REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO MODIFIED CELLULOSE: EQUILIBRIUM, KINETICS AND THERMODYNAMICS STUDY

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ABSTRACT

Cellulose dialdehyde has been prepared and reacted with thiosemicarbazide to give thiosemicarbazone modified cellulose (CTSC). A new and a relatively green methodology have been developed for the selective separation of Ga (III) and In (III) ions. The batch removal of Ga (III) and In(III) from aqueous solution under different experimental conditions using economic adsorbent were investigated in this study. The effects of Ga (III) and In (III); initial concentration, contact time, adsorbent dosage, solution pH and temperature on CTSC adsorption were investigated. Ga (III) and In (III) adsorption uptake were found to decrease with increase in initial concentration, contact time and increase with the increase in temperature solution, whereas adsorption of Ga (III) and In (III) were more favorable at acidic pH 2.5 for Ga (III) and (2-2.5) for In (III). The isotherm results were analyzed using the Langmuir, Freundlich and Temkin isotherms. The pseudo-first order and pseudo-second order equations are applied to model the kinetics of Ga (III) and In (III) ions adsorption onto CTSC kinetic model. Thermodynamic parameters such as standard enthalpy (ΔH), standard entropy (ΔS), standard free energy (ΔG) were determined. A single stage batch adsorber was designed for adsorption of Ga (III) ions from aqueous solutions based on the optimum isotherm, and the treated volume was calculated for different initial concentrations for Ga (III).

1   INTRODUCTION

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava &Majumder, 2008) With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. An increase in population initiating rapid industrialization was found to consequently increase the effluents and domestic wastewater into the aquatic ecosystem. Thus, the treatment of wastewater containing heavy metals has become a major concern. Among the various metals, Ga(III) and In(III) are widely distributed in the earth's crust and water system and present toxic manifestations when ingested by living systems (Bailar et al, 1973).These elements find several uses in industry. Gallium is used in electronic devices, especially in the manufacture of gallium arsenide laser diodes, semiconductors and superconductors. It has applications in aerospace, shipbuilding, cryogenics, medicine, atomic reactors and electronic industry. Tooth decay, pain in joints and bones, nervous and gastrointestinal disorders, heart pain and general disability are the effects of excessive exposure or

ingestion of Ga(III) or In(III), is a well-known poison and its action is cumulative. It causes polyneuritis, convulsion, coma and even death (Bailar et al, 1973). Low concentrations of Ga(III) and In(III) are not easily detected and high levels of potentially interfering constituents preclude their direct determination. Various preconcentration tools are employed prior to their analysis (Zhang et al, 2003). Liquid-liquid extraction (Rydberg et al,1992) is effective for separation and preconcentration of cations, including these metals. Several researchers have studied the fundamental extraction behavior and the mutual extractive separation of trivalent group 13 metal cations using many kinds of extractants (Horiguchi et al, 2002; Liu et al 2006) . In spite of its versatility, multi-stage extraction procedures, disposal of large volumes of organic wastes and expensive treatment are the main problems. Solid phase extraction (SPE) has major advantages over liquid-liquid extraction, including the fast, simple, direct application in micro level, no waste generation, low risk of contamination, time and cost-saving. Modified resins containing methylene-diphosphonate (Alexandratos et al, 1996) ,carboxy methylphosphonate (Trochimczuk, &Jezierska 1997), substituted malonamides (Trochimczuk 1998) and substituted phenylphosphinic acid (Trochimczuk, 2000) have been applied for the separation of Ga(III) and In(III). The use of many of the solvent extraction techniques has been limited because they are expensive, often require long process times, and cause the release of toxic materials. Cellulose, which is a naturally occurring complex polysaccharide, is biodegradable and the most abundant renewable organic raw material at low costs in the world. Modification of cellulose by graft copolymerization and direct chemical modification techniques allows one to chemically change the cellulose chain by introducing functional groups, which leads tonew cellulose products with new properties (Mansour et al, 2015).

   This paper reports on the use of modified cellulose to remove Ga(III) and In(III) from aqueous solutions. The effect of metal ions concentrations, adsorbent dosage, pH, temperature, contact time, adsorbent pretreatment is discussed.

2   MATERIALS AND TECHNIQUES

2.1. Buffered solution

   Hydrochloric acid, sodium hydroxide and the other reagents were analytical grade (BDH Chemicals Ltd. Poole, England). Solutions of pH 1- 8 were prepared by using hydrochloric acid (0.1M) in double distilled water and adjusting the solutions to be required value with sodium hydroxide (0.1M).

2.2. Preparation of the adsorbent

   Microcrystalline cellulose (Sigma-Aldrich) with a particle size 51 μm was used. The cellulose derivate; dialdehyde cellulose (DAC) can be produced by employing periodate as an oxidizing agent. During the periodate oxidation, selective cleavage of the C2-C3 bond of the cellulose occurs, and two aldehyde groups are formed "Fig.1". (David William O'Connell et al, 2008). Cellulose is stirred in a 0.5% $NaIO_4$ solution for 6h. The precipitate is washed with bidistilled water with six times (30 ml for each time) and dried. Chemical immobilization with thioseemicarbazide (CH_5N_3O) was performed as in our previous work (Mansour et al, 2015;) and (David William et al 2008).
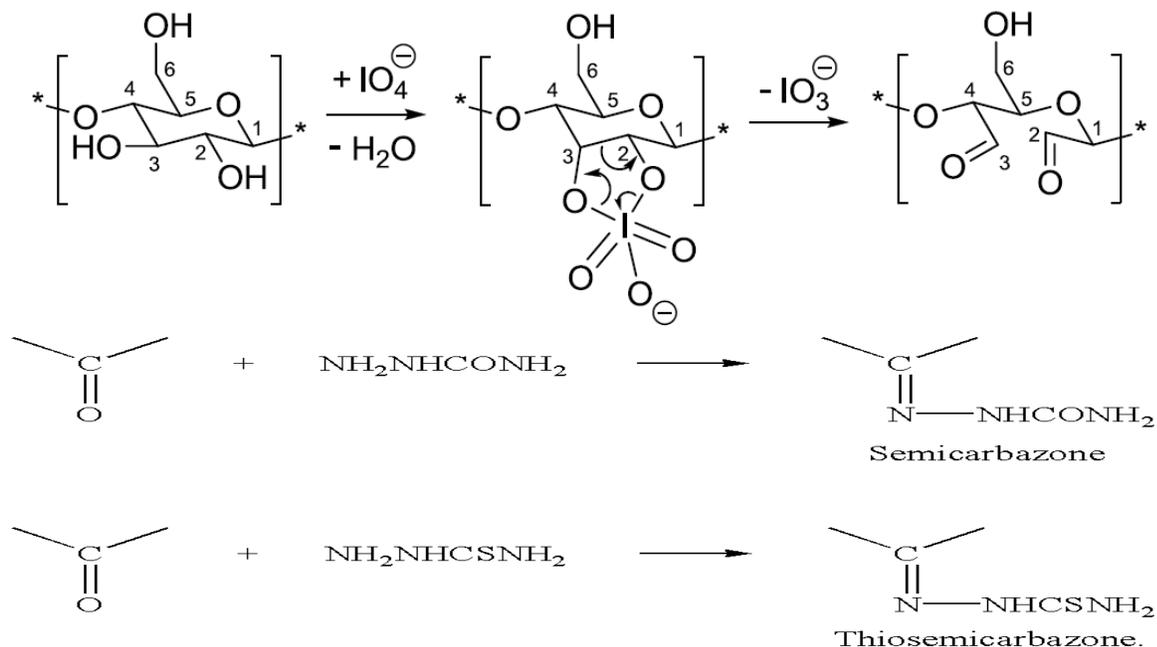
Figure 1.Oxidation of cellulose by periodate followed by formation of thiosemicarbazone

2.3.Preparation of adsorbate

A stock solution of In (III) (1000 µg ml^{-1}) was prepared by dissolving 1g of In (Aldrich) in 5ml concentrated nitric acid, the mixture was evaporated till dryness and then another 3ml were added and the volume was completed to 1L with bidistilled water. Here a 1000µg ml^{-1} solution of Ga(III) was prepared by dissolving 1g of Ga (Aldrich) in aqua regia (3ml HCl: 1ml HNO$_3$) and the mixture was diluted to 1L of bidistilled water. (Mohammad M. Hassanien, et.al 2007)

2.4.Instrumentation

The electronic spectra and the absorbance measurements of the Ga^{3+} ion with xylenol orange (Makoto Otomo, 1965) at λ_{max} = 573 nm and In^{3+} with 1-(2-pyridyl methylidene amine)-3-(salicylideneamine) thiourea is proposed (Rosales et al, 1986) at λ_{max} = 520 nm were recorded using computer – controlled double beam UV–Vis spectrophotometer UV -2401 PC (Shimadzu, Japan) with quartz cell (10 mm). The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with accuracy of ±0.01 and standardized with variable mechanical shaker (Corporation Precision Scientific, Chicago, USA) with constant speed of 240 rpm. A simulated wastewater contaminated by Ga (III) and In (III) were used for all experiments in this study. Synthetic stock solutions were prepared by dissolving accurately weighed amounts of Ga (III) and In (III) ions (1gm) in one liter of double distilled water to form a stock solution (1000ppm) and a stock solution was diluted to the required initial concentration (range: 25 to 300 mg/l) for both heavy metal ions.

2.5.Experimental technique

Adsorption studies were performed by the batch technique to obtain equilibrium data. The batch technique was selected because of its simplicity. Batch experiment was carried out at various pH (1-8), adsorbent dose (0.01 – 0.1g) and stirring speed (240 rbm) for a contact time of 20 min for Ga^{3+} and 30 min for In^{3+}. For each batch experiment, sample solution (100 ml) containing 50 µg ml^{-1} of the studied metal ion was transferred to a 250 ml stopper glass bottle. After setting pH and added desired amount of

adsorbent (50mg) the mixture was agitated on mechanical shaker for optimum time at 25^0C, after that the mixture was filtered to separate the adsorbent from supernatant. The residual concentration of metal ions in supernatant was determined by UV – vis spectrophotometer. The removal percentage (R%) of the studied metal ions were calculated for each run by the following expression:

$$\% \text{ Removal} = \left(\frac{c_i - c_f}{c_i} \right) * 100 \tag{1}$$

Where C_i and C_f are the initial and final concentration of studying ions (Ga^{3+} and In^{3+}) in the solution (mg/l).

2.6. Adsorption isotherms study

The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume V is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of Ga (III) and In (III) at equilibrium were calculated using equation (2):

$$q_e = (c_i - c_{e)} \times \frac{V}{m} \times 10^{-3} \tag{2}$$

where, q_e represents the amount of metal uptake per unit mass of adsorbent (mg/g) at equilibrium time, v is the volume of test solution (l), m is the mass of dry adsorbent (g), Ci and Ce are the concentrations of metal ions in mg/l at initially and at equilibrium, respectively. The equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature. Freundlich, Langmuir and Temkin isotherms are the earliest and simplest known relationships describing the adsorption equation (Muhamad et al, 1998; Jalali et al, 2002). Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorption and desorption, while others are purely empirical and intended to correlate the experimental data in simple equations with two or at most, three empirical parameters: the more the number of empirical parameters, the better the fit between experimental data (Motoyuki, 1990). Several isotherm models are available to describe this equilibrium sorption distribution.

2.6.1. Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by (Gesgel et al, 2003;   Khambhaty Y et al 2009):

$$q_e = (q_m K_L C_e) / (1 + K_L C_e) \tag{3}$$

The linearised form of the above equation after rearrangement is given by:

$$\frac{c_e}{q_e} = \frac{1}{q_m} c_e + \frac{1}{q_m k_l} \tag{4}$$

The experimental data is then fitted into the above equation for linearization by plotting C_e/q_e against C_e.

2.6.2.   Freundlich isotherm

The Freundlich model named after Freundlich (1926) is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by (Kavith&Namasivayam, 2007; Li Y. et al 2009)

$$q_e = K_F (C_e)^{1/n} \tag{5}$$

The nature of isotherm is indicated by the slope 1/n. The adsorption is favorable if values of slope 1/n lay between zero and one (Gecgel et al, 2003). The above equation is conveniently used in linear form as:

$$\ln q_e = \ln K_F + (1/n) \ln Ce \tag{6}$$

A plot of ln Ce against ln qe yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The constants 1/n and ln K_F can be determined from the slope and intercept, respectively.

2.6.3.   Temkin isotherm

The Temkin isotherm assume that the adsorption heat of all molecules in the layer decreases linearly with coverage as a result of adsorbate/adsorbate interaction, and adsorption characterized by a uniform distribution of binding energy (Kavith&Namasivayam, 2007; Han R. et al 2009) .The linear form of Timken can be exposed as:

$$q_e = q_m \ln K_t + q_m \ln C_e \tag{7}$$

Where: k_t is Temkin constant which is related to adsorption capacity and maximum binding energy (l/g), q_e and C_e are the equilibrium concentration in solid phase (mg/g) and liquid phase respectively (mg/l), q_m is constant related to the heat of adsorption (J/mole) (Adouby et al, 2007).

2.7.Adsorption dynamics study

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid–solution interface. Kinetics of Ga(III) and In(III) adsorption on the modified cellulose were analyzed using pseudo first-order (Lagergren, 1898), pseudo second-order (Ho et al., 2000). The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2, values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of Ga(III) and In(III) adsorption (Muhamad et al, 1998).

2.7.1.   The pseudo first-order model

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{8}$$

After integration and applying boundary conditions t=0 to t=t and qt=0 to qt=qt, the integrated form of Eq. (9) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

The values of log (q_e−q_t) were linearly correlated with t. The plot of log (q_e−q_t) vs. t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

2.7.2.   The pseudo second-order model

 Ho and McKay pseudo second order kinetic model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}\, t \qquad\qquad\qquad (10)$$

Where: k_2 is the second order rate constant (g/mg min) (Hameed et al., 2009; Eren et al., 2010).

2.8. Effect of pH

 In order to establish the effect of pH on the sorption of Ga^{3+} and In^{3+} ions, the batch equilibrium studies at different pH values was carried out in the range of 1-8. The pH was adjusted using NaOH and HCl solutions (0.1M). The experiment was elaborated by shaking the solution containing the metal ion with the CTSC of variable acidity for sufficient equilibrium time.

2.9. Thermodynamic studies

 The aim of thermodynamic study is to determine thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). Thermodynamic parameters used to determine the spontaneity of the adsorption (Suteu&Zaharia, 2011)

$\Delta G = -RT\ln k$ (11)
$K = q_e/C_e$ (12)
$\Delta G = \Delta H - T\, \Delta S$ (13)

 The sorption enthalpy (ΔH, Jmol^{-1}) was specified by the slopes ($\Delta H/R$), and the entropy (ΔS, Jmol^{-1} k^{-1}) was specified by the intercepts ($\Delta S/R$). Finally, free Gibbs energy was calculated using the above equation number (13) (Recep&Birnur, 2013).

3   RESULTS AND DISCUSSION

3.1. Effect of contact time

 Effect of contact time on the rate of adsorption using CTSC was achieved as shown in "Fig.2". The experiments were performed at natural pH, 25^0 C temperature and adsorbent dose of 0.05gm /100mL solution. The rate of percent removal for Ga^{3+} reached to 100% after 20 min and In^{3+} after 30 min. This is probably due to larger surface area being available at beginning for the adsorption of Ga^{3+} and In^{3+} ions. The rate of adsorption decreased with time due to decrease in the concentration gradient (driving force) which indicates that the adsorbent is saturated at this level and the adsorption reaches its maximum value (Hameed et al, 2009).
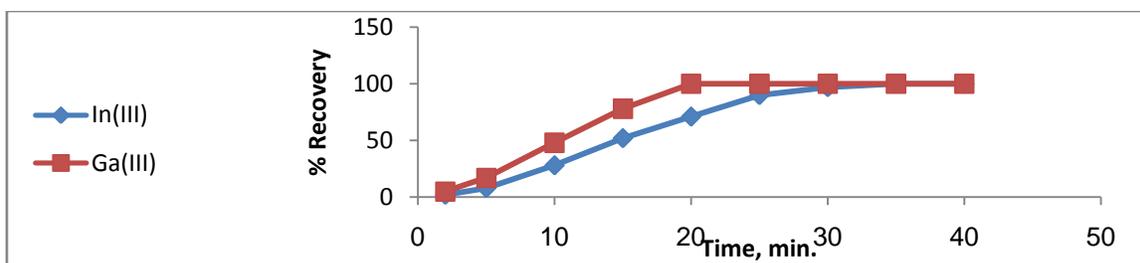
Figure 2. The effect of time on the removal of Ga(III) and In(III) using CTSC

3.2. Effect of pH

The pH of solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of adsorbate (Panday et al, 1985;Nomanbhay et al, 2005). It is generally known that at low pH values, solution is strongly acidic and the surface of the sorbent is surrounded by hydrogen ions, which prevent the metal ions from approaching the binding sites on the sorbent. Figure 3 shows the maximum sorption efficiency of CTSC for Ga(III) at pH 2.5 and for In(III) at 2- 2.5. The adsorption rate not decrease due to replacement of hydrogen ion on the surface of CTSC with Metal ions molecules on the solution. At higher pH sorption capacity and % removal decreased and this can be explained by the fact that at higher pH, the number of hydroxyl ions is more and chances of formation of metal hydroxides are also more that result in precipitation. This precipitation caused a decrease in sorption capacity and % removal with increase in pH.
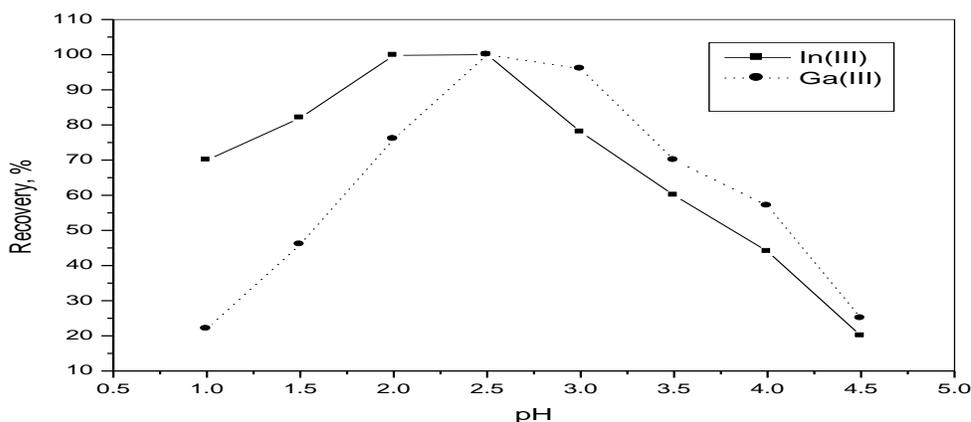

Figure 3. **Effect of pH on the adsorption of Ga(III) and In (III) using CTSC**.

3.3. Effect of temperature

Thermodynamic parameters are dependent on temperature which indicates if the adsorption is exothermic or endothermic(Barakat et al, 2009). In this study, the effect of temperature on the separation efficiency of Ga^{3+} and In^{3+} ions was studied by applying the optimal conditions with different temperatures (26 - 55^{0}C). The data present in "Fig.4" indicate that, there is an increase in the removal percentage of the studying metal ions with increasing temperature that indicate the adsorption is endothermic for both Ga (III) and In(III) ions onto CTSC.
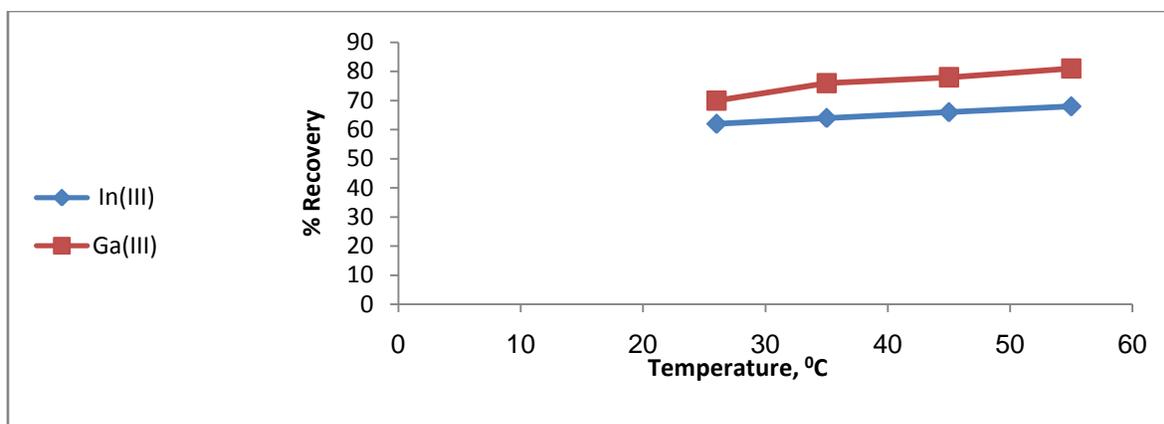
Figure 4. Effect of temperature on the adsorption of studying metal ions

3.4. Effect of concentration

The effect of initial concentration of both Ga (III)and In(III) on percentage removal and specific uptake by CTSC are shown in "Fig. 5". The percentage removal of Ga (III) and In(III) from aqueous solution decreased as concentration increased from 25 to 300mg/L at constant pH. With increase in the concentration, the percentage removal of the metal ion from aqueous solution decreases because at higher concentration, metal ions diffuse to the adsorbent surface by intraparticale diffusion and the hydrolyzed ions diffused at slower rate, thus decreasing the percentage removal (Arshad et al., 2008). Also at higher metal ions concentration to adsorbent ratio, higher energy sites get saturated and adsorption starts on lower energy sites, resulting in lower percentage removal of metal ions (Bhattachara et al., 2006).
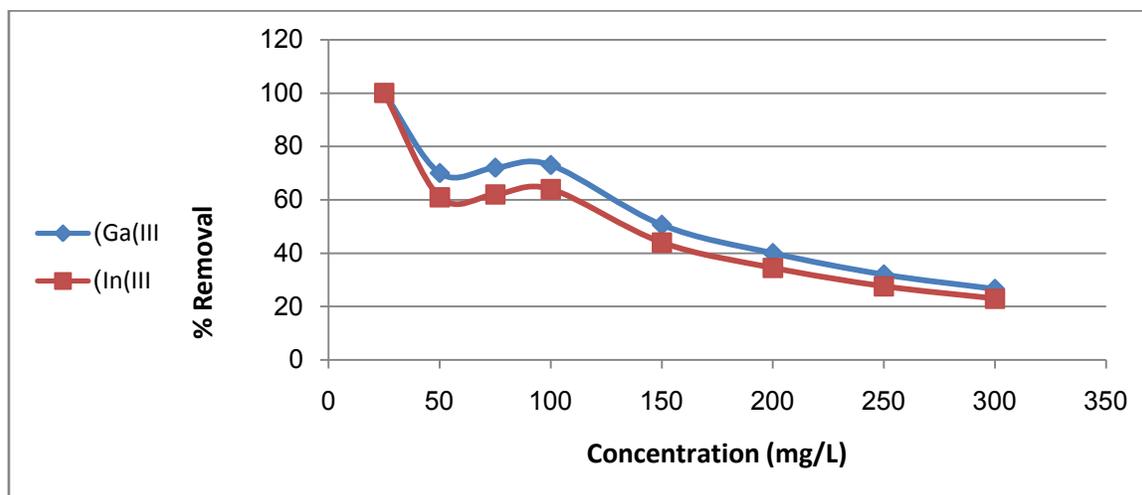

Figure 5. Effect of concentration on the adsorption of studying metal ions

3.5. Adsorption kinetics

Adsorption kinetics provides the details on the adsorption mechanism of adsorbate onto an adsorbent. The kinetics of heavy metals (Ga^{3+} and In^{3+}) adsorption on CTSC was examined with the pseudo first-order and pseudo-second order to fit the experimental data (Ho, Y.S.& McKay, G., 1998; Juang, R.S., Wu, F.C., & Tseng, R.L., 2010). The kinetic models tested for an initial concentration of 50ppm of studying heavy metals are shown in table 1. It was clearly that the kinetics of Ga^{+3} and In^{+3} removed by

CTSC followed the pseudo second kinetic model "Fig.6" with correlation coefficient R^2 is 0.987 for Galium III and 0.975 for Indium III yields very good straight lines.

Table 1. Calculated kinetic parameters for pseudo first order and pseudo second order kinetic models for the adsorption of Ga^{3+} and In^{3+} using CTSC as adsorbent

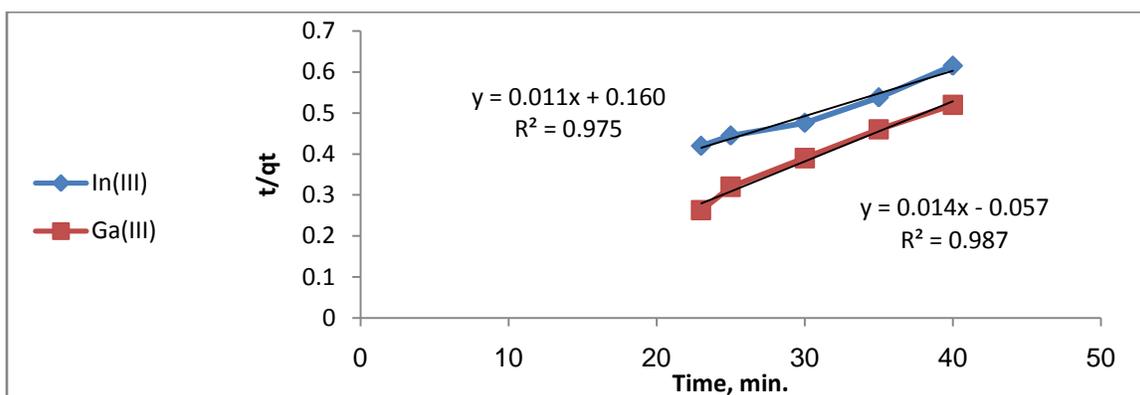| NO	Adsorption Kinetics	Isotherm parameters		R^2	
		Ga (III)	In(III)	Ga(III)	In(III)
1	Pseudo First-Order	$k_1 = 2.001$ $q_e = -0.0483$	$k_1 = 2.076$ $q_e = 0.0494$	0.94	0.88
2	Pseudo Second-Order	$k_2 = 0.0574$ $q_e = 0.0146$	$k_2 = 0.1617$ $q_e = 0.011$	0.987	0.975

Figure 6. Pseudo second order kinetics for Ga(III) and In(III) onto CTSC

3.6. Adsorption isotherms

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface and is important for the design of adsorption system (Tunali, S., et al, 2006) . The isotherm results were analyzed using the Langmuir, Freundlich and Temkin isotherms models (shown in Table 2) find common use for describing adsorption isotherms for water and wastewater treatment application (Gecgel et al, 2013). Table 3 shows the values of constants and correlation coefficients of the three isotherms. The correlation coefficient from the three equations indicates that Langmuir model yields a better fit for experimental data than the other model, for both Ga(III) and In(III) (See figs 7-12.). This means that the adsorption is monolayer and takes place on homogeneous surfaces.

Table 2. Isotherm models and their linearized expression with their parameters.

Isotherm	Equation	Linear expression	Plot	Parameters
Langmuir	$q_e = (q_m K_L C_e)/(1 + K_L C_e)$			
		Type I: $C_e/q_e = 1/(q_m K_L) + C_e/q_m$	C_e/q_e vs. C_e	K_L & q_m
		Type II: $1/q_e = 1/(q_m K_L C_e) + 1/q_m$	$1/q_e$ vs. $1/C_e$	K_L & q_m
		Type III: $q_e = q_m + q_e/(K_L C_e)$	q_e vs. q_e/C_e	K_L & q_m
		Type IV: $q_e/C_e = K_L q_m - K_L q_e$	q_e/C_e vs. $\ln q$	K_L & q_m
Freundlich	$q_e = K_F (C_e)^{1/n}$	$\ln q_e = \ln K_F + (1/n)\ln C_e$	$\ln q_e$ vs. $\ln C_e$	K_F & n
Temkin	$q_e = q_m \ln(K_T C_e)$	$q_e = q_m \ln K_T + q_m \ln C_e$	q_e vs. $\ln C_e$	K_T & q_m

Table 3. Isotherm parameters for adsorption of Ga(III) and In(III) ions from aqueous solutions onto CTSC.

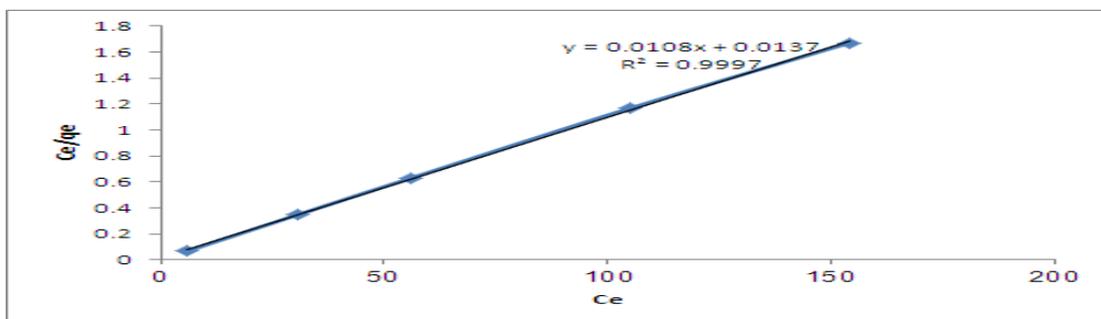| NO	Adsorption Isotherm	Isotherm Parameters		R^2	
		Ga(III)	In(III)	Ga(III)	In(III)
1	Langmuir	$q_m = 92.59$	$q_m = 89.28$	0.9997	0.9963
		$K_L = 0.7886$	$K_L = 0.048$		
2	Freundlich	$K_f = 84.7$	$K_f = 16.6$	0.8161	0.841
		$n = 73.5$	$n = 3.06$		
3	Tempkin	$q_m = 1.048$	$q_m = 0.0279$	0.7118	0.859
		$Kt = 2.78 \times 10^{35}$	$Kt = 3.8 \times 10^{24}$		

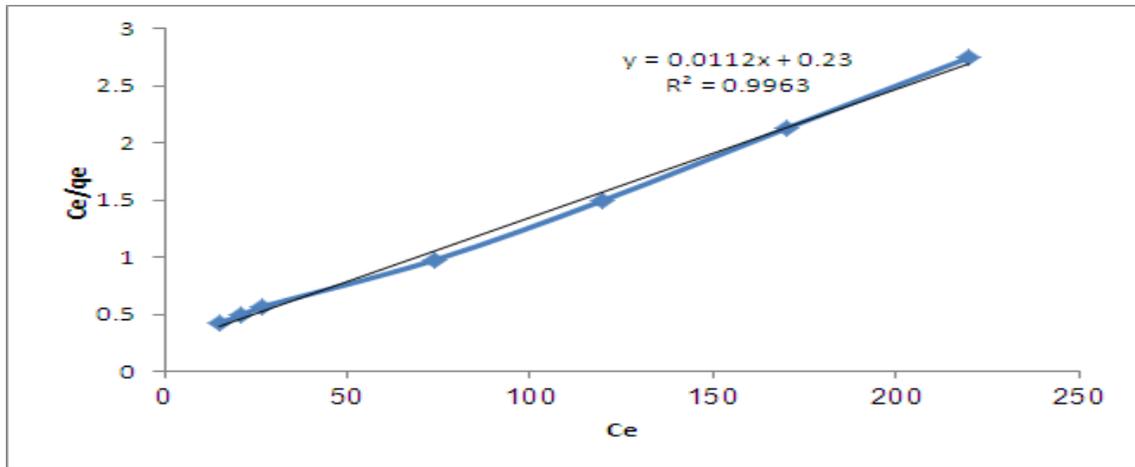**Figure 7. Langmuir model for adsorption of Ga(III) onto CTSC**

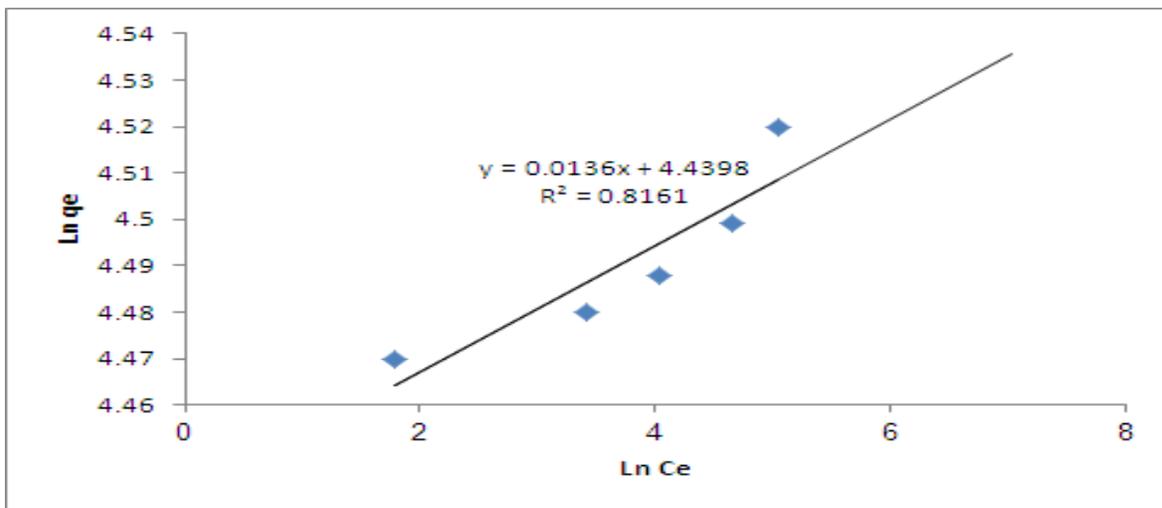**Figure 8. Langmuir model for adsorption of In(III) onto CTSC**

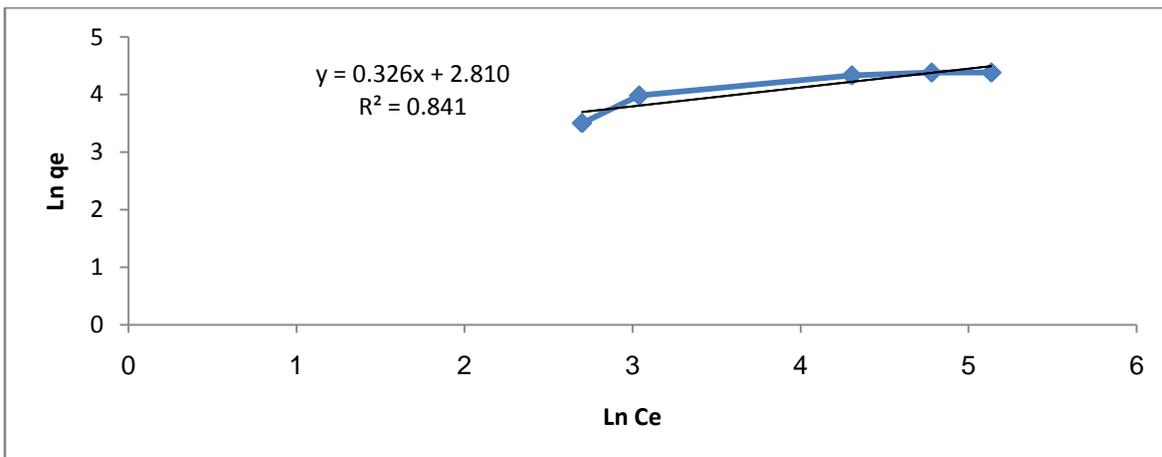**Figure 9. Freundlich model for of Ga(III) onto CTSC**

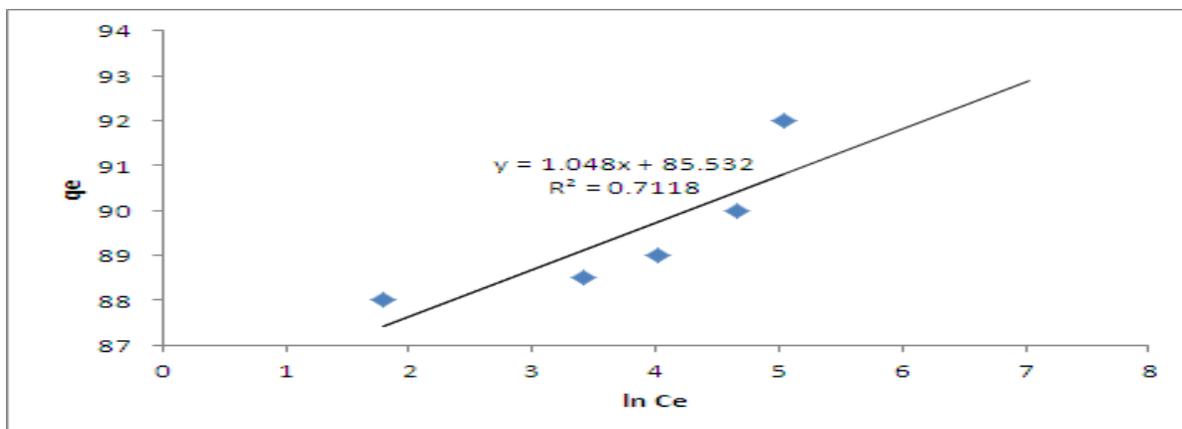**Figure 10. Freundlich model for adsorption of In(III) onto CTSC**

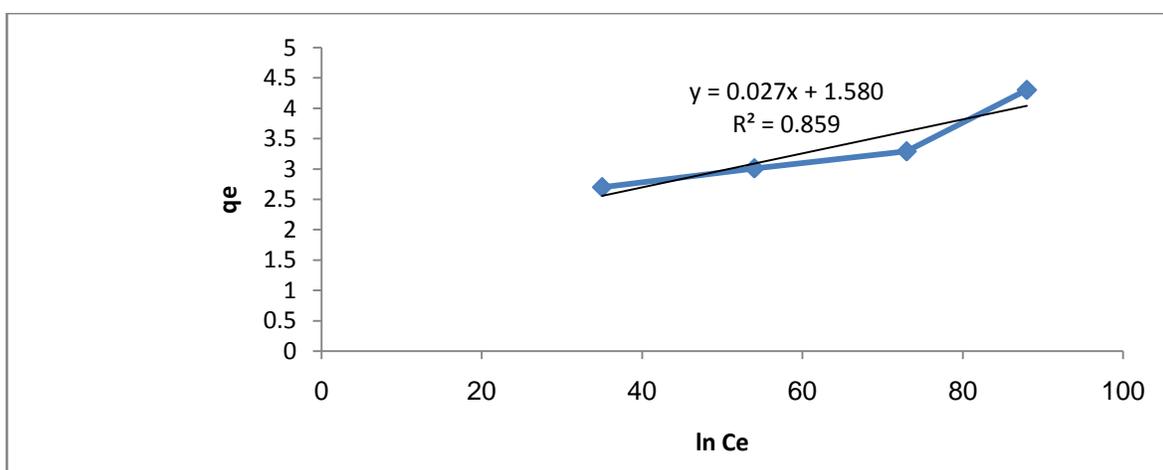**Figure 11. Temkin model for adsorption of Ga(III) onto CTSC**

Figure 12. Temkin model for adsorption of In(III) onto CTSC

3.7. Adsorption Thermodynamics

1/T as a function of $\ln q_e/C_e$ is depicted in "Fig.13"and shows the temperature dependence of the adsorption of the studied ions. The thermodynamic parameters ΔH, ΔG and ΔS were calculated employing the equations, the value of enthalpy are for the Ga(III) and In(III) ions (Ga^{3+}: 17.3 KJmol^{-1}; In^{3+} 6.648 KJmol^{-1}). The enthalpy change for the adsorption was $\Delta H > 0$ for Ga(III) and In(III) ions for CTSC; that is to say, the overall process are endothermic. ΔG for Ga(III) - 2.799 KJmol^{-1} and for In(III) -1.49 KJmol^{-1}. The negative value of ΔG indicates the spontaneous nature of the adsorption of Ga(III) and In(III) onto CTSC (Jaycock, M.J.,& Parfitt, G.D., 1981). The entropy change was positive $\Delta S > 0$ for Ga(III) and In(III) ions (Ga^{3+}: 64.9 mol^{-1}K^{-1} ; In^{3+}26.39 mol^{-1}K^{-1}).
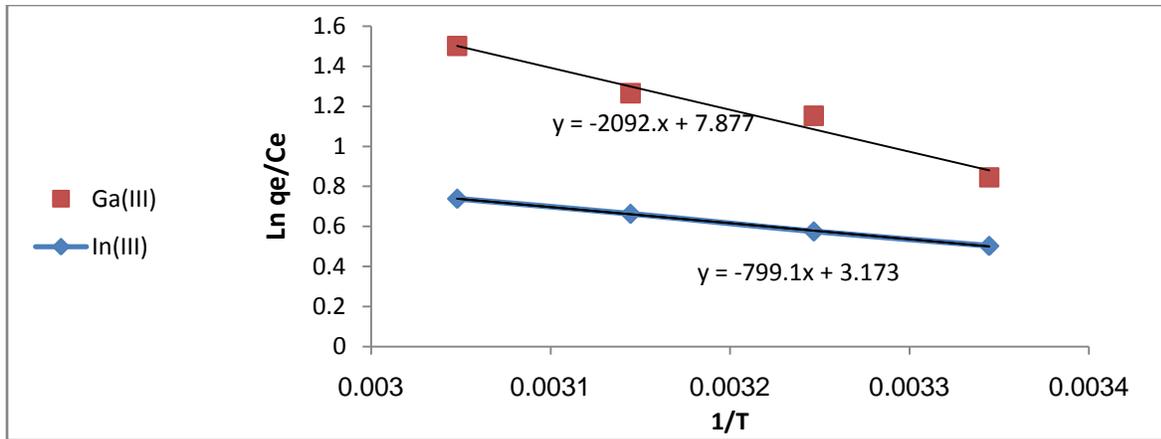
Figure 13. Graphical determination of thermodynamic parameters

3.8. Process design

Adsorption process proceeds through varies mechanism such as external mass transfer of solute onto adsorbent followed by intraparticle diffusion. Unless extensive experimental data are available concerning the specific sorption application design procedures based on sorption equilibrium conditions are the most common methods to predict the adsorber size and performance. The design of batch adsorber depend on equilibrium data obtained from experimental work (Mahmoudi et al., 2014) are the most common method to predict the amount of adsorbent needed and the size of adsorber.

A schematic diagram of a batch sorption process is shown in "Fig14". The design objective is to reduce the Ga(III) liquid volume V(l) from an initial concentration of C_0 to C_1 (mg/l). The amount of adsorbent (CTSC) is M and the solute loading changes from q_0 to q_1 (mg/g). At time t=0, q_0=0 and as time proceeds the mass balance equates Ga(III) removed from the liquid to that picked up by the solid.
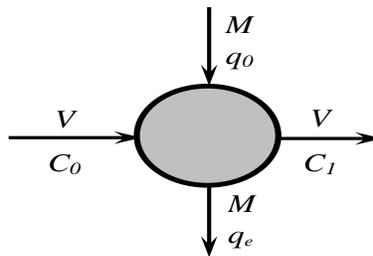

Figure 14. A single-stage batch adsorber for removal of Ga(III) from aqueous solutions

The mass balance for the Ga^{3+} in the single-stage is given by:

$$V(C_0 - C_1) = M(q_1 - q_0) = Mq_1 \qquad (14)$$

At equilibrium conditions, $C_1 \rightarrow Ce$ and $q_1 \rightarrow q_e$

For the adsorption of Ga^{3+} on CTSC, the Langmuir isotherm gives the best fit to experimental data. Consequently equation can be best substituted for q_1 in the rearranged form of Eq. (15) giving adsorbent/solution ratios for this particular system,

$$\frac{M}{V} = \frac{C_0 - C_1}{q_1} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\left[(qmkLCe)/(1+kLCe)\right]} \tag{15}$$

"Fig.15" shows a series of plots (60, 70, 80 and 90% Ga^{3+} removal at different solution volumes, i.e., 1, 2, 3, 4, 5, 6, 7 and 8 L) derived from Eq. (16) for the adsorption of Ga^{3+} on CTSC at initial concentration of 50 mg/L. The amount of CTSC required for the 90% removal of Ga^{3+} solution of concentration 50 mg/L was 1.43, 2.867, 4.29 and 5.72 g for Ga^{3+} solution volumes of 1, 2, 3 and 4 L, respectively.
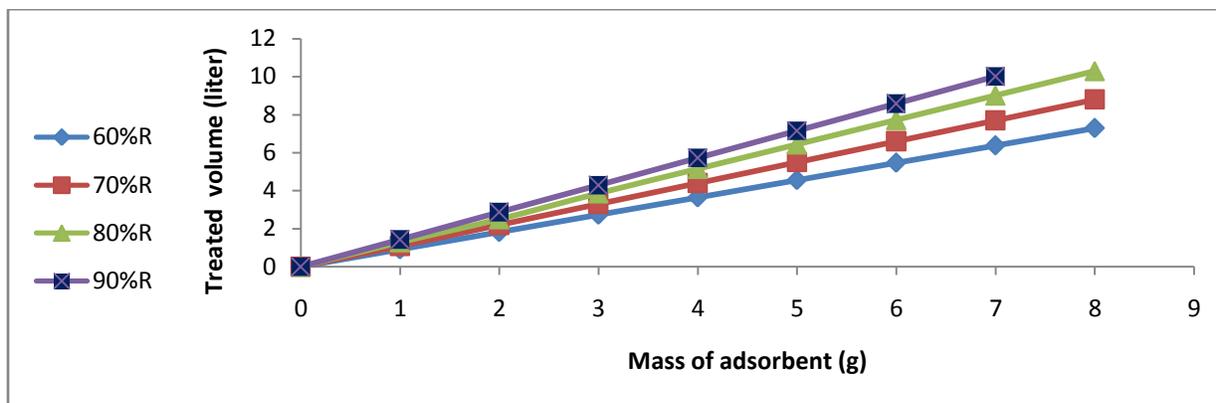

Figure 15. Volume of effluent treated versus mass of CTSC for different percentage removal of 100 mg/l Ga(III) ion concentration.

4   CONCLUSION

The present study shows that, a novel adsorbent (CTSC), was synthesized, and its adsorpative features were investigated for Ga (III) and In (III) ions. The removal of Ga^{3+} and In^{3+} from aqueous solution is a rapid process, at pH 2.5 for Ga (III) and pH 2-2.5 for In(III). The adsorptive capacities for the metals Ga (III) and In (III) were respectively 92.59 mgg^{-1} and 89.28 mgg^{-1}. The equilibrium data of both heavy metals (Ga^{3+} and In^{3+}) fits well with Langmuir isotherm. The kinetic data are very well with the pseudo second order for Ga^{3+} and In^{3+}. The positive value of ΔH indicates that the process is endothermic for both Ga (III) and In (III) ions. The percent removal of heavy metals onto CTSC reached to 100% after 20 min for Ga(III) and 30 min In(III) at 50ppm. Thus, Application of this study may be highly useful in designing the cost effective and highly efficient technique for heavy metals effluent techniques.

ABBREVIATIONS

Ce   Equilibrium metal ion concentration (mg/L)
Ci   Initial metal ion concentration (mg/L)
Cf   Final metal concentration, mg/L
CTSC Cellulose thiosemicarbazone
DAC Dialdehydecellulose
Kf   Adsorption capacity
M   Mass of adsorbent (g)
M   Molarity

n Adsorption intensity by Freundlich isotherm model
qe   Equilibrium adsorption capacity (mg/g)
qm   Empirical Constant by Langmuir isotherm model, mg/g
R   Universal gas constant (8.314 J/mol/K)
T   Temperature in Kelvin (K)
V   Volume of the solution (L)

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