

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

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ABSTRACT

One of the significant developments in the new range of applications is the study of the ability of chitosan, as a potentially major environmental treatment material, to remove metal ions from wastewaters. Chitosan is the deacetylated form of chitin, and this process produces a chain of amino groups along the chitosan structure. The adsorption of Al (III) ions from unique solutions (Aqueous, Acidic, and Basic) onto modified chitosan granular adsorbent was studied. SEM and FTIR techniques were used to characterize the composition of adsorbent chitosan. The impact of number parameters has been investigated by means of the following batch adsorption technique. The quite a number variables studied include the initial attention of the adsorbate, agitation time, adsorbent dosage, chemical, as well as the solution methodologies to explain and model the rate of adsorption of the metal ions from solution, in addition to the influence of temperature values were studied. The experimental statistics used to be fit properly to the Freundlich isotherm. Thermodynamic parameters such as ΔH , ΔS and ΔG were calculated, indicating that the adsorption was spontaneous and endothermic nature.

KEYWORDS: Removal, Al(III), Modified Chitosan, Aqueous, Acidic and Basic medium, Adsorption Isotherm.

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1. INTRODUCTION

Chitosan, as a attribute polysaccharide, has receptive amino and hydroxyl groups in its linear poly glucosamine chains, can be utilized to functionalize and modify. In any case, traditional change approach using single chitosan cross linking with glutaraldehyde normally leads to reduce of useful crew (- NH₂-) and loading capacity, it's interested to prepare multifunctional chitosan-x which used in many functions such as water treatment by means of using diethylene tri a- mine Penta acetic acid (DTPA) with sufficient wide variety of carboxyl group son the backbones, is a frequently used as chelating agent for heavy metal [1].

The object of this study [2] is to assess the removal of Fe(III) ions from aqueous solutions onto modified chitosan. The effect of various parameters has been investigated by the following batch adsorption technique. The various variables studied include the initial concentration of the adsorbate, agitation time, adsorbent dosage, kinetics, the influence of temperature. The experimental data was fit well to the Freundlich isotherm. Thermodynamic parameters such as ΔH , ΔS and ΔG were calculated, indicating that the adsorption was spontaneous and endothermic nature [2].

Algerian's municipal sewage treatment plants generate around 106 m³ of sewage sludge annually. Recently, the rapid expansion of wastewater treatment plants without equal attention to the treatment of the produced sludge has genera- ted increasing concerns. While the sludge is usually incinerated or used as an agricultural fertilizer and may contain numerous nutrients, there may also be harmful substances that complicate sludge management. Hence the removal of pollutants from the sludge is necessary before further usage. This paper discusses the characteristics of potable water treatment sludge containing a high aluminum content. Furthermore, an electrokinetic treatment is proposed to remove aluminum from this sludge by varying the type of solution contained in the cathode compartment and modifying the treatment time to optimize the efficiency of the process. Successful results were achieved where 60% of aluminum was collected on the cathode side with a consumed energy around of 1000-2000 kWh kg⁻¹ of sludge weight. [3-6].

In this study, a low-cost, eco-friendly adsorbent was prepared from Eucalyptus camaldulensis barks through chemical activation. The effect of operating variables namely initial pH, sorbent dose, initial metal concentration, shaking speed and temperature on the aluminum removal percentage and uptake capacity has been studied. The optimal pH was found as 5.0 and the sorbent dosage 5.0 g/L. Temperature effect proved the process to be endothermic. The experimental observations were fitted to Langmuir and Freundlich isotherms were Langmuir proved to be a better 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 operating conditions. From the thermodynamic studies, the activation energy was evaluated as 43.23 kJ mol⁻¹.

This study attempts to introduce a procedure to remove Aluminum ions from drinking water and industrial effluents by using active carbon with different grading as absorbent. Absorption of Aluminum ions was discussed in different conditions of Aluminum concentration, contact time, the impact of electrolytes and pH on Aluminum ions absorbency. Both Freundlich and Langmuir isotherms

used to investigate the adsorption. Thermodynamics relations governing process, such as specification of (ΔG°), (ΔS°) and the enthalpy of adsorption, were calculated, which showed that Aluminum absorption on active carbon is an endothermic and spontaneous process.

2. EXPERIMENTAL

2.1. Materials and methods

2.1.1. Studies of Adsorption Processes for Aluminum ions

Batch equilibrium isarithm and dynamics studies were administrated within the same manner. In every sort of studies, we have a tendency to ready metal particle solutions containing Al ions (0.01M) and transferred them into (250 ml) wide-mouth propane check bottles with screw closure caps employing a Finn pipette. Every bottle contained a illustrious volume (50 ml) of the metal particle solution. A illustrious quantity (0.5 g) of the changed chitosan was additional into every bottle. Afterward, the bottled were shaken ceaselessly (1-120 min). At certain intervals of contact time, the solution sample was withdrawn and filtered, and therefore the final concentration of Al ions decided within the filtrate By exploitation atomic absorption.

2.1.2. Kinetic studies of the adsorption processes for metal ions aluminum ions:

Limited batch approach determined the charge of the adsorption process. Series of adsorption experiments was set up at a consistent temperature. Solutions (50 ml) of Aluminum ions at consistent ionic strength (0.01 M) were thermo stated at the required temperature (298 K) in (250 ml) wide-mouth propylene check bottles with screw closure caps the use of a finn pipette (accurate to ± 0.03). A weighed quantity of the adsorbent (0.5 gm) used to be added to every solution. The bottles were completely shaken. After suitable intervals (30, 60, 90, 120 min), the contents of each bottle one at a time were filtered, and the trivalent metal ion concentration in the liquid segment was once determined.

The Lagergren pseudo first and second order models, commonly used for sorption systems, assumed that the adsorption rate is related to the difference between the amounts of adsorbate bound at any given time *versus* the adsorbate bound at equilibrium. The first- and second-order models can be respectively expressed as Equations:

$$q_{ads} = q_{e,ads}(1 - e^{-k_1,ads t})$$

$$q_{ads} = q_{e,ads} k_2,ads t / (1 + k_2,ads t)$$

where k_1,ads and k_2,ads are the 1st and 2nd order adsorption rate constants (hr^{-1}), in which a larger rate constant demonstrates that a shorter time is required for reaching a specific fractional uptake compared with a smaller rate constant, while q_{ads} is the amount of As adsorbed at time t and $q_{e,ads}$ is the amount of As adsorbed at equilibrium.

The adsorption kinetic curve of the chitosan was modeled by fitting the pseudo-first-order and the pseudo-second-order adsorption kinetic equation:

$$\log(q_e - q_t) = \log q_e - k_1 t$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where q_e (mg/g) is the amount of Al ions adsorbed upon reaching equilibrium, q_t (mg/g) is the amount of Al ions adsorbed at time t (min), and k_1 (min^{-1}) and k_2 [$g \cdot (mg/min)^{-1}$] are the rate constants of the pseudo-first-order and pseudo-second-order adsorption kinetic equations, respectively.

The Weber and Morris intra-particle diffusion model is expressed as following:

$$q_t = k_i t^{1/2} + I$$

Where k_i is the rate constant of intra-particle diffusion. I is a constant that gives idea about the thickness of the boundary layer (mg/g). The larger the value of I , the greater the boundary layer effect is [10]. The values of k_i and I can be determined from the slope and intercept of the linear plot of q_t versus $t^{1/2}$, respectively. If the plot of q_t versus $t^{1/2}$ gives a straight line and passes through the origin, the adsorption process is controlled only by the intra-particle diffusion. But if the plot shows multi-linear characteristic or does not pass

through the origin, the adsorption process is controlled by two or more diffusion mechanisms.

The rate constant of intraparticle diffusion (k_{id}) at different temperatures were determined using the following equation:

Where (q_t) is the amount adsorbed at time t , ($t^{1/2}$) is the square root of time.

$$q_t = k_{id} t^{1/2} \text{-----} (3)$$

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2.2.3. Thermodynamic of the Adsorption Processes for Metal Ions Aluminum ions:

Proper assessment of thermodynamics can provide in-depth information regarding the inherent energy and structural changes of adsorbent after adsorption and also provide the mechanism involved in adsorption process. The thermodynamics parameters studies include enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS). They can be calculated from the following equations.

$$K_d = q_e / c_e$$

$$\ln K_d = -\Delta H / RT + \Delta S / R$$

$$\Delta G = \Delta H - T\Delta S$$

Where K_d is the distribution coefficient, L/g; q_e is the equilibrium adsorption capacity, mg/g; c_e is the equilibrium reserpine concentration of, mg/L; R is the gas constant, 8.314 kJ/ (molK); And T is the absolute temperature, K.

The plots of $\ln K_d$ versus $1/T$ at different initial concentrations were shown in Fig 8. The plots were all linear with good correlation coefficients ($R^2 > 0.92$), suggesting that Van't Hoff equation was suitable to be applied for the calculations of enthalpy change (ΔH) and entropy change (ΔS). The values of ΔH and ΔS could be obtained from the slopes and intercepts of the plots, respectively. The results were listed in Table 3.

2.2.4. Mechanisms of the Adsorption Processes For Aluminum ions

It is constantly necessary to predict the rate-limiting step in an adsorption procedure to recognize the mechanism related with the phenomena. For a solid-liquid adsorption process, the solute switch is generally characterized by way of either external mass transfer or intraparticles diffusion or both. Three sorts of mechanisms are involved in the adsorption process, stated as two follows:
 Film diffusion: This involves the motion of adsorbate molecules from the adsorbent.
 Particle diffusion: where the adsorbate molecules pass in the interior of the adsorbent particles.
 Adsorption of the adsorbate molecules on the interior of the porous adsorbent takes place.

2.1.5. Effect of Temperature on the Adsorption Processes for Aluminum Ions

To decide the impact of temperature on the adsorption of metal (Me(III)) ions equilibrium adsorption used to be carried out in a number of (250 ml) wide- mouth polypropylene bottles with screw closure caps at two desired two temperature (298, 308, and 313 K) in absence and in the presence of (0.1 M) two HCl solution.

The dose of (0.5 g) of modified chitosan was once first off weighed accurately and introduced without delay into (250 ml) polypropylene bottles. Then, (50 ml) two of aqueous options containing metal ions with (0.01 M) concentration have been added to every bottle and shacked for (120 min) to obtain the equilibrium. The supernatant used to be eliminated immediately by using filtration. The concentration of the residual aqueous phase used to be determined by means of atomic absorption). The quantity of Aluminum ions adsorbed used to be then calculated by way of subtracting its ultimate concentration from initial concentration [1, 2 and 3].

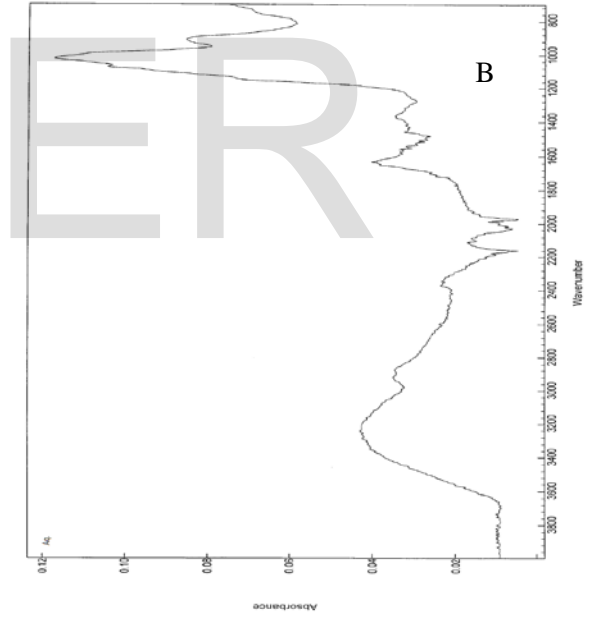
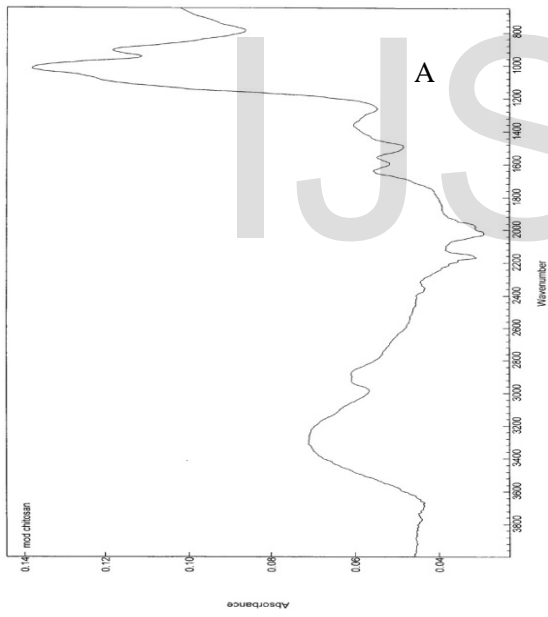
3. RESULTS AND DISCUSSION

3.1. Characterization of Modified Chitosan

3.1.1. FTIR Spectroscopy

The FTIR spectrum figure 1(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 the amino group of chitosan [7-8]. 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 (figure 1 (d)), low basic medium (figure 1 (f)) and aqueous medium (figure 1 (d)) respectively.

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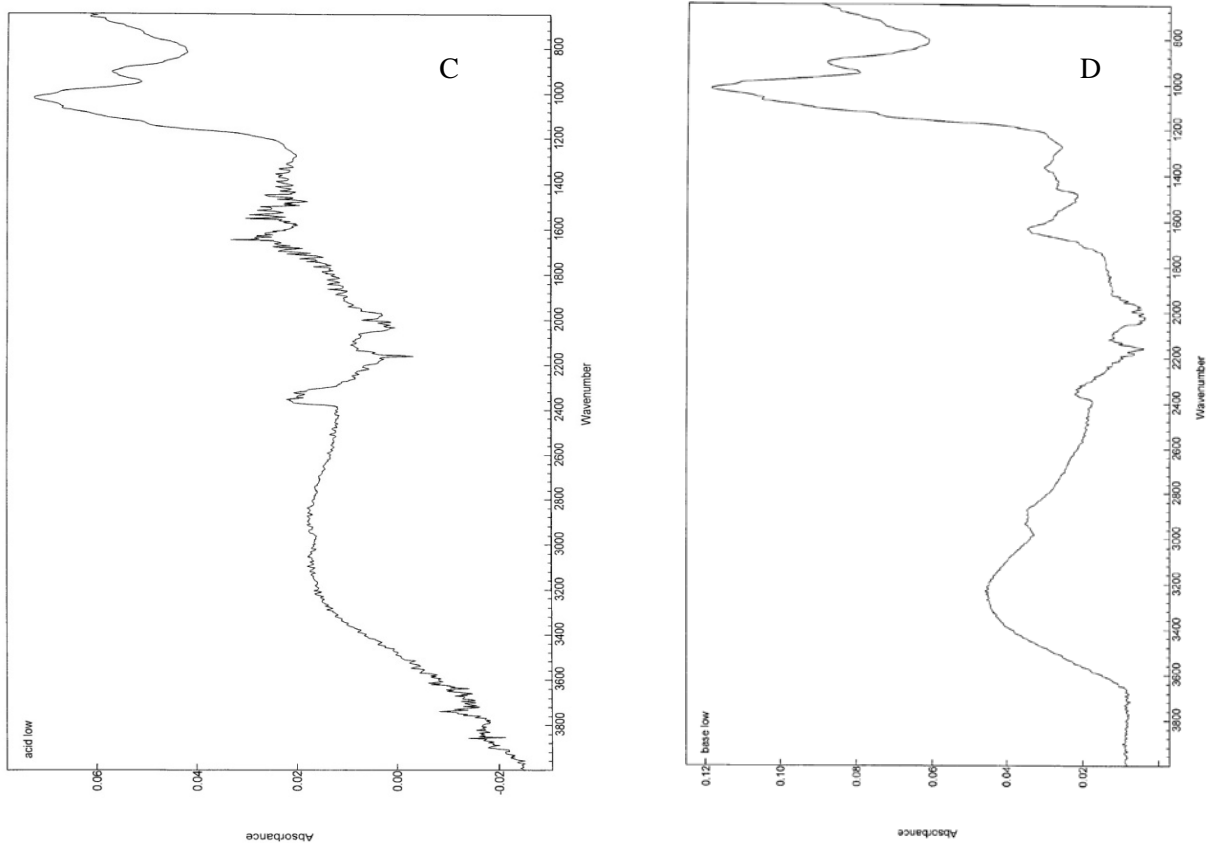


Figure 1. Infrared of A) Modified Chitosan b) Infrared of Modified Chitosan in aqueous solution, c) Infrared of Modified Chitosan in acidic solution d) Infrared of Modified Chitosan in basic solution

3.1.2-X-ray Diffraction Analysis (XRD)

The XRD pattern of chitosan prepared from shrimp shells waste at Figure 2a, exhibits the weak diffraction peaks centered at diffraction angle $2\theta = 11.9^\circ$ and sharp diffraction peaks at $2\theta = 20^\circ$ are indicative of the high degree of crystallinity morphology of chitosan. The X-ray diffraction analysis for modified chitosan, the characteristic peaks at $2\theta = 10^\circ$ and 20° disappeared, and a very weak and broad peak centered at $2\theta = 15^\circ$ appeared Figure (2b). This

difference in XRD patterns weak and broad peak centered at $2\theta = 15^\circ$ appeared in figure2b. 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-linked into chitosan allowed the synthesis of hydrogels with higher hydrophilicity [9] which can facilitate the active surface area, That plays a very important role in adsorption process in our study.

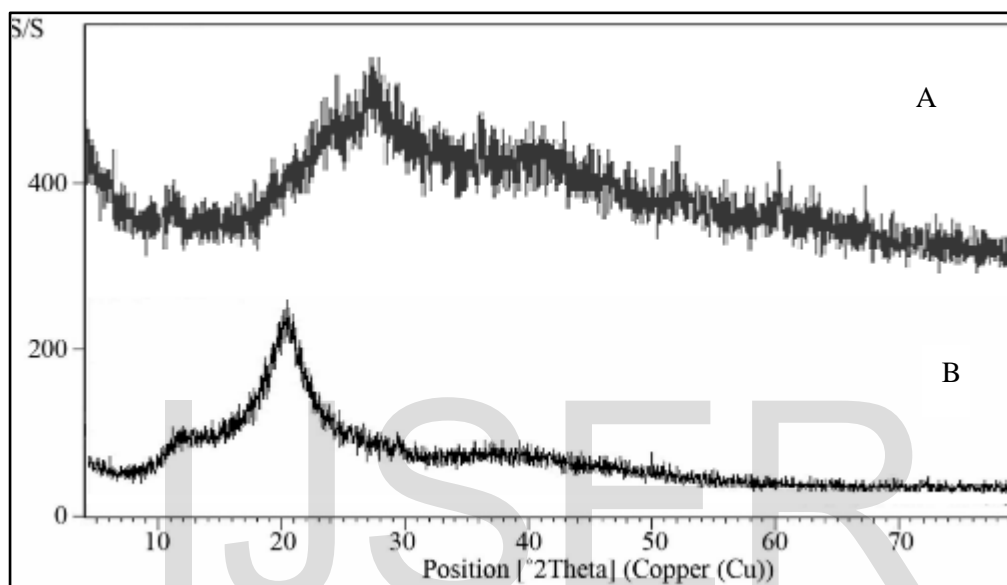


Figure1. X-ray diffraction of a) chitosan and b) modified chitosan

3.1.3. Scanning Electron Microscope (SEM):

The porous structure of modified chitosan in this study may offer more adsorption sites for adsorbate, which supported the fact that starch glutaraldehyde-cross linked chitosan has been widely applied in the uptake of heavy metals [13,14] and drug delivery [15]. Also, modified chitosan with a higher total surface area and a more open pore structure could be supposed to adsorbate Al(III), which may at least partially explain this result that the adsorption by modified chitosan, but not solid chitosan.

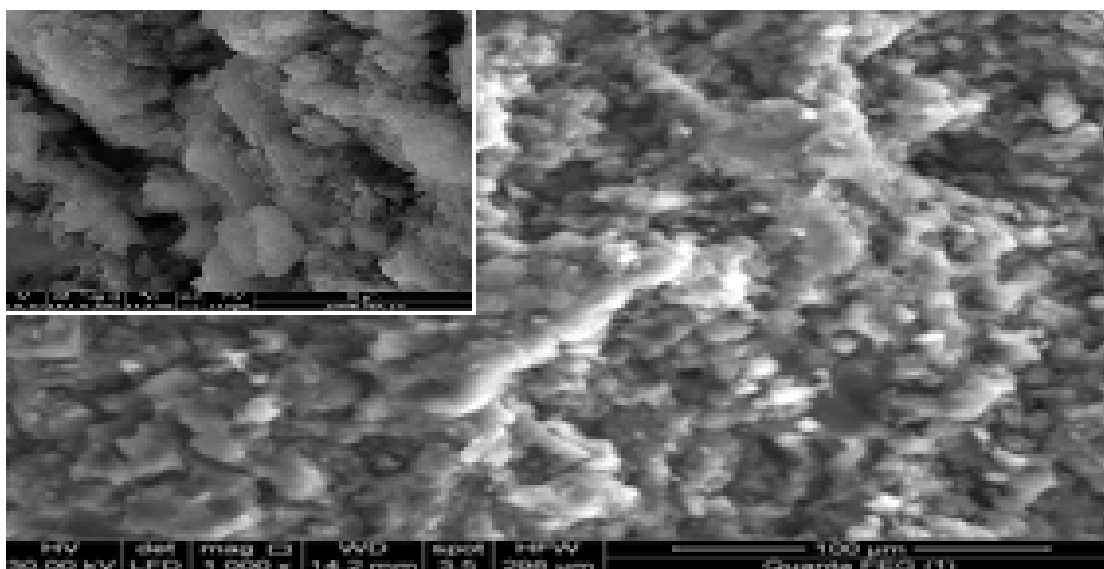


Figure 3. Scanning electron microscope of modified chitosan

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3.4. Studies of Adsorption Processes for the Removal of Aluminum Al (III) By Using Modified Chitosan (In Aqueous Solution)

Langmuir isotherm:

Langmuir isotherm as in Table (1) is regularly used to describe adsorption of solute from liquid options and this model assumes monolayer adsorption onto a homogeneous surface with a finite number of equal sites and expressed through the following (eq. (1)).

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

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

Langmuir parameters				Freundlich parameters				
	Q ₀	b (L/mg)	RL	R ²		N	k _f	R ²
Aqueous	11.0864745	-1.11911	-0.00332	0.9990		0.5000	1.0000	1.0000

Characteristic constants of Langmuir equation, Q₀ the theoretical maximum adsorption capacity and k_L associated to affinity of the binding sites, Q₀ and k_L Langmuir isotherm constants can be decided from the Linearized of Eq(1) as eq(2):

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \dots \dots \dots (2)$$

The slope and intercept of the linear plot of (C_e/q_e) Verses (C_e) provide the values of Q₀ and k_L respectively. To comprehend the feasibility of the isotherm, the essential points of Langmuir model can be expressed in terms of separation factor or equilibrium parameter RL, which was once described by means of Eq(3):

$$R_L = \frac{1}{1 + bC_0} \dots \dots \dots (3)$$

The values of RL indicate the shapes of isotherms to be either unfavorable (RL>1), linear (RL=1),

favorable ($0 < RL < 1$) or irreversible ($RL = 0$) [16]. The RL values for Al(III) were calculated and indicated that adsorption is even favorable for the higher metal ion concentration that has been investigated. The data of RL values the adsorbent is suitable adsorbent (modified chitosan) for the adsorption of Al(III) ions from aqueous solutions.

Freundlich isotherm:

The Freundlich model is expressed as follows (Eq. 4):

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

The Linearized form of Freundlich equation is given by (Eq. 5): $\ln q_e = \ln k_f + (1/n) \ln C_e$ (5)

Where k_f and $1/n$ are characteristic constants representing the adsorption Capacity and adsorption intensity of the device 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 the intercept is $(\ln k_f)$. The magnitude of $0 < n$ shows the favorability of method of adsorption.

The adsorption parameters obtained from both the models were given in Table (1). The experimental data have been fitted nicely with Langmuir isotherm suggesting that the Al(III) adsorbed from monolayer insurance on the adsorbent surface. To a lesser extent, the equilibrium data had been also well described with the Freundlich model probable due to the real heterogeneous nature of the floor sites concerned in the system of adsorption and Table (1).

On the other hand, the equilibrium data were analyzed using Freundlich isotherm model and (R^2) values were estimated. The cost of (n) suggests that the adsorption capacity is only barely suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by way of Al (III) ions; this infinite surface coverage is predicted to show up indicating multilayer adsorption on the surface. It can be concluded that the Langmuir isotherm was once greater appropriate than Freundlich one as in most instances the correlation coefficient used to be greater as viewed in Table(1) thus indicating the applicability of monolayer coverage of the Al(III) ions on the surface of adsorbent. This can be defined via two the two reality that two the adsorbent two has two a high surface area for Al (III) ions adsorption. Therefore solely monolayer adsorption came about on their surface [18].

Temkin and Pyzhev isotherm:

The Temkin and Pyzhev isotherm have commonly been applied in the following Equation:

$$q_e = (RT/b) \ln(AC_e)$$

$$q_e = (RT/bT) \ln A_T + (RT/bT) \ln C_e$$

$$BT = RT/bT$$

Where (AT) (L/g) and (bT) (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). Where bT Related to the heat of adsorption. We located that the Values greater than 8 shows a strong interaction between Al (III) and adsorbent. However, a greater value suggests the presence of highly superior cohesive forces in between the adsorbent and Al (III).

The Dubinin-Radushkevich (D-R) isotherm [19] was once also employed to find out the adsorption mechanism primarily based on the practicable principle assuming a heterogeneous surface. Dubinin-Radushkevich isotherm is expressed as follows Equation:

$$q_e = X_m e^{-\beta \epsilon^2}$$

The linear form was Equation:

$$\log q_e = \log X_m - \beta \epsilon^2$$

Where (Xm) 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 Equation:

$$\epsilon = RT \ln (1+(1/C_e))$$

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

A plot of (ln qe) Vs (ε²) as in gave a straight line of the slope, (β) and intercept, (Xm) of special systems have been evaluated. The distinction in the free energy between the adsorbed section and the saturated liquid adsorbate is referred to as the potential, a term first advanced with the aid of Polanyi [20]. In the present study Dubinin-Radushkevich isotherm constants, monolayer capability (Xm) and adsorption electricity (β) are tabulated in Table (2).

The magnitude of (β) is used to decide the kind of adsorption mechanism. When one mole of Al(III) ions is transferred the adsorbent surface, its price is higher than 8 KJ/mol which suggests chemical adsorption, the calculated values of (E) for the present find out about is greater than 8.0 KJ/mol for the adsorption of Al(III), which propose 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			
AT	BT	R ²	B	q ₀	E	R ²

Aqueou	2.3887 x10 ⁻	-1.6179	0.9884	-3 x10 ⁻⁰⁶	11.2290	408.2483	0.9883
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3.5. Study The Adsorption Kinetics Modeling In Aqueous Solution:

The data of the kinetics of Al (III) adsorbed from aqueous solution onto modified chitosan had been analyzed using pseudo first-order, pseudo 2d order intraparticles diffusion kinetic models, respectively. The conformity between experimental facts and each mannequin envisioned values was expressed by means of the correlation coefficient (R2). Relatively high (R2) values indicated that two the model successfully describes the kinetics of Al (III) ions adsorption removal.

The adsorption kinetics of Al(III) ions from the liquid phase to strong is considered as a reversible response with an equilibrium kingdom being mounted between two phases. A simple pseudo first-order model was consequently used to correlate the rate of reaction and expressed as follows Equation:

$$dq_t/dt = k_1(q_e - q_t)$$

Where (q_e) and (q_t) (mg/g) are concentration of Al (III) ions in the adsorbent at equilibrium and at time (t), respectively integration and making use of boundary stipulations (t=0 to t=t) and (q_t=0 to q_t=q_t), the integrated form showed in the following Equation:

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

Plots for the last equation were made for the Al (III) ions adsorption at one of a kind studied temperature. Approximately linear matches had been determined for the Al(III) ions, over the whole 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 legitimate for the present systems.

A pseudo-second-order rate model is also used to describe the kinetics of the adsorption of Al(III) ion adsorbent materials. The integrated form is:

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e) t$$

The relationships are linear, and the values of correlation coefficient (R2), suggest a strong relationship between the parameters and also explain that the process of adsorption of Al(III) ions follows pseudo-second order kinetic model.

TABLE (3): Kinetic parameters for removal of Al(III) ions by modified chitosan:

	Pseudo	first-order		Pseudo-second-order				
	qe,1	K1	R ²	qe,2	K2	H	R ²	t
Aqueous	4.00866	0.02763	0.8809	11.13586	0.010899	1.35153	0.9992	25
Aqueous	4.07099	0.021879	0.9842	13.79310	0.007745	1.473405	0.9991	35
Aqueous	1.00832	0.01589	0.8945	13.58696	0.029961	5.53097	0.9997	45

From the results, it can be proven that the value of the rate constant (k2) was once elevated with expand in temperature the correlation coefficient (R2) has an extremely excessive value, and theoretical (qe) two values agree with experimental ones. These results suggest that the pseudo-second-order adsorption mechanism is predominant and that the normal rate regular of each Al(III) ion appears to be controlled with the aid of the chemisorptions process.

3.6. Study the Intra-Particle Diffusion Model (Weber- Marries) In Aqueous Solution:

At present 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:

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

The direction of diffusion is radial and the concentration.

The pore diffusivity is constant and does not change with time, the pore diffusion parameter, kid ((mg/g min^{0.5}) is expressed as Equation :

$$qt = kidt^{0.5} + C$$

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

The (kid) values were obtained as in Table (4) from the slope of the linear parts of the curve of extraordinary initial concentration of the Al(III) ions in aqueous solution. It can be viewed that the plots possess multilinear portions; it shows that the two or more steps have an effect on the adsorption process. It was determined that straight strains relate the points, the sharp first linear portion is due to the film diffusion and the 2d linear component is due to the pore diffusion. Non- linearity of the plots had indicated the multi-stage adsorption of toxic metal as Al(III) by the adsorbent. The extrapolation of the first linear element offers the intercept equal to the boundary layer thickness or film thickness. The values of intercept provide an idea about the boundary layer thickness such as the layer the intercept, the increased the boundary layer effect.

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

3.7. Study The Effect of Temperature and Calculation of Activation Energy (E_a) In

Aqueous Solution:

The adsorption of Al(III) ions has been located to amplify with an increase in temperature from (25 to forty five °C). The extend in adsorption capacity of the adsorbent with temperature indicates an endothermic manner as in desk (5).

The increase in adsorption with temperature can also be attributing to both trade in pore size of the adsorbent inflicting intraparticles diffusion within the pores or to enhancement in the chemical affinity of the Al(III) ions to the surface of adsorbent leading to some form of chemical interaction to take at some stage in adsorption method which outcomes into make bigger in adsorption capacity. At greater temperature, the opportunity of diffusion of solute inside the pores of adsorbent might also not rule out as stated via formerly workers [21].

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

t °C		ΔG	ΔS	ΔH	A	E _a
Aqueous	25	8892.706	-102.719	-21758.800	3.36 x 10 ¹³	64483.740
Aqueous	35	9789.447				
Aqueous	45	10952.864				

The a number of thermodynamic parameters further substantiated the above results. Enthalpy exchange (ΔH), Entropy change (ΔS), Gibbs free energy change (ΔG) and Activation energy (E_a) evaluated for adsorption.

The effect of temperature on adsorption is similarly established by means of the vant Holf plots as based totally on the fowling equations [22]:

$$kD = q_e / C_e$$

$$\Delta G = -RT \ln kD$$

$$\Delta G = \Delta H - T \Delta S$$

$$\ln kD = (\Delta S / R) - (\Delta H / RT)$$

Where (T) is the absolute temperature in Kevin (K), R is gas constant (8.314 J/mol K) and kD 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 kD) versus

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(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).

Therefore the positive value of ΔS suggested some structure 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 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.

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 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 (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 results show that the process is one of activated chemical adsorption and the positive value of the activation energy (E_a) suggested that the rise in the solution temperature favors the Al(III) ions adsorption onto the modified Chitosan

3.8. 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 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 on 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 the amount of Al(III) immobilized onto the modified Chitosan.

Furthermore, at high acidic the function groups are present in protonated forms which have electrostatic repulsion to aluminum ions (Al(III)) and are hard to donor their electron pair to coordinate with aluminum ions (Al(III)), thus weakening the complexation between them and further decreasing the aluminum ions (Al(III)) adsorption capacity. With the decrease of solution acidity, due to the decrease in H⁺ concentration, the competition effect between Al(III)(and 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, enhancing the complexation between Al(III) and the functional groups, accordingly, an increase of

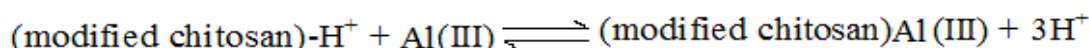
Al(III) uptake.

The relationships between the amount of Al(III) adsorbed on modified chitosan, and their equilibrium concentration solution was 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

Langmuir parameters					Freundlich parameters		
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 AT				D-R parameters q ₀ E			
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	-6.40-06	8.8534	288.6751	0.5390

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



The equilibrium adsorption data indicate that: (a) At low acid concentration the metal cations exhibit 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 for 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 Al(III) by modified chitosan in the acidic medium were analyzed using

pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models, respectively as in Table (7 and 8).

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				
				qe,2	K2	H	R ²	t
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	0.02464	0.9946	12.06273	0.02232	3.2478	0.9999	35
0.005 M	1.554175	0.02233	0.9848	13.29787		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	0.08728	0.8079	6.29114	3.01x10 ⁻⁵	0.1206	0.2457	35
0.025 M	2.968930	0.012667	0.9363	11.79245		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		0.0346	0.1998	35
0.050 M	7.627812	0.011745	0.8530	-37.594	3.49x10 ⁻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	t °C	Kid	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

The relationships are linear, and the values of correlation coefficient (R²) suggest a strong relationship between parameters and also give an explanation for that the process of adsorption of the steel ions Al(III) follows pseudo-second-order kinetic models.

The thermodynamic assumptions of the great becoming isotherm grant perception into the surface properties and mechanism of getting rid of process. The thermodynamic parameters particularly enthalpy change (ΔH) and two the entropy alternate (ΔS) can be calculated from the slope and intercept of the straight line plotted by means of $\ln kD$ versus $1/T$. The Gibbs free energy change (ΔG) we decided at 25, 35, 45 °C. The obtained thermodynamic parameters (ΔG , ΔH , ΔS , and E_a) have been listed in Table (9).

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

Molarity (mol/L)	t (s)	ΔG (KJ/mol)	ΔS (J/mol.K)	ΔH (KJ/mol)	A	Ea (KJ/mol)
ACIDIC MEDIUM (HCl)						
0.005 M	25	8976.715	-53.710	-7038.11	1.7x10 ¹⁴	68757.39
0.005 M	35	9484.791				
0.005 M	45	10052.194				
0.025 M	25	10610.338	-36.646	-1818.63	8.6x10 ¹⁸	99957.65
0.025 M	35	6245.656				
0.025 M	45	11552.528				
0.050 M	25	11615.088	-4.860	9879.16	1.7x10 ²⁶	148765.60
0.050 M	35	10761.386				
0.050 M	45	11752.194				

3.9. Studies 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 a basic medium according to the Langmuir, Freundlich, Temkin, and Dubinin- Redushkevich (D-R) models as in the Table (10).

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

Langmuir parameters				Freundlich parameters			
		B	RL	R ²	N	kf (mg/g)	R ²
BASIC MEDIUM (NH₄OH)							
0.001 M	11.061946	-0.73917	-0.00504	0.9984	-15.7233	14.69265	0.9535
0.003 M	11.248593	-0.85072	-0.00438	0.9988	-15.6006	14.79449	0.9115
0.005 M	11.350737	-1.20850	-0.00308	0.9998	-13.1406	15.23702	0.9631
Temkin parameters				D-R parameters			
	AT	BT	R ²	B	q ₀ (mg/g)	E	R ²
BASIC MEDIUM (NH₄OH)							
0.001 M	9.86374	-0.7882	0.9565	4.4x10 ⁻⁰⁷	12.04802	1118.0340	0.5858
0.003 M	1.02051x10 ⁻⁰⁶	-0.7948	0.9213	5.4x10 ⁻⁰⁷	11.97954	1000.000	0.6410
0.005 M	6.03274	-1.0558	0.9758	1.4x10 ⁻⁰⁶	11.20993	707.1068	1.0000

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

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					
	k_1	$q_{e,2}$	K_2	H	R^2	t		
BASIC MEDIUM (NH₄OH)								
0.001 M	1.525808	0.02280	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	7.00003	0.043527	0.9121	12.61034	0.011452	1.821162	0.9994	35
0.005 M	0.457299	0.00783	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)	$t_{0.5}$	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

In the studies of the kinetics of the removal of Al(III) by modified chitosan in a basic

medium at the different temperature, we obtained the thermodynamic parameters (ΔG , ΔH , ΔS and E_a) as illustrated in the following Table (13).

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

Molarity	t	ΔG	ΔS	ΔH	A	E_a
BASIC MEDIUM (NH₄OH)						
0.001 M	25	9369.434	-117.701	-25182.300	1019.313	-27118.111
0.001 M	35	12204.487				
0.001 M	45	11650.495				
0.003 M	25	10090.634	-132.712	-30034.2	266808.703	41771.421
0.003 M	35	9632.624				
0.003 M	45	11601.023				
0.005 M	25	9468.004	-103.711	-12276.0	1179.821	27908.932
0.005 M	35	8027.723				
0.005 M	45	12824.414				

Conclusion

From the current study, it can be concluded that the chemical modification of Chitosan with the different organic compounds and polymeric materials can lead to promising materials in the light of their application directions. In this work, the modification of Chitosan adsorbent was prepared and characterized by FTIR and SEM to confirm the functional groups and the morphological structure, respectively. The obtained results showed that the optimum adsorbent dose was 2 g/l at pH of 3.5 and equilibrium time of 60 min. The adsorption kinetics of aluminum ions onto modified Chitosan followed the Langmuir model well fitted the pseudo-second order model and the adsorption isotherm. The maximum adsorption capacity of the adsorbent was 166.98 mg/g, and the equilibrium parameter (RL) at different concentrations was less than unity indicating the adsorption of aluminum ions onto Modification of Chitosan is favorable.

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