

Investigate the Adsorption Mechanism of Heavy Metals as Aluminum Ions (Al^{+3}) from Different Solutions Using Modified Chitosan

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The aim of this revise is to charge the taking away of Al(III) ions from different solutions (Aqueous, Acidic and Basic) against modified chitosan. The result of a choice of parameters has been investigated by the following set adsorption method. The different variables calculated take in first concentration of the adsorbate, agitation time, adsorbent dosage, chemical kinetics, influence of temperature. The experimental data was fit well to the Freundlich isotherm. Thermodynamic parameters such as ΔH , ΔS and ΔG were calculated, representing that the adsorption was spontaneous and endothermic nature.

Keywords: Al(III), Modified Chitosan, Aqueous, Acidic/Basic Media, Adsorption Isotherm.

Introduction

Chitosan, as a normal polysaccharide, has reactive amino and hydroxyl groups in its linear polyglucosamine chains, can be used to functionalize and modify. However, conventional modification method using single chitosan crosslinking with glutaraldehyde generally leads to cut of practical group ($-NH_2-$) and loading facility, its attracted to set up multifunctional chitosan-x which used in a lot of applications such as water treatment by using diethylenetriamine pentaacetic acid (DTPA) with satisfactory number of carboxyl groups on the backbones, is a generally used as chelating agent for heavy metal [1]. The aim of this learn [2] is to assess the taking away of Fe(III) ions from aqueous solutions against modified chitosan. The effect of different parameters has been investigated by the next batch adsorption method. The different variables studied take in initial concentration of the adsorbate, agitation time, adsorbent amount, kinetics, control of temperature. The new facts was fit well to the Freundlich isotherm. Thermodynamic parameters such as ΔH , ΔS and ΔG were calculated, representing that the adsorption was spontaneous and endothermic nature [2].

This learn [3] was performed to investigated the variables that control Fe(III) ions taking

away in acidic and basic medium by modified chitosan. The quantity of Fe(III) ions adsorbed on the modified chitosan increases with increasing its first concentration, also the adsorption of ferric ions Fe(III) has been found to increase with an increase in temperature, this indicates an endothermic process. The positive value of (ΔS) suggested some structure change in adsorbent and adsorbate. The ($+\Delta H$) further confirmed the endothermic nature of the processes. The ($-\Delta G$) value for the Fe(III) indicates the spontaneous nature of the adsorption process [3]. Algerian's public manure action vegetation generates about 10^6 m³ of manure slush yearly. Freshly, fast growth of wastewater action plants not including like notice to the action of the shaped slush has generated increasing concerns. Although the slush is more often than not incinerated or used as farming manure and could have various nutrients, there could also be damaging substances that make difficult slush organization. Therefore the taking away of pollutants as of the slush is needed by more habit. This article discusses the characteristics of drinkable water action slush containing high aluminum content. Also, an electro kinetic action is projected to take away aluminum from this slush by unstable the type of solution controlled in the cathode compartment and modifying the treatment time to optimize the

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efficiency of the process. Successful outcome were achieved where 60% of aluminum was collected on the cathode face with a consumed power about of 1000-2000 kWh kg⁻¹ of slush mass. [4].

In this learn [5], a low-cost eco-friendly adsorbent was organized from *Eucalyptus camaldulensis* barks during chemical activation. The result of working variables that is original pH, sorbent dosage, original metal concentration, shaly rapidity and temperature on the aluminum taking away gain and uptake ability has been calculated. The best pH was found as 5.0 and the sorbent dosage 5.0 g/L. Temperature effect proved the process to be endothermic. The investigational remarks were fixed to Langmuir and Freundlich isotherms where Langmuir proved to be a well again fit [5]. Pseudo-second order and intra-particle diffusion kinetic models were employed to the experimental data to verify the mechanism of sorption. The constants of isotherms and kinetic models were evaluated at different working conditions. From the thermodynamic studies, the activation energy was evaluated as 43.23 kJ mol⁻¹ [5]. This learns attempts to bring in a process to take away Aluminum ions from drinking water and manufacturing effluents by active carbon through different grading as adsorbent. Adsorption of Aluminum ions were discussed in different conditions of Aluminum concentration, contact time, impact of electrolytes and pH on Aluminum ions adsorbency. Both Freundlich and Langmuir isotherms used to examine the adsorption. Thermodynamics associations leading method, such as order of (ΔG°), (ΔS°) and the enthalpy of adsorption, were considered, which showed to Aluminum adsorption on active carbon is an endothermic and spontaneous process [6].

Experimental

Materials and methods

All the chemical used were of analytical grade, distilled water was in experimental [1, 2 and 3]

Results and discussion

Classification OF MODIFIED CHITOSAN

FTIR SPECTROSCOPY

The FTIR spectrum (a) of blended beads shows a wide band approximately 3600-3200 cm⁻¹, improved hydrogen bonding compared that of chitosan or starch only. In the spectrum of starch and chitosan mix together, the amino group peak of chitosan shifted from 1634 to 1650.245 cm⁻¹. This fact pointed out that interactions were here between the hydroxyl group of starch and amino
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group of chitosan [7-8]. In the spectrum of starch and chitosan mix together, the amino group peak of chitosan shifted from 1634 to 1634.5, 1636.3 and 1636.7 cm⁻¹ in low acidic medium (chart (d)), low basic medium (chart (f)) and aqueous medium (chart (d)) respectively.

X-ray Diffraction investigation (XRD)

The X-ray diffraction analysis for modified chitosan, the characteristic peaks at $2\theta = 10^\circ$ and 20° moved out, and a very weak and large peak centered at $2\theta = 15^\circ$ appeared Figure (h). This variation in XRD patterns weak and large peak centered at $2\theta = 15^\circ$ appeared Chart (g). 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 chitosan decreases after cross linking by starch and glutaraldehyde. This could be accredited to the bend of the strong hydrogen bond in original chitosan due to the exchange of hydroxyl and amino groups, which ably damaged the lateness of the filler of the new chitosan chains and resulted in the creation of vague modified chitosan. Lately, discovered to the merging of hydrophilic cross-linker into chitosan permitted the fusion of hydrogels with higher hydrophilicity [9] which is able to help the active surface area that plays a very important role in adsorption process in our study.

Scanning Electron Microscope (Sem)

The spongy structure of modified chitosan during this learn may here more adsorption sites for adsorbate, which usually supported the fact that starch glutaraldehyde-crosslinked chitosan has been usually useful in the uptake of heavy metals [13,14] also medicine delivery [15]. In addition, modified chitosan with a higher total surface area and a more open pore composition could be invented to adsorbate Al(III), which may at least partially give details this cause that the adsorption by modified chitosan, but not solid chitosan.

(Ii):Studies Of Adsorption Processes For The Taking Away Of Aluminum Al(Iii) By Modified Chitosan (In Aquoeus Soltion)

[1] By using Langmiur isotherm:

Langmiur isotherm as in Table (1) is a lot worn to explain adsorption of solute from liquid solutions and this model assumes monolayer adsorption onto a homogeneous surface with fixed number of the same sites and articulated by the following (eq. (1))

$$q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e} \dots \dots \dots (1)$$

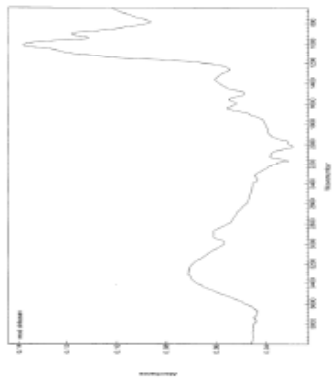


Chart (a) Infrared of Modified Chitosan

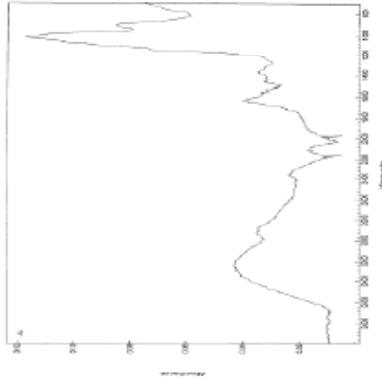


Chart (b) Infrared of Modified Chitosan in aqueous solution

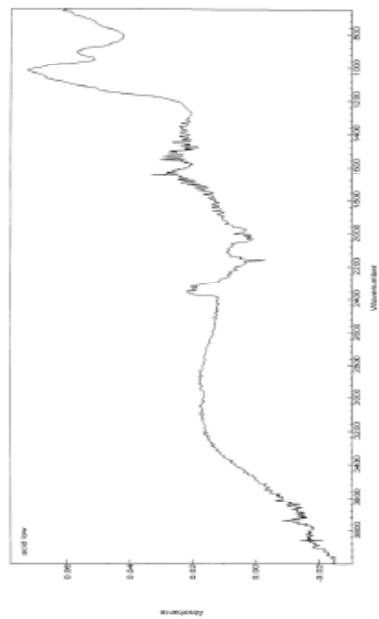


Chart (c) Infrared of Modified Chitosan in acidic solution

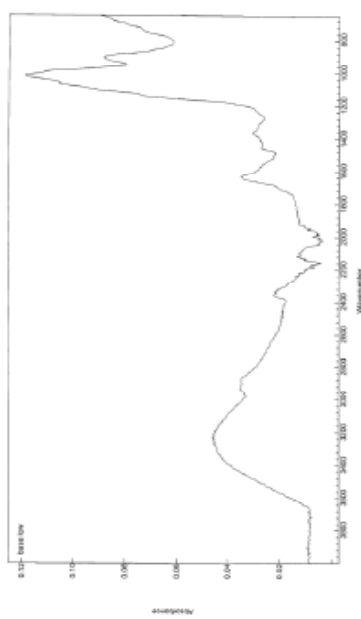


Chart (d) Infrared of Modified Chitosan in basic solution

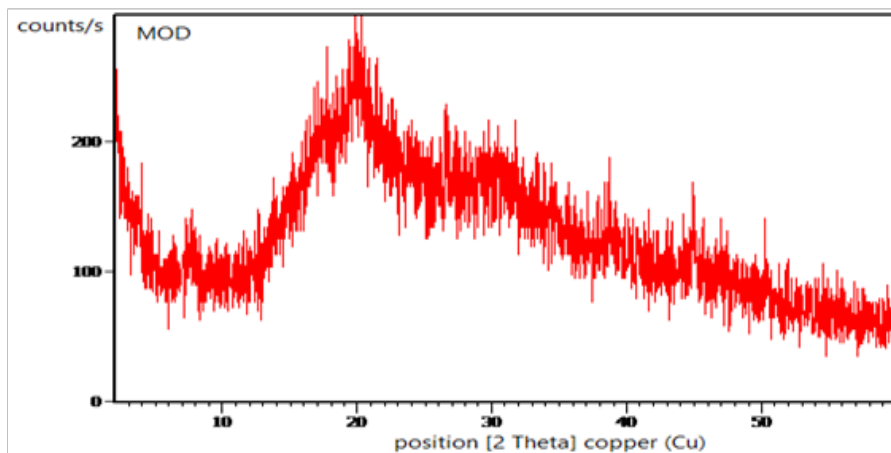


Chart (h) X-ray diffraction of modified chitosan

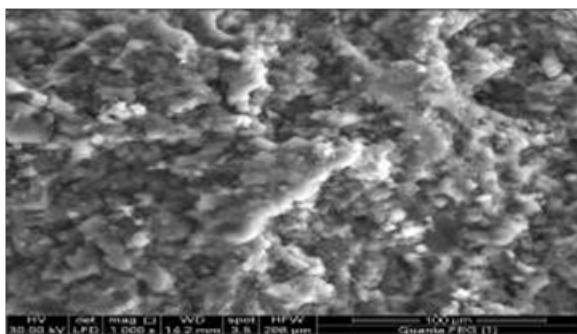


Chart (j) Scanning electron microscope by magnification 1000 of modified chitosan.

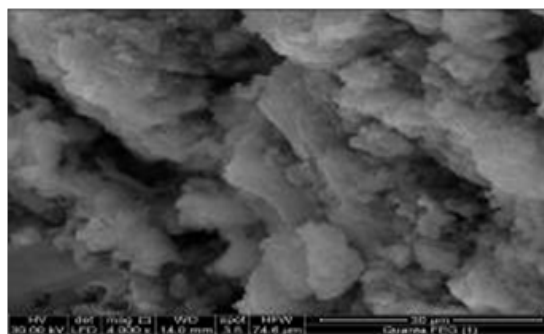


Chart (l) Scanning electron microscope by magnification 4000 of modified chitosan.

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

| Langmiur parameters | | | | | Freundlich parameters | | |
|---------------------|-----------------|-------------|----------|--------|-----------------------|-----------------|--------|
| | Q_o (mg/g) | b (L/mg) | R_L | R^2 | n | k_f (mg/g) | R^2 |
| Aqueous | 11.0864745 | -1.11911 | -0.00332 | 0.9990 | -19.3424 | 14.0572 | 0.8391 |

Characteristic constants of Langmiur equation, Q_o the theoretical greatest adsorption facility and k_L linked to affinity of the required sites, Q_o and k_L Langmiur isotherm constants can be determined from the linearized of Eq(1) as inq(2):

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \dots\dots\dots(2)$$

The slope and intercept of the linear plot of (C_e/q_e) Verses (C_e) provide the values of Q_o and k_L respectively. In order to know the feasibility of the isotherm, the essential features of Langmiur model can be expressed in the terms of separation factor or equilibrium parameter R_L , which was defined by Eq(3):

$$R_L = \frac{1}{1+bC_o} \dots\dots\dots(3)$$

The values of R_L show 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 Al(III) were calculated and indicated that adsorption is even favorable for the higher metal ion concentration that have been

investigated. The data of R_L values the adsorbent is suitable adsorbent (modified chitosan) for the adsorption of Al(III) ions from aqueous solutions.

[2] By *Freundlich isotherm*:

The freundlich mode is articulated as follows (Eq. 4):

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

The linearized form of Freundlich equation is given by (Eq. 5):

$$\ln q_e = \ln k_f + (1/n) \ln C_e \dots\dots\dots(5)$$

where k_f and $1/n$ are typical constants instead of the adsorption ability and adsorption strength of the system respectively. The linear plot between ($\ln q_e$) verses ($\ln C_e$) gives a slope which is like to the value of ($1/n$) and intercept is ($\ln k_f$). The magnitude of $0 < n < 1$ indicates the favorability of method of adsorption.

The adsorption parameters obtained from both the models were given in Table (1). The investigational data were fixed well with Langmiur isotherm suggesting that the Al(III) adsorbed from monolayer treatment on the adsorbent surface. To

smaller extent, the equilibrium data were also well described with the Freundlich model possibly due to the real heterogeneous nature of the surface sites involved in the process of adsorption and Table (1). On the other hand, the equilibrium data were analyzed using Freundlich isotherm model and (R²) values were projected. The value of (n) generally indicates that the adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not see coming any saturation of the adsorbent by Al(III) ions; this endless surface coverage is expected to occur indicating multilayer adsorption on the surface. It can be concluded that the Langmuir isotherm was more suitable than Freundlich one as in most cases the correlation co-efficient was higher as seen in Table(1) thus indicating the applicability of monolayer coverage of the Al(III) ions on the surface of adsorbent. This can be explained by the fact that the adsorbent have a high surface area for Al(III) ions adsorption. Therefore only monolayer adsorption occurred on their surface [18].

[3] By using Temkin and Pyzhev isotherm:

The Temkin and Pyzhev isotherm has usually 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 associated parameters are set in Table (2). (b_T) related to heat of adsorption. Values higher than 8 indicates strong interaction connecting Al(III) and adsorbent. but, higher value indicates presence of relatively stronger cohesive forces in

between the adsorbent and Al(III).

The Dubinin-Radushkevich (D-R) isotherm [19] was as well engaged to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. Dubinin-Radushkevich isotherm is articulated as follows (Eq.9):

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

The liner form was (Eq. 10):

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

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):

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

where (R) is the gas constant (8.314 J/mol K) and (T) is absolute temperature

A plot of (ln q_e) Vs (ε²) as in gave a straight line of slope, (β) and intercept, (X_m) of unlike systems were evaluated. The variation 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 resolve the type of adsorption mechanism. When one mole of Al(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 Al(III), which suggest that adsorption process onto the surface of the adsorbent modified chitosan is following chemical adsorption type.

TABLE 2. Adsorption isotherm parameters for Al(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 |
| Aqueous | 2.3887 x10 ⁻⁰⁵ | -1.6179 | 0.9884 | -3 x10 ⁻⁰⁶ | 11.2290 | 408.2483 | 0.9883 |

(A) Study The Adsorption Kinetics Modeling In Aqueous Solution:

The information of the kinetics of Al(III) adsorbed from aqueous solution on modified chitosan were analyzed by pseudo first order, pseudo second order intraparticle diffusion kinetic models, respectively. The agreement between investigational data and each model predicted values was articulated by the correlation coefficient (R^2). A comparatively high (R^2) values indicated that the model effectively describes the kinetics of Al(III) ions adsorption taking away.

The adsorption kinetics of Al(III) ions as of liquid phase to solid is measured as a reversible effect with an equilibrium state being established between two phases. A simple pseudo first-order model was consequently used to associate the rate of reaction and expressed as follows (Eq. 12):

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

where (q_e) and (q_t) (mg/g) are concentration of Al(III) ions in the adsorbent at equilibrium and at time (t), respectively calculation and applying limit setting ($t=0$ to $t=t$) and ($q_t=0$ to $q_t=q_t$), the integrated from of (Eq. 12) becomes (Eq. 13):

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \text{-----(13)}$$

Plots for (Eq. 13) were made for the Al(III) ions adsorption at diverse studied temperature. around linear hysteresis were observed for the Al(III) ions, more than the complete series of shaking time explored and at all temperatures through low link coefficient as in Table (3), representing that the

pseudo first order kinetic model is not suitable for the here systems.

A pseudo second-order rate model is also used to explain the kinetics of the adsorption of Al(III) ion adsorbent materials. The differential equation for chemisorptions kinetic rate reaction is expressed as (Eq. 14):

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

where k_2 is the rate constant of pseudo second-order equation, for the limit setting ($t=0$ to $t=t$) and ($q_t=0$ to $q_t=q_t$), the integrated from of (Eq. 14) becomes (Eq. 15):

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

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

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e) t \text{-----(16)}$$

The associations are linear, and the values of link coefficient (R^2), advise a strong link between the parameters and also give details that the process of adsorption of Al(III) ions follows pseudo second order kinetic model.

As of the consequences, it can be exposed that the value of the rate constant (k_2) were increased by increase in temperature the association coefficient (R^2) has an very high value, and theoretical (q_e) values agree with investigational ones. These outcome advise that the pseudo second-order adsorption mechanism is major and that the overall rate constant of each Al(III) ion appears to be controlled by the chemisorptions process.

| | 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 °C |
| Aqueous | 4.008667 | 0.027636 | 0.8809 | 11.13586 | 0.010899 | 1.351534 | 0.9992 | 25 |
| Aqueous | 4.070990 | 0.021879 | 0.9842 | 13.79310 | 0.007745 | 1.473405 | 0.9991 | 35 |
| Aqueous | 1.008324 | 0.015891 | 0.8945 | 13.58696 | 0.029961 | 5.530973 | 0.9997 | 45 |

TABLE 3. Kinetic parameters for removal of Al(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 °C |
| Aqueous | 4.008667 | 0.027636 | 0.8809 | 11.13586 | 0.010899 | 1.351534 | 0.9992 | 25 |
| Aqueous | 4.070990 | 0.021879 | 0.9842 | 13.79310 | 0.007745 | 1.473405 | 0.9991 | 35 |
| Aqueous | 1.008324 | 0.015891 | 0.8945 | 13.58696 | 0.029961 | 5.530973 | 0.9997 | 45 |

(B) Study The Intra-Particle Diffusion Model (Weber-Marries) In Aqueous Solution:

At the near time Weber and Morris's and pore-diffusion is the most generally used models for studying the mechanism of adsorption. On the other hand, Weber and Morris's pore-diffusion model assumes that:

- (i) The outer film mass remove is only major for a very small time at the start of diffusion.
- (ii) The path of diffusion is radial and the concentration.
- (iii) The pore diffusivity is constant and does not vary 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 unusual initial concentration of the Al(III) ions in aqueous solution. It can be seen that the 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 hole diffusion. Non-linearity of the plots had indicated the multi phase adsorption of toxic metal as Al(III) by the adsorbent. The extrapolation of the first linear portion gives the intercept equal to the limit layer thickness or film thickness. The values of intercept offer an idea about the limit layer depth such as the layer the intercept, the greater the limit layer effect.

(C) Study The Result Of Temperature And Calculaion Of Activation Energy (Ea) In Aqueous Solution:

The adsorption of Al(III) ions has been create to raise with an raise in temperature from (25 to 45 °C).The increase in adsorption ability of the adsorbent with temperature indicates an endothermic process as in table (5).

The raise in adsorption with temperature my be attributing to either change in hole size of the adsorbent causing inter-particle diffusion within the pores or to enrichment in the chemical kinship of the Al(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 ability. At higher temperature, the option of diffusion of solute inside the pores of adsorbent can not lined out as reposted by earlier workers [21].

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

| | t °C | K_{id} | C | R ² |
|---------|------|----------|---------|----------------|
| aqueous | 25 | 0.3644 | 7.4468 | 0.8769 |
| Aqueous | 35 | 0.3929 | 8.6390 | 0.9750 |
| Aqueous | 45 | 0.1052 | 12.2000 | 0.9357 |

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

| | t °C | ΔG (KJ/mol) | ΔS (J/mol K) | ΔH (KJ/mol) | A | Ea (KJ/mol) |
|---------|------|---------------------|----------------------|---------------------|--------|-------------|
| Aqueous | 25 | 3423.51 | 443.45 | 135820.30 | 118.61 | 39148.25 |
| Aqueous | 35 | -235.89 | | | | |
| Aqueous | 45 | -5479.91 | | | | |

The over outcome were more substantiated by the different thermodynamic parameters. Enthalpy change (ΔH), Entropy change (ΔS), Gibbs free energy change (ΔG) and Activation energy (E_a) evaluated for adsorption.

The result of temperature on adsorption is more definite 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 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 E_a) were listed in Table (5).

So the positive value of ΔS suggested some structure vary in the adsorbent and adsorbate. In fact, the positive value of enthalpy (ΔH) further established the endothermic nature of the processes, so increasing temperature supplied with a more favorable adsorption of Al(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 Al(III) is physical in nature [23]. The activation energy (E_a) was calculated by the linearized Arrhenius equation (eq. 22):

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

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

As of the pseudo second-order kinetic studies, k_2 is the rate constant which control the process, i.e (k) In this study, activation energy (E_a) 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 (E_a)

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 (E_a) is between (8.4) and (83.7) KJmol^{-1} [21] noted that chemical adsorption includes activated and non activated forms.

The consequences shows that the method is one of activated chemical adsorption and the positive value of the activation energy (E_a) optional that the rise in the solution temperature favors the Al(III) ions adsorption onto the modified chitosan

(III) Studies Of Adsorption Processes For The Removal Of Chromium Al(III) By Modified Chitosan In Acidic Medium

The acidity ranging from 0.005 to 0.050 M HCl, aluminum ions Al(III) adsorption ability decreases. But, at higher acid molarities bad setting are set up to exist for adsorption, so, no adsorption happen. This drift was observed by earlier workers when investigative metal adsorption no different adsorbents [17], and can be interpreted as follows. Under acidic conditions, as strong competition effect between H^+ and aluminum Al(III) caused by high concentration of H^+ leads to decrease amount of Al(III) powerless on the modified chitosan.

Also, at high acidic the function groups are present in protonated forms which have electrostatic disgust to aluminum ions (Al(III)) and are firm to giver their electron pair to coordinate with aluminum ions (Al(III)), thus weakening the complexation amid them and more decreasing the aluminum ions (Al(III)) adsorption capacity. With the decrease of solution acidity, due to the decrease of H^+ concentration, the war result between Al(III)(and/or Al(OH⁺)) and H^+ becomes weak, resulting in more Al(III) immobilized onto the modified chitosan. Besides, the combined H^+ ions gradually dissociate from functional groups at low acidity, attractive the complexation between Al(III) and the functional groups, so, raise of Al(III) uptake.

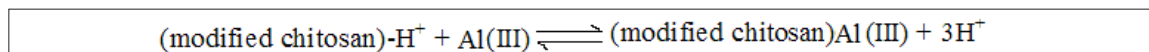
The relations between the amount of Al(III) adsorbed on modified chitosan and their equilibrium concentration solution were described by the adsorption isotherms as in Table (6). The adsorption data of the metal complexes on modified chitosan according to the Langmuir, Freundlich, Temkin and Dubinin-Redushkevich (D-R) models.

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

| Langmiur parameters | | | | Freundlich parameters | | | |
|----------------------------|--------------------------|------------------------|----------------|-----------------------|--------------------------|--------------------------|----------------|
| Molarity | Q _o (mg/g) | B (L/mg) | R _L | R ² | n | k _f (mg/g) | R ² |
| ACIDIC MEDIUM (HCl) | | | | | | | |
| 0.005 M | 10.7643 | -0.5096 | -0.0073 | 0.9983 | -1.6239 | 122.4052 | 0.9585 |
| 0.025 M | 6.2814 | -1.0571 | -0.0035 | 0.8800 | -1.87652 | 82.45177 | 0.9794 |
| 0.050 M | 2.5867 | -0.0123 | -0.4295 | 0.9884 | -4.74383 | 22.00392 | 0.8501 |
| Temkin parameters | | | D-R parameters | | | | |
| Molarity | A _T (L/g) | B _T (J/mol) | R ² | B | q _o (mg/g) | E (KJ/mol) | R ² |
| ACIDIC MEDIUM (HCl) | | | | | | | |
| 0.005 M | 0.0020 | -4.7498 | 0.9895 | -0.0003 | 5.0289 | 40.8248 | 0.9018 |
| 0.025 M | 0.0072 | -4.3038 | 0.9873 | -0.0002 | 5.8462 | 50.0000 | 0.7918 |
| 0.050 M | 0.0002 | -2.1305 | 0.8914 | -6x10 ⁻⁰⁶ | 8.8534 | 288.6751 | 0.5390 |

The adsorption experiments were approved away with Al(III) by modified chitosan in inorganic acid solution. According to the above offered guess

of complexation setting, the modified chitosan process of Al(III) complexes in Al(III)-inorganic acid (hydrochloric acid) systems can be as follows:



The equilibrium adsorption data show that: (a) At low acid concentration the metal cations show in general strong uptake and high attraction with the modified chitosan environment. This actions is a famous for all adsorption processes. On the other hand, (b) with rising acid concentration the H⁺ increase and more competes sites. The study of adsorption dynamics describes the solute uptake speed and clearly this rate controls the residence time of adsorbate uptake at the solid/solution line. The data of the kinetics of the removal of Al(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 Table (7 and 8).

The relations are linear, and the values of link coefficient (R²) propose a strong link between parameters and also give details that the method of adsorption of the metal ions Al(III) follows pseudo second-order kinetic models.

The thermodynamic assumptions of the top fitting isotherm offer near 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 °C. The obtained thermodynamic parameters (ΔG, ΔH, ΔS and Ea) were listed in Table (9).

(Iv) Stduies Of Adsorption Processes For The Removal Of Chromium Al(Iii) By Modified Chitosan In Basic Medium

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

The information of the kinetics of the removal of Al(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 Table (11 and 12).

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

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

| 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 °C |
| ACIDIC MEDIUM (HCl) | | | | | | | | |
| 0.005 M | 5.481507 | 0.026715 | 0.8282 | 12.18027 | 0.006261 | 0.9289 | 0.9930 | 25 |
| 0.005 M | 1.865950 | 0.024642 | 0.9946 | 12.06273 | 0.02232 | 3.2478 | 0.9999 | 35 |
| 0.005 M | 1.554175 | 0.022339 | 0.9848 | 13.29787 | 0.025056 | 4.4307 | 0.9998 | 45 |
| 0.025 M | 4.919263 | 0.013818 | 0.9642 | 9.372071 | 0.001557 | 0.1368 | 0.8953 | 25 |
| 0.025 M | 217.3702 | 0.087284 | 0.8079 | 63.29114 | 3.01×10^{-05} | 0.1206 | 0.2457 | 35 |
| 0.025 M | 2.968930 | 0.012667 | 0.9363 | 11.79245 | 0.074534 | 10.3648 | 0.9931 | 45 |
| 0.050 M | 5.140437 | 0.009212 | 0.9996 | -8.2713 | 0.000339 | 0.0232 | 0.8530 | 25 |
| 0.050 M | 6.212981 | 0.014970 | 0.8362 | -15.2439 | 0.000149 | 0.0346 | 0.1998 | 35 |
| 0.050 M | 7.627812 | 0.011745 | 0.8530 | -37.594 | 3.49×10^{-05} | 0.0494 | 0.1094 | 45 |

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

| Molarity (mole/L) | t °C | K_{id} | C | R ² |
|----------------------------|------|----------|---------|----------------|
| ACIDIC MEDIUM (HCl) | | | | |
| 0.005 M | 25 | 0.3925 | 6.7596 | 0.9173 |
| 0.005 M | 35 | 0.1647 | 9.9619 | 0.9726 |
| 0.005 M | 45 | 0.1392 | 11.487 | 0.9999 |
| 0.025 M | 25 | 0.5541 | -0.0226 | 0.949 |
| 0.025 M | 35 | 1.5319 | -5.0496 | 0.9192 |
| 0.025 M | 45 | 0.3433 | 7.1067 | 0.9209 |
| 0.050 M | 25 | 0.6615 | -3.1589 | 0.8862 |
| 0.050 M | 35 | 0.7473 | -2.9486 | 0.9332 |
| 0.050 M | 45 | 0.9731 | -3.9119 | 0.9195 |

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

| Molarity (mole/L) | t °C | ΔG (KJ/mol) | ΔS (J/mol K) | ΔH (KJ/mol) | A | Ea (KJ/mol) |
|----------------------------|------|-------------|--------------|-------------|----------------------|-------------|
| ACIDIC MEDIUM (HCl) | | | | | | |
| 0.005 M | 25 | 3643.070 | 135.288 | 44076.720 | $1.7x \cdot 10^{14}$ | 68757.39 |
| 0.005 M | 35 | 2814.319 | | | | |
| 0.005 M | 45 | 803.903 | | | | |
| 0.025 M | 25 | 7721.154 | 185.902 | 62394.92 | $8.6x \cdot 10^{18}$ | 99957.65 |
| 0.025 M | 35 | 3867.521 | | | | |
| 0.025 M | 45 | 3874.176 | | | | |
| 0.050 M | 25 | 8998.750 | 70.098 | 29926.983 | $1.7x10^{26}$ | 148765.60 |
| 0.050 M | 35 | 8707.511 | | | | |
| 0.050 M | 45 | 7508.941 | | | | |

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

| Langmiur parameters | | | | | Freundlich parameters | | |
|--|---------------------------|------------------------|----------------|----------------------|-----------------------|-----------------------|----------------|
| Molarity | Q _s (mg/g) | B (L/mg) | R _L | R ² | n | k _f (mg/g) | R ² |
| BASIC MEDIUM (NH₄OH) | | | | | | | |
| 0.001 M | 11.0619469 | -0.73917 | -0.00504 | 0.9984 | -15.7233 | 14.69265 | 0.9535 |
| 0.003 M | 11.2485939 | -0.85072 | -0.00438 | 0.9988 | -15.6006 | 14.79449 | 0.9115 |
| 0.005 M | 11.3507378 | -1.20850 | -0.00308 | 0.9998 | -13.1406 | 15.23702 | 0.9631 |
| Temkin parameters | | | | D-R parameters | | | |
| Molarity | A _T (L/g) | B _T (J/mol) | R ² | B | q ₀ (mg/g) | E (KJ/mol) | R ² |
| BASIC MEDIUM (NH₄OH) | | | | | | | |
| 0.001 M | 9.86374×10^{-09} | -0.7882 | 0.9565 | -4×10^{-07} | 12.04802 | 1118.0340 | 0.5858 |
| 0.003 M | 1.03951×10^{-08} | -0.7948 | 0.9213 | -5×10^{-07} | 11.97954 | 1000.0000 | 0.6410 |
| 0.005 M | 6.03274×10^{-06} | -1.0558 | 0.9758 | -1×10^{-06} | 11.20993 | 707.1068 | 1.0000 |

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

| Pseudo first-order | | | | Pseudo second-order | | | | t °C |
|--|-------------------------|-------------------------------------|----------------|-------------------------|---------------------------|--------------|----------------|------|
| 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 | |
| BASIC MEDIUM (NH₄OH) | | | | | | | | |
| 0.001 M | 1.525808 | 0.022800 | 0.9624 | 11.86240 | 0.025795 | 3.629764 | 0.9999 | 25 |
| 0.001 M | 1.653484 | 0.008521 | 0.8369 | 13.49528 | 0.012224 | 2.226180 | 0.9963 | 35 |
| 0.001 M | 2.226384 | 0.012206 | 0.9829 | 13.38688 | 0.052593 | 9.425071 | 0.9998 | 45 |
| 0.003 M | 1.756305 | 0.017042 | 0.8861 | 11.90476 | 0.017002 | 2.409639 | 0.9992 | 25 |
| 0.003 M | 3.026217 | 0.023260 | 0.9991 | 13.22751 | 0.012132 | 2.122692 | 0.9996 | 35 |
| 0.003 M | 0.629071 | 0.012436 | 0.9768 | 13.35113 | 0.050045 | 8.920607 | 0.9998 | 45 |
| 0.005 M | 1.787722 | 0.022339 | 0.9146 | 11.60093 | 0.020715 | 2.787845 | 0.9998 | 25 |
| 0.005 M | 7.000032 | 0.043527 | 0.9121 | 12.61034 | 0.011452 | 1.821162 | 0.9994 | 35 |
| 0.005 M | 0.457299 | 0.007830 | 0.9659 | 13.28021 | 0.042955 | 7.575758 | 0.9997 | 45 |

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

| Molarity (mole/L) | t °C | K_{id} | C | R ² |
|--|------|----------|--------|----------------|
| BASIC MEDIUM (NH₄OH) | | | | |
| 0.001 M | 25 | 0.1461 | 10.019 | 0.9545 |
| 0.001 M | 35 | 0.2107 | 10.535 | 0.8136 |
| 0.001 M | 45 | 0.0613 | 12.575 | 0.9186 |
| 0.003 M | 25 | 0.1997 | 9.3148 | 0.9464 |
| 0.003 M | 35 | 0.2698 | 9.7127 | 0.9943 |
| 0.003 M | 45 | 0.0632 | 12.509 | 0.9079 |
| 0.005 M | 25 | 0.1791 | 9.3363 | 0.9323 |
| 0.005 M | 35 | 0.2902 | 8.8605 | 0.9633 |
| 0.005 M | 45 | 0.0721 | 12.311 | 0.8988 |

TABLE 13. thermodynamic parameters for the removal of Al(III) by modified chitosan in basic medium.

| Molarity (mole/L) | t °C | ΔG (KJ/mol) | ΔS (J/mol K) | ΔH (KJ/mol) | A | Ea (KJ/mol) |
|--|------|---------------------|----------------------|---------------------|------------|-------------|
| BASIC MEDIUM (NH₄OH) | | | | | | |
| 0.001 M | 25 | 3410.785 | 308.078 | 94431.790 | 1019.313 | -27118.111 |
| 0.001 M | 35 | 2498.989 | | | | |
| 0.001 M | 45 | -1825.036 | | | | |
| 0.003 M | 25 | 3047.037 | 285.350 | 88264.495 | 266808.703 | 41771.421 |
| 0.003 M | 35 | 758.867 | | | | |
| 0.003 M | 45 | -2685.151 | | | | |
| 0.005 M | 25 | 2942.335 | 258.103 | 80856.466 | 1179.821 | 27908.932 |
| 0.005 M | 35 | -1132.409 | | | | |
| 0.005 M | 45 | -3175.238 | | | | |

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تحقق من آلية الامتزاز للمعادن الثقيلة مثل أيونات الألومنيوم (Al + 3) من حلول مختلفة باستخدام الشيتوزان المعدل

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الهدف من هذه الدراسة هو تقييم إزالة أيونات (Al + 3) من المحاليل المختلفة (مائي ، حمضي ، القاعدي) على الشيتوزان المعدل. لقد تم دراسة تأثير العوامل المختلفة من خلال تقنية الامتزازية التالية. تشمل المتغيرات المختلفة التي تمت دراستها التركيز الأولي للمادة الممتصة ، وقت الامتزاز ، الجرعة الممتزة ، الحركية الكيميائية ، تأثير درجة الحرارة. كانت البيانات التجريبية مناسبة تمامًا لمعادلة Freundlich. تم حساب المعلمات الديناميكية الحرارية مثل ΔH و ΔS و ΔG ، مما يشير إلى أن الامتزاز كان طبيعيًا و ماص للحرارة.