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BENTONITE/CHITOSAN BIOCOMPOSITE AS AN ADSORBENT FOR HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS

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ABSTRACT

The present work focuses on the study of the application of abundant and less expensive materials such as chitosan and bentonite/chitosan biocomposite in the removal of hexavalent chromium. Spectroscopic analysis like techniques FTIR, XRD and BET have been used to characterize the adsorbents. The data indicate that the adsorption of chromium proceeds kinetically according to a pseudo-second order model on both samples and the apparent activation energy (Ea) have been measured to be 22.9 $kJ.mol^{-1}$ and 84.4 $kJ.mol^{-1}$ for chitosan and 5%Bt/CS, respectively. The adsorption isotherm experiments show that the adsorption capacity depends on the studied chromium adsorption temperature. It has been found that the data could be well described by the Langmuir as well as the Freundlich models. Thermodynamic parameters (i.e., change in the free energy ($\Delta G°$), the enthalpy ($\Delta H°$), and the entropy ($\Delta S°$) have been also, evaluated.

Keywords: chitosan; bentonite; biocomposite; biosorption; chromium.

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1. INTRODUCTION

Currently, the continuing degradation of the environment is a universal concern for humanity. Efforts in various areas of research are being made for its preservation by reducing the concentration of various pollutants. Among these heavy metals are the most harmful to the environment pollutants. View of their importance, they are used in many sectors of industry in the worldwide. For example, chromium compounds are widely used as leader tanning, textile and woodworking [1-3]. Discharges from these industries are often overloaded by the Cr (VI) which is recognized by its adverse effects on human health, flora and fauna. Chromium mainly occurs in the trivalent and hexavalent oxidation states. Cr(III) is usually not toxic at low and medium concentrations, whereas Cr(VI) is highly toxic, a suspected carcinogenic agent, and has negative effect on the nervous system and bone narrow that is highly soluble and mobile in the aquatic environment [4–6].

Several treatment processes such as chemical reduction, precipitation, ion exchange, membrane separation and adsorption have been applied to remove Cr(VI) from wastewater [7]. During the last decade attention has been given to treatment processes involving adsorption of Cr(VI) on low-cost materials. Natural zeolite and clay minerals are low-cost materials which exhibit significant cation exchange capacities due to their negatively charged framework structure [8,9]. However, these materials have little affinity for anion groups [10]. The treatment of water and wastewater contaminated with Cr(VI) using low-cost adsorbents is a feasible process, provided that the adsorbents have received adequate modification. The modification of the negatively charged surface of minerals with cationic surfactants can effectively remove inorganic anions such as hexavalent chromium species and non-polar organic contaminants from solution. The most widely used organic modifiers is a commercial hexadecyltrimethylammonium (HDTMA), cetyltrimethylammonium (CTMA) and their homologues with ahydrophobic alkyl long tail and a hydrophilic quaternary ammonium cation charged part [11-15].However, there are only a few reports on the adsorption of Cr(VI) by modified clay minerals with chitosan biopolymer [16]. Chitosan, (1,4)-2-amino-2-deoxy-β-D-glucan, is a natural polymer easily derived from chitin, mainly by extensive N-deacetylation with alkaline treatment. The importance of chitin and chitosan motivates extensive research undertaken for their industrial and agricultural industrial utilities. In addition, since chitin and its derivative, chitosan are a kind of environment-friendly polymer material, their use as adsorbent is often of primary interest to the scientific community, due to their adsorptive properties.

The aim of the present study is to investigate chromium species biosorption by bentonite modified with natural chitosan (Bt/CS composite). Batch adsorption process has been used to evaluate the maximum adsorption capacity of CS alone and Bt/Cs composite. Bentonite (Bt) and chitosan (CS) have been chosen because of their low cost and abundance in nature and are not toxic to human beings.The chitosan used in this work is extracted from shrimp shells collected from the fishmongers of Meknes city in Morocco. The characterization of these samples was done by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), MET and BET. The adsorption kinetics, isotherms and thermodynamics parameters for the chromium removal efficiency have been investigated.

2. Materials and methods

2.1 Materials

The bentonite (Bt) was provided from Rhone Poulenc Company (France). Chitosan was prepared in our laboratory by deacetylation of chitin (see below). Potassium dichromate ($K_2Cr_2O_7$), HCl and NaOH have been purchased from Aldrich chemicals and specified to be = 99% purity. Deionised water was used in all experiments.

2.2 Preparation of Bt/chitosan biocomposite

Chitosan (CS) with deacetylation degree (DD) of 83% has been prepared by deacetylation of chitin which is extracted from shrimp shells collected from the fishmongers of Meknes city in Morocco [17]. The deacetylation reaction has been carried out at T= 120°C, by treating chitin with a concentrated NaOH solution (C = 12N). The nanocomposite (5%Bt/CS) has been prepared as follows: chitosan solution was prepared by dissolving chitosan in a 5% (v/v) aqueous acetic acid solution and the resulting solution was stirred vigorously for about 4 h. Before its use the Bt has been swollen in 50 ml of distilled water and sonificated for 15 min. Thereafter, the chitosan solution was slowly added to the Bt suspension at 60 °C. During the mixing process, the weight ratio of clay to chitosan was 5% Bt/CS. The reaction mixture has stirred for 24 h, separated by centrifugation and washed with distilled water. Then, the nanocomposite has been dried at 80°C for 12 h and ground to powder.

2.3 Characterization methods

Samples of CS and 5%Bt/CS were prepared for FT-IR, XRD, MEB and BET Analysis: a) XRD patterns were obtained using a X'PERT MPD-PRO wide angle X-ray powder diffractometer operating at 45 kV and 40 mA with CuK_α radiation (λ = 1,542 Å), b) FTIR spectra have been recorded in absorption frequencies (400 – 4000 cm^{-1}) in an FTIR (Shimadzu, JASCO 4100). The samples were prepared in KBr discs from very well dried mixtures of about 4% (w/w) and stored in a desiccator, c) N_2 adsorption measurements at -196 °C were performed with a Micromeritics ASAP 2010. The specific surface area and the average pore diameter were determined according to the standard Brunauer, Emmett and Teller (BET) and Barrett, Joyner and Halenda (BJH) methods, respectively.

2.4 Adsorption experiments

Batch experiments have been carried out to evaluate the adsorption capacity of the samples for chromium species. The effect of temperature on the adsorption of chromium by CS and 5%Bt/CS was studied at T = 298, 308 and 318 K. A mass m of the adsorbent was mixed with 20 ml of an aqueous solution of $K_2Cr_2O_7$ with initial concentration C_0 (mol/l). The mixture has then been stirred for a period "t" at constant pH = 5. After the adsorption time, the solid is separated from the solution by filtration through 0.45 µm Millipore nylon filter. The chromium concentration in the aqueous phase has been analysed by UV–VIS spectrophotometer (Schimadzu Mini 4100) at 350 nm. The removed amount of chromium from the aqueous solution was calculated by the following equation:

$$qe = V.\frac{(Ci - Ce)}{m}$$

Where qe is the removed amount of chromium, from the liquid phase (mg/g). Ci and Ce are the initial and residual concentrations in mg/l, respectively; V is the volume of liquid phase (L) and m is the mass of the sorbent (mg).

3. EXPERIMENTAL RESULTS

3.1. Adsorbent characterization

3.1.1 FTIR characterization

FTIR spectra of natural chitosan, Bentonite and 5%Bt/CS are shown in Fig.1 and compared with each other. The bands at 3452 $cm^{-1}$and the shoulder at 3225 cm^{-1} are attributed to the O-H and N-H stretching vibrations and water hydrogen bonded to other water molecules within the interlayer [18], respectively. The characteristic bands in the region 900–1200 cm^{-1} are attributed to different types of Si–O and Si–O–Si stretching vibrations. Additional bands between 450 and 900 cm^{-1}in the spectrum of Bt have been assigned to typical Si–O and Si–O–Al bending modes [19]. The appearance of new bands located at 2850 cm^{-1} and 2925 cm^{-1} in the spectrum of 5%Bt/CS sample can be noted. These bands are related to the symmetric and asymmetric stretching vibration of CH_2 and CH_3 which give two bending vibrations located at 1463 and 1474 cm^{-1}, due to the methylene scissoring modes. The presence of these C-H vibrations suggest that the composition of the modified Bt in the interlayer space may have resulted from ion exchange of Na^+ with the quaternary ammonium cation in chitosan [16, 20]. The bands assigned to the stretching vibrations of C-O-C linkages in the polysaccharide structure appear at 1155 cm^{-1}, 1085 cm^{-1} and 1025 cm^{-1} is the antisymmetric stretching of C-O-C bridge. The bands observed between 1700 and 1250 cm^{-1} are characteristic of chitosan and have been reported to be the amide I and II bands. Similar results have been reported by other authors using bentonite or other clays [19-21].

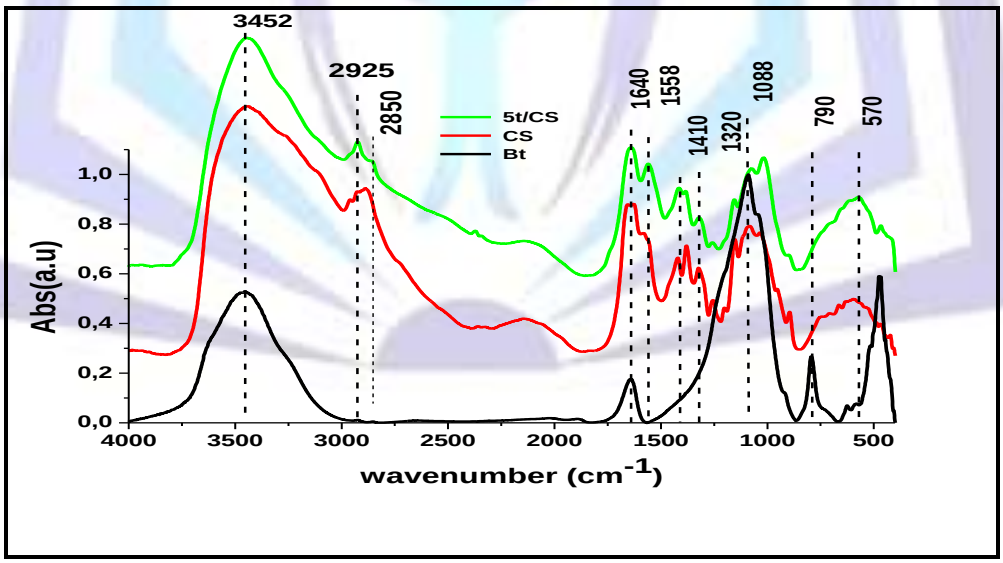

Fig 1: FTIR spectra ofchitosan andbiocomposite 5%Bt/CS

3.1.2 XRD Analysis of CS, Bt and 5% Bt/CS

Fig. 2 illustrates the XRD patterns of Bt, CS and 5% Bt/CS. The formation of the intercalated/exfoliated structure of the composite 5%Bt/CS is confirmed by the disappearance of the peak at 2θ° value corresponding to a basal spacing of d(001) = 14.92 Å in Bt. The higher d(001) value obtained for the biocomposite is related to the chitosan chains which enter in the lamellar space of Bt and exfoliate the silicate layers [22,23]. For chitosan, two main diffraction peaks at 2θ° = 9.28 and 4.57 are observed. The broadened peak around 2θ° = 9.28 indicates the existence of an amorphous structure. After

being formed into the biocomposite, these two crystalline peaks still exist, but their positions have been moved from the initial values of 2θ° and become somewhat stronger and sharper. The result suggests a higher crystallinity or denser packing in the main chain in comparison with the neat chitosan. This result is consistent with other reports in the literatures [24, 25]. It is evident that the addition of Bt greatly changed the crystallinity of chitosan, confirming the strong interaction between chitosan and Bt leading to the exfoliation of Bt scheets.

3.1.3 BET surface area

In order to investigate the effect of Bt exfoliation on the pore structure of 5%Bt/CS biocomposite, N_2 adsorption isotherms have measured and the isotherms are presented in Fig.3. It is interesting to note that a type IV adsorption isotherm is exhibited in all samples with H3 type hysteresis loops according to the original IUPAC classification [26], implying that the samples mainly contain mesopores and macropores. The results show that the BET surface area of Bt (37.8 m^2/g) decreases to 0.6 m^2/g when it's modified with chitosan biopolymer which has longer carbon chain, and the pore volume decreases also from 0.1005 to 0.0026 cm^3/g. The decease of surface area and the pores volume may be attributed to exchange sites which are satisfied by chitosan with large molecular size resulting in inaccessibility of the internal surface to nitrogen gas and the blocking of the pores in the 5%Bt/CS. The pore-size distribution calculated from the BJH desorption isotherm are inserted in Figure 3. The pore-size distribution centers around 100Å for Bt and 140Å for 5%Bt/CS indicate a mesoporous structures of the samples. This is in accordance with the conclusions drawn in the literatures [27-29].

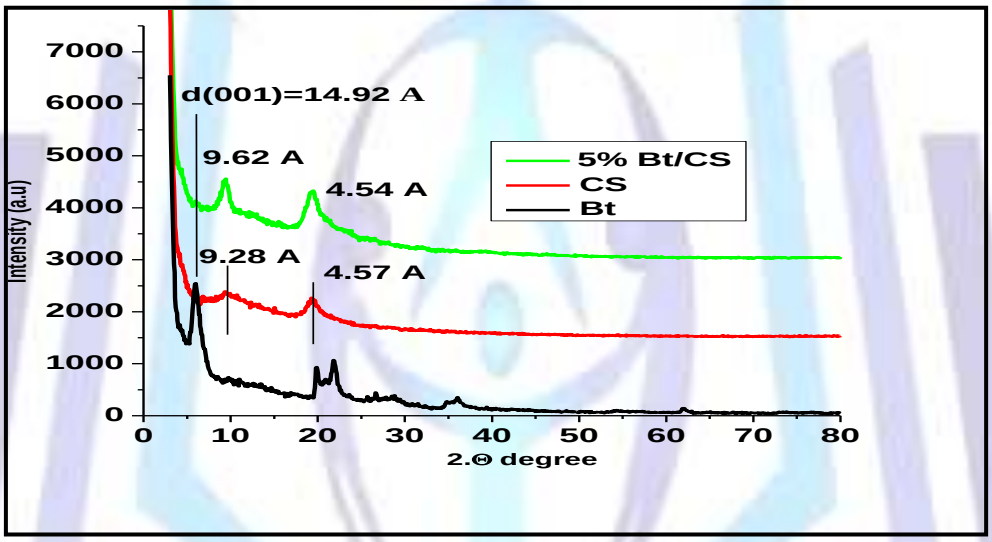

Fig 2: XRD patterns of Bt, CS and 5%Bt/CS

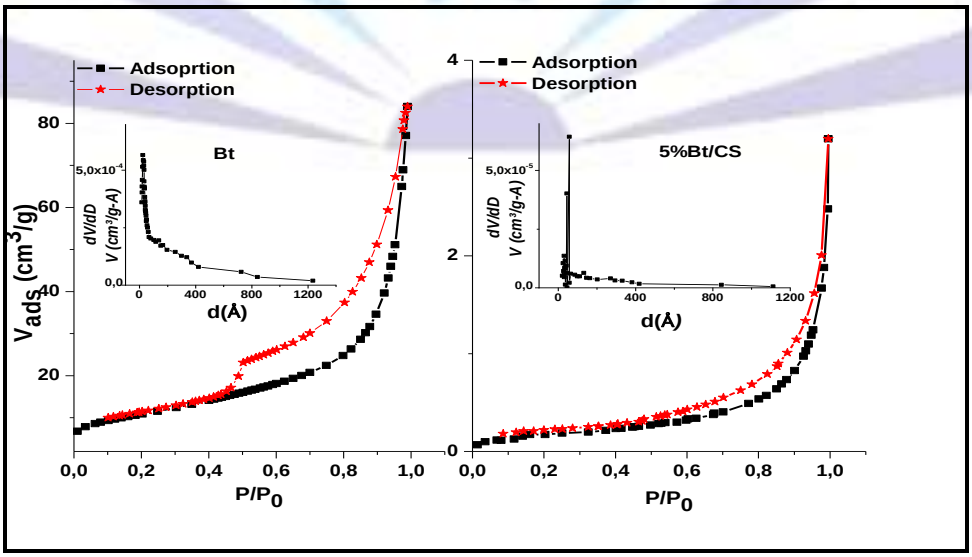

Fig 3: N_2 adsorption/desorption isotherms of Bt and 5% Bt/CS

3.2 Chromium removal studies

3.2.1 Adsorption kinetics

The plots of qe versus t at different temperatures of Cr(VI) adsorption onto CS and 5%Bt/CS carried out at pH = 5 are shown inFig 4. It has been found that Cr(VI) adsorption rate is relatively fast for the first 40 min with the plateau occurring at approximately 80 min for both samples. The data reveal that the adsorption uptake qe(mg/g) decreases with increased adsorption temperature and the adsorption rate declines and reaches the equilibrium position over time. The amounts of chromium adsorbed at equilibrium are 58 mg/g and 59 mg/g, , for chitosan and 5%Bt/CS, respectively. These quantities are mainly due to the adsorption of chromium onto the chitosan.

The kinetic data have been evaluated using the Lageregen, first order [30, 31] and Ho et coll [32, 33] pseudo second order kinetic equations. The equations corresponding to the above models are given in table 1. The kinetic constants can be obtained from the plot of log(qe–q) (Fig.5A) and t/qe(Fig.5B) against different time intervals, for the three temperatures considered in the adsorption of chromium onto CS and 5%Bt/CS. As it is shown in the table 1, the equilibrium adsorption capacity (qe) obtained experimentally correlates better with the second order kinetic model. The regression coefficient obtained from this model is higher (Table 1), thereby leading to the conclusion that the experimental data fit well with the second order kinetics.

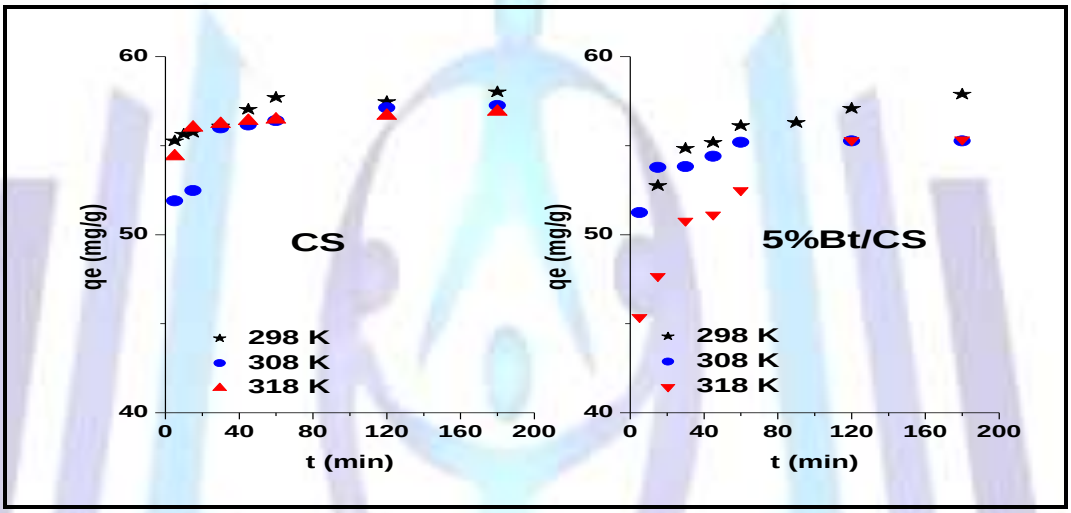

Fig 4: Effect of the contact time on adsorption capacity of CS and 5%Bt/CS for Cr (VI) atdifferent temperatures C_0(Cr(VI)) = 10^{-3} mol/l.

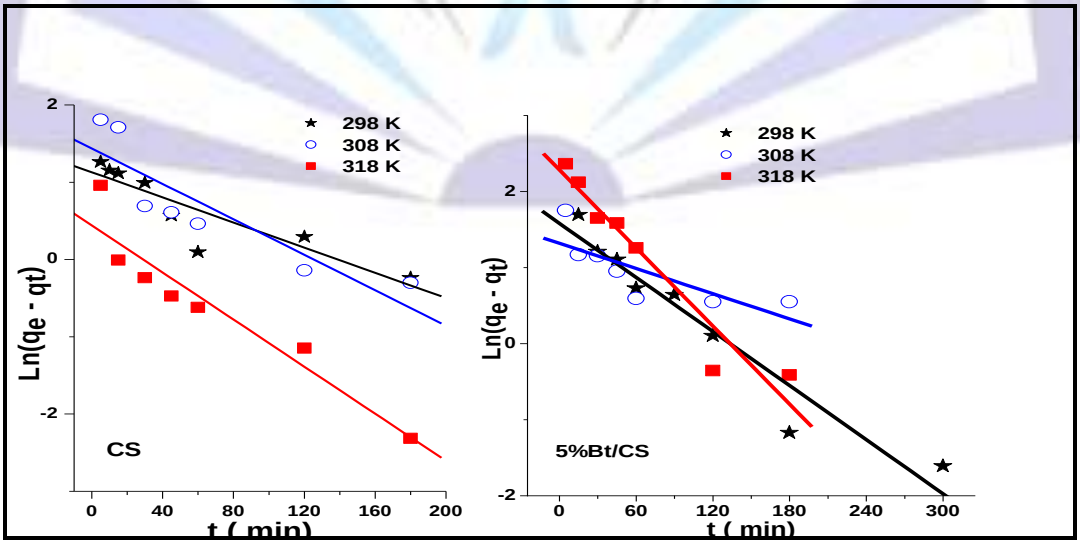

Fig 5A: Adsorption kinetics fitted by pseudo-first order equation for retention of Cr(VI) on CS and 5%Bt/CS at different temperatures

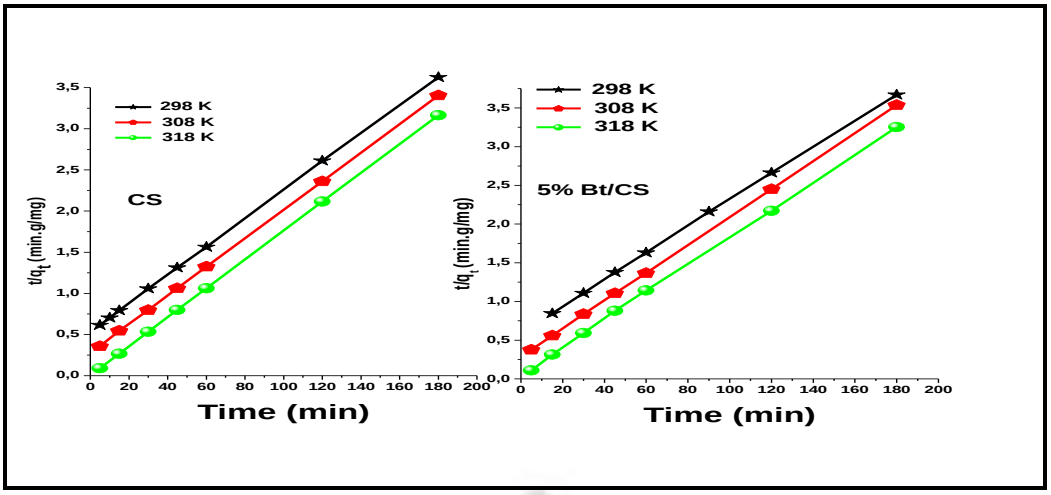

Fig 5B: Adsorption kinetics fitted by pseudo-second order equation for retention of Cr(VI) on CS and 5%Bt/CS at different temperatures

Table 1. Kinetic parameters for the adsorption of Cr (VI) on CS and 5% Bt/CS.

			Lagergren (pseudo 1st order) $\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$			Ho et coll (pseudo 2nd order) $\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} - \frac{1}{q_e}t$		
Adsorbent	q_{Exp} (mg/g)	T (K)	k_1 (min^{-1})	q_{eq}cal (mg/g)	R_1^2	k_2 (g/mg.min)	q_{eq}cal (mg/g)	R_2^2
CS	58.20	298	8.14×10^{-3}	3.10	0.896	2.74×10^{-2}	58.07	0.999
	58.04	308	1.14×10^{-2}	4.21	0.885	3.35×10^{-2}	57.57	0.999
	57.12	318	1.15×10^{-2}	1.55	0.951	4.89×10^{-2}	56.94	1
5%Bt/CS	58.15	298	1.18×10^{-2}	4.86	0.965	7.41×10^{-3}	58.44	0.999
	57.07	308	5.52×10^{-3}	3.73	0.788	3.09×10^{-2}	55.46	0.999
	56.01	318	1.71×10^{-2}	9.82	0.963	6.26×10^{-2}	56.21	0.999

3.2.2 Adsorption activation energy

The magnitude of the activation energy is commonly used as the basis for differentiating between physical and chemical adsorption. The pseudo second order rate constants of chromium adsorption onto CS and 5%CS/Bt is expressed as a function of temperature by Arrhenius equation: $\ln(k_2) = \ln A - Ea/R.T$

where k_2 is the rate constant of the pseudo second order (g/mg.min), Ea the activation energy of sorption ($kJ.mol^{-1}$), R the universal gas constant (8.314 $J.mol^{-1}$ K) and T the solution temperature (K).

A plot of $\ln k_2$ versus 1/T yields a straight line, with slope −Ea/R (Fig. 6). The activation energy for Cr(VI) adsorption onto CS is found equal to be 22.9 $kJ.mol^{-1}$ and 84.4 $kJ.mol^{-1}$ for that of chromium adsorption onto 5%Bt/CS, suggesting that the Cr(VI) is physically adsorbed onto CS and chemically adsorbed onto the 5%Bt/CS sample. It is known that when activation energy is low, the rate is controlled by intra-particle diffusion mechanism, which is a physical step in the adsorption process.

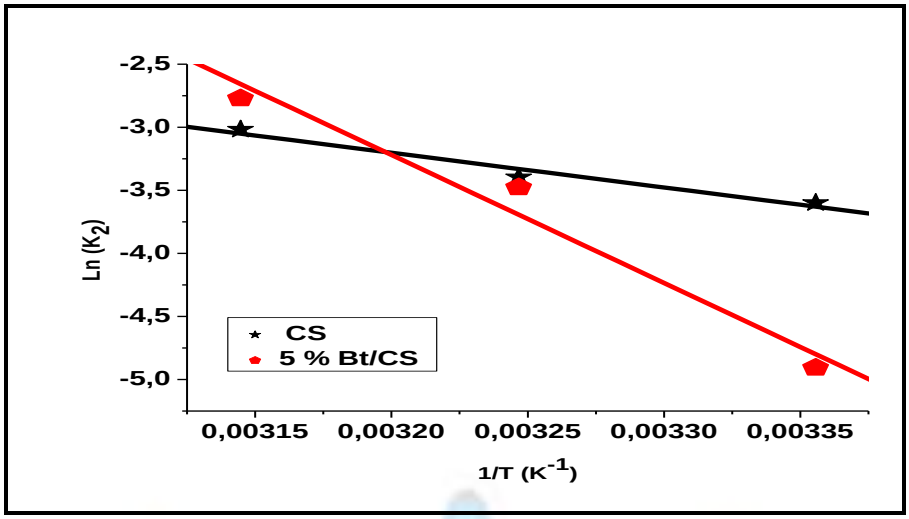

Fig 6: Arrhenius plot of lnK_2 vs 1/T

3.2.3 Adsorption isotherms

The sorption isotherms of chromium on CS and 5%Bt/CS at various temperatures are presented in Fig. 7. The amounts of chromium adsorbed on 5%Bt/CS increase slightly by increasing the temperature, while in the case of CS, the temperature has a negative effect. This may be due to a decrease in the degree of freedom of adsorbed species and a decrease in number of active sites or to a desorption of physically adsorbed chromium on chitosan when the adsorption temperature is increased. The Cr(VI) adsorption uptake has beenfound to decrease with an increase in solution temperature for all initial concentration. This indicates that the adsorption reaction of Cr(VI) on CS is exothermic.

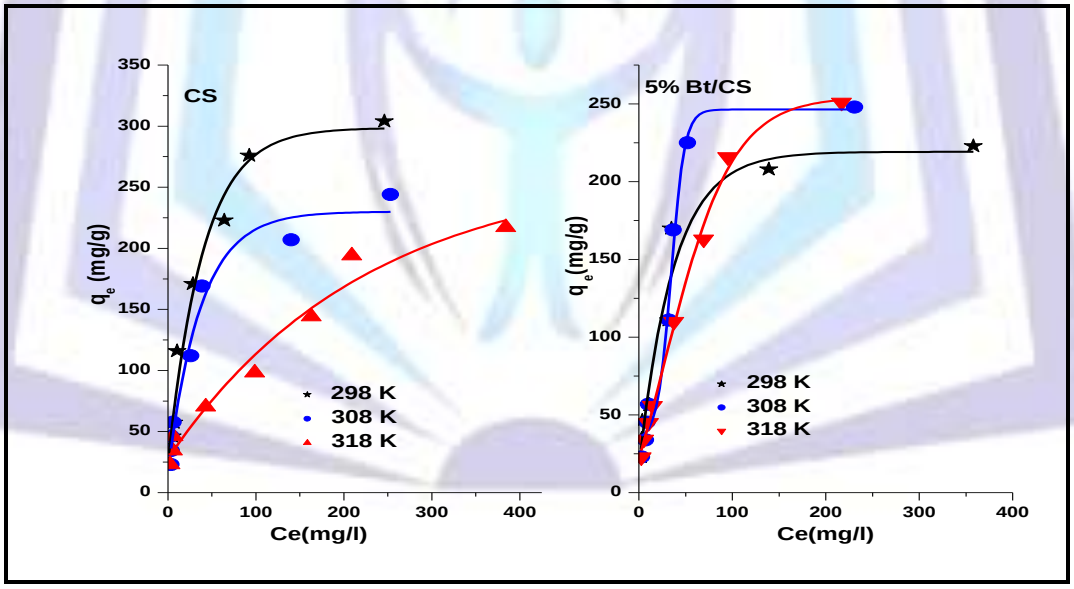

Fig 7: Effect on the Cr(VI) concentration on adsorption capacity of CS and 5%Bt/CS at various T

The experimental sorption data are fitted according to two models, Freundlich adsorption model and Langmuir adsorption model:

- **Langmuir model**:

The expression of this model is: $$qe = \frac{qm.K_L.Ce}{1+K_L.Ce}$$

where qe is the equilibrium Cr(VI) concentration on adsorbent (mg/g), Ce is the equilibrium Cr(VI) concentration in solution (mg/L), Qm is the monolayer capacity of the adsorbent (mg/g) and K is the Langmuir adsorption constant (L/mg).

The Langmuir equation is applicable to homogeneous sorption where the sorption of each sorbate molecule onto the surface has equal sorption activation energy.

- **Freundlich isotherm:**

The Freundlich isotherm is an empirical equation which can be used for non ideal sorption that involves heterogeneous sorption. The Freundlich isotherm is commonly given by the followingequation:

$$qe = K_F . C_e^{1/n}$$

whereqeis the equilibrium concentration on adsorbent (mg/g),Ce is the equilibrium concentration in solution (mg/L), K_F(mg/g)and 1/n are the Freundlich constants characteristic of the system indicators of adsorption capacity and adsorption intensity, respectively.

The values of qm, K_L, K_F, 1/n and the correlation coefficients are given in Table 2 where it is shown that R^2 values obtained for Langmuir isotherm model are generally higher than those obtained by the Freundlich model. Nevertheless, the values of n ranged between 0<1/n<1 in the Freundlich model for various temperatures demonstrated that the adsorption of Cr(VI) on these adsorbents is also favourable. These are also consistent with the results in the adsorption kinetics. If the values of K_F and 1/n are compared at all the studied temperatures, the results indicate that higher values of 1/n and lower values of K_F have been obtained at higher temperatures.

Table 2. Isotherm constants for Cr(VI) adsorption onto CS and 5%Bt/CS.

Sample	T (K)	Langmuir			Freundlich		
		R^2	K_L (L/mg)	Q_m(mg/g)	R^2	1/n	K_F(mg/g)
CS	298	0.987	0.028	395.25	0.953	0.484	27.571
	308	0.960	0.026	331.12	0.955	0.509	18.324
	318	0.984	0.068	151.97	0.986	0.421	17.498
5%Bt/CS	298	0.972	0.07	187.97	0.957	0.446	21.90
	308	0.963	0.04	190.11	0.952	0.625	12.69
	318	0.969	0.09	151.06	0.992	0.585	12.50

3.2.4 Thermodynamic studies

The thermodynamic parameters such as standard free energy (ΔG^0), standard enthalpy (ΔH^0) and the standard entropy (ΔS^0) changes have been calculated from the adsorption studies at different temperatures. These parameters are obtained from the equations below, and the graph shown in Fig.8:

with: $\Delta G° = -RT\ln Kc$,

where R is the gas constant ($kJmol^{-1} K^{-1}$), T is the temperature (K), and K_c is the distribution coefficient defined as the ratio of the amount adsorbed (qe in mg/g) to the equilibrium concentration (Ce in mg/l): $Kc = q_e / C_e$.

The Gibbs free energy change is also related to enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the following equation:

$$\ln Kc = \frac{\Delta S°}{R} - \frac{\Delta H°}{R.T}$$

The values of ΔH° and ΔS° have been obtained from the slope and intercept of the linear plot of ln(Kc) versus 1/T (Fig. 8). Thenegative values of ΔG°(Table 3) indicate that the adsorption process was favourable and spontaneous in nature. The negative value of ΔH°suggests that the adsorption is exothermic and the positive value confirm the endothermic process. The positive value ofΔS° shows increase randomness at the solid–solution interface during the adsorption of chromium onto 5%Bt/CS and reflects the affinity of the adsorbent for Cr(VI).

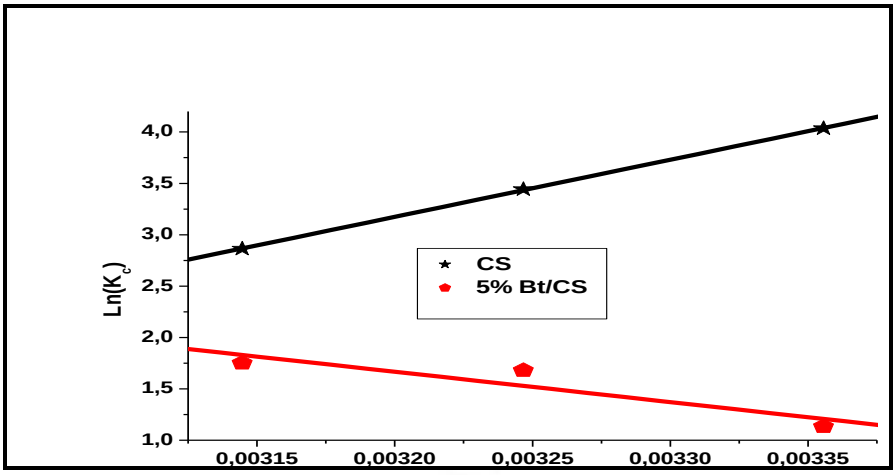

Fig 8: Van't Hoff plot for estimating thermodynamic parameters

Table 3: Thermodynamic parameters for the adsorption of Cr (VI) onto CS and 5%Bt/CS

Sample	T(K)	ΔG^0 (KJ .mol^{-1})	ΔS^0 (J .mol^{-1} .K^{-1})	ΔH^0 (KJ .mol^{-1})	R^2
CS	298	-9.99	- 46.18	- 121.41	0.988
	308	-8.81			
	318	-7.57			
5%Bt/CS	298	-2.81	92.40	24.54	0.922
	308	-4.30			
	318	-4.63			

4 CONCLUSIONS

Bt/CS biocomposite has prepared from the raw materials and used as a biosorbent for the removal of chromium ion from aqueous solution. FTIR, XRD and surface area measurement clearly shows that the chitosan biopolymer entered into the interlayer space of the bentonite. Adsorption of Cr(VI) on CS and 5%Bt/CS can be considered as a simple, fast and economic method for its removal from water and wastewater. A very good agreement with the obtained experimental data indicates that a pseudo-second-order kinetic model is favorable for chromium ion adsorption on these samples. The activation parameters of the adsorption process helped in the prediction of how the adsorption of chromium ions might vary with temperature changes. The activation energy, Ea, is 22.9 kJ.mol^{-1} and 84.4 kJ.mol^{-1}, respectively for chromium adsorption onto CS and 5%Bt/CS. The Langmuir and Freundlich isotherms models, has provided the best fit for experimental data. The maximum monolayer adsorption capacity of CS and 5%Bt/CS adsorbents as obtained from Langmuir adsorption isotherms has been found to be 395.25 and 187.97 mg/g, respectively, for Cr(VI) at pH = 5. The thermodynamic analysis confirms the spontaneous character of adsorption process. The decrease in randomness of species, has resulted with negative value of $\Delta S°$. Therefore, chitosan and 5%Bt/CS could be used as adsorbent for Cu(VI) removal from wastewater.

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