

Synthesis, Characterization and Kinetic Study of poly(vinyl acetate)-g-Chitosan and its Use in Removal of Cadmium (II) ions from Water

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Abstract

The grafted vinyl acetate copolymerization lying on chitosan in weak acidic aqueous solution was examined via using $K_2S_2O_8$ as initiator. FTIR spectra, DSC, DTG and TGA were used for graft polymer characterizing. The monomer to chitosan ratio was tested and the optimal grafting conditions were affixed. The highest grafting percentage PG of production polymers have been applied to remove Cd(II) ions from water samples through adsorption experiments at pH=7. The amounts of adsorbed metal ion on the polymers was estimated using atomic absorption spectrophotometer. The temperature effect on Cd(II) adsorption was studied too. Langmuir and Freundlich isotherms as well as kinetic study equations were employed to fit the experimental data. The results of the adsorption equilibrium for Cd(II) fitted well to Langmuir isotherm and the removal percentage at 30°C after 5 min is 76.65 % and the thermodynamic parameters for the adsorption are $\Delta H= 96.87$ kJ/mol $\Delta S= 339.19$ J/mol K and $\Delta G= -5.11, -11.13$ and -11.78 kJ/mol in different temperatures. The kinetic study of these adsorption isotherms showed that all these isotherms correlates well with the second order equation.

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Keywords: Adsorption, Chitosan, Graft Copolymerization, Kinetics, Water treatment.

1-Introduction

Chitosan is a nontoxic, semicrystalline, biodegradable, and biocompatible linear polysaccharide of arbitrarily connected β -(1 \rightarrow 4) linked D-glucosamine de-acetylated units also N-acetyl D-glucosamine, acetylated units which signify as homo-polymer [1-4]. The wonderful chemical, biological as well as pharmaceutical chitosan uses have concerned notice to the achievable value of chitosan-grafted polymers in diverse fields such drug delivered system [5], hydrogel formation [6], and wastewater treatment [7]. So chitosan has possible uses variety as of biomedicine also pharmacy to water treatment.

Chitosan is a weak base and easy bio-adsorber with a very good gel formation capacity, and it has together reactive hydroxyl and amino groups that were applied to modify its chemical characteristics [8].

Adsorption is a specific interactions between an adsorbent like a component to be adsorbed on the adsorbate surface [9,10]. These interactions are highly related to the chemical structure of chitosan or its functional, which are able to make interactions through hydroxyl and amine groups are tending to be

ionized, as a function of pH (pKa in the range 6.0–6.7). In that case, the chitosan amine group in will be active as a poly-cationic and bind with electrostatic interactions or ion exchange. In addition, when the amine groups are non-ionized, nitrogen atoms which have a free electron pair tend to interact with cations as an electrons poor species. It may be interact with hydrophilic, charge anionic or cationic and natural species, the basic structural factors in the acetylation degree [11] a definite amiphilic character owing to the acetyl groups presence has been mention [12] addition the interaction possibility with species presenting a little hydrophobic nature.

This work aims to study and reports the adjustment of chitosan via grafted vinyl acetate monomer and investigate the effects of monomer ratio to chitosan. TGA, DTGA & DSC thermal analyses and FTIR were applied for the identification of polymers synthesis. Although, the adsorption of Cd(II) ions on synthetic polymer has been examined characterization of prepared polymers. Also the adsorption of Cd(II) onto prepared polymer via batches experiments at several contact time and temperature at pH=7 buffer solution. The

total ion adsorbed on the new synthetic polymers was estimated via atomic absorption spectrophotometer.

2-Experimental

2.1. Materials

All reagents as well as compounds were locally obtained also used without any purification. Solvent used in this work were distilled from the appropriate drying agent immediately prior to use.

2.2. Measurements

FTIR spectroscopy for Polymers were obtained using Shimadzu 8400S FTIR in a wave number ranged between (4000–800 cm^{-1}). TGA, DTG & DSC for polymers thermal analyses were achieved at R.T. under argon inert conditions; flow rate 10 mL/min, heating rate=5°C/min using Linseis STA PT-1000. Atomic absorption spectrophotometer. data were completed with Phoenix-986 AA spectrophotometer. Samples were shaken and thermostated using BS-11 thermostated shaker.

2.3. General Synthetic procedure

2.3.1. Graft Chitosan copolymerization by vinyl acetate:

Grafting reaction was completed in 250 ml round bottle flask by dissolving 1g chitosan in 60ml of 2% acetic acid with overnight stirring at R.T. followed by reflux to 70°C then 0.135g, 0.5mmol of potassium persulfate was added after 15min, diverse amounts of monomers was adding to the mixture for 180min. The mixture was treated with methanol to precipitate the polymer then washed with methanol too followed by drying under vacuum oven. The dried polymers were extracted using 40:60 methanol: water mixture for 24hrs to remove the homo vinyl acetate polymer.

2.4. Adsorption study

2.4.1. Adsorption of cadmium(II) ions on the vinyl acetate grafted Chitosan:

Cadmium (II) adsorption on grafted chitosan polymer resin was examined using batches method. 0.1g of each dry grafted polymers was placed in 15ml of pH=7 phosphate buffer solution (potassium dihydrogen phosphate and sodium hydroxide)

for about 1hr with continuous shaking until equilibrate.

An accurate 15ml of standard Cd solution (400, 300, 200 and 100 mg/L). The mixture was shaken at 30 °C for precise time. Each sample was filtered and the total Cd(II) ions remain in the solution was estimated via AAS at λ 228.8nm using Cd(II) ions standard curve. The temperature effect on the Cd(II) adsorption was examined by repeating the procedure again at 40 and 50 °C temperatures [13].

3-Result and discussions

3.1. Synthesis of Chitosan grafted vinyl acetate

A grafted copolymer is a series of macromolecular chain with one or more block connected to the main chain as side chain(s) [14]. Chitosan was grafted by vinyl acetate in aqueous weak acidic solution by applied $\text{K}_2\text{S}_2\text{O}_8$ as initiator.

Synthetic route for the preparation of chitosan grafted vinyl acetate polymer was shown in Scheme (1).

3.2. Polymerization parameters effects on percentage of grafting of Chitosan graft polymer

3.2.1. The monomer concentration

The monomer concentration effect on the vinyl acetate grafting on chitosan was tested, then the grafting percentage was determined as follows:

$$PG = \frac{W_P}{W_A} \times 100 \dots\dots\dots (1)$$

Where PG: is the grafting percentage %, W_P is the weight of polymer result, W_A is the vinyl acetate weight. The grafting percentage (PG) was established on the monomer amount to chitosan and found= 16.19 %, 33.73 % and 47.39 % which are represented in Fig.(1).

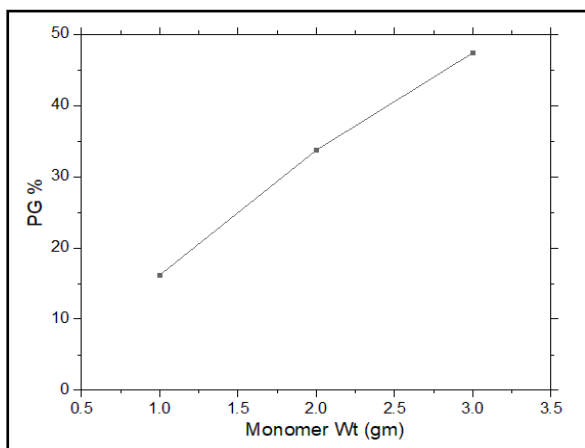


Fig.(1): Effect of monomer on percentage grafting % of grafted copolymer; Chitosan=1g, PPS =0.3mmol, t =180 min, T=70 °C.

3.3.Characterization of Chitosan grafted vinyl acetate:

FTIR, TGA, DTG and DSC thermal analyses were applied for the identification of synthetic graft copolymer. FTIR spectrum, of graft copolymer, Fig.(2) illustrate typical band at 1732.13cm^{-1} , which allocate to the carbonyl ester group vibrational stretching in grafted chain. This band was sited at 1757.21cm^{-1} in the spectrum of vinyl acetate monomer Fig.(3). This lower frequency shifting is owing to inter and/or intra molecular interactions through hydrogen bonding. Naturally the insolubility of graft polymer in spite of containing a large number of ester groups is produced by the crosslinking [15], $1556.61\text{--}1573.97\text{ cm}^{-1}$ due to (COO^-) vibrations of free acetic acid. Further details of the other bands and their assignment are summarized in Table (1).

The DSC thermogram, Fig.(4) showed two endothermic peaks at 83.3°C and 237.8°C are due to the evaporation of adsorbed and bound water [16] as well as the temperature glass transition (T_g) respectively, furthermore one exothermic peak of chitosan at 293.6°C , which may matched to the polysaccharide decomposition [17].

While, poly(vinyl acetate)-g-chitosan DSC curve, Fig.(5) showed an endothermic peak at 87.6°C correlated to the adsorbed also bound water evaporation in the polymer with another endothermic peak at 243.7°C related to the glass transition grafted copolymer temperature (T_g) Furthermore, two endothermic also exothermic peaks at 307.7°C and 339.4°C may

due to grafted copolymer decomposition. Whereas, two endothermic also exothermic peaks at 426.8°C and 490.2°C respectively, may due to the decomposition of poly vinyl acetate chains grafted to chitosan, these peaks are powerful signify about the grafted formation.

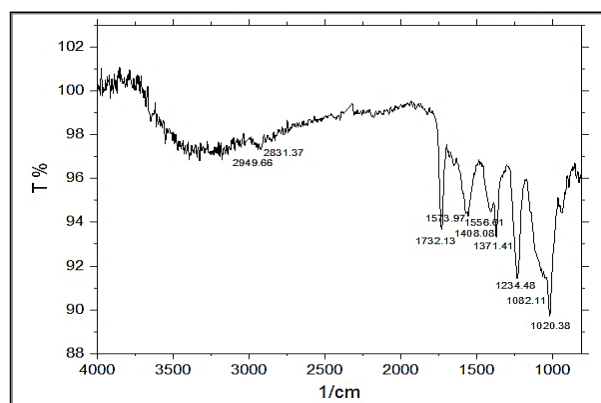


Fig.(2): FTIR spectrum of poly (vinyl acetate)-g-Chitosan.

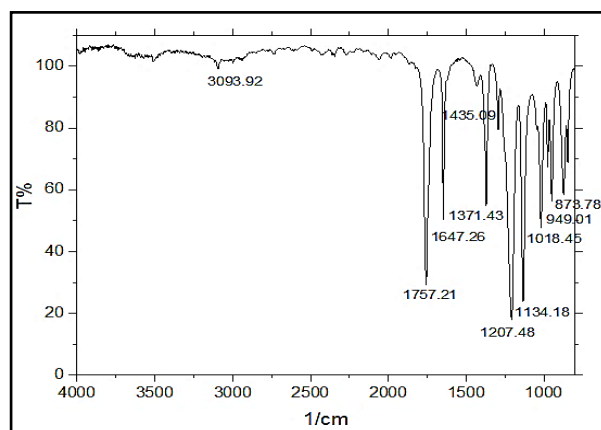
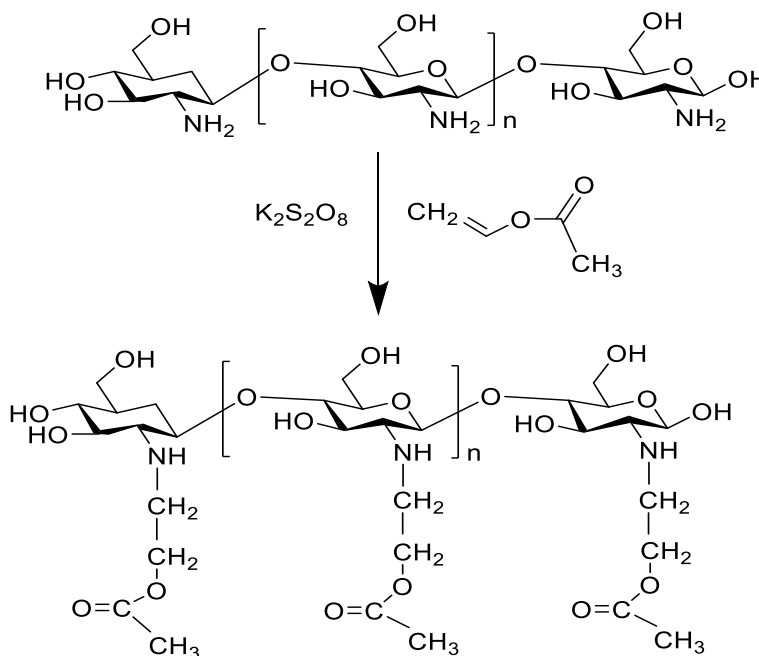


Fig.(3): FTIR spectrum of vinyl acetate.

Table (1)
IR spectral data of poly(vinyl acetate)-g-Chitosan.

$\nu(N-H)+(O-H)$ (Hydrgen bonding) (cm^{-1})	$\nu(CH_2)$ (asymmetric) (symmetric) (cm^{-1})	$\nu(C=O)$ (cm^{-1})	$\delta(O-H)$ $\delta(C-H)$ wagging (cm^{-1})	$\nu(C-O-C)$ (Aymmetric) (Symmetric) (cm^{-1})	$\nu(C-O)$ grafted chains (cm^{-1})
(3120–3640)(br.)	(2949.66)(w) (2831.37)(w)	(1732.13)(s)	(1408.08)(m) (1371.41)(s)	(1082.11)(s) (1020.38)(s)	(1234.48)(m)

ν =stretching, δ =bending, s=strong, m=medium, w=weak, br.=broad



Scheme (1): General route of Chitosan grafted vinyl acetate.

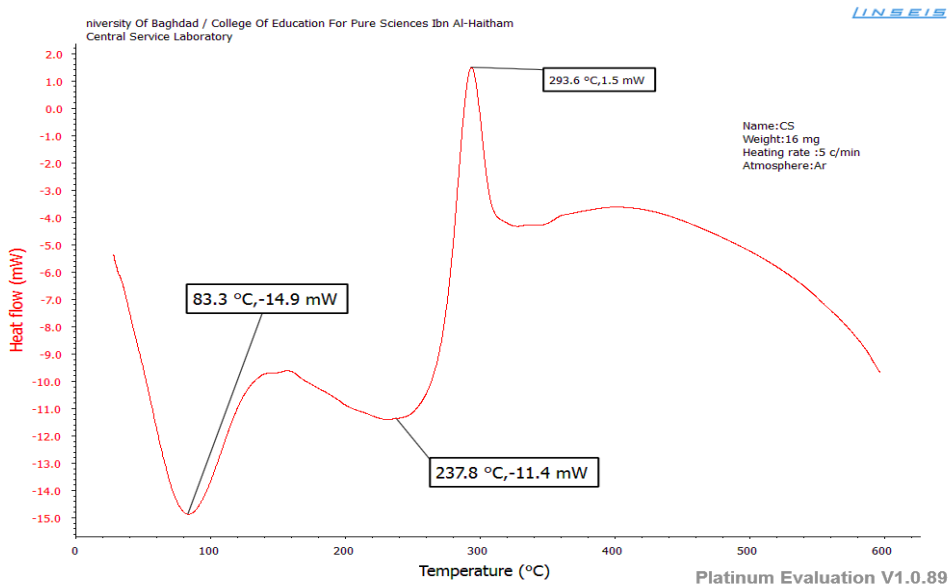


Fig.(4): DSC thermogram of pure Chitosan.

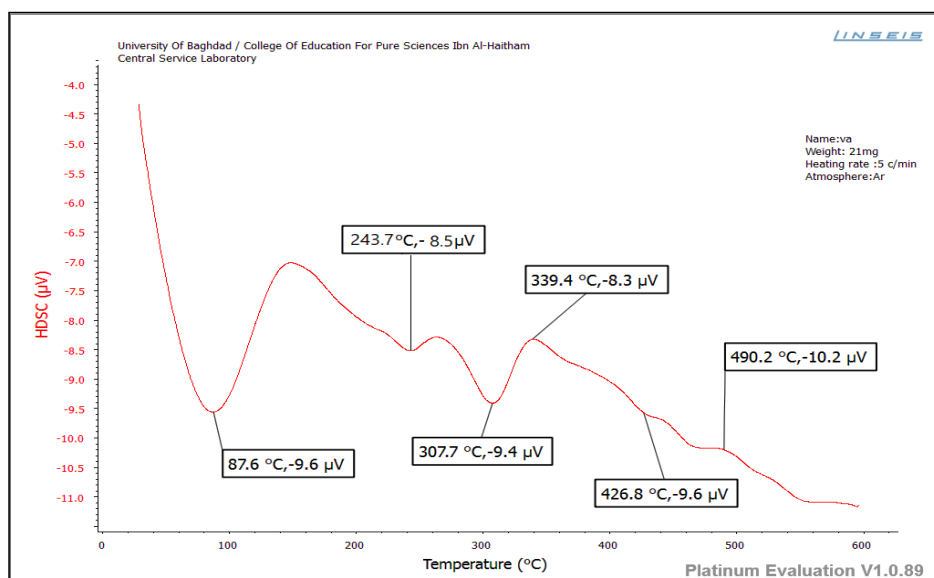


Fig.(5): DSC thermogram of poly(vinyl acetate)-g-Chitosan.

The DTG and TGA of pure chitosan, Fig.(6) exhibited two stages of different weight loss between 60°C and 597.062°C. The first stage ranges from 60°C to 222.505°C with 10.53 % weight loss of the adsorbed and bound water. The second stage of weight loss starts at 222.505°C and that keep on 597.062°C through $T_{max} = 290^{\circ}\text{C}$ with 65.355 % of weight loss owing to the chitosan degradation [18].

While, DTG and TGA curve of poly vinyl acetate Fig.(7) showed four stages of diverse weight loss between among 60°C and 596.402°C. The primary first stage ranges from 60°C to 199.787°C with 2.922 % weight loss may related to the adsorbed also bound water loss.

The second stage of weight loss initiates at 199.787°C and 277.311°C with 14.57% of weight loss owing to ungrafted chitosan degradation. A 56.112 % weight losses in the third stage between 277.311°C to 382.675°C through $T_{max} = 316^{\circ}\text{C}$ that contributes to the decomposition of chitosan grafted copolymer. So, it is evident that grafting vinyl acetate onto chitosan could enhance the stability of pure chitosan at higher temperature. There is 13.245% weight loss in the fourth stage from 382.675°C to 596.402°C that contributes to the decomposition of poly vinyl acetate chains grafted to chitosan.

3.4 Calibration curve of Cd(II) ions

A working calibration graft for Cd(II) ions quantitative analysis was create and valid by AAS at λ 228.8nm using standard solutions in the concentration range 0.2 mg/L to 0.8 mg/L in buffer pH=7 aqueous solution, Fig.(8).

3.5. Rate of Cd(II) ions adsorption as a function of equilibrium time

The synthetic polymers have a maximum grafting percentage were chosen to study their ability for Cd(II) ions removals from aqueous samples. The interaction rate of Cd(II) ions with polymer was examined via batch method at several contact or equilibration time at pH= 7, Fig.(9). The results showed that a usual reliance on Cd(II) ions absorbed with contact time, also illustrate a fast equilibration rate within 76.65 % Cd(II) ions ions absorbed were attained after 5 min and get to a steady state within 1 hr.

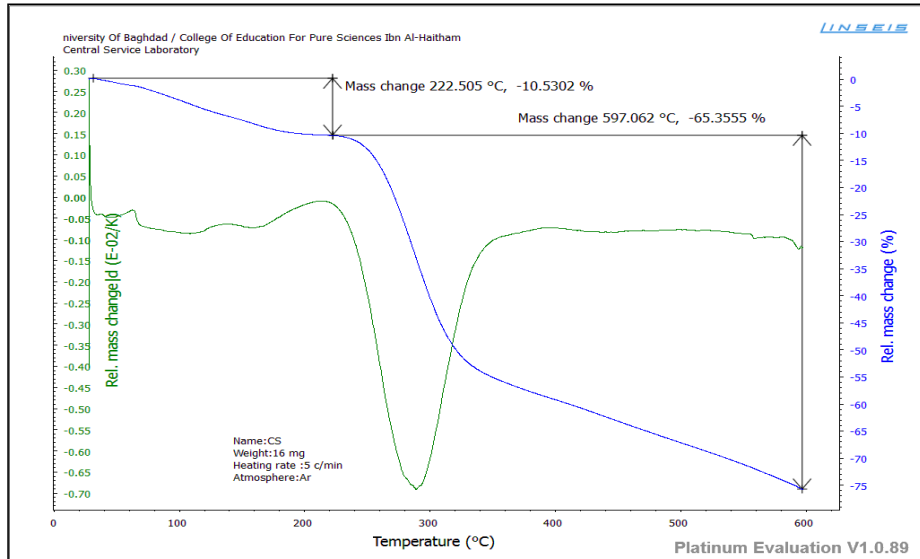


Fig.(6): DTG and TGA thermogram of pure Chitosan.

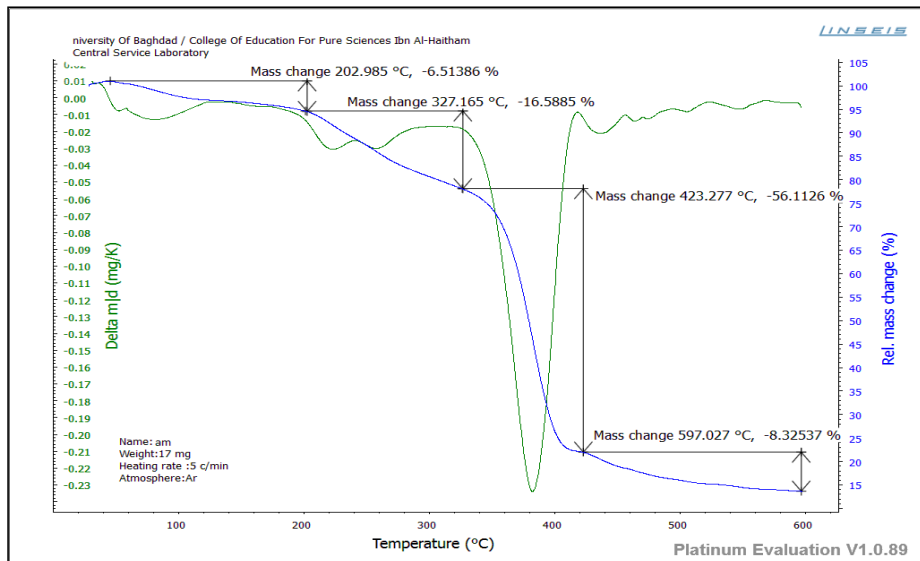


Fig.(7): DTG and TGA thermogram of poly(vinyl acetate)-g-Chitosan.

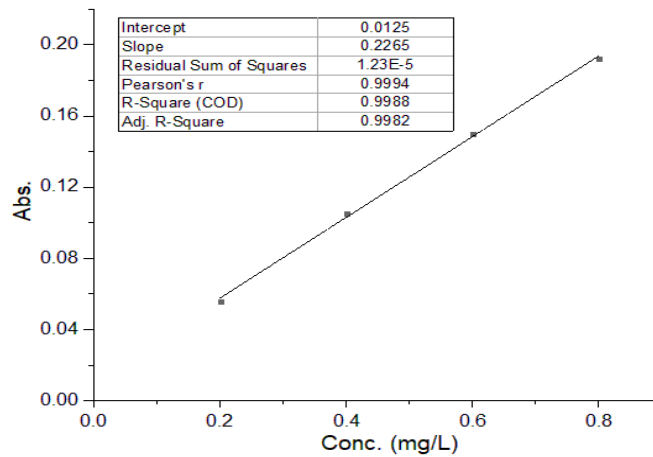


Fig.(8): Calibration curve for Cd(II) ions.

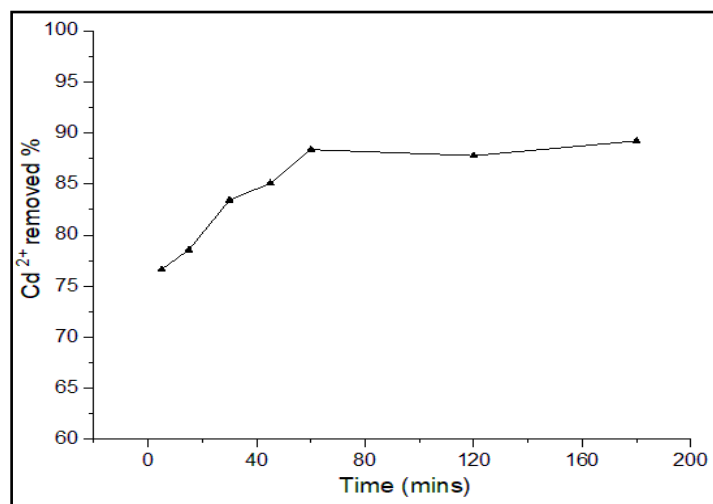


Fig.(9): Removal percentage of Cd(II) ions by the graft copolymer with time.

3.6. Modeling isotherms

Fig.(10) showed the adsorption isotherm of grafted copolymer, the isotherm graphs are like L type isotherm, this indicate that the adsorbate (Cd(II) ions) undergoes a high sorption on to the adsorbent surface in very high concentration of Cd (II) ions.

Langmuir and Freundlich isotherms are the common adsorption models applied to explaining the experimental data [19]. Langmuir model suppose that the equilibrium was achieved after the formation of monolayer of the particles adsorbate formed on the adsorbent. The form of the linear Langmuir model was set as:

$$\frac{C_e}{Q_e} = \frac{1}{b Q_o} + \frac{1}{Q_o} C_e \dots\dots\dots (2)$$

Where C_e is equilibrium adsorbate concentration, Q_o is Langmuir constant associated to adsorption capacity while b : constant correlated to the affinity among the adsorbent also the adsorbate. The Q_o and b values were estimated by plotting C_e/Q_e vs. C_e . Where Q_e is the quantity of adsorbate uptake for each component adsorbent weight at equilibrium:

$$Q_e = \frac{(C_o - C_e)V}{W} \dots\dots\dots (3)$$

Where C_o : is the initial adsorbate concentration, V : the volume of solution, W weight of dry resin. The Langmuir isotherm characteristics are able to express as a dimensionless equilibrium parameter term, R_L [20]:

$$R_L = \frac{1}{1 + b C_o} \dots\dots\dots (4)$$

The value of (R_L) indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The practical Freundlich isotherm is a major significant multi-site adsorption isotherm for heterogeneous surfaces. It assumes an initial surface adsorption followed by the condensation effect resulting from extremely strong solute-solute interaction. The linear form of Freundlich model is as follows equation:

$$\text{Log } Q_e = \text{Log } K_F + \left(\frac{1}{n}\right) \text{Log } C_e \dots\dots\dots (5)$$

Where K_F is Freundlich isotherm constant and correlated to maximum adsorption capacity. n is a Freundlich isotherm exponent constant which gives an indication of how favorable the adsorption process is [21]. The K_F and n values were achieved by plotting $\text{Log } Q_e$ vs. $\text{Log } C_e$. Langmuir and Freundlich models were applied to fit the testing results, Figs.(11) and (12), which illustrate excellent fit of the testing results for Langmuir isotherm at 40°C and 50°C compared to Freundlich isotherm model and correlates well with both Langmuir and Freundlich equations at 30°C. The results confirmed that the Cd(II) ions adsorption by grafted copolymer is distinguished by monolayer coated the Cd(II) ions on the external adsorbent surface of the synthetic polymer also the adsorption process had the same activation energy for all

adsorbed particals. Additionally, the separation factor values R_L found are ranged among $0 < R_L < 1$ which indicates a favorable Cd(II) ions adsorption on the polymers particles Fig.(13.) Thermodynamic function; ΔG° , ΔH° and ΔS° for the adsorption route was obtained using the following equation [22]:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (6)$$

Where R is the common gas constant, T: is the absolute temperature of the solution also K_d is the distribution coefficient which be achieved through:

$$K_d = \frac{C_{AE}}{C_e} \dots\dots\dots (7)$$

Where C_{AE} is the equilibrium amount adsorbing on the polymer also C_e is the equilibrium concentration. A plot of $\ln K_d$ versus $1/T$. produced a direct line used for find the ΔH° and ΔS° from the slop also the intercept correspondingly. ΔG° was obtained using the lower equation:

$$\Delta G^\circ = - RT \ln K_d \dots\dots\dots (8)$$

The obtained values of standard enthalpy ΔH° and standard entropy ΔS° of graft copolymer are 96.87 kJ/mol and 339.19 J/mol K respectively. The positive ΔS° values indicate the affinity of vinyl acetate grafted chitosan for adsorbates such as Cd(II) ions as a result of the increased randomness at the interface between the solid liquid phases.

The values of ΔG° are -5.11 KJ/mol at 30°C, -11.13 KJ/mol at 40°C and -11.78 KJ/mol at °C which demonstrate that the ΔG° value decreases with the temperatures increases. This indicates the spontaneous nature and feasibility of the process [23].

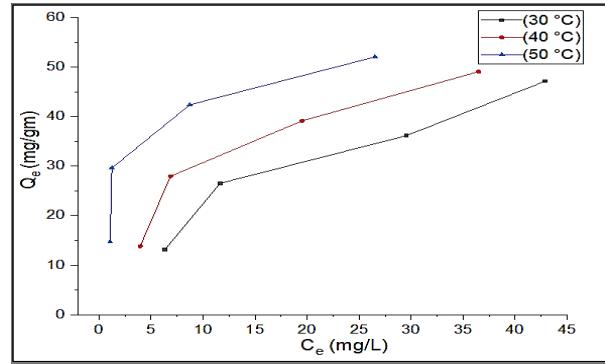


Fig.(10): Cd(II) ions Adsorption isotherm by grafted copolymer at different temperatures.

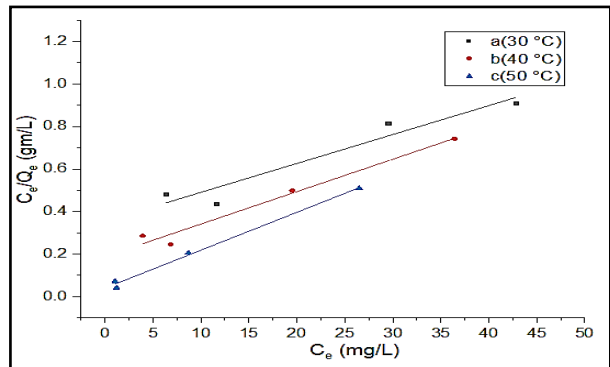


Fig.(11): Linearized Langmuir equation for Cd(II) ions uptake with grafted copolymer at different temperatures.

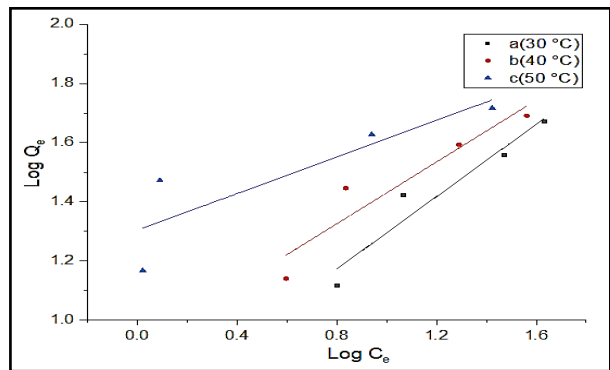


Fig.(12): Linearized Freunlich equation for Cd(II) ions uptake with grafted copolymer at different temperatures.

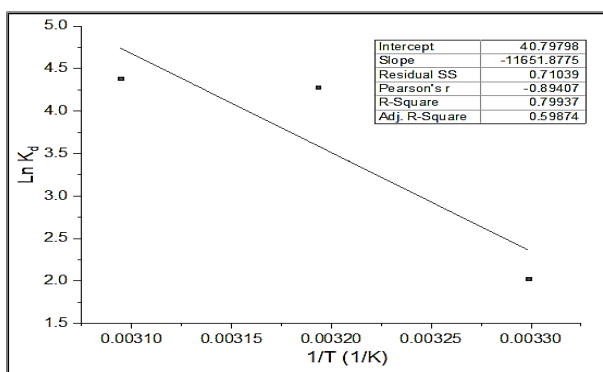


Fig.(13): Variation of thermodynamic parameters through temperature for the of Cd(II) ions adsorption on grafted copolymer.

3.7 Kinetic study

To illustrate the adsorption kinetics of graft copolymer, correlations of adsorbed amounts with time required through the investigation of special statistical expressions related to different models, which are first and second order equation [24].

3.7.1 First order equation

The first-order equation was commonly applied for the solute adsorption from liquid solution. The equation rearranged and linear it reads:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \dots\dots\dots (9)$$

Where k_1 is the kinetic constant related to first-order adsorption, whereas Q_e and Q_t are the graft copolymer amounts be adsorbed at equilibrium also at t time. A graph of $\ln(Q_e - Q_t)$ versus t produced a linear line.

3.7.2 Second order equation

The second-order equation expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \dots\dots\dots (10)$$

Where Q_t and Q_e have the similar meaning as before, k_2 is the related kinetic constant.

A draw of t/q_t against t gives a slope line of $1/Q_e$. The kinetic study of these adsorption isotherms showed that all have a good correlated through the second order equation according to their determination coefficient, Figs.(14) and (15).

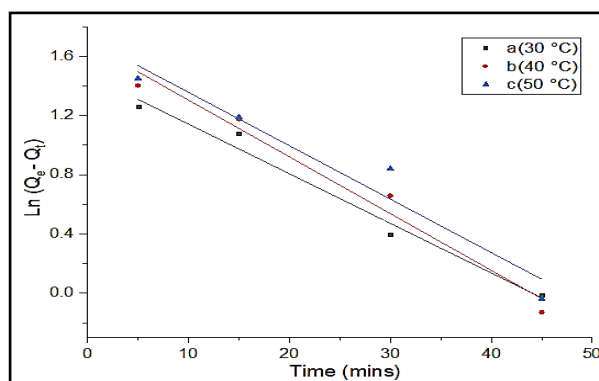


Fig.(14): Kinetic study for Cd(II) ions uptake on grafted copolymer by using of first order equation.

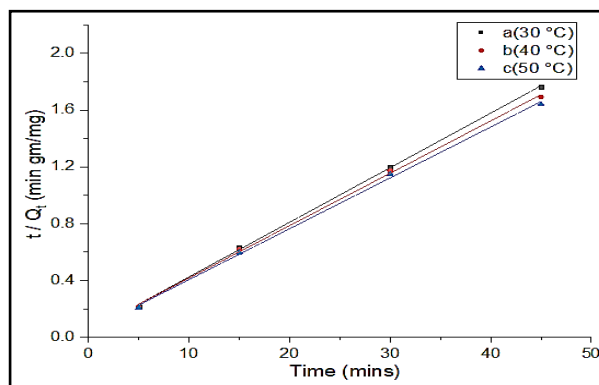


Fig.(15): Kinetic study for Cd(II) ions uptake on grafted copolymer by using of second order equation.

Conclusions

Poly(vinyl acetate)-g-chitosan was prepared by a copolymerization reaction between chitosan and vinyl acetate monomer. Grating percentage PG found to be increase with increasing of the monomer concentration PG polymer was used to study the sorption of Cd(II) ions at different concentrations, temperatures and pH=7. In all cases, the adsorption kinetics could be very satisfactorily fitted by a second-order equation. All the adsorption isotherms could be very well adjusted by Langmuir's equation, but we found that the adsorption isotherm at 30°C was correlates well with both Langmuir and Freunlich equations. Results show that for the same equilibrium concentration on the loading capacity of the adsorbent increases with the increasing of temperature. It is confirmed the endothermic nature of Cd(II) ions adsorption onto grafted copolymer. The adsorption nature happened in monolayer with a very fast adsorption.

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