken at a constant rpm for a specified amount of time. Upon completion a sample of the suspension was filtered through a whatmann No 1 filter and the filtrate was analyzed for residual Cr (VI) using the AAS. And the adsorbent (chitosan) regenerated was washed successively with distilled water and dried to initiate another cycle. The absence of a noticeable

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change in the desorption capacities of the reused chitosan confirms the reusable potential of chitosan.

$$\text{Metal present in biosorbent after desorption } (q_d, \text{mg/g}) = \frac{V \text{ x } C_f}{m} \qquad (2)$$

Development of mathematical model using RSM:

Modeling and optimization of the experiments were done using RSM to validate the experimental results. Where the effects of test variable alone and/or in combination on the processes were analyzed and generated a methodology for mathematical model. The graphical perspective of mathematical model has been derived using the contour plots. Simulations were used to explore the performance of systems for analytical solutions.

The mathematical-statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA). This batch studies employed three test variables adsorbent dosage (x_1), metal concentration (x_2) and pH (x_3), following the second-order polynomial equation:

$$\begin{aligned} y &= \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_1\alpha_2 x_1 x_2 \\ &+ \alpha_1\alpha_1 x_1 x_1 + \alpha_2\alpha_2 x_2 x_2 + \alpha_3\alpha_3 x_3 x_3 + \varepsilon \end{aligned} \qquad (3)$$

Optimization

Optimization studies for the adsorption of Cr (VI) from synthetic Cr (VI) solutions were carried out by studying the effect of variables including adsorbent dosage, initial Cr (VI) ion concentrations, pH of solutions, shaking time and shaking speed by means of a central composite design (CCD) using RSM [32].

III RESULTSAND DISCUSSION

Effect of pH and mechanism of Cr (VI) adsorption onto chitosan

The results of batch studies on the effect of initial pH on Cr (VI) removal over a range of 2–10, showed 96.02% of Cr (VI) removal at a pH of 4 (initial Cr (VI) concentration = 6 mg/l and the corresponding optimum dose of chitosan = 50 mg). However, above pH 5 there was a decrease in the uptake and the removal was found to be 74.2 % at a pH of 10 (Fig.1). With increase in pH from 4 to 10, the degree of protonation of the adsorbent functional group decreased gradually and hence removal was decreased[33]. The experiments were repeated for varying adsorbent dosage (10-70 mg), contact time (30-240 min) and at different temperatures (30-60 ^{0}C) to attain the maximum amount of chromium removal (Fig.1). The maximum removal of 99.257 % was achieved under optimized conditions. Isotherm studies were conducted with an initial chitosan concentration of 0.2–1.4 g/l. The mechanism of Cr (VI) sorption by chitosan gave good fits with the Langmuir and Freundlich models with a maximum q value of 35.7 mg/g. It has been found that the kinetics of Cr (VI) adsorption onto chitosan can be explained well by the pseudo second order kinetic model with R^2 = 0.999 as illustrated in Fig.2, Fig.3, Table 3 & Table 4.

Effect of pH and mechanism of Cr (VI) adsorption onto saw dust

Adsorption studies were conducted with an initial saw dust dosage concentration of 0.5 –4.0 g per 50 ml of synthetic Cr (VI) solutions. Results revealed that increase of saw dust dose from 0.5 g to 2 g increased the Cr (VI) adsorption from 2.15 % to 52.13 % after 60 min of equilibration (Fig.4). The results on the effect of initial pH on Cr (VI) removal over a range of 2–8, showed 59.34% of Cr (VI) removal at a pH of 5 and the corresponding optimum dose of saw dust = 2 g. However, above pH 5 there was a decrease in the uptake and the removal was found to be 51.07 % at a pH of 8 (Fig.4). Decrease in the Cr (VI) removal at a pH above and below 5 can be explained by the rapid changes in chemical nature of saw dust [34]. The experiments were repeated for varying contact time (30-480 min) and shaking speed (30-150 rpm) to attain the maximum amount of chromium removal. The maximum removal of 67.33 % was achieved under optimized conditions. Kinetic and isotherm modeling studies demonstrated that the experimental data best fit a pseudo second order and Freundlich model with the maximum adsorption capacity of 0.04 mg/g, as illustrated in Table 3 & Table 4.

Effect of pH and mechanism of Cr (VI) adsorption onto tea waste

Adsorption studies were conducted with an initial dosage concentration of 25 mg – 2000 mg per 50 ml of synthetic Cr (VI) solutions. Results revealed that increase of tea waste dose from 25 mg to 500 mg increased the Cr (VI) adsorption from 33.6 % to 88.53 % after 60 min of equilibration (Fig.5). The results on the effect of initial pH on Cr (VI) removal over a range of 3–9, showed 95.0% of Cr (VI) removal at a pH of 3 and the corresponding optimum dose of tea waste = 500 mg. However, above pH 3 there was a decrease in the uptake and the removal was found to be 86.5 % at a pH of 9 (Fig.5). The experiments were repeated for varying contact time (30-240 min) and at different temperatures (30-50 ^{0}C) to attain the maximum amount of chromium removal**.** The maximum removal of 98.88 % was achieved under optimized conditions. Kinetic and isotherm modeling studies demonstrated that the experimental data best fit a pseudo second order and Freundlich model with the maximum adsorption capacity of 0.097 mg/g, as illustrated in Table 3 & Table 4.

The energy of sorption was below 20.0 KJ/mol as per Dubinin-Radushkevich expression, confirms the adsorption was physical nature (physisorption) for the aforementioned experiments (Fig.6). And the value of D is sufficiently higher that 10 $^{-10}$ m^2/min for all the three adsorbents concludes that pore diffusion is not the main rate determining step and the Table 5 points out clearly that the external diffusion cannot be neglected since all the $t^{0.5}$ are greater than 1. Hence it is appropriate to assume that the Cr (VI) adsorption is controlled by external mass transfer at earlier stages and by intra particle diffusion at later stages[35].

Thermodynamic Studies

Thermodynamic studies were done by carrying out equilibrium studies at various temperatures to obtain corresponding values of Ca and Ce.

$$K = \frac{C_a}{C_e} \qquad (4)$$

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Where, Ca represents adsorption in mg/l at equilibrium; Ce is the equilibrium concentration of the metal in mg/l; K represents the thermodynamic equilibrium constant.
The Gibb's free energy ΔG is related to the thermodynamic equilibrium constant by the following:

$$\Delta G = -R\,T \ln K \qquad (5)$$

where, ΔG is the Gibb's free energy in J/mole;
R is the ideal gas constant whose value is 8.314 J/molK;
K represents the thermodynamic equilibrium constant,
T is temperature in Kelvin.
In thermodynamics, the Gibb's free energy is related to the enthalpy change (ΔH) and entropy change (ΔS) at constant temperature by the following van't Hoff equations:

$$\ln K = -\left(\frac{\Delta H}{R\,T}\right) + \frac{\Delta S}{R} \qquad (6)$$

where, ΔH stands for enthalpy change in J/mol;
ΔS represents entropy change in J/molK;
The values of ΔH and ΔS are obtained from the slopes and intercepts, respectively, of the plot of lnK against 1/T.
Negative enthalpy ΔH and ΔS was obtained in thermodynamic study which indicates that the adsorption is exothermic and stable as there is increase in orderliness of the system [36] (Table 6 & Fig.7).

DESORPTION OF CR (VI) FROM METAL LOADED CHITOSAN

A maximum desorption (88%) of Cr(VI) from chitosan was achieved under optimized conditions of contact time (60 min), agitation speed (120 rpm) and temperature (40°C). Desorption was well described in all the cases studied. Adsorption efficiency remained the same for regenerated adsorbent[37]. The results confirm that environmental pollution due to chromium can be minimized to a larger extent.

IV MODELING AND OPTIMIZATION

Model fitting:

The empirical relationship for % metal removal (% adsorption) (Y) versus the three test variables in coded units obtained by the application of RSM is given by

$$\%\ \text{Metal removal} = +99.20 - 117.73X_1 - 11.738X_2 + 36.31X_3 + 18.28X_1X_2 + 5.77X_1^2 - 0.228\,X_2^2 - 4.05\,X_3^2 \qquad (7)$$

where y (response) is the % metal removal (% adsorption), x_1, $x_2$and x_3 are the coded values of the tests variables, adsorbent dosage (x_1), metal concentration (x_2) and pH (x_3). Polynomial regression analysis has been conducted for second-order response surface model and the results are given in Table 7.
The results of the % Metal removal as a function of the independent variables adsorbent dosage, metal concentration and pH showed that this regression is statistically significant The Model F-value of 35.52 implies that there is only a 0.01% chance that a "Model F-Value" is not significant this could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case α_2, α_3, α_1 α_2 , $\alpha_2^{\,2}$, $\alpha_3^{\,2}$ are significant model terms. The fit of the model was checked by the determination of coefficient (R^2). In this case, the value of the determination coefficient (R^2 = 0.9540) indicates that 4.6% of the total variable is not explained by the model. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 24.112 indicates an adequate signal. This model can be used to navigate the design space. The Response surface and contour plots for % Metal removal are shown in Fig. 8.

Optimization using Desirability Functions

A multiple response method was applied for optimization of adsorbent dosage, Cr (VI) concentration, contact time, agitation speed and adsorption (%). Numerical optimization found a point that maximizes the desirability function. A minimum level of adsorbent (chitosan) dosage (25.27 mg), agitation speed (69.88 rpm), a maximum level of initial Cr (VI) concentration (8.18 mg/l) and shaking time (103.82 min) resulted in 99.3 % of Cr (VI) removal at the initial pH within a range of 2–10 for Cr (VI) adsorption (Fig.9). Optimization studies for desorption of Cr (VI) from chitosan were carried out by means of a central composite design (CCD) using response surface methodology (RSM). A minimum level of speed (130 rpm), maximum levels of contact time (81 min) and desorption (99.77%) were set for maximum desirability. Ramp desirability was generated using Design Expert 8.0.6.1.

V. CONCLUSION

From the experiments discussed above, the following conclusions can be drawn.

- The adsorption of Cr (VI) onto natural adsorbents has been examined. The comparative study showed that chitosan had the maximum adsorption capacity for Cr (VI).
- The Langmuir model has been found to be the most suitable with a maximum adsorption capacity of 35.7 mg/g and a correlation coefficient,R^2= 0.952. The experimental data have been found to fit well with the pseudo second order kinetic model with $R^{2=}$ 0.999.
- The energy of sorption was below 20.0 KJ/mol as per Dubinin-Radushkevich expression, confirms the adsorption was physisorption for all the cases studied.
- The experimental study results revealed that the rate of adsorption was controlled by adsorbent dosage; metal concentration and pH compared to other factors like shaking time and speed. Whereas optimization using Design Expert 8.0.6.1 software resulted metal concentration and pH as the most significant terms compared to other operating parameters.
- Chitosan is a best alternate to the conventional absorbents for wastewater treatment due to its high sorption capacity and regeneration character.

VI. SCOPE FOR FUTURE WORK

- ✓ Adsorption of heavy metals using natural adsorbents can be achieved in continuous multistage columns so that the technology can be transferred to industrial level.

✓ Exact cost analysis can be done to find the economical adsorbent among the identified ones for heavy metal adsorption.

VII. ACKNOWLEDGEMENT

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Nomenclature

C_{in}	Cr (VI) concentration in aqueous solutions before adsorption (mg/l)
C_o	Cr (VI) concentration in aqueous solutions after adsorption (mg/l)
B	BET Constant
k_F	Freundlich constant
n	Freundlich constant
K_L	Langmuir adsorption energy (L/mg).
q_{max}	Monolayer adsorption capacity of adsorbent (mg/g), Langmuir
q_m	Maximum adsorption capacity (mg/g),BET
B_E	Free energy of sorption per mole of the sorbate
q_D	Dubinin-Radushkevich isotherm constant
α	The initial adsorption rate (mg.g^{-1}.min^{-1}) , Elovich Model
β	Desorption constant (mg.g^{-1}.min^{-1}),Elovich Model
q_T	Adsorption capacity at time t(mg/g)
k_{int}	Intra particle diffusion rate constant
m	Weight of adsorbent (g)
V	Eluant volume (l)
C_f	Chromium concentration in synthetic eluant solution after desorption (mg/l)
y	RSM response
α_0	constant term
α_1	The coefficients of the linear parameters, Adsorbent dosage (mg)
α_2	The coefficients of the linear parameter, Metal Concentration (mg/l)
α_3	The coefficients of the linear parameter,pH
$\alpha_1{}^2$	The coefficients of the quadratic parameter, Adsorbent dosage
$\alpha_2{}^2$	The coefficients of the quadratic parameter, Metal Concentration
$\alpha_3{}^2$	The coefficients of the quadratic parameter, pH
$\alpha_1\ \alpha_2$	The coefficients of the interactive parameter
ε	The residual associated with the experiment
x_1	coded values of the tests variables, Adsorbent dosage (mg)
x_2	coded values of the tests variables, Metal Concentration (mg/l)
x_3	coded values of the tests variables, pH

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Table Captions

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TABLE.1 ADSORPTION ISOTHERM MODELS

Isotherm	Linear form	Plot	Inference
Langmuir	$\frac{1}{q_e} = \frac{1}{k_L q_{max}}\left(\frac{1}{C_e}\right) + \frac{1}{q_{max}}$	$\frac{1}{q_e}\ vs\ \frac{1}{C_e}$	Monolayer adsorption can only occur at a fixed number of definite localized sites, that are identical and equivalent. Langmuir isotherm refers to homogeneous adsorption
Freundlich	$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e$	$\ln q_e\ vs\ \ln C_e$	The stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation**.**
Brunauer-Emmett Teller	$\frac{C_e}{[(C_0 - C_e)q_e]} = \frac{1}{Bq_m} + \frac{B-1}{Bq_m}\frac{C_e}{C_0}$	$\frac{C_e}{[(C_0 - C_e)q_e]}\ vs\ \frac{C_e}{C_0}$	Multilayer adsorptions with the following hypotheses: (a) molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer. Explain the physical adsorption of molecules on a solid surface and basis for the measurement of specific surface area of a material.
Dubinin-Radushkevich	$\ln(q_e) = \ln(q_d) - B_E\,[RT\ln(1+\frac{1}{Ce})]^2$	$\ln q_e$ vs $[RT \ln 1+1/C_e)]^2$	The constant B_E gives an idea about the mean free energy E. It is a parameter used in predicting the type of adsorption. An E value < 8 kJmol^{-1} is an indication of physisorption ,a value in between 8 and 16 kJ mol^{-1} indicates ion exchange and if E>20 kJ it is chemisorptions[24-26]

TABLE.2 ADSORPTION KINETIC MODELS

Isotherm	Linear Form	Plot	Inference
Pseudo first order	$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303}$	$\log(q_e - q_t)$ vs t	It is only an approximate solution to the first order rate mechanism. The parameter log(qe) is an adjustable parameter and it is not often equal to the intercept of a plot of log(qe - qt) against t, whereas in a true first order system, log(qe) should be equal to the intercept of a plot. Describe the adsorption rate based on the adsorption capacity.
Pseudo second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(t/q_t) vs.t	Film diffusion might be involved in the sorption process.
Elovich model	$q = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$	q vs ln t	The Elovich kinetic equation is based on adsorption capacity, The rate of adsorption of solute on adsorbent decrease exponentially with an increase in the amount of solute adsorbed.
Intra particle diffusion	$q_t = k_{int}\, t^{1/2}$	q_t vs $t^{1/2}$	For Weber-Morris model, It is essential for the q_t vs $t^{1/2}$ plot to go through the origin, if the intra particle diffusion is the sole rate-limiting step. However, it is not always the case and adsorption kinetics may be controlled by film diffusion and intra particle diffusion simultaneously. Thus, the slope is not equal to zero[28-29]

TABLE 3 ISOTHERM PARAMETERS FOR CR (VI) ADSORPTION ONTO NATURAL ADSORBENTS

Isotherm	Adsorbent	Isotherm parameters		
Langmuir	Chitosan	$q_{max = 35.7\ mg/g}$	K_L= 4 L/mg	R^2 =0.952
	Saw dust	$q_{max = 0.995\ mg/g}$	K_L= 0.024 L/mg	R^2 =0.626
	Tea waste	$q_{max = 4.5\ mg/g}$	K_L=0.13	R^2 = 0.865
Freundlich	Chitosan	k_F =29.4	n =1.87	R^2 =0.940
	Saw dust	k_F=0.027	n =1.195	R^2 =0.860
	Tea waste	k_F = 0.66	n=0.79	R^2 =0.923
BET	Chitosan	q = 24.5 mg/g	B = 38.04	R2 = 0.922
	Saw dust	q = 0.018 mg/g	B = -1.81	R2 = 0.821
	Tea waste	q =1.515 mg/g	B =3.235	R2 = 0.695

TABLE 4 KINETIC PARAMETERS FOR CR (VI) ADSORPTION

	Pseudo first order				Pseudo second order			Elovich		
Adsorbent	**q_e exp (mg/g)**	**q_e calculated (mg/g)**	**k_1 (min^{-1})**	**R^2**	**q_e calculated (mg/g)**	**k_2 (min^{-1} g. mg^{-1})**	**R^2**	**β ($g.mg^{-1}$)**	**α (min^{-1} $g.mg^{-1}$)**	**R^2**
Chitosan	5.95	0.99	0.017	0.764	6.06	0.074	0.999	5.076	$2.2x10^{10}$	0.888
Saw dust	0.094	0.022	0.020	0.545	0.094	2.943	0.999	357.1	$2.5\ x10^{9}$	0.956
Tea waste	0.522	0.044	0.021	0.940	0.526	1.050	0.999	100	$1.9x10^{18}$	0.978

TABLE 5 INTRA PARTICLE DIFFUSION COEFFICIENTS FOR CR (VI) ADSORPTION

System/ Adsorbent	**t**	**q_t**	**$t^{0.5}$**	**K_{id}**	**R^2**
Chitosan	20	5.64	4.47	0.062	0.935
	40	5.709	6.32		
	60	5.761	7.74		
	80	5.925	8.94		
	90	5.949	9.48		
	100	5.949	10		
Saw dust	30	5.477	0.074	0.002	0.908
	60	7.745	0.078		
	120	10.954	0.093		
	180	13.416	0.0945		
	240	15.491	0.0955		
	300	17.32	0.0985		
	360	18.973	0.101		
Tea waste	30	3.16	0.552	0.023	0.972
	60	4.47	0.559		
	90	5.47	0.566		
	120	6.32	0.575		
	150	7.07	0.587		
	180	7.74	0.591		
	210	8.36	0.593		
	240	8.94	0.593		

TABLE 6 THERMODYNAMIC PARAMETERS FOR ADSORPTION OF CR (VI) ONTO CHITOSAN

Temperature (^{o}C)	$K = \frac{C_a}{C_e}$	$\ln K$	$\Delta G = -RT \ln K$ J/mol	ΔH J/mol	ΔS J/mol K
30	0.979	-0.021	52.90	- 6699.42	- 22.115
40	0.973	-0.027	70.26		
50	0.993	-0.23	617.64		
60	0.78	-0.22	609.08		

TABLE 7 ANOVA TEST FOR % METAL REMOVAL USING THE CENTRAL COMPOSITE DESIGN

Model term	**Coefficient estimate**	**Sum of square**	**Mean square**	**DF**	**F-Value**	**P-Value**
α_0 Intercept	+99.20	388.27	55.47	**7**	35.52	< 0.001
α_1 Adsorbent dosage	-117.73	0.46	0.46	1	0.30	0.5958
α_2 Metal concentration	-11.74	98.18	98.18	1	62.87	< 0.001
α_3 pH	+36.313	117.68	117.68	1	75.35	< 0.001
$\alpha_1{}^2$	+5.77	0.35	0.35	1	0.22	0.6448
$\alpha_2{}^2$	-0.229	9.22	9.22	1	5.91	0.0317
α_3 2	-4.049	180.61	180.61	1	115.65	< 0.001
$\alpha_1\ \alpha_2$	+18.28	122.04	122.04	1	78.15	< 0.001
Residual	-	18.74	1.56	12	-	-

Std. Dev. : 1.25
Mean : 96.72
C.V. % : 1.29
R-Squared : 0.954
Adeq Precision : 24.112

Figure captions

Fig.1 Effect of pH , adsorbent dosage , contact time and Cr(VI) concentration on Cr (VI) adsorption on chitosan
Fig.2 Isotherm plot for adsorption Cr (VI) onto chitosan at different temperature (Langmuir, Freundlich & BET)
Fig.3 Kinetics plot for adsorption Cr (VI) onto chitosan (Pseudo first order, Pseudo second order, Elovich and Intra particle diffusion model)
Fig.4 Effect of adsorbent dosage, pH & contact time on Cr (VI) adsorption onto saw dust
Fig.5 Effect of adsorbent dosage , pH ,contact time and shaking speed on Cr (VI) adsorption onto tea waste
Fig.6 Dubinin- Radushkevich isotherm for adsorption Cr (VI) onto chitosan, saw dust and tea waste
Fig.7 Plot of ln K versus 1/T for the adsorption of Cr (VI) onto chitosan
Fig.8 Response surface and contour plots for Cr(VI) adsorption capacity as a function of the test variables adsorbent dosage (x_1), metal concentration (x_2) and pH (x_3)
Fig.9 Desirability ramp for six goals - adsorbent dosage, metal concentration, pH, agitation speed, shaking time and % adsorption

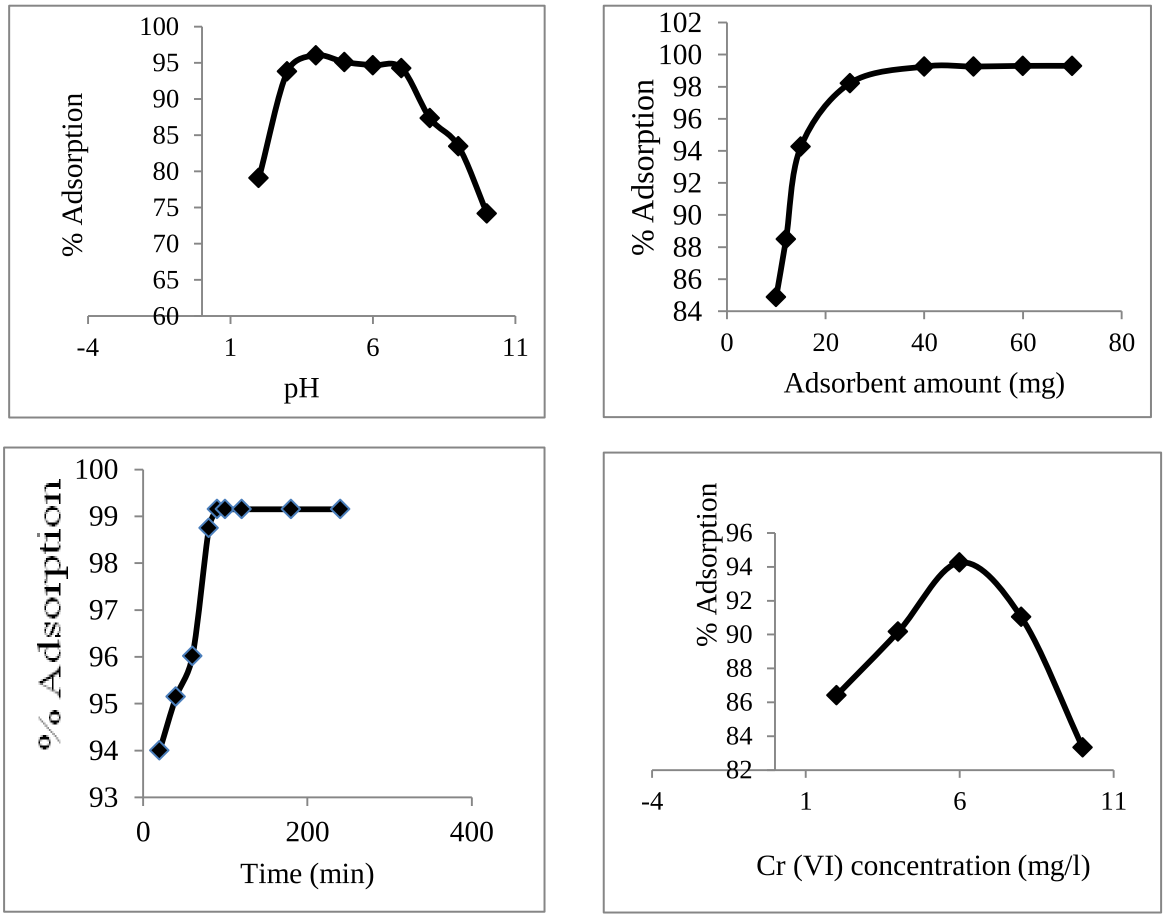
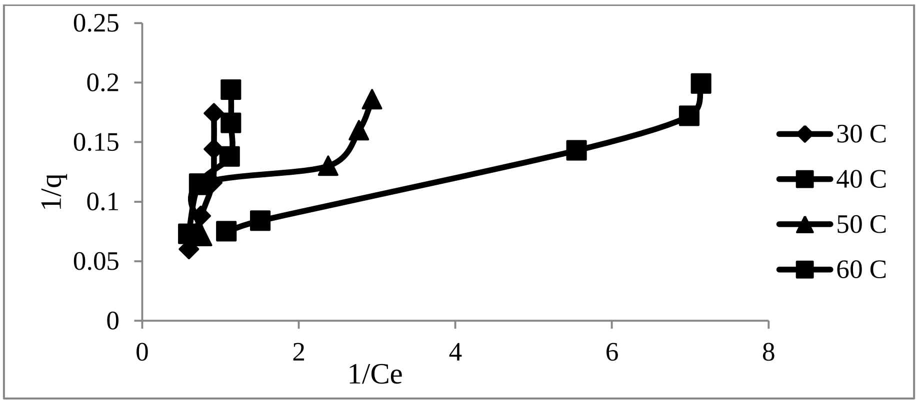


Fig.1 Effect of pH , adsorbent dosage , contact time and Cr(VI) concentration on Cr (VI) adsorption on chitosan



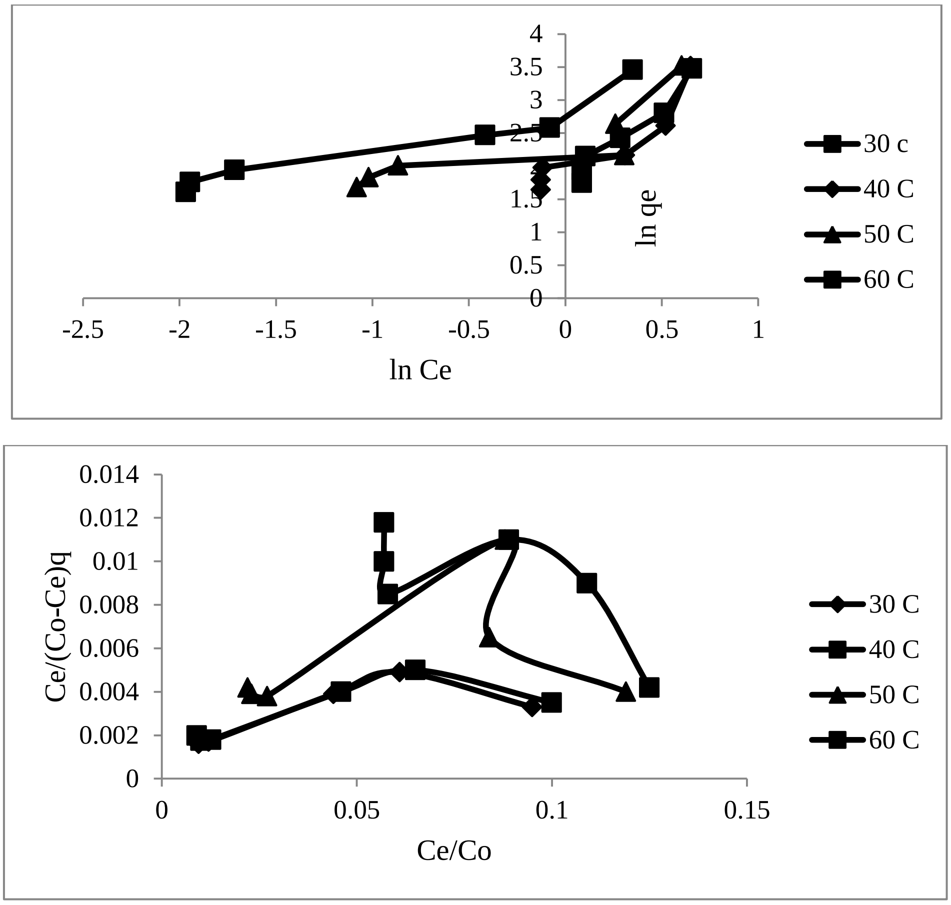


Fig.2 Isotherm plot for adsorption Cr (VI) onto chitosan at different temperature (Langmuir, Freundlich & BET)

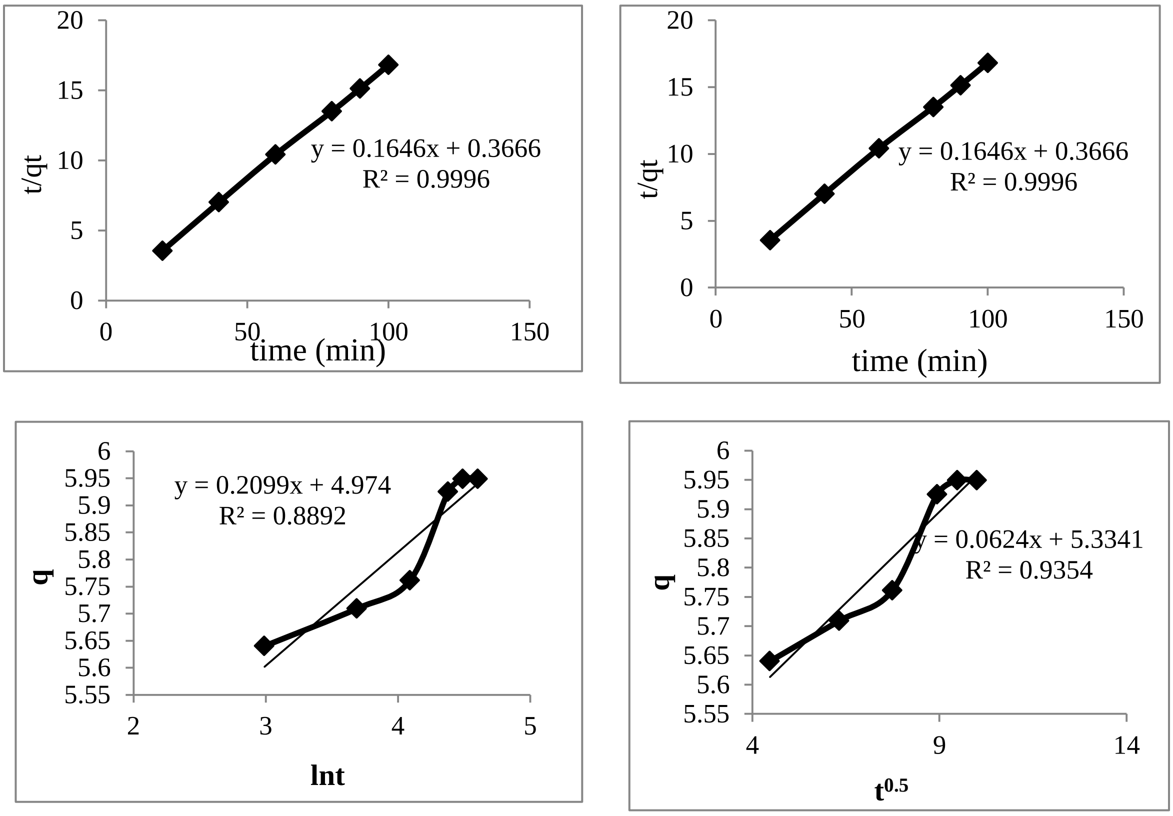


Fig.3 Kinetics plot for adsorption Cr (VI) onto chitosan (Pseudo first order, Pseudo second order, Elovich and Intra particle diffusion model)

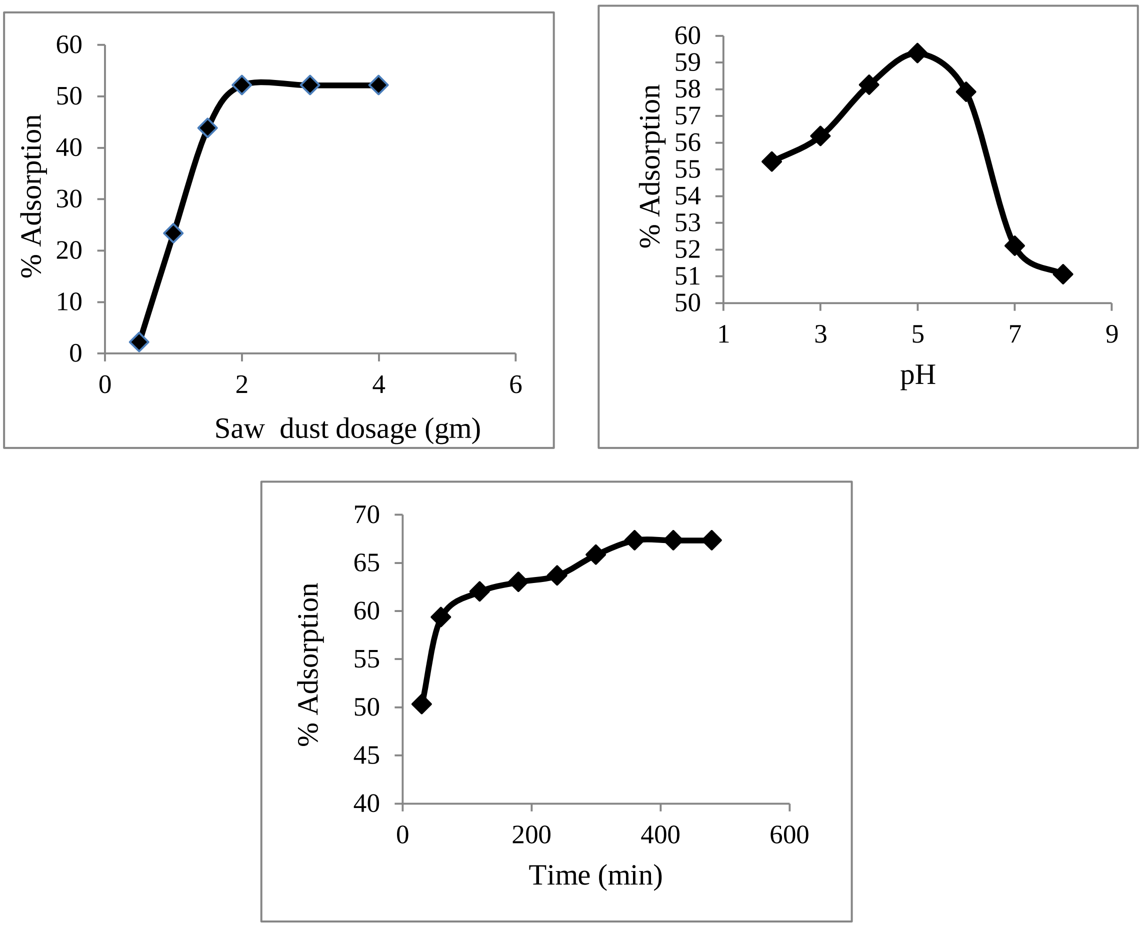


Fig.4 Effect of adsorbent dosage, pH & contact time on Cr (VI) adsorption onto saw dust

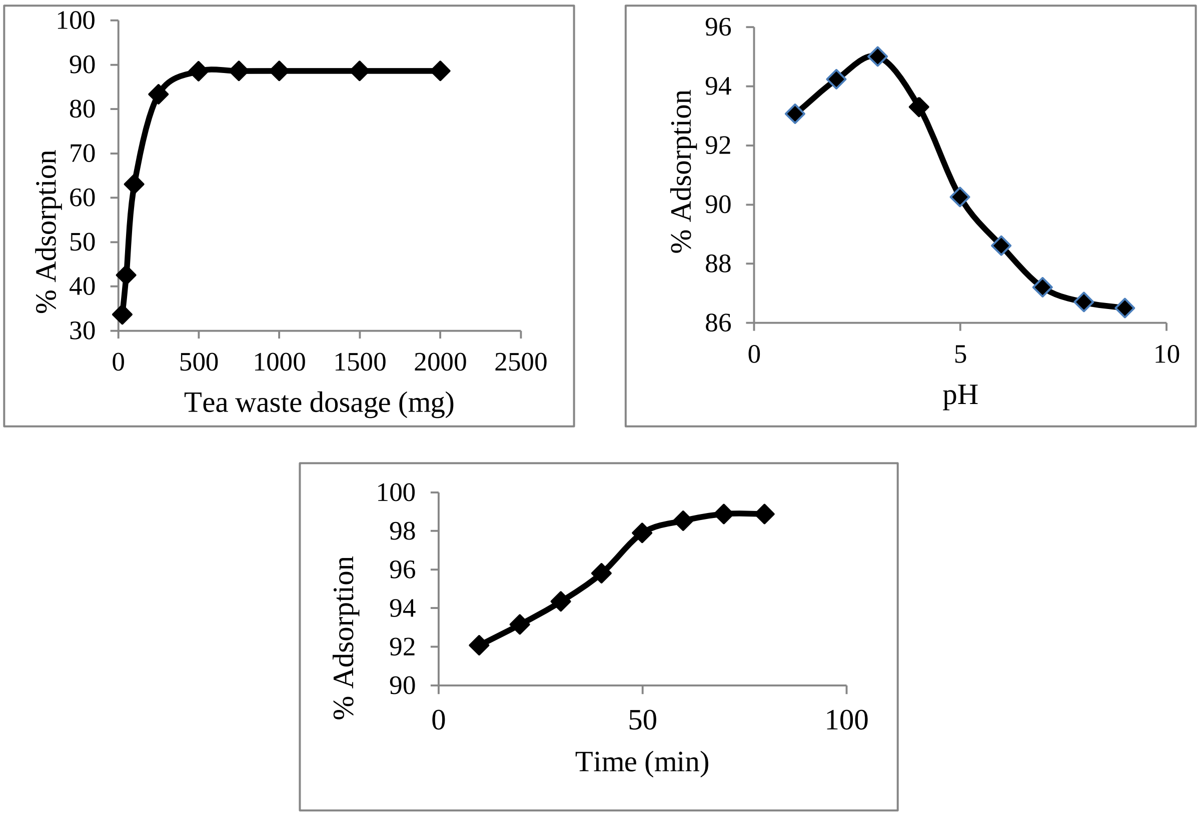


Fig.5 Effect of adsorbent dosage, pH & contact time on Cr (VI) adsorption onto tea waste

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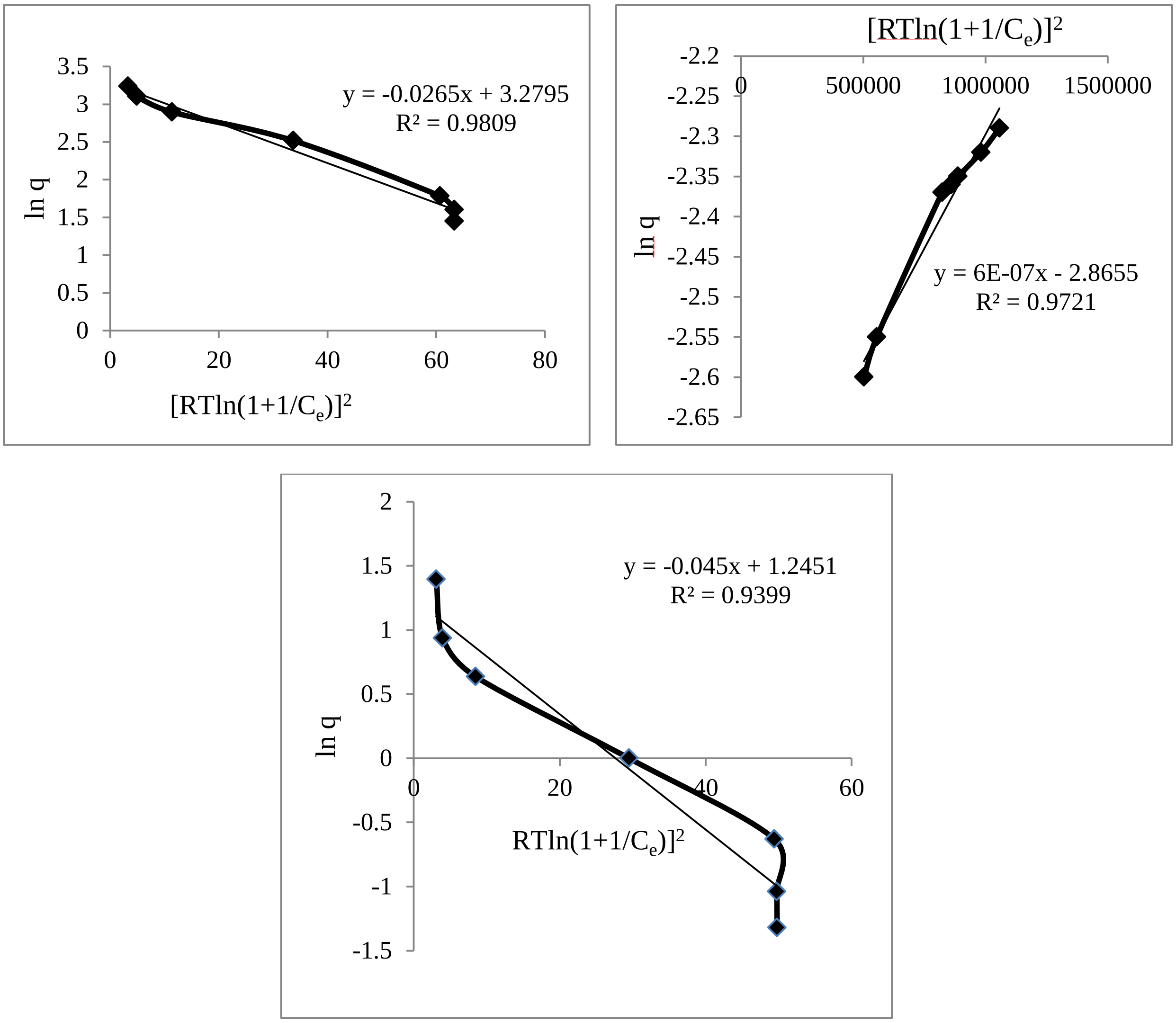

Fig.6 Dubinin- Radushkevich isotherm for adsorption Cr (VI) onto chitosan, saw dust and tea waste

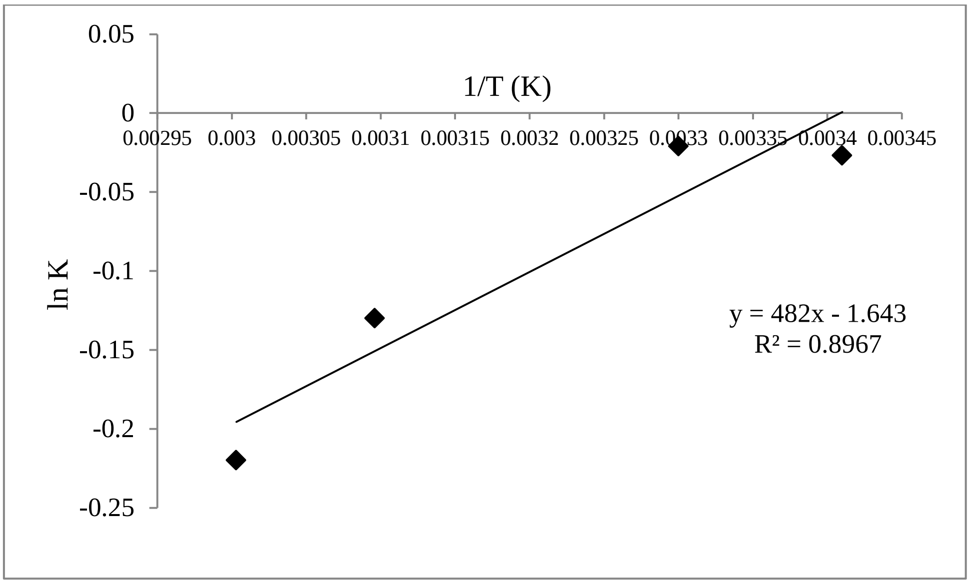

Fig.7 Plot of ln K versus 1/T for the adsorption of Cr (VI) onto chitosan

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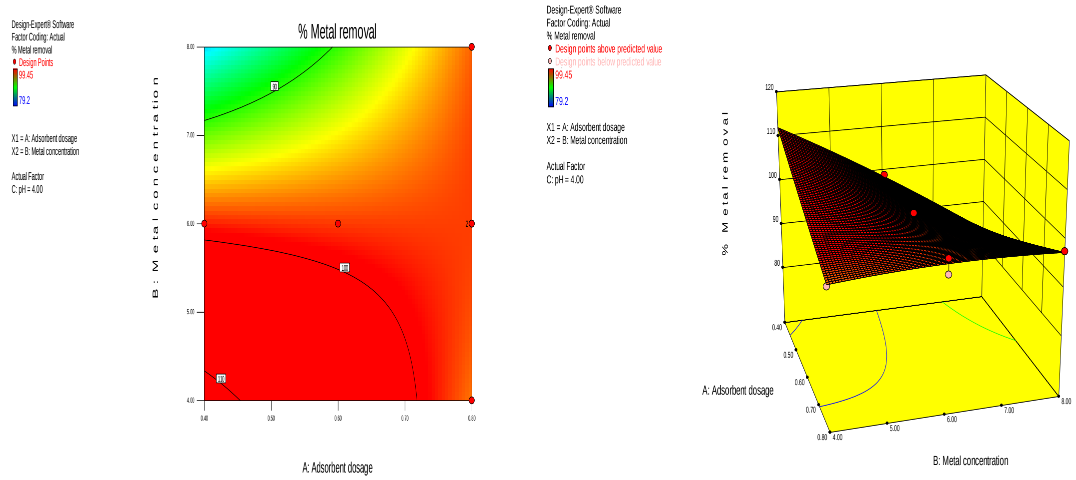

Fig.8 Response surface and contour plots for Cr(VI) adsorption capacity as a function of the test variables adsorbent dosage (x_1), metal concentration (x_2) and pH (x_3).

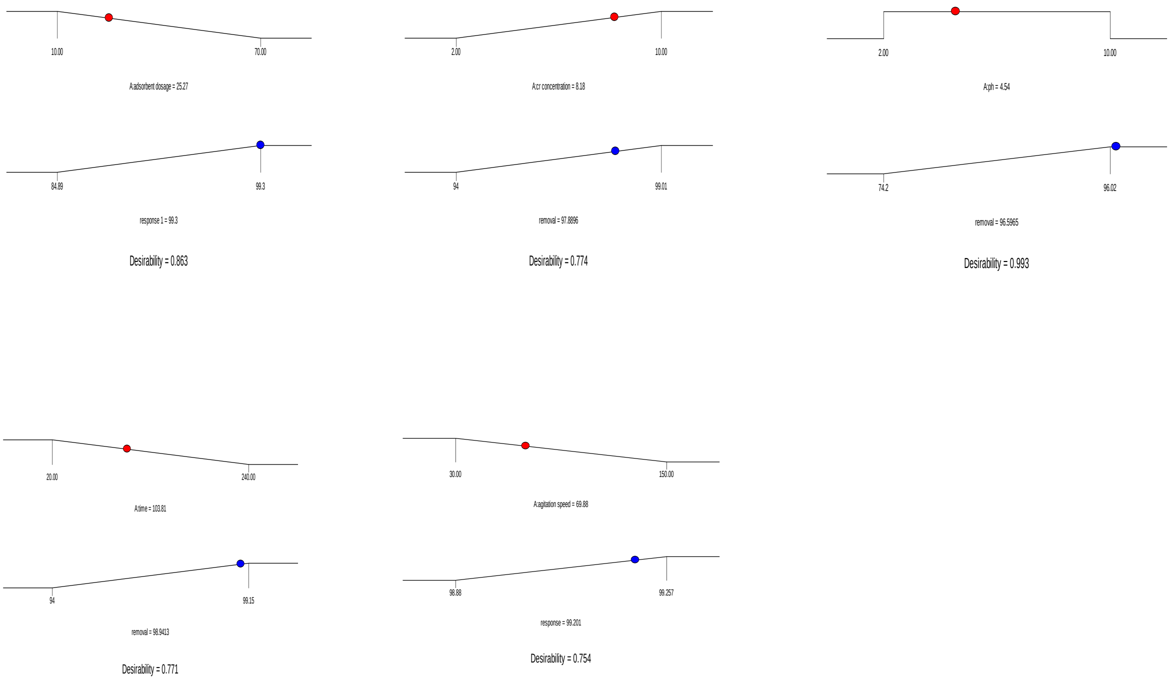

Fig.9 Desirability ramp for six goals - adsorbent dosage, metal concentration, pH, agitation speed, shaking time and % adsorption

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