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Investigate the Adsorption Mechanism of Heavy Metals as Chromium Ions (Cr+3) from Different Solutions Using Modified Chitosan

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THE OBJECTIVE of this study is to assess the removal of Cr (III) ions onto modified chitosan-starch from aqueous solutions under both acidic and basic conditions. The effect of various parameters has been investigated via batch adsorption technique. Such parameters include initial concentration of adsorbate, agitation time, adsorbent dosage, chemical kinetics, and influence of temperature. The experimental data were fit well to Frendlich adsorption isotherm. The thermodynamic parameters such as ΔH, ΔS and ΔG were calculated, indicating that the adsorption was spontaneous and endothermic in nature.

Keywords: Cr (III) Modified Chitosan, Starch, Aqueous Solutions, Acid/Alkaline, Adsorption Isotherm.

Introduction

Chitosan is prepared by alkaline treatment of chitin shells of shrimps. Chitosan is used in a variety of biomedical and agricultural applications such as biopesticides, fining agents, preventing spoilage, self-healing paints, antibacterial agent on bandage, and drug delivery throughout the skin. It can be employed for water filtration because of its ability to bind to fine sediment particles followed by removal in sand filtration. It can also be used to purify water from phosphorus, heavy metals, and oils without any negative environmental impacts. When supported by other fining agents such as bentonite, gelatin, and silica gel, chitosan can be used to eliminate suspended particles from water. Chitosan is a natural polysaccharide comprising reactive amino and hydroxyl groups in its linear polyglucosamine chains that could be functionalized or modified. Chitosan can be modified via either grafting or crosslinking reactions which leads to the development of chitosan derivatives able to display better adsorption capability and resistance in severe media circumstances. However, cross-linking of chitosan slightly reduce the adsorption aptitude because both amino and hydroxyl groups of chitosan are bound with the crosslinker and consequently cannot interact with the pollutants. As a general comment, in more recent years, researchers have attempted to prepare chitosan-based modifying the molecules of chitosan [1-6].

Herein, we report the preparation of modified chitosan with starch as an adsorbent substrate toward removal of Cr (III) from water. The characterization of chitosan and modified chitosan was determined by infrared, X-ray diffraction and scanning electron microscope. The concentration of Cr (III) was determined by atomic absorption microscope.

Experimental

Materials and method

Analytical X-Ray Diffraction equipment; model X-Pert with secondary monochromator, Cu-radiation (λ=1.542 Å) at 45 K.V., 35 M.A. and scanning speed 0.02°/sec. were used. The diffraction peaks between 2Θ = 0° and 60°,

corresponding spacing (d, Å) and relative intensities (I/I$_o$) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files of solid chitosan and modified chitosan. The Scanning Electron Microscope identified chitosan and modified chitosan samples using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1,000,000 and resolution for Gun.1n, FEI company, Netherlands. The atomic absorption microscope (Thermo Fisher Scientific) was used to determine the concentration of Cr (III) ions before and after solution treatment.

Chitosan (MW 5000) was purchased from Tako Kasei Kogyo CO. Ltd., Japan. Starch (C$_6$H$_{10}$O$_5$)$_n$ (MW 162.1406) soluble GR was purchased from Merch chemicals, India. Glutaraldehyde (C$_5$H$_8$O$_2$) (MW 100.12 and density 1.13 Kg/lit) was purchased from central Drug House, New Delhi, India. Sodium hexametaphosphate, physical crosslinker, was purchased from Pioneer Chemical Company, New Delhi, India.

Preparation of modified chitosan crosslinked resin

A 20 ml of 2% acetic acid solution was taken in a beaker and a known quantity of chitosan was added slowly under stirring condition followed by stirring for about 2 hours. A starch solution was prepared separately by dissolving a known quantity of starch in 10 ml of distilled water. The prepared starch solution was added into chitosan solution under stirring conditions and mixed together for 3 hours at room temperature. The prepared mixture was kept at room temperature (293 K) overnight. Chitosan and starch mixture was extruded through a syringe into a homogenous solution of sodium hydroxide-methanol (1:20 w/w) solution. Freshly prepared beads were washed three times with distilled water and resultant beads were allowed to reach with 20 ml of sodium hexametaphosphate (SHMP) 25% solution for 10 minutes at room temperature. Physically cross linked beads were washed and dipped into 20 ml of glutraldehyde (GA) (25%) solution for 10 minutes at 333 K. Finally, the crosslinked beads were washed with distilled water and dried in oven at 313 K for 12 hr.

Preparation of Cr (III) solution

By dissolving (33.3060 g of CrCl$_3$.6H$_2$O in 250 ml beaker transfer into 250 ml measuring flask, take 100 ml to prepare 0.1 M in 500 ml measuring flask, take 50 ml to prepare 0.01 M in 500 ml measuring flask.

The adsorption procedure of Cr (III)

Batch equilibrium isotherm and kinetics studies, were carried out in the same manner. In each type of studies we prepared metal ion solutions containing Cr (III)) ions (0.01M) and transferred them into (250 ml) wide-mouth propylene test bottles with screw closure caps using a Finn pipette. Each bottle contained a known volume (50 ml) of the metal ion solution. A known amount (0.5 g) of the modified chitosan was added into each bottle. Afterwards, the bottle was shaken continuously (1-120 minutes). At certain intervals of contact time, the solution samples were withdrawn and filtered and the final concentration of metal ions Cr (III) was determined in the filtrate: By using atomic absorption. Amount of Cr (III) ions adsorbed was then calculated by subtracting its final concentration from initial concentration.

Kinetic study

Rate of adsorption process was determined by limited batch technique. Series of adsorption experiments were established at constant temperature. Solutions (50 ml) of Cr (III) ions at constant ionic strength (0.01 M) were heated at constant temperature (298 K) in (250 ml) wide-mouth propylene test bottles with screw closure caps using a pipette (accurate to ±0.03). A weighed amount of the adsorbent (0.5 gm) was added for each solution. The bottles were thoroughly shaken. After appropriate intervals (30, 60, 90, 120 min), the contents of each bottle separately were filtered and the trivalent metal ion concentration in the liquid phase was determined. To describe the kinetic process, kinetic data were analyzed based on Lagergren pseudo first-order model, pseudo second order reaction rate model, and intraparticle diffusion [2].

Thermodynamic study

Thermodynamic parameters for the adsorption processes, including Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were used to decide whether the adsorption process is spontaneous, (ΔG) was calculated according to reported literature [2].

Adsorption mechanism

It is always important to predict the rate-limiting step in an adsorption process to understand the mechanism associated with the phenomena.

For a solid liquid adsorption process, the solute transfer was usually characterized by either external mass transfer or intraparticle diffusion or both. Generally three types of mechanisms were involved in the adsorption process, mentioned as follows:

(1) Film diffusion, which involves the movement of adsorbate molecules from the adsorbent.
(2) Particle diffusion, where the adsorbate molecules move in the interior of the adsorbent particles.
(3) Adsorption of the adsorbate molecules on the interior of the porous adsorbent.

Effect of temperature on adsorption process

To determine the effect of temperature on the adsorption of metal Cr (III)) ions equilibrium adsorption was performed in several (250 ml) wide-mouth polypropylene bottles with screw closure caps. Temperature (298, 308, and 313 K) in absence and in the presence of (0.1 M) HCl solution. Dose of (0.5 g) of modified chitosan was firstly weighed accurately and introduced directly into (250 ml) polypropylene bottles. Then, (50 ml) of aqueous solutions containing metal ions with (0.01 M) concentration were added to each bottle and shacked for (120 min) to attain the equilibrium. The supernatant was removed immediately by filtration. The concentration of the residual aqueous phase was determined (Cr(III)) by atomic absorption. Amount of metal ion (Cr(III)) adsorbed was then calculated by subtracting its final concentration from initial concentration.

Cr (III) uptake during the adsorption process

The study of adsorption kinetics describes the rate of solute uptake and evidently this rate controls the residence time of adsorbate uptake at the solid solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process [2].

Results and Discussion

FTIR of modified chitosan

The FTIR spectrum (a) of blended beads shows a broad band around 3600-3200 cm^{-1}, enhanced hydrogen bonding compared that of chitosan or starch alone. In the spectrum of starch and chitosan blend, the amino group peak of chitosan shifted from 1634 to 1650.245 cm^{-1}. This phenomenon pointed out that interactions were present between the hydroxyl group of starch and amino group of chitosan [7-9]. In the spectrum of starch and chitosan blend, the amino group peak of chitosan shifted from 1634 to 1634.5, 1636.3 and 1636.7 cm^{-1} in low acidic medium, low basic medium, and aqueous medium, respectively.

X-ray diffraction analysis

The X-ray diffraction analysis for modified chitosan, the characteristic peaks at 2θ = 10° and 20° disappeared, and a very weak and broad peak centered at 2θ = 15° (Fig. 1). This difference in XRD patterns weak and broad peak centered at 2θ = 15°. This difference in XRD patterns between chitosan and modified chitosan should be attributed to the cross-linking reaction between chitosan and glutaraldehyde. In agreement with the result of previous studies [10-12], the crystallinity of modified chitosan decreases after crosslinking with starch and glutaraldehyde. This could be attributed to the deformation of the strong hydrogen bond in original chitosan due to the substitution of hydroxyl and amino groups, which efficiently destroyed the regularity of the packing of the original chitosan chains and resulted in the formation of amorphous modified chitosan. Recently, revealed that the incorporation of hydrophilic cross-linker into chitosan allowed the synthesis of hydrogels with higher hydrophilicity [9] which is able to facilitate the active surface area, that plays a very important role in adsorption process in our study.

Scanning electron microscope

The scanning electron microscope images shown in Fig. 2 display porous structure of modified chitosan which may offer more adsorption sites for adsorbate, which generally supported the fact that starch glutaraldehyde-crosslinked chitosan has been widely applied in the uptake of heavy metals [13, 14] and drug delivery [15]. In addition, modified chitosan with a higher total surface area and a more open pore structure could be supposed to adsorbate Cr (III), which may at least partially explain this result that the adsorption by modified chitosan, but not solid chitosan.

Study the adsorption of Cr (III) on chitosan-starch By using Langmuir isotherm

Langmuir isotherm, as in Table 1, is often used to describe adsorption of solute from liquid solutions and this model assumes monolayer adsorption onto a homogeneous surface with
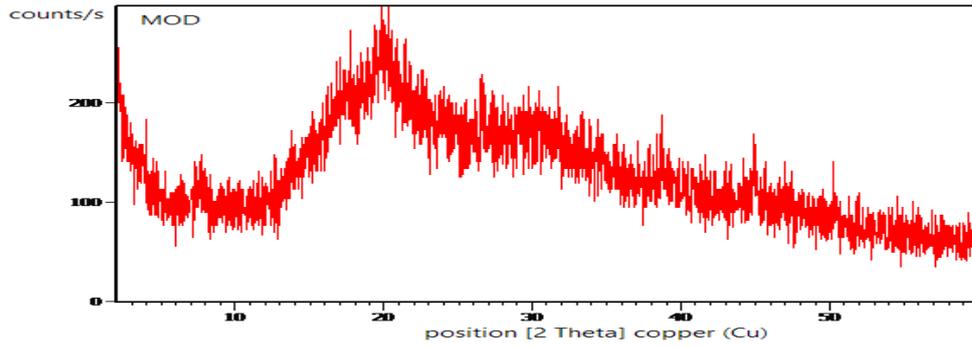
**Fig. 1. X-ray diffraction of modified chitosan.**
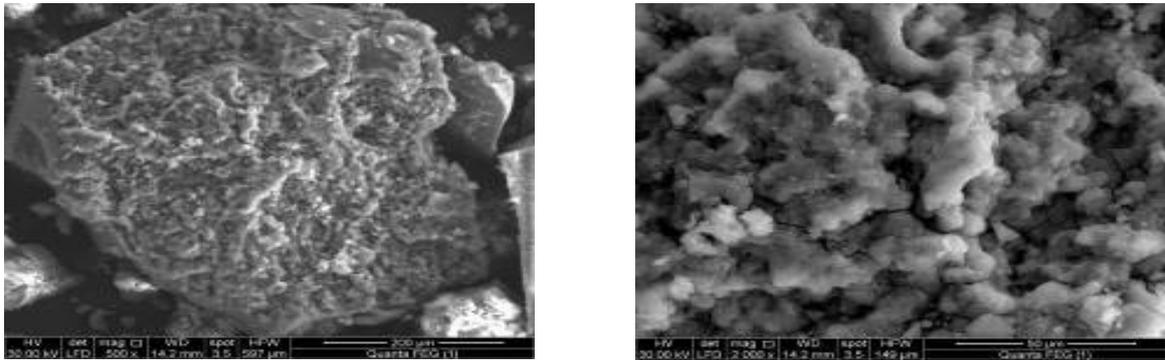
Fig. 2. Scanning electron microscope of modified chitosan.

finite number of identical sites and expressed by the following (eq. (1)).

$$q_e = \frac{Q_o k_L C_e}{1 + k_L C_e} \quad\text{.. (1)}$$

Characteristic constants of Langmuir equation, Q_o the theoretical maximum adsorption capacity and k_L related to affinity of the binding sites, Q_o and k_L Langmuir isotherm constants can be determined from the linearized of Eq(1) as in Eq(2):

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \quad\text{.. (2)}$$

The slope and intercept of the linear plot of (C_e/q_e) Verses (C_e) give the values of Q_o and k_L

respectively. In order to know the feasibility of the isotherm, the essential features of Langmuir model can be expressed in the terms of separation factor or equilibrium parameter R_L, which was defined by Eq (3):

$$R_L = \frac{1}{1 + bC_o} \quad\text{.. (3)}$$

The values of R_L indicate the shapes of isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [16]. The R_L values for Cr(III) were calculated and indicated that adsorption is even favorable for the higher metal ion concentration that has been investigated. The data of R_L values the adsorbent is suitable adsorbent (modified chitosan) for the

TABLE 1. Adsorption isotherm parameters for Cr (III) by modified chitosan.

Langmuir parameters					Freundlich parameters		
Q_o (mg/g)	b (L/mg)	R_L	R^2		N	k_f (mg/g)	R^2
14.92537	-0.0331	0.061687	0.9996		-3.16556	90.63585	0.9985

adsorption of Cr(III) ions from aqueous solutions.

By using Frendlich isotherm

The Frendlich mode is expressed as follows (Eq. 4):

$$q_e = k_f C_e^{1/n} \text{---------------------------------(4)}$$

The linearized form of Frendlich equation are given by Eq. 5:

$$\ln q_e = \ln k_f + (1/n)\ln C_e \text{--------------(5)}$$

Where k_f and $1/n$ are characteristic constants representing the adsorption capacity and adsorption intensity of the system respectively. The linear plot between ($\ln q_e$) versus ($\ln C_e$) gives a slope which is equal to the value of ($1/n$) and intercept is ($\ln k_f$). The magnitude of $0<n<1$ indicates the favorability of process of adsorption.

The experimental data were fitted well with Langmuir isotherm suggesting that the Cr (III) adsorbed from monolayer coverage on the adsorbent surface. To lesser extent, the equilibrium data were also well described with the Frendlich model probably due to the real heterogeneous nature of the surface sites involved in the process of adsorption. On the other hand, the equilibrium data were analyzed using Frendlich isotherm model and (R^2) values were estimated. The value of (n) generally indicates that the adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by Cr(III) ions; this infinite surface coverage is expected to occur indicating multilayer adsorption on the surface. It can be concluded that the Langmuir isotherm was more suitable than Frendlich one as in most cases the correlation co-efficient was higher thus indicating the applicability of monolayer coverage of the Cr(III) ions on the surface of adsorbent. This can be explained by the fact that the adsorbent has a high surface area for Cr(III) ions adsorption. Therefore only monolayer adsorption occurred on their surface [17, 18].

By using Temkin and Pyzhev isotherm

The Temkin and Pyzhev isotherm has commonly been applied in the following (Eq. 6).

$$q_e = (RT/b) \ln(AC_e) \text{----------------------(6)}$$

$$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e \text{--------(7)}$$

$$B_T = RT/b_T \text{----------------------------------(8)}$$

Where (A_T) (L/g) and (b_T) (J/mol) are Temkin isotherm constants, (R) is the gas constant (8.314 J/mol) (T) is the absolute temperature. The related parameters are given in Table 2. (b_T) related to heat of adsorption. Values higher than 8 indicates strong interaction between Cr(III) and adsorbent. However, higher value indicates presence of relatively stronger cohesive forces in between the adsorbent and Cr(III). The Dubinin-Radushkevich (D-R) isotherm [19] was also employed to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. Dubinin-Radushkevich isotherm is expressed as follows (Eq.9):

$$q_e = X_m e^{-\beta \varepsilon 2} \text{-------------------------------(9)}$$

The liner form was (Eq. 10):

$$\log q_e = \log X_m - \beta \varepsilon^2 \text{------------------------(10)}$$

Where (X_m) is the Dubinin-Radushkevich monolayer capacity (mg/g), (β) is a constant related to adsorption energy, and (ε) is the polanyi potential [20] which is related to the equilibrium concentration as follows in Eq. 11:

$$\varepsilon = RT \ln (1+(1/C_e)) \text{--------------------(11)}$$

Where (R) is the gas constant (8.314 J/mol K) and (T) is absolute temperature. A plot of ($\ln q_e$) Vs (ε^2) as in gave a straight line of slope, (β) and intercept, (X_m) of different systems were evaluated. The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the potential, a term first advanced by Polanyi [20]. In the present study Dubinin-Radushkevich isotherm constants, monolayer capacity (X_m) and adsorption energy (β) are tabulated in Table 2. The magnitude of (β) is used to determine the type of adsorption mechanism. When one mole of Cr(III) ions is transferred the adsorbent surface, its value is higher than 8.0 KJ/mol which indicates chemical adsorption, the calculated values of (E) for the present study is higher than 8.0 KJ/mol for the adsorption of Cr(III), which suggest that adsorption process onto the surface of the adsorbent modified chitosan is following chemical adsorption type.

The data of the kinetics of Cr(III) adsorbed from aqueous solution onto modified chitosan

TABLE 2. Adsorption isotherm parameters for Cr(III) by modified chitosan.

Temkin parameters			D-R parameters			
A_T (L/g)	B_T (J/mol)	R^2	B	q_o (mg/g)	E (KJ/mol)	R^2
0.00338	-6.2347	0.9991	7×10^{-08}	12.09147	3779.645	0.9964

were analyzed using pseudo first order, pseudo second order intraparticle diffusion kinetic models, respectively. The conformity between experimental data and each model predicted values were expressed by the correlation coefficient (R^2). A relatively high (R^2) values indicated that the model successfully describes the kinetics of Cr(III) ions adsorption removal. The adsorption kinetics of Cr(III) ions from liquid phase to solid is considered as a reversible reaction with an equilibrium state being established between two phases. A simple pseudo first-order model was therefore used to correlate the rate of reaction and expressed as follows (Eq. 12):

$$dq_t/dt = k_1(q_e-q_t) \text{----------------------(12)}$$

Where (q_e) and (q_t) (mg/g) are concentration of Cr(III) ions in the adsorbent at equilibrium and at time (t), respectively integration and applying boundary conditions (t=0 to t=t) and (q_t=0 to q_t=q_t), the integrated from of (Eq. 12) becomes (Eq. 13):

$$\log (q_e-q_t)=\log qe -(k_t/2.303)t \text{-----------(13)}$$

Plots for (Eq. 13) were made for the Cr(III) ions adsorption at different studied temperature. Approximately linear fits were observed for the Cr(III) ions, over the entire range of shaking time explored and at all temperatures with low correlation coefficient as in Table 3, indicating that the pseudo first order kinetic model is not valid for the present systems. A pseudo second-order rate model is also used to describe the kinetics of the adsorption of Cr(III) ion adsorbent materials. The differential equation for chemisorptions kinetic rate reaction is expressed as (Eq. 14):

$$dq_t/dt = k_2(q_e-q_t)^2 \text{------------------------(14)}$$

Where k_2 is the rate constant of pseudo second-order equation, for the boundary conditions (t=0 to t=t) and (q_t=0 to q_t=q_t), the integrated form of (Eq. 14) becomes (Eq. 15):

$$1/(q_e-q_t) = 1/q_e \, t \text{----------------------------(15)}$$

Eq. (15) can be rearranged to obtain a linear form equation as Eq. (16):

$$(t/q_t) = (1/k_2q_e^2) + (1/q_e) \, t \text{----------------(16)}$$

The relationships are linear, and the values of correlation coefficient (R^2), suggest a strong relationship between the parameters and also explain that the process of adsorption of Cr(III) ions follows pseudo second order kinetic model.

From the results, it can be shown that the values of the rate constant (k_2) were increased with increase in temperature the correlation coefficient (R^2) has an extremely high value, and theoretical (q_e) values agree with experimental ones. These results suggest that the pseudo second-order adsorption mechanism is predominant and that the overall rate constant of each Cr(III) ion appears to be controlled by the chemisorptions process. At the present time Weber and Morris's and pore-diffusion is the most widely used models for studying the mechanism of adsorption. On the other hand, Weber and Morris's pore-diffusion model assumes that:

(i) The external resistance mass transfer is only significant for a very short period at the beginning of diffusion.

(ii) The direction of diffusion is radial and the concentration.

(iii) The pore diffusivity is constant and does not change with time, the pore diffusion parameter, k_{id} ((mg/g min$^{0.5}$) is expressed as (Eq. 17):

$$q_t = k_{id}t^{0.5} +C \text{----------------------(17)}$$

Where (q_t) is the amount adsorbed (mg/g) at time (t).

The (k_{id}) values were obtained, as in Table 4, from the slope of the linear portions of the curve of different initial concentration of the Cr(III) ions in aqueous solution. It can be seen that the

TABLE 3. Kinetic parameters for removal of Cr(III) ions by modified chitosan.

	Pseudo first-order			Pseudo second-order				
	$q_{e,1}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,2}$ (mg/g)	K_2 (g/mg min)	H (mg/g min)	R^2	T ^{o}C
Aqueous	4.210174	0.038230	0.9780	19.60784	0.126907	6.19195	1.0000	25
Aqueous	4.347104	0.035236	0.9995	20.32520	0.120994	6.04230	1.0000	35
Aqueous	3.180534	0.020957	0.9106	21.05263	0.105038	4.88998	0.9999	45

plots possess multilinear portions; it indicates that the two or more steps influence the adsorption process. It was found that straight lines relate the points, the sharp first linear portion is due to the film diffusion and the second linear portion is due to the pore diffusion. Non-linearity of the plots had indicated the multi stage adsorption of toxic metal as Cr(III) by the adsorbent. The extrapolation of the first linear portion gives the intercept equal to the boundary layer thickness or film thickness. The values of intercept give an idea about the boundary layer thickness such as the layer the intercept, the greater the boundary layer effect.

The adsorption of Cr (III) ions has been found to increase with an increase in temperature from (25 to 45 ^{o}C).The increase in adsorption capacity of the adsorbent with temperature indicates an endothermic process as in Table 5. The increase in adsorption with temperature may be attributing to either change in pore size of the adsorbent causing inter-particle diffusion within the pores or to enhancement in the chemical affinity of the Cr(III) ions to the surface of adsorbent leading to some kind of chemical interaction to take during

adsorption process which results into increase in adsorption capacity. At higher temperature, the possibility of diffusion of solute within the pores of adsorbent may not be ruled out as reposted by earlier workers [21].

The above results were further substantiated by the various thermodynamic parameters. Enthalpy change (ΔH), Entropy change (ΔS), Gibbs free energy change (ΔG) and Activation energy (Ea) evaluated for adsorption. The effect of temperature on adsorption is further confirmed by the vant Holf plots as based on the equations (18, 19, 20 and 21) [22]:

$$k_D = q_e/C_e \text{----------------------(18)}$$

$$\Delta G = -RT \ln k_D \text{-----------------(19)}$$

$$\Delta G = \Delta H - T \Delta S \text{----------------(20)}$$

$$\ln k_D = (\Delta S/R) - (\Delta H/RT) \text{----(21)}$$

Where (T) is absolute temperature in Kevin (K), R is gas constant (8.314 J/mol K) and k_D is the distribution coefficient (ml/g). The thermodynamic parameters namely enthalpy

TABLE 4. The intra-particle diffusion model (Weber-Marries) model for removal of Cr(III) by modified chitosan.

	T ^{o}C	K_{id}	C	R^2
Aqueous	25	0.2653	16.372	0.8658
Aqueous	35	0.2727	16.942	0.9373
Aqueous	45	0.3355	16.801	0.9477

TABLE 5. Thermodynamic parameters for removal of Cr (III) by modified chitosan.

	T ^{o}C	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)	A	Ea (KJ/mol)
Aqueous	25	-342.911	6.834108	1694.31	0.000217	7151.62
Aqueous	35	-408.024	-	-	-	-
Aqueous	45	-480.465	-	-	-	-

change (ΔH) and entropy change (ΔS) can be calculated from the slope and intercept of straight line plotted by (ln k_D) versus (1/T). The Gibbs free energy change (ΔG) was determined. The obtained thermodynamic parameters (ΔH, ΔS, ΔG and Ea) were listed in Table 5. Therefore the positive value of ΔS suggested some structural change in the adsorbent and adsorbate. In fact, the positive value of enthalpy (ΔH) further confirmed the endothermic nature of the processes, so increasing temperature supplied with a more favorable adsorption of Cr(III) ions onto the adsorbent. The negative Gibbs free energy (ΔG) value for the metal adsorption process on the adsorbent indicates the spontaneous nature of the adsorption process.

Generally, The values of the change in enthalpy (ΔH) indicated that adsorption process of Cr(III) is physical in nature [23]. The activation energy (Ea) was calculated by the linearized Arrhenius equation (eq. 22):

$$\ln (k) = \ln (A) - (Ea/RT) \text{----------------(22)}$$

Where (Ea) is the activation energy of adsorption (kJmol^{-1}), (k) is the rate constant which controls the process, (A) is Arrhenius constant, (R) is the ideal gas constant and (T) is the absolute temperature (K).

From the pseudo second-order kinetic studies, k_2 is the rate constant which controls the process, i.e (k) In this study, activation energy (Ea) value of different systems under study (KJ/mol) was obtained from the plot of (ln k_2) versus (1/T). In physical adsorption, the activation energy (Ea) usually more than 8.0 KJmol^{-1}, since the forces involved in chemical adsorption is high. Chemical adsorption involves forces much stronger than in physical adsorption and the activation energy (Ea) is between (8.4) and (83.7) KJmol^{-1} [21] noted that chemical adsorption includes activated and non activated forms. The results show that the process is one of activated chemical adsorption and the positive value of the activation energy (Ea) suggested that the rise in the solution temperature favors the Cr(III) ions adsorption onto the modified chitosan. The acid concentration occurs between 0.001 and 0.005 M HCl, chromium ions Cr(III) adsorption capacity decreases. However, at further higher acid molarities unfavorable conditions are found to exist for adsorption, accordingly, no adsorption

occurs. This trend was observed by earlier workers when examining metal adsorption no different adsorbents [17], and can be interpreted as follows. Under acidic conditions, as strong competition effect between H$^+$ and chromium Cr(III) caused by high concentration of H$^+$ leads to decrease amount of Cr(III) immobilized onto the modified chitosan. Furthermore, at high acidic the function groups are present in protonated forms which have electrostatic repulsion to chromium ions (Cr(III)) and are hard to donor their electron pair to coordinate with chromium ions (Cr(III)), thus weakening the complexation between them and further decreasing the chromium ions (Cr(III)) adsorption capacity. With the decrease of solution acidity, due to the decrease of H$^+$ concentration, the competition effect between Cr(III)(and/or Cr(OH$^+$) and H$^+$ becomes weak, resulting in more Cr(III) immobilized onto the modified chitosan. Besides, the combined H$^+$ ions gradually dissociate from functional groups at low acidity, enhancing the complexation between Cr(III) and the functional groups, accordingly, increase of Cr(III) uptake. The relationships between the amount of Cr(III) adsorbed on modified chitosan and their equilibrium concentration solution were described by the adsorption isotherms as in Table 6. The adsorption data of the metal complexes on modified chitosan according to the Langmuir, Freundlich, Temkin and Dubinin-Redushkevich (D-R) models.

The adsorption experiments were carried out with Cr(III) by modified chitosan in inorganic acid solution. According to the above presented assumption of complexation conditions, the modified chitosan process of Cr(III) complexes in Cr(III)-inorganic acid (hydrochloric acid) systems can be as follows:

$$(\text{modified chitosan})\text{-}H^+ + Cr(III) \rightleftharpoons (\text{modified chitosan})Cr(III) + 3H^+$$
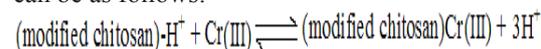
The equilibrium adsorption data indicate that: (a) At low acid concentration the metal cations exhibit generally strong uptake and high affinity with the modified chitosan matrix. This behavior is prominent for all adsorption processes. However, (b) with increasing acid concentration the H$^+$ increase and further competes sites. The study of adsorption dynamics describe the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid/solution interface. The data of the kinetics of the removal of Cr(III) by modified chitosan in acidic medium were analyzed using pseudo-first-order,

pseudo-second-order and intra-particle diffusion kinetic models, respectively as in Tables 7 and 8.

The relationships are linear, and the values of correlation coefficient (R^2) suggest a strong relationship between parameters and also explain

TABLE 6. Adsorption isotherm parameters for the removal of Cr (III) by modified chitosan in acidic solutions.

	Langmiur parameters				Frendlich parameters		
Molarity (mole/L)	Q_o (mg/g)	B (L/mg)	R_L	R^2	N	k_f (mg/g)	R^2
			ACIDIC SOLUTIONS (HCl)				
0.001 M	16.37	-45.5×10^{-3}	40.5×10^{-3}	0.9998	-3.85505	69.2309	0.9992
0.003 M	15.8	-40.7×10^{-3}	45.2×10^{-3}	0.9999	-3.57143	76.0852	0.9990
0.005 M	12.5	-20.9×10^{-3}	84.3×10^{-3}	0.9988	-2.29358	163.6440	0.9965
	Temkin parameters				D-R parameters		
Molarity (mole/L)	A_T (L/g)	B_T (J/mol)	R^2	B	q_o (mg/g)	E (KJ/mol)	R^2
			ACIDIC SOLUTIONS (HCl)				
0.001 M	1.98×10^{-4}	-5.3	0.9995	-2×10^{-4}	18.43775	50.000	0.9993
0.003 M	2.48×10^{-4}	-5.7	0.9996	-2×10^{-4}	17.81249	50.000	0.9996
0.005 M	6.39×10^{-4}	-7.9	0.9982	-2×10^{-7}	6.540411	26.7261	0.9639

TABLE 7. Parameters of pseudo first-order and pseudo second-order models for the removal of Cr(III) by modified chitosan in acidic solutions.

	Pseudo first-order			Pseudo second-order				
Molarity (mole/L)	$q_{e,1}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,2}$ (mg/g)	K_2 (g/mg min)	H (mg/g min)	R^2	T ºC
			ACIDIC SOLUTIONS (HCl)					
0.001 M	5.075728	0.045830	0.8104	20.449898	0.118600	5.882353	0.9996	25
0.001 M	0.038690	6.112234	0.9810	20.833300	0.108393	5.099439	1.0000	35
0.001 M	0.032703	4.555122	0.9029	21.929825	0.112396	6.075334	0.9997	45
0.003 M	10.57791	0.055733	0.9745	19.880716	0.114083	5.144033	0.9999	25
0.003 M	4.314197	0.033394	0.7901	20.040080	0.115116	5.321980	0.9992	35
0.003 M	4.449385	0.025103	0.9698	22.026432	0.096183	4.488330	0.9997	45
0.005 M	8.218641	0.037769	0.8116	17.857143	0.086824	2.403846	0.9975	25
0.005 M	6.596294	0.018654	0.9013	20.120724	0.062271	1.569859	0.9941	35
0.005 M	7.857782	0.020727	0.9871	21.231423	0.059153	1.572871	0.9972	45

TABLE 8. The intra-particle diffusion (Weber-Marries) model for removal of Cr(III) by modified chitosan in acidic solutions.

Molarity (mole/L)	t ºC	K_{id}	C	R^2
ACIDIC SOLUTIONS (HCl)				
0.001 M	25	0.3296	16.518	0.7502
0.001 M	35	0.3247	16.750	0.9524
0.001 M	45	0.2748	18.370	0.9718
0.003 M	25	0.3162	15.971	0.8940
0.003 M	35	0.2403	16.858	0.8740
0.003 M	45	0.3605	17.326	0.9972
0.005 M	25	0.4709	11.862	0.9491
0.005 M	35	0.6320	11.366	0.9562
0.005 M	45	0.7360	11.243	0.9993

that the process of adsorption of the metal ions Cr(III) follows pseudo second-order kinetic models. The thermodynamic assumptions of the best fitting isotherm provide insight into the surface properties and mechanism of removing process. The thermodynamic parameters namely enthalpy change (ΔH) and the entropy change (ΔS) can be calculated from the slope and intercept of the straight line plotted by ln k_D versus 1/T. The Gibbs free energy change (ΔG) we determined at 25, 35, 45 ºC. The obtained thermodynamic parameters (ΔG, ΔH, ΔS and Ea) were listed in Table 9.

The adsorption data of the Cr(III) complexes on modified chitosan in basic medium according to the Langmuir, Freundlich, Temkin and Dubinin-Redushkevich (D-R) models as in Table 10.

The data of the kinetics of the removal of Cr(III) by modified chitosan in basic medium were analyzed using pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models, respectively as in Tables 11 and 12.

In the studies of the kinetics of the removal of Cr (III) by modified chitosan in basic medium at different temperature we obtained the thermodynamic parameters (ΔG, ΔH, ΔS and Ea) as illustrated in Table 13.

TABLE 9. Thermodynamic parameters for the removal of Cr(III) by modified chitosan in acidic solutions.

Molarity (mole/L)	T ºC	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)	A	Ea (KJ/mol)
ACIDIC SOLUTIONS (HCl)						
0.001 M	25	-398.138	10.00839	2602.033	0.048495	-940.563
0.001 M	35	-440.040	-	-	-	-
0.001 M	45	-602.211	-	-	-	-
0.003 M	25	-349.774	11.73272	3172.622	0.000825	-2858.770
0.003 M	35	-382.537	-	-	-	-
0.003 M	45	-589.867	-	-	-	-
0.005 M	25	-228.898	7.76195	2081.327	0.000183	-6582.190
0.005 M	35	-314.053	-	-	-	-
0.005 M	45	-384.651	-	-	-	-

TABLE 10. Adsorption isotherm parameters for the removal of Cr(III) by modified chitosan in basic solutions.

	Langmuir parameters				Frendlich parameters		
Molarity (mole/L)	$Q_\circ$ (mg/g)	B (L/mg)	R_L	R^2	N	k_f (mg/g)	R^2
BASIC SOLUTIONS (NH$_4$OH)							
0.001 M	11.64144	-0.01972	-0.10556	0.9981	-2.96033	100.832376	0.9997
0.002 M	15.57632	-0.03836	-0.10256	0.9996	-3.24149	87.498378	0.9992
0.003 M	15.77287	-0.0402	-0.10412	0.9996	-3.68053	73.097075	0.9832

	Temkin parameters				D-R parameters		
Molarity (mole/L)	A_T (L/g)	B_T (J/mol)	R^2	B	$q_\circ$ (mg/g)	E (KJ/mol)	R^2
BASIC SOLUTIONS (NH$_4$OH)							
0.001 M	39.47 x10^{-4}	-6.5607	0.9998	-6 x10^{-8}	13.20374	2886.75135	0.8864
0.002 M	2.751468	-5.8525	0.9989	-9 x10^{-8}	10.88080	2357.0226	0.9621
0.003 M	2.46 x10^{-4}	-5.6690	0.9988	-9 x10^{-8}	11.16071	2357.0226	0.9409

TABLE 11. Parameters of pseudo first-order and pseudo second-order models for the removal of Cr (III) by modified chitosan in basic solutions.

	Pseudo first-order			Pseudo second-order				
Molarity (mole/L)	$q_{e,1}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,2}$ (mg/g)	K_2 (g/mg min)	H (mg/g min)	R^2	T ºC
BASIC SOLUTIONS (NH$_4$OH)								
0.001 M	1.762382	0.019345	0.9941	19.0114068	0.170388	10.4931794	1.0000	25
0.001 M	3.869011	0.033163	0.8297	20.1207244	0.130654	6.91085004	0.9990	35
0.001 M	29.53929	0.080835	0.7943	20.661157	0.112014	5.3561864	0.9984	45
0.002 M	1.938653	0.021418	0.9798	19.4931774	0.159075	9.61538462	0.9991	25
0.002 M	1.735002	0.005758	0.9948	21.0970464	0.097675	4.2462845	0.9961	35
0.002 M	2.350715	0.010133	0.9615	21.5982721	0.454639	4.46428571	0.9980	45
0.003 M	1.534617	0.024872	0.882	19.7628459	0.1682	11.0497238	1.0000	25
0.003 M	2.236145	0.010364	0.9864	21.1864407	0.101558	4.62962963	0.9983	35
0.003 M	3.063374	0.024412	0.8662	21.8340611	0.110273	5.79710145	0.9994	45

Conclusion

We studied the removal of Cr (III) ions using modified chitosan-starch from aqueous solutions under both acidic and basic conditions. The amount of Cr(III) ions adsorbed on the modified chitosan increases with increasing its initial concentration, also the adsorption of ferric ions Cr(III) has been found to increase with an increase in temperature, this indicates an endothermic process. The positive value of (ΔS) suggested

TABLE 12. The intra-particle diffusion (Weber-Marries) model for removal of Cr(III) by modified chitosan in basic solutions.

Molarity (mole/L)	T ºC	K_{id}	C	R^2
BASIC SOLUTIONS (NH₄OH)				
0.001 M	25	0.1732	17.032	0.9977
0.001 M	35	0.2200	17.373	0.9175
0.001 M	45	0.2635	17.180	0.8946
0.002 M	25	0.1777	17.374	0.9987
0.002 M	35	0.2409	17.482	0.7762
0.002 M	45	0.2925	17.564	0.8843
0.003 M	25	0.1476	17.935	0.8975
0.003 M	35	0.2785	17.391	0.8985
0.003 M	45	0.2415	18.495	0.9472

TABLE 13. Thermodynamic parameters for the removal of Cr(III) by modified chitosan in basic solutions

Molarity (mole/L)	T ºC	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)	A	Ea (KJ/mol)
BASIC SOLUTIONS (NH₄OH)						
0.001 M	25	-332.978	5.217035	1215.008	0.00021732	7151.62
0.001 M	35	-405.445	-	-	-	-
0.001 M	45	-436.849	-	-	-	-
0.002 M	25	-359.008	9.92359	2593.635	6468446.64	18407.2
0.002 M	35	-470.692	-	-	-	-
0.002 M	45	-557.969	-		-	-
0.003 M	25	-371.636	8.363884	2107.017	0.00017286	7302.02
0.003 M	35	-496.527	-	-	-	-
0.003 M	45	-537.789	-	-	-	-

some structure change in adsorbent and adsorbate. The (+ΔH) further confirmed the endothermic nature of the processes. The (-ΔG) value for the Cr(III) indicates the spontaneous nature of the adsorption process.

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التحقيق في آلية امتصاص المعادن الثقيلة كأيونات الكروم الثلاثي من حلول مختلفة باستخدام الشيتوزان المعدل

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الهدف من هذه الدراسة هو تقييم إزالة أيونات الكروم الثلاثي بواسطة الشيتوزان المعدل بالنشا من المحاليل المائية تحت كل من الظروف الحمضية و القاعدية. و دراسة تأثير مختلف العوامل المختلفة على تقنية الامتصاص . وتشمل هذه المعايير التركيز الأولي قبل الامتزاز، وقت الإثارة، جرعة الممتزات، حركية العملية الكيميائية، وتأثير درجة الحرارة. كانت البيانات التجريبية تناسب جيدا نموذج فريندليش للامتزاز. وقد تم حساب المعلمات الحرارية مثل ΔH، ΔS و ΔG، مشيرا إلى أن الامتزاز كان ماصا للحرارة في الطبيعة.