REMOVAL OF CHROMIUM (VI) FROM WASTE WATER USING MIXED ADSORBENT

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Abstract

The potential for removal of hexavalent chromium from waste water through biosorption using mixed adsorbent powder (Borasus flabellifer coir powder and Ragi husk powder) was investigated in batch experimentation. The percentage removal of chromium (VI) has been found to be dependent on several parameters, like, agitation time, the mixed adsorbent particle size, mixed adsorbent dosage, initial chromium (VI) ion concentration, temperature and pH. The adsorption mechanism was found to follow both the Langmuir and Freundlich models for chromium (VI) adsorption onto mixed adsorbents based on high regression coefficient R2 value. The adsorption behavior followed the second order kinetics. The maximum chromium (VI) metal percentage removal observed at pH 2 is 72.98% and also maximum metal uptake of 18.518 mg/g. The results obtained based on the experimental study showed that mixed adsorbent powder is found to be an effective and economically viable adsorbents for chromium (VI) removal from wastewater.

Key words: chromium (VI), adsorption, mixed adsorbents, adsorption isotherms, adsorption kinetics, thermodynamic parameters.

1 Introduction

Ongoing trends in urbanization and industrialization enormously contribute towards voluminous increase in wastewater generated from chemical, petrochemical and refinery processes. Heavy metals are important constitutes of wastewater streams that are often discharged into water bodies disregarding specified discharge limits in environmental regulations. Thereby, heavy metals pose significant risk to human beings, aquatic species and other living organisms and hence water contamination with heavy metals needs to be addressed globally [1-2]. Among heavy metal contaminants in wastewater, chromium is highly toxic, carcinogenic and mutagenic when it is present in hexavalent state and $Cr_2O_7^{2-}$ can cause lung cancer [3-4]. Typically chromium sources in wastewater are from industries involved in metal finishing, leather tanning, electroplating and textile industries.

Among various constituents, Cr (III) and Cr (VI) are often identified to be relevant for the risk of toxicity. It is well known that Cr (VI) is 100 fold more toxic than Cr (III) due to its high water solubility, mobility and ease to undergo reduction [5]. Cr (VI) toxicity is primary due to its oxidizing nature and ability to form free radicals during reduction from Cr (VI) to Cr (III) inside living cells [6]. Typical tolerance limit for Cr (VI) in wastewater streams is 0.05 mg/L [7].

Conventional techniques for Cr (VI) removal from wastewater include chemical precipitation, ion exchange technique, reduction technique, electrochemical process, extraction technique, membrane process, evaporation technique and foam separation process. While these processes offer several advantages, they are expensive at lower concentrations. An alternative process to address such issues is the bio-sorption which has been proven to be effective as a low cost option to address Cr (VI) removal from wastewater streams as available agricultural waste materials are proven to be quite useful. Several bio-

materials like tamarind seeds, rice husk, maize bran, wall nut hull, groundnut hull, limonia Acidissima hull (Elephant hull) powder and ragi husk powder etc, have been used as adsorbents to remove Cr (VI) from aqueous solutions [8].

Though process industries did not focus much on use of the naturally available adsorbents, various investigators have been exploring use of such adsorbents for removal of heavy metals in effective manner and these may find application in future. In this direction, mixed adsorbents have been used for the removal of chromium (VI) from waste water and their performance in comparison with individual adsorbent such as Borasus flabellifer (palm fruit) coir powder and Ragi husk powder are shown in Table 1.

This work addresses the use of Borasus flabellifer coir and Ragi husk mixed adsorbent powder as an effective and inexpensive material for the removal of chromium (VI) from waste water in batch experimentation.

2 Materials and methods

2.1 Preparation of synthetic chromium (VI) solution

All chemicals used for study are of analytical grade. Stock solution of 1000 mg/L was prepared by adding distilled water in measured quantity of $K_2Cr_2O_7.5H_2O$ placed in 1 L volumetric flask upto the mark. $K_2Cr_2O_7.5H_2O$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) used as standard chemicals and are procured from the manufacturers. Various concentrations of test solution of chromium (VI) ranging from 20 mg/L to 100 mg/L were prepared by subsequent dilution of the stock solution.

2.2 Preparation of Borasus flabellifer coir powder and Ragi husk powder

The adsorbents used were borasus flabellifer coir powder and Ragi husk powder as mixed adsorbent. Both the borasus flabellifer coir and Ragi husk were collected from agriculture farms in the close vicinity of the college in Vizianagaram. To ensure its purity, materials were washed thoroughly and dried for removal of moisture, after which, they were crushed in a roll mill. The material so processed was screened through British standard screen (BSS) meshes (63 μm-125 μm). Finally the product obtained is stored in air tight plastic bottle, so as to prevent from degradation for further use. All the materials were used as such and not subjected to any pretreatment.

2.3 Batch experimental procedure

Batch process adsorption studies were carried out to investigate the effect of different parameters and their ranges in the present work shown in Table 2. Solution containing adsorbate and adsorbent was agitated at a fixed value of 180 rpm in a mechanical shaker at known time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper.

Final residual metal concentration after adsorption was measured using Atomic absorption Spectrophotometer (PinAAcle, 500, Perkin Elmer Pvt Ltd). To estimate the percentage removal of chromium (VI) from waste water, the following equation was used.

$$\text{Removal of chromium (VI)} = \frac{Initial - Final\ metal\ ion\ concentration}{Initial\ metal\ ion\ concentration} \times 100 \quad (1)$$

3 Results and discussion

3.1 Effect of contact time at various mixed adsorbent dosages

The agitation time profile for adsorption of chromium (VI) for fixed mixed adsorbent dosage of 0.6g for various concentrations of chromium solution is depicted in Figure 1. The data shows that the agitation time at equilibrium is achieved at 60 minutes at optimum pH value of 2 for the removal of chromium (VI). After equilibrium time, no further change in percentage removal of chromium (VI) metal has been noticed. Figure 1 shows that percentage removal of chromium (VI) decreases with increase in concentration of chromium solution.

3.2 Effect of pH

The literature reveals that pH is one of the most important parameters that effects on adsorption process. Figure 2 illustrates the effect of pH on adsorption of chromium (VI) at different initial concentrations. With increase in adsorption of chromium (VI), pH values vary from 1 to 2, which decrease when pH is greater than 2. The maximum percentage removal of chromium (VI) was noticed at pH 2.

3.3 Effect of mixed adsorbent dosage and size in aqueous solution

The variations in percentage removal of chromium (VI) and also metal uptake with mixed

adsorbent dosage is illustrated in Figure 3. It has been noticed that the percentage removal of chromium (VI) increases from 45.65% to 72.98% and also metal uptake decreases from 4.565 mg/g to 0.6923 mg/g with an increase in the mixed adsorbent dosage from 0.1 g to 1.0 g in 50mL solution at 303 K for 63µm mixed adsorbent size. After wards, it revealed that further increase in mixed adsorbent dosage does not result in increased percentage removal of chromium (VI). This may be due to non-availability of binding sites and also due to the blockage of binding site with the excess mixed adsorbent dosage. The percentage removal of chromium (VI) from waste water with mixed adsorbent size is reported in Table 3. The percentage removal of chromium (VI) increases from 68.52% (1.142 mg/g) to 72.98% (1.2163 mg/g) with decrease in the mixed adsorbent size from 125µm to 63µm. This phenomenon is expected as the decrease in size of adsorbent results in the increase of the surface area of it, thereby the number of active sites are better exposed to the adsorbate.

3.4 Effect of Temperature

The effect of temperature on adsorption of chromium (VI) on mixed adsorbent is one of important parameter at different initial concentrations. Figure 4 reveals that the maximum percentage removal of chromium (VI) is achieved at temperature of 323 K. It also reveals that adsorption of chromium (VI) increases with increase in temperature being endothermic reaction in nature. Further, low initial metal ion concentrations of the solution shows favorable adsorption in comparison with higher metal ion concentration solutions. The percentage removal of chromium (VI) is increased from 67.69% to 74.32% in the temperature range of 283 K-323 K for 20 mg/L initial concentration of chromium (VI). Maximum adsorption of 74.32% was observed at 323 K. This increase in binding might be due to increase in surface activity and increased kinetic energy of the chromium (VI) metal ions.

3.5 Adsorption Isotherms

An applicability of Langmuir, Freundlich, Tempkin isotherms for mixed adsorbents of Borasus flabellifer coir powder and Ragi husk powder was tested to characterize the interaction of the metal ions with the mixed adsorbent. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed in the solid phase when the two phases are at equilibrium.

3.5.1 Langmuir model

The applicability of Langmuir isotherm [11] was tested to estimate the maximum metal uptake which occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules.

The non-linear model of Langmuir isotherm is as under

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \qquad (2)$$

q_e is the metal uptake (mg/g), C_e is the equilibrium metal ion concentration (mg/L). q_{max} is the maximum metal uptake, and b is the ratio of sorption rates.

The linear model of Langmuir isotherm is as under

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \qquad (3)$$

Figure 5 illustrates the linearity for Langmuir isotherm for the adsorption of chromium (VI) on mixed adsorbent. Their equations along with the q_{max} and b calculated from the slope and the intercept are depicted in Table 4. It has been noticed that there was strong binding of chromium (VI) onto the surface of mixed adsorbent. The separation factor, R_L determined from Table 5 at Temperature 303 K and pH 2 is in between 0.4367-0.7949 for various concentrations shows favorable adsorption $(0<R_L<1)$.

3.5.2 Freundlich model

The applicability of Freundlich isotherm [12] was tested for nonlinear multilayer adsorption model with heterogeneous energetic distribution active sites and reversible adsorption, followed by interaction between adsorbed molecules.

Non-linear model of Freundlich isotherm is as under

$$q_e = K_f C_e^{\frac{1}{n}}$$

$$\qquad (4)$$

K_f and n are the adsorption capacity and adsorption intensity respectively. q_e is the equilibrium metal uptake and C_e is concentration of chromium (VI) at equilibrium.

The linear model of Freundlich isotherm is as under

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (5)$$

The values of K_f and n obtained from intercept and slope of a plot of log q_e versus log C_e are given in Table 6. Figure 6 illustrates the linearity based on high regression coefficient value for Freundlich isotherm for the adsorption of chromium (VI) on mixed adsorbent and linearity of the relationship reveals strong binding of chromium (VI) to the mixed adsorbent. As the slope of isotherm (n) is greater than 1, it favors for the adsorption of chromium (VI) on mixed adsorbent.

3.5.3 Tempkin model
The applicability of Tempkin isotherm model [13] was tested for direct/indirect the adsorbent-adsorbate interactions.
Both the nonlinear and linear form of Tempkin equations are as under

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \qquad (6)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad (7)$$

$B_T = (RT/b_T)$. T is the temperature (K) and R is the universal ideal gas constant. Constant b_T represents the heat of adsorption. A_T is the equilibrium binding constant at the maximum binding energy. A plot of q_e versus ln C_e at a fixed temperature will give Tempkin isotherm constants, A_T and b_T.

Figure 7 depicts the linearity for Tempkin isotherm for the adsorption of chromium (VI) on mixed adsorbent. Their equations with regression coefficients are given in Table 7 and Linearity relationship of Figure 7 reveals that strong binding of chromium (VI) on the mixed adsorbent.

3.6 Studies on kinetics of adsorption
The adsorption kinetic models describe the metal uptake and also the reaction rate controls the process time of metal uptake on the solid – solution interface along with reaction pathways and time to reach equilibrium. Two kinetic models have been tested to investigate the mechanism of adsorption using pseudo first order and pseudo second order kinetic models at various parameters. Based on value of regression coefficient (R^2), the closeness of experimental data to the model predicted values are decided A relatively high R^2 value (close or equal to one) is preferred for better adsorption of chromium (VI) on to the mixed adsorbent.

3.6.1 Pseudo-first order kinetic model
The pseudo first order kinetic model is as under

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (8)$$

q_e and q_t are the metal uptake at equilibrium and time t, respectively (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). This equation (8) is rearranged as under

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t \qquad (9)$$

Figure 8 illustrates the first order kinetics for adsorption of chromium (VI) on mixed adsorbent. The model equations with regression coefficients are given in Table 8. From the graph, the q_e is estimated for different process parameters and the estimated value is checked with the experimental value. From Table 8, it is seen that q_{ecal} and q_{eexp} are not the same. Therefore, first order kinetics may not represent the first order kinetic model. The above model is not fit for chromium (VI) removal on mixed adsorbent.

3.6.2 Pseudo–second order kinetic model
The pseudo-second-order kinetic model is as under

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (10)$$

k_2 is the rate constant (g mg^{-1}min^{-1}). The linear form of Equation (10) after integration is given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (11)$$

And k_2 is obtained from the intercept of the plot of t/q_t vs t. Figure 9 depicts the second order kinetic model for adsorption of chromium (VI) on mixed adsorbent. The model equations with correlation coefficients are shown in Table 9, it is seen that q_{ecal} and q_{eexp} are almost the same. Therefore, the second order kinetic model is fit for chromium (VI) removal by mixed adsorbent.

3.6.3 Intra-particle diffusion model
The combination of four consecutive steps [14], like diffusion in the bulk solution, diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles are used for

chromium (VI) removal from waste water on mixed adsorbent. According to Weber and Moris [15] if the rate limiting step is the intra-particle diffusion, then the amount adsorbed at any time is directly proportional to the square root of contact time t as shown mathematically below

$$q_t = K_{diff} t^{0.5} + C \qquad (12)$$

q_t, t and K_{diff} are the metal uptake, contact time and the intra-particle diffusion coefficient respectively. A plot of q_t against $t^{0.5}$ will give a straight line with a positive intercept for intra particle diffusion. The value of K_{diff} will be calculated from slope. The higher value of K_{diff} indicates the enhancement of the rate of adsorption.

Figure 10 illustrates almost linearity for intra particle diffusion model on the basis of the regression coefficient values. The R^2 values (refer to Table 10) are almost close to unity, conforming that the rate-limiting step is mostly the intra-particle diffusion process.

3.7 Thermodynamics of adsorption

Adsorption is temperature dependent, associated with three thermodynamic parameters like change in enthalpy (ΔH), change in entropy (ΔS) and change in Gibb's free energy (ΔG) [16].
The Von't Hoff equation is as under

$$K_D = \frac{C_{Ae}}{C_e} \qquad (13)$$

$$\Delta G = -RT \ln K_D \qquad (14)$$

K_D is the equilibrium constant and C_{Ae} and C_e(both in mg/L) are the equilibrium concentrations for solute on the mixed adsorbent and in the solution, respectively. The K_D values calculated from equation (13) are used in equation (14) to find out the ΔG, ΔH and ΔS. Then K_D is expressed below as function of ΔH (KJ/mol) and ΔS (KJ/mol K) and absolute temperature.

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (15)$$

The values of ΔH and ΔS are calculated for the slope and intercept respectively by plotting ln K_D vs (1/T).

The experimental data was plotted in Figure 11 which illustrates almost linearity for Von't Hoff equation. Their equations with correlation

coefficients are given in Table 11. From values of ΔH, ΔS and ΔG, the thermodynamic parameters such as ΔG, ΔH and ΔS for the adsorption of chromium (VI) on mixed adsorbent indicates the feasibility, spontaneity, irreversibility and endothermic nature.

4 CONCLUSIONS

The findings of this study revealed that the Borasus flabellifer coir and Ragi husk mixed adsorbent have the potential for use as cheap naturally available bio-sorbent for the removal of chromium (VI) from waste water, up to 72.98% for an initial concentration of chromium (VI) 20 mg/L and at a temperature of 303 K, which are specified below;

- The equilibrium agitation time is achieved at 60 minutes for all initial concentration of chromium (VI) solution.
- The maximum percentage removal of chromium is achieved at pH value of 2.
- With the increase in mixed adsorbent dosage from 0.1 to 1.0 g (for 50 mL of solution of 20 mg/L at temperature of 303K), the percentage adsorption of chromium (VI) is increased from 45.65 to 72.98%.
- The maximum metal uptake observed from model is 18.518 mg/g
- The percentage removal of chromium (VI) on mixed adsorbent increases with increase in the temperature from 283K to 323K for all initial concentrations of chromium (VI).
- The adsorption mechanism is found to follow both the Langmuir and Freundlich models.
- The adsorption behaviour is described by the pseudo second-order kinetics.
- The thermodynamic parameters such as (ΔG), (ΔH) and (ΔS) reveal the feasibility, irreversibility, spontaneity and endothermic nature and an increased randomness at the surface of the mixed adsorbent.

The present study was conducted in the batch process as this can form the basis for designing of continuous flow systems. Both borasus flabellifer coir powder and ragi husk powder are easily available, economically viable and biodegradable and proved to be very effective biosorbent for the removal of chromium (VI).

5 References

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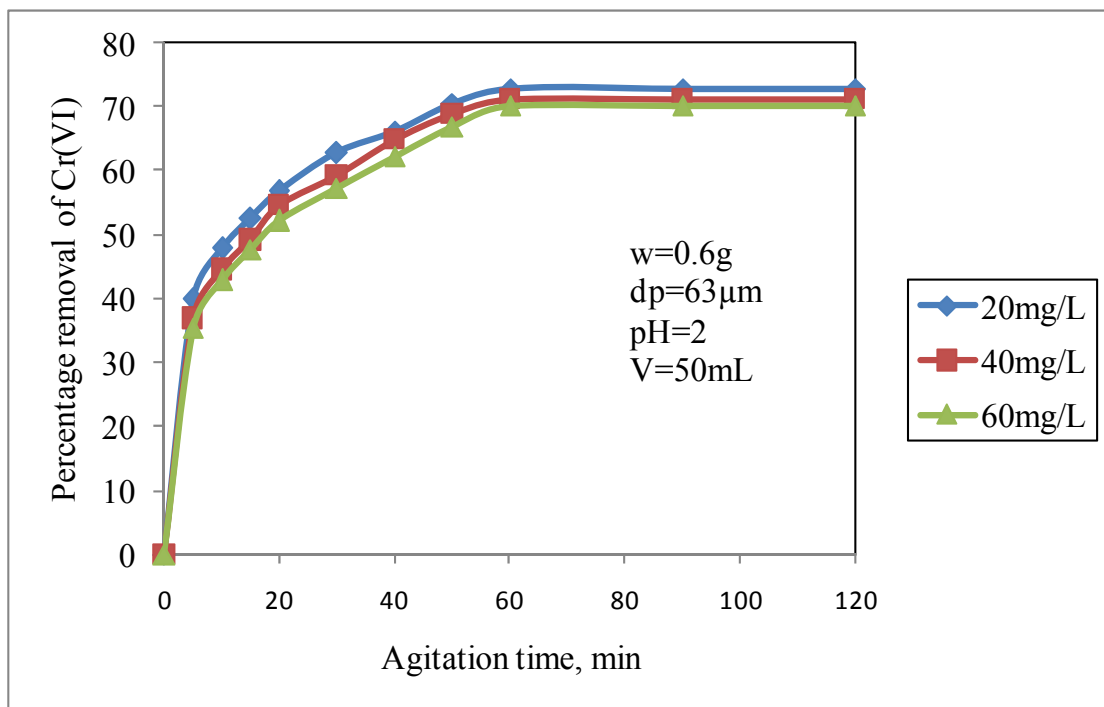
Figure 1. Effect of agitation time on adsorption of chromium (VI) by mixed adsorbent.
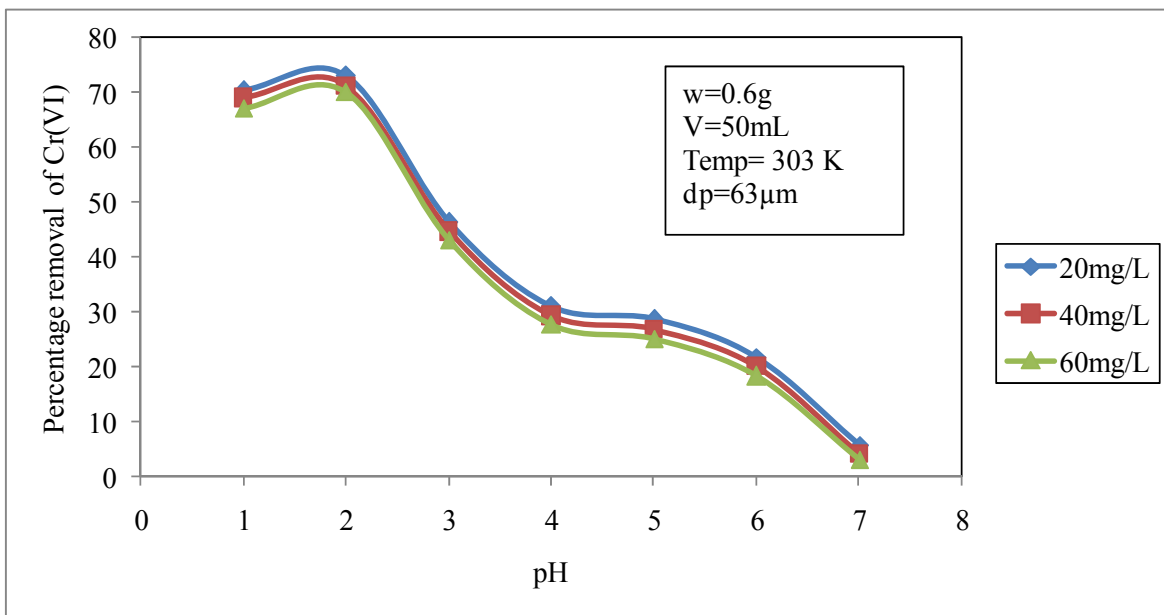

Figure 2. Effect of pH on adsorption of chromium (VI) at different initial concentrations by mixed adsorbent.
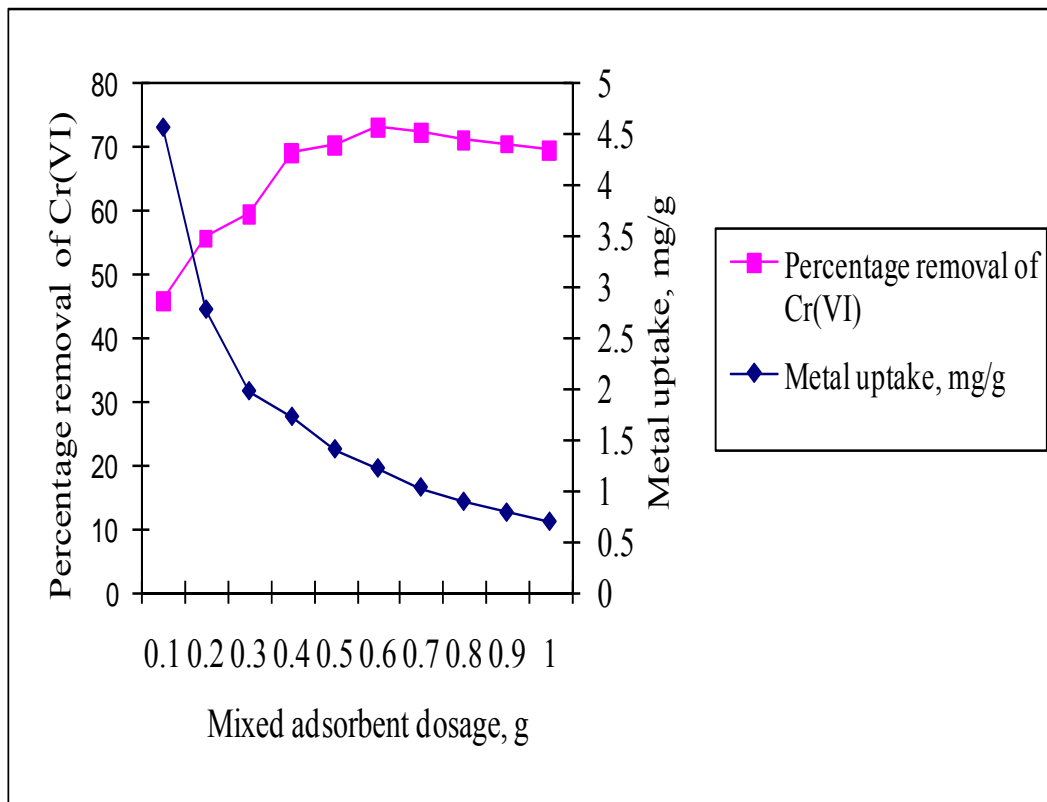
Figure 3. Effect of mixed adsorbent dosage (1:1) on percentage removal of chromium (VI) and metal uptake
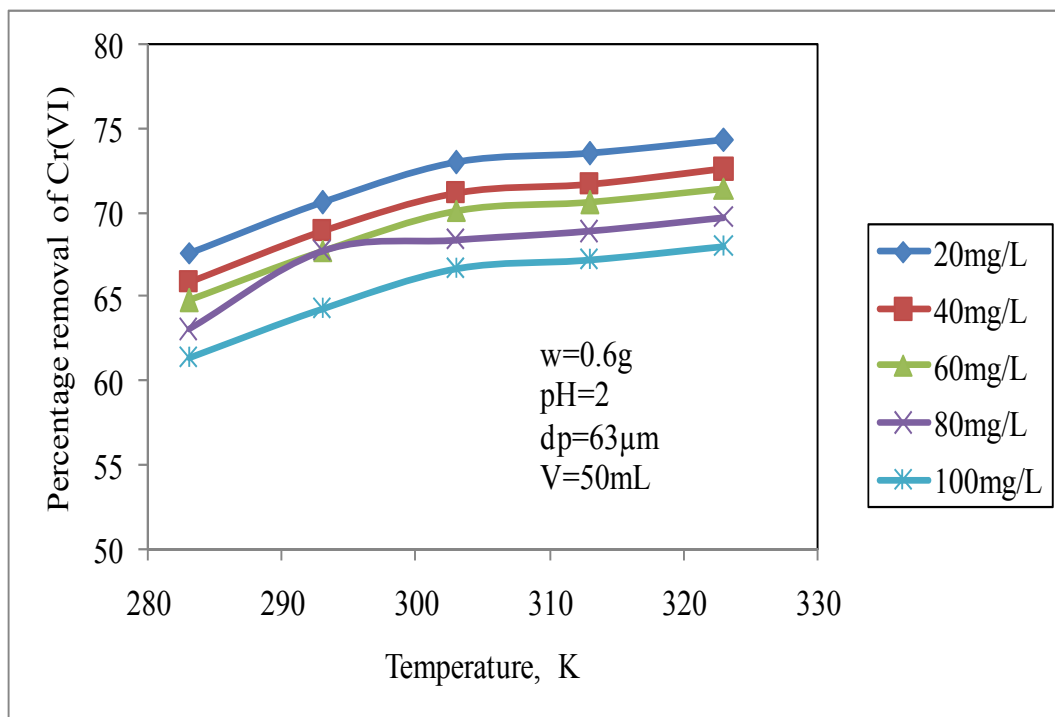

Figure 4. Effect of temperature on percentage removal of chromium (VI) by mixed adsorbent.
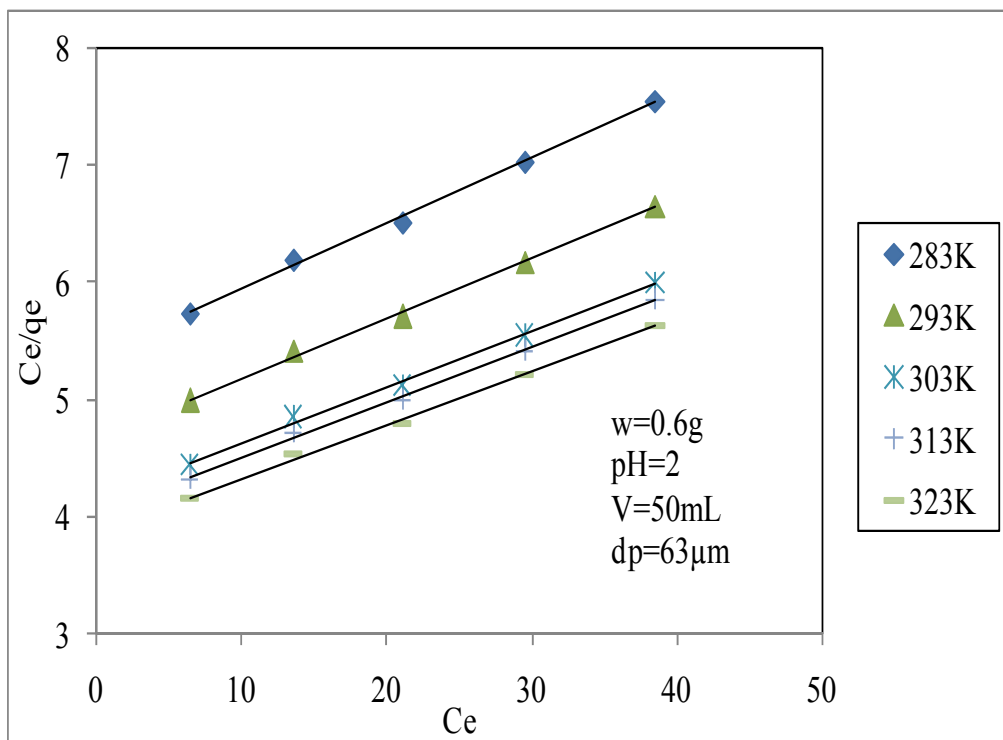
Figure 5. The Langmuir isotherm for adsorption of chromium (VI) by mixed adsorbent.
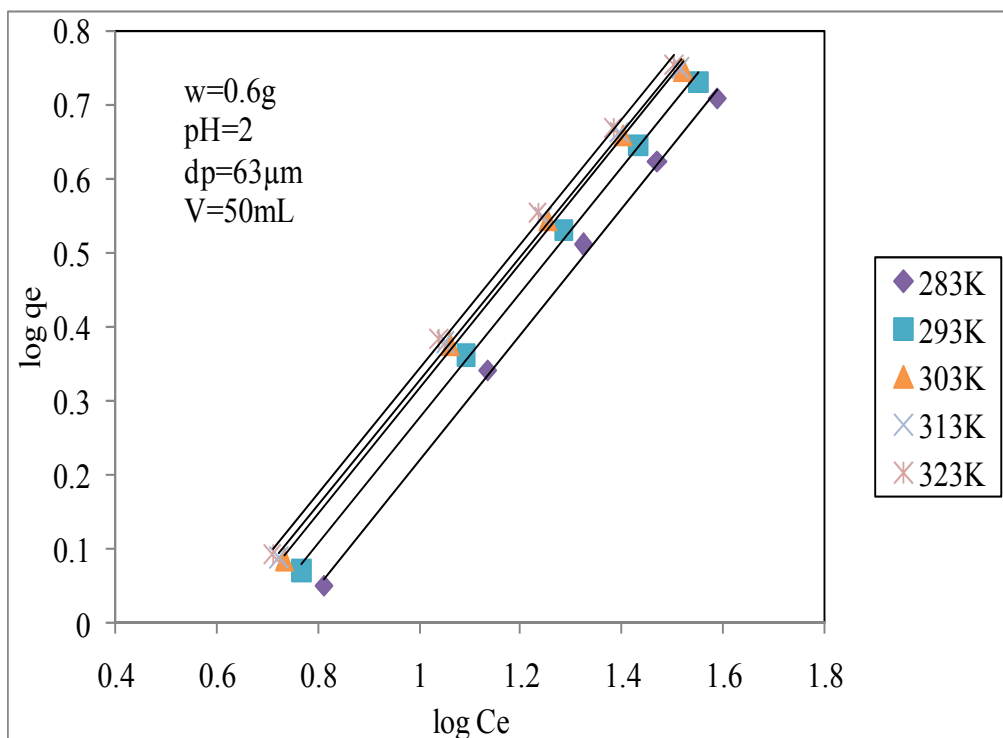

Figure 6. The Freundlich isotherm for adsorption of chromium (VI) by mixed adsorbent.
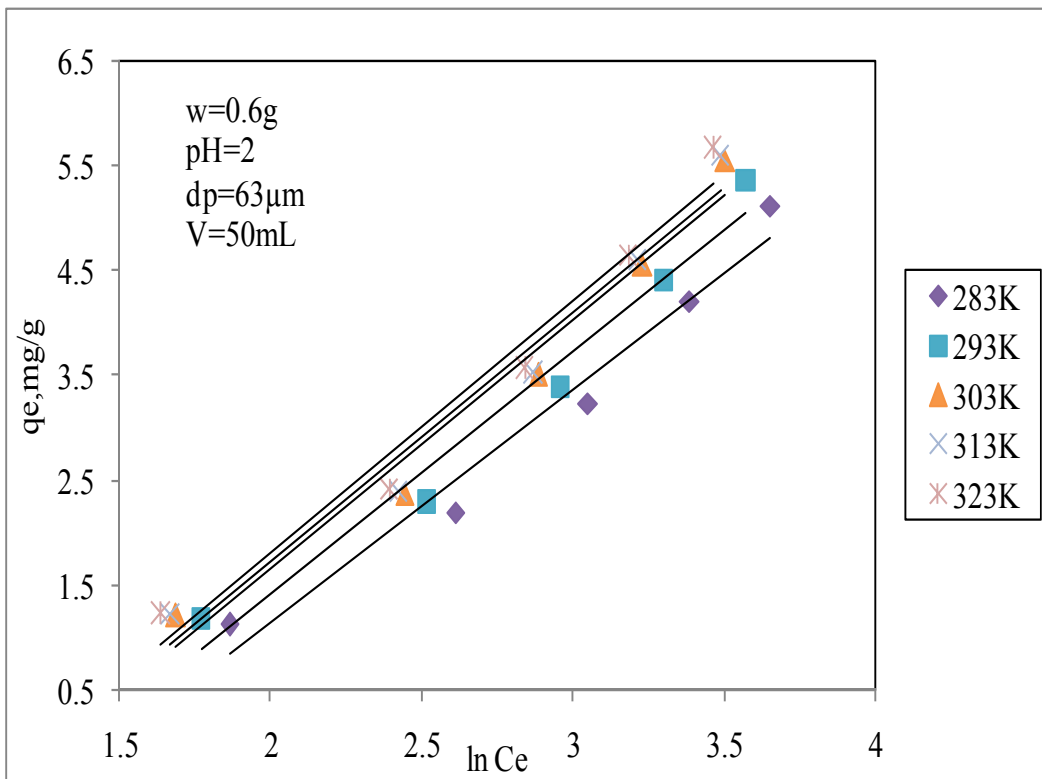
Figure 7. The Tempkin isotherm for adsorption of chromium (VI) by mixed adsorbent powder.
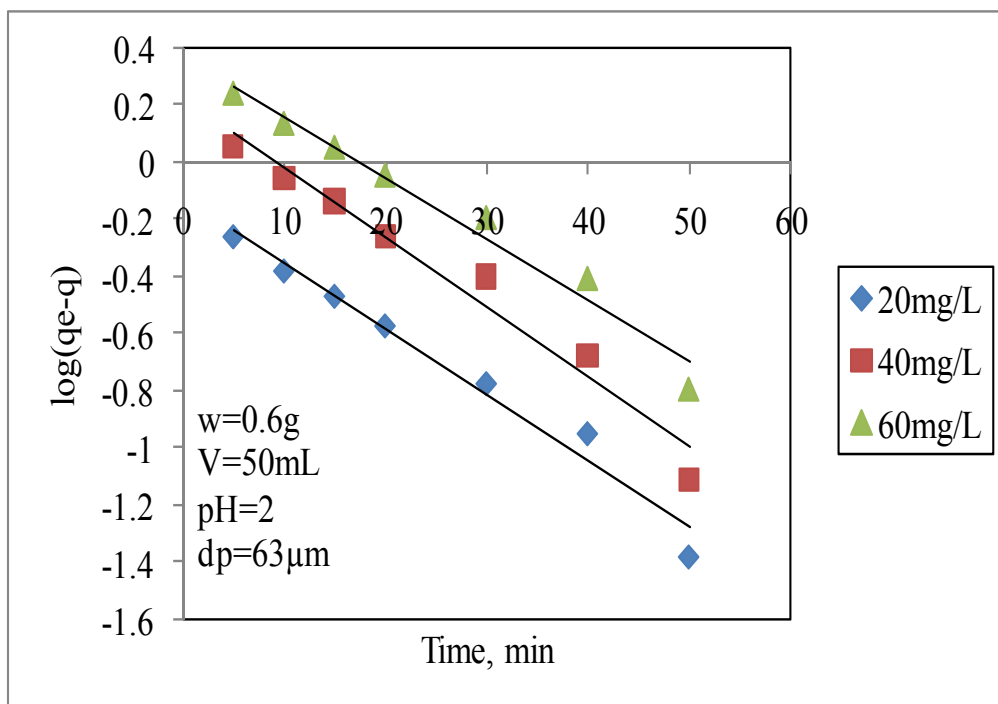

Figure 8. Testing the first order kinetics for adsorption of chromium (VI) by mixed adsorbent.
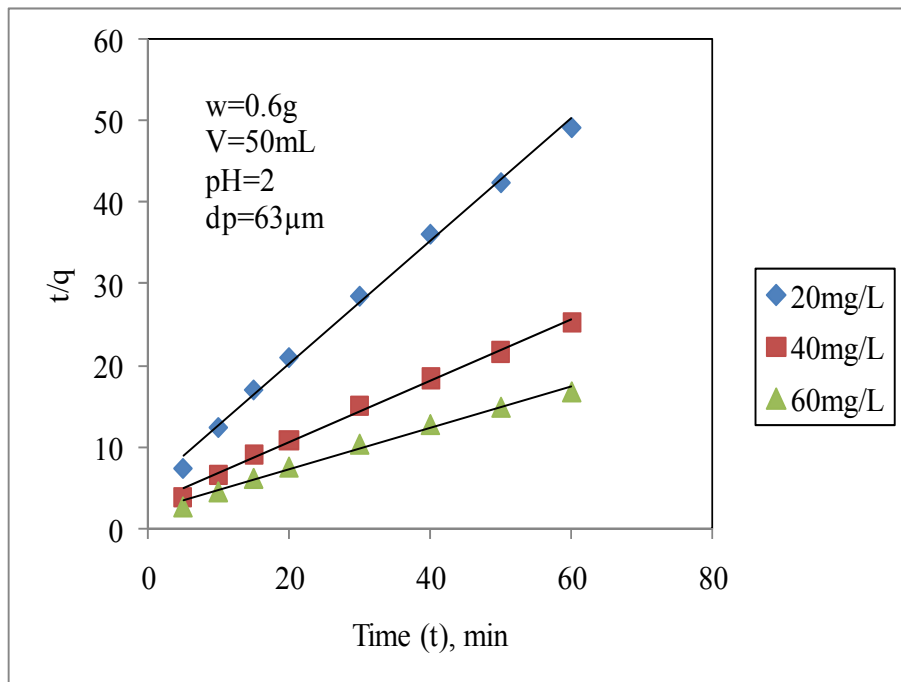
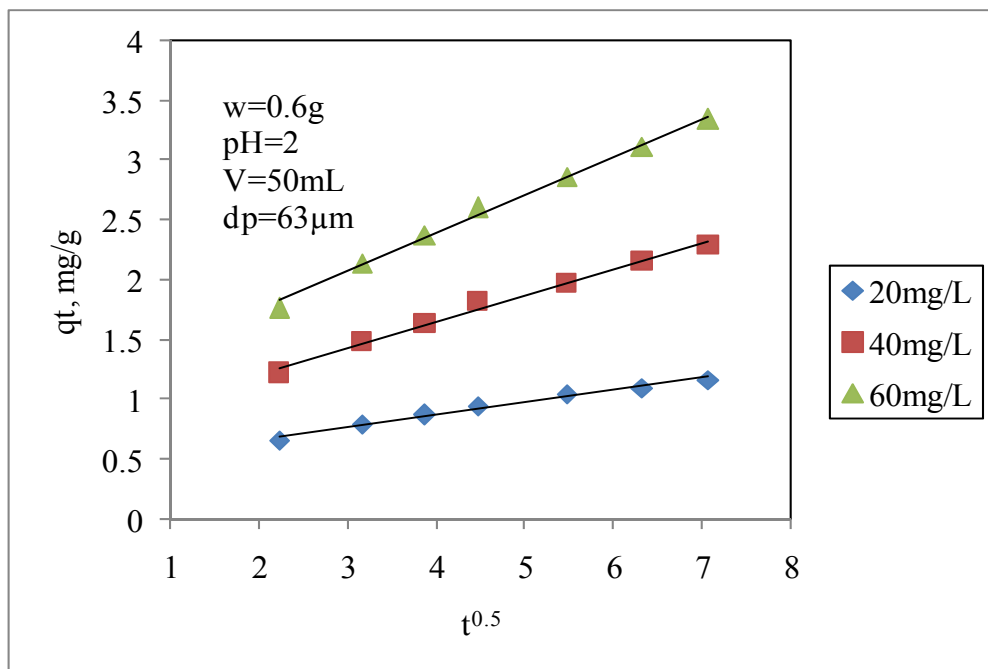Figure 9. Testing the second order kinetics for adsorption of chromium (VI) by mixed adsorbent.

Figure 10. Testing the intra particle diffusion model for adsorption of chromium (VI) by mixed adsorbent.
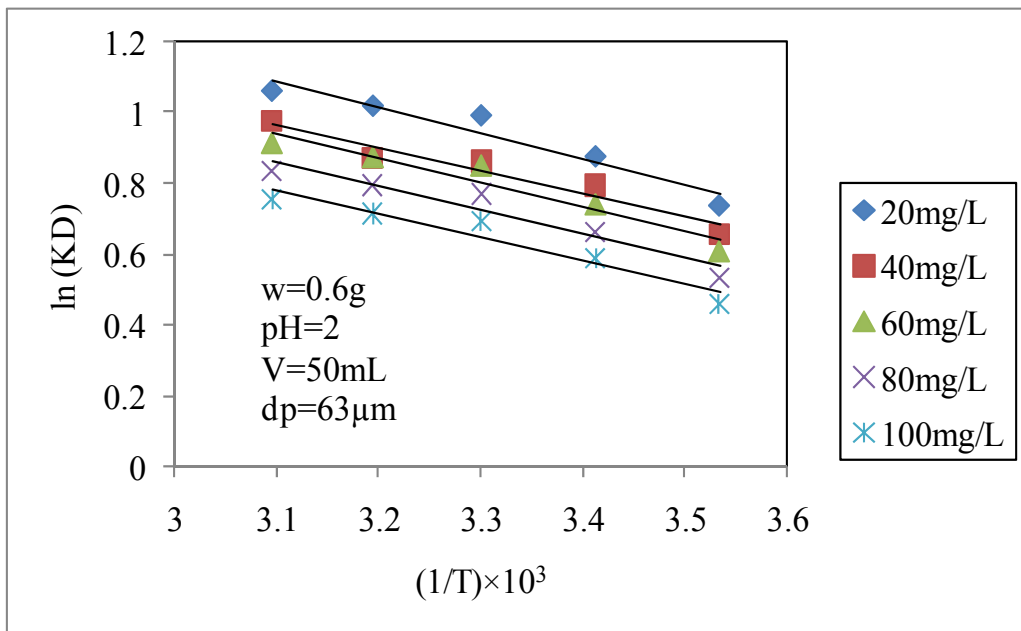
Figure 11.The Von't Hoff equation.

Table 1: Performance of mixed adsorbents in comparison with the individual adsorbents.

S.No.	Name of adsorbent	pH	Percentage removal of chromium (VI)	Reference
1	Borasus flabellifer coir powder	2	97.16	[9]
2	Ragi husk powder	2	72.48	[10]
3	Mixed adsorbent powder	2	72.98	Present study

Table 2. Various parameters and its ranges investigated in present experimentation

Parameter	Range of parameters
Agitation time (t), min	5, 10, 15, 20, 25, 30, 40, 50, 60, 90 and 120
Mixed adsorbent dosage (w), g	0.1, 0.2, 0.3, 0.4 , 0.5, 0.6, 0.7, 0.8, 0.9 and 1
Initial chromium (VI) concentration (C_0), mg/L	20, 40, 60, 80 and 100
pH	2, 3, 4, 5, 6, 7, 8, 9 and 10
Temperature, K	273, 283, 293, 303.313, 323
Adsorbent particle size, μm	63, 89, 125

Table 3. Effect of adsorbent particle size, C_0=20 mg/L; Temp=303 K; v=50mL; t=60min; pH=6.

S.No.	Mixed adsorbent average particle size, μm	Final concentration, mg/L	Percentage removal of Cr(IV)	Metal uptake (mg/g)
1	63	5.404	72.98	1.2163
2	89	5.532	72.34	1.2056
3	125	6.296	68.52	1.142

Table 4. Parameters of the Langmuir isotherms for removal of chromium (VI) by mixed adsorbent.

S.No.	Temperature, K	Model Equations	q_m	b	R_L	R^2
1	283	$\dfrac{C_e}{q_e} = 0.055C_e + 5.382$	18.182	0.0102	<1	0.997
2	293	$\dfrac{C_e}{q_e} = 0.054C_e + 4.679$	18.518	0.0115	<1	0.997
3	303	$\dfrac{C_e}{q_e} = 0.054C_e + 4.165$	18.518	0.0129	<1	0.997
4	313	$\dfrac{C_e}{q_e} = 0.054C_e + 4.055$	18.518	0.0133	<1	0.997
5	323	$\dfrac{C_e}{q_e} = 0.054C_e + 3.885$	18.518	0.0139	<1	0.997

Table 5. $R_L = \dfrac{1}{1 + bc_i}$ values at pH=2; T=303K.

Initial concentration, C_i (mg/l)	R_L
20	0.7949
40	0.6596
60	0.5637
80	0.4921
100	0.4367

Table 6. Parameters of the Freundlich isotherms for removal of chromium (VI) by mixed adsorbent.

S.No.	Temperature, K	Equations	K_f	n	R^2
1	283	$\log q_e = 0.851 \log C_e - 0.629$	0.2349	1.1751	0.998
2	293	$\log q_e = 0.846 \log C_e - 0.571$	0.2685	1.182	0.998
3	303	$\log q_e = 0.841 \log C_e - 0.522$	0.3006	1.1891	0.998
4	313	$\log q_e = 0.839 \log C_e - 0.511$	0.3083	1.1918	0.998
5	323	$\log q_e = 0.837 \log C_e - 0.493$	0.3214	1.1947	0.998

Table 7. Parameters of the Tempkin isotherm for removal of chromium (VI) by mixed adsorbent

S.No.	Temperature, K	Equations	b_T	A_T	R^2
1	283	$q_e = 2.21 \ln C_e - 3.262$	1064.64	0.2285	0.968
2	293	$q_e = 2.3 \ln C_e - 3.172$	1059.13	0.2518	0.968
3	303	$q_e = 2.367 \ln C_e - 3.068$	1064.27	0.2736	0.968
4	313	$q_e = 2.38 \ln C_e - 3.036$	1093.39	0.2792	0.968
5	323	$q_e = 2.404 \ln C_e - 2.99$	1117.06	0.2883	0.968

Table 8. Kinetic data of Lagergren pseudo first order coefficients for removal of chromium (VI)

Kinetics	Parameters Mixed adsorbent dosage=0.6g pH=2, Temperatue=303K Initial concentration	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, K_1, min^{-1}
1st order	20mg/L	$\log(q_e - q) = -0.023t - 0.119$	0.7603	1.2163	0.971	0.0529
	40mg/L	$\log(q_e - q) = -0.024t + 0.225$	1.6788	2.375	0.965	0.0553
	60mg/L	$\log(q_e - q) = -0.021t + 0.375$	2.3713	3.5069	0.971	0.0484

Table 9. Kinetic data of Lagergren pseudo second order coefficients for removal of chromium (VI).

Kinetics	Parameters Mixed adsorbent dosage=0.6 g pH=2, Temperatue=30^{0}C Initial concentration, ppm.	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, K_1, g mg^{-1} min^{-1}
2nd order	20mg/L	$\dfrac{t}{q} = 0.751t + 5.297$	1.332	1.2163	0.996	0.1065
	40mg/L	$\dfrac{t}{q} = 0.377t + 3.096$	2.6525	2.375	0.994	0.0459
	60mg/L	$\dfrac{t}{q} = 0.252t + 2.298$	3.9682	3.5069	0.990	0.0276

Table 10. Parameters of intra particle diffusion model for removal of chromium (VI).

S.No.	Initial concentration, mg/L	Model equations	R^2	K_{diff}	Constant, C
1.	20	$q_t = 0.102t^{0.5} + 0.465$	0.987	0.102	0.465
2.	40	$q_t = 0.217t^{0.5} + 0.785$	0.992	0.217	0.785
3.	60	$q_t = 0.318t^{0.5} + 1.118$	0.994	0.318	1.118

Table 11. Thermodynamic parameters for removal of chromium (VI) by mixed adsorbent.

Initial Conc, mg/L	Model Equations	ΔH, KJ/mole	ΔS, J/mole K	ΔG, KJ/mole				
				283	293	303	313	323
20	$\ln K_D = -0.728(\frac{1}{T}) + 3.34$ $R^2 = 0.929$	6.0626	27.835	-1.814	-2.093	-2.371	-2.649	-2.928
40	$\ln K_D = -0.644(\frac{1}{T}) + 2.96$ $R^2 = 0.933$	5.3542	24.659	-1.624	-1.871	-2.117	-2.364	-2.611
60	$\ln K_D = -0.688(\frac{1}{T}) + 3.07$ $R^2 = 0.925$	5.72	25.598	-1.524	-1.780	-2.036	-2.292	-2.548
80	$\ln K_D = -0.676(\frac{1}{T}) + 2.95$ $R^2 = 0.927$	5.6203	24.585	-1.337	-1.583	-1.829	-2.075	-2.321
100	$\ln K_D = -0.656(\frac{1}{T}) + 2.81$ $R^2 = 0.927$	5.4539	23.412	-1.172	-1.406	-1.639	-1.874	-2.108