

## Effect of adsorption parameters on biosorption of $Zn^{++}$ ions from aqueous solution by graft copolymer of locust bean gum and polyacrylamide

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Graft copolymers of locust bean gum (LBG) and polyacrylamide have been synthesized using ammonium persulphate (APS) as initiator for removal of  $Zn^{++}$  ions from water systems. The effect of reaction variables including the concentration of acrylamide 10 to 30 g/L, APS  $0.1 \times 10^{-3}$  to  $10 \times 10^{-3}$  mol/L, LBG 10 to 25 g/L, time duration 30-180 min and temperature 40-80°C have been studied. Grafted copolymer has been characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). To optimize the adsorption conditions several experimental parameters were varied. The sorption data obeyed Langmuir and Freundlich sorption isotherms. The Langmuir sorption capacity ( $Q_{max}$ ) is found to be 30.30 mg/g. Freundlich constants,  $K_F$  and  $n$ , are found to be 9.04 and 3.73, respectively. The adsorption of  $Zn^{++}$  ions by graft copolymer has been assessed by FTIR and SEM analysis. A metal capped structure is observed by SEM analysis after  $Zn^{++}$  biosorption. The results of the study indicate that the synthesized graft copolymer is an efficient adsorbent for removal of  $Zn^{++}$  ions from water systems.

**Keywords:** Metal removal, Water treatment, Kinetics, Zinc, Optimization

One of the significant pollution sources in the pollution of the water milieu is industrial wastewater. An enormous amount of industrial wastewater was discharged into rivers, lakes, and coastal areas during the last century. This resulted negative effects to the eco-system and human's life. The metal-working industries discharge zinc, nickel, chromium, cadmium, lead, iron, and titanium compounds, which enter the water bodies through waste water<sup>1,2</sup>.

The waste water from plumbing, petrochemical, painting, printing process and pharmaceutical industries contains undesired amount of  $Zn^{++}$  ions. Concentrations of zinc greater than 2 ppm negatively affects the amount of oxygen that fish can carry in their blood<sup>3</sup>. In the absence of other complexing or adsorbing agents the free zinc ion is coordinate with six water molecules to form the octahedral aquo ion  $(Zn(H_2O)_6)^{2+}$  in water<sup>4</sup>. Aquo ions and other toxic species have their utmost effects on aquatic organisms under low pH and low alkalinity<sup>4</sup>. Excess zinc inhibit DNA synthesis resulting teratogenic to frog and fish embryos<sup>5,6</sup>. Water concentration of 1.1 mg Zn/L caused a 50% decrease in the number of algal species and freshwater aquatic plants are usually absent from

areas containing  $> 2$  mg Zn/L<sup>4</sup>. Increased tissue total proteins, decreased glycogen, and decreased acid phosphatase activity in crabs are the result of undesirable effects of zinc<sup>7</sup>. Overdose of zinc can lead to depression, lethargy, neurologic signs such as seizures and ataxia, and increased thrust<sup>8</sup>. In order to prevent the harmful impact of zinc on ecosystem and public health, it is necessary to remove zinc from the source water.

Several methods are used such as, chemical precipitation, oxidation/reduction, filtration, ion exchange, membrane separation, and adsorption for the removal of heavy metals from aqueous solution<sup>9</sup>. Recently there is a great interest in developing cost effective and environmental friendly technologies for the management of wastewater polluted with heavy metals<sup>10</sup>. Biosorption has been extensively studied over recent years due to its wide range of target pollutants, high sorption capacity, exceptional performance, ecofriendly nature, and low cost<sup>11</sup>.

The biopolymers represent an interesting and attractive choice as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, and excellent selectivity towards

aromatic compounds and metals. There is a recent interest in the synthesis of new adsorbent materials containing polysaccharides due to increasing number of publications on adsorption of heavy metals by these natural polymers. Polysaccharides can be modified to more useful materials in several ways. Grafting with synthetic polymeric materials is one of the most successful methods of modification and the resultant grafted material can have perfect properties towards any particular application. To get efficient metal ion adsorbents various polysaccharides have been grafted on to synthetic polymers e.g., N-vinyl-2-pyrrolidone grafted guar gum for  $\text{Fe}^{2+}$  and  $\text{Cr}^{6+}$  removal<sup>12</sup>, polyacrylamide grafted guar gum for  $\text{Cr}^{6+}$  removal<sup>13</sup>, polyacrylamide grafted starch for  $\text{Zn}^{2+}$  removal<sup>14</sup> and polyacrylamide grafted chitosan for  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  removal<sup>15</sup>.

No report so far is available on the polyacrylamide grafting onto locust bean gum (LBG) for removal of  $\text{Zn}^{2+}$  ions. In the present work, we have synthesized graft copolymers of LBG and acrylamide using ammonium persulfate (APS) as initiator. The optimum graft polymer has been evaluated for the removal of zinc ions from solution containing metal ion.

## Experimental Section

### Materials

LBG was procured from victory Essence Mart (Bangalore, India). Acrylamide (AAM), APS and methanol were purchased from Loba Chemie (Mumbai, India). All other chemicals were analytical grade and used as received.

### Preparation of graft copolymers

Required amount of LBG was dissolved in water (40 mL) in a 500 mL three-necked round bottom flask. The flask was stoppered and deaerated by purging with nitrogen and were equilibrated at required temperature (40-80°C) with constant stirring. 5 mL of AAM solution was added to the reaction mixture and stirred for 15 min. Then 5 mL of APS solution was added and the reaction was allowed to continue for specific period of time. After the desired time interval the reaction was stopped by letting air into the flask. Then the grafted sample was precipitated by pouring the reaction mixture into methanol and kept overnight. The precipitate was filtered and washed three times with methanol: water (80:20, v/v) mixture to remove unreacted monomer, initiator, and homopolymer. The final graft copolymer was then dried to a constant weight at 45°C.

Percentage grafting (%G) and percentage grafting efficiency were calculated in the following manner:

$$\%G = \frac{(w_1 - w_o)}{w_o} \times 100 \quad \dots (1)$$

$$\%GE = \frac{(w_1 - w_o)}{w_2} \times 100 \quad \dots (2)$$

where  $w_0$ ,  $w_1$  and  $w_2$  denote the weight of LBG, graft copolymer, and AAM.

### Study of zinc ion adsorption

Different concentrations of zinc ions were prepared from zinc nitrate in distilled deionized water. Adsorption experiments using the graft copolymer as adsorbent were carried out on a temperature controlled incubator shaker. A known amount of adsorbent was thoroughly mixed with 25 mL of respective zinc solutions with known concentrations and pH. After specified time, the mixtures were filtered. Then the amounts of the adsorbed metal ions were determined by titration with 0.01 M EDTA using Eriochrome Black-T as indicator. The operating variables studied were time, pH, adsorbent dosage, initial metal ion concentration, and temperature. The amount of metal ions adsorbed was determined by the following equation:

$$q_e = \frac{(C_o - C_e)}{W} \times V \quad \dots (3)$$

where  $q_e$  is the amount of heavy metal ions adsorbed at time  $t$  (mg/g);  $W$  is the adsorbent mass(g);  $C_o$  and  $C_e$  are the initial and equilibrium solution concentrations of metal ions in aqueous solution (mg/L), respectively, and  $V$  is the volume of the solution(L).

### Fourier transform infrared spectroscopy

The Fourier transform infrared spectra of locust bean gum, acrylamide, and locust bean gum grafted acrylamide samples have been recorded with Fourier-transform infrared spectrophotometer (Prestige-21, Shimadzu, Japan) in the range 400 and 4000  $\text{cm}^{-1}$ .

### X-ray diffraction (XRD)

X-ray diffractogram of acrylamide, locust bean gum, and locust bean gum grafted acrylamide samples were recorded employing X-ray diffractometer (Ultima-III, Rigaku, Japan) using copper target slit 10 mm in the differential angle range of 0-60° (2 $\theta$ ).

### Scanning electron microscopy

Scanning electron micrograph of acrylamide, locust bean gum, and locust bean gum grafted acrylamide samples were taken using a SEM (JEOL, JSM6360, UK). The photomicrograph of sample was taken at an accelerating voltage at 15 kV at different magnifications.

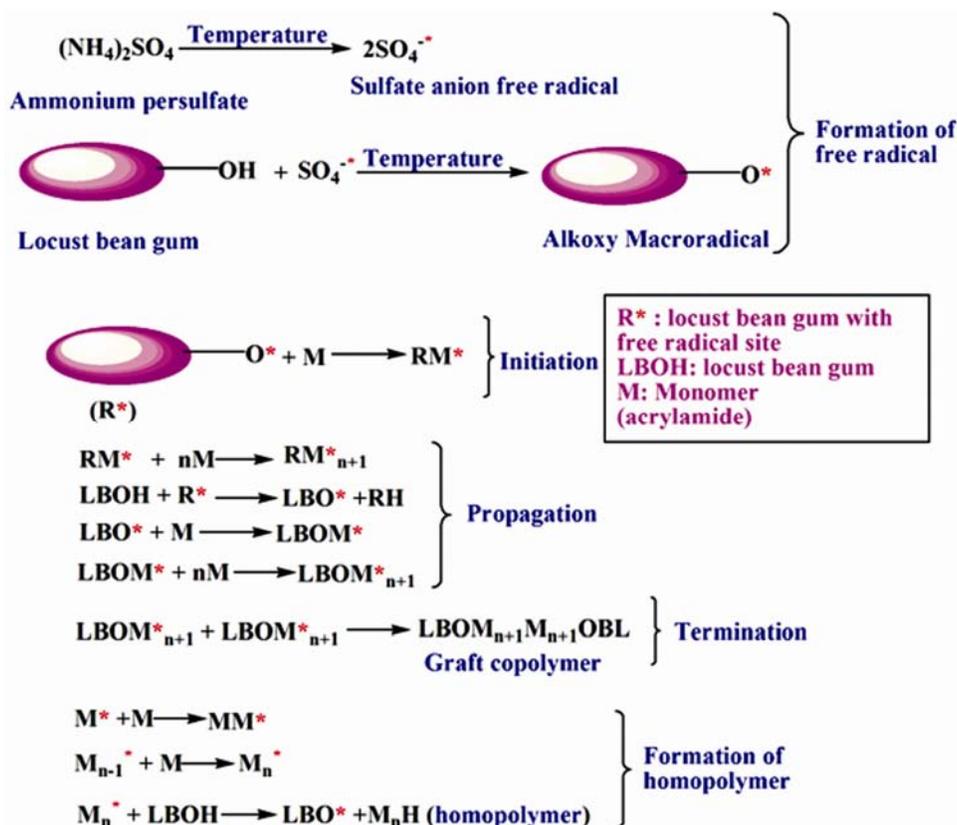
### Results and Discussion

The graft copolymer has been synthesized by conventional method using APS as a free radical initiator in an inert atmosphere of nitrogen. The probable mechanism of graft copolymer synthesis has been depicted in Scheme 1.

#### Characterization of grafted polymer

The IR spectra of locust bean gum, acrylamide, and grafted copolymer are shown in Fig. 1. A broad absorption band in locust bean gum at  $3367.71\text{ cm}^{-1}$  is observed due to the stretching frequency of the OH group (Fig. 1a). The bands around  $1026.13$  and  $2887.43\text{ cm}^{-1}$  are assigned to CO stretching as well as CH stretching respectively. A band at  $1386.81\text{ cm}^{-1}$  for the  $CH_2$  scissoring vibration. Similar spectra of locust bean gum are presented in the literature<sup>16</sup>.

Acrylamide showed peak at  $1674.21$  and  $1612.49\text{ cm}^{-1}$  indicate amide carbonyl stretching and amide N-H bending vibrations, respectively (Fig. 1b). Bands at  $3352.52$  and  $3180.61\text{ cm}^{-1}$ , related with asymmetrical and symmetrical stretching of the NH bond, respectively. The band shown at  $2812.21\text{ cm}^{-1}$  represents stretching of CH bonds. Band at  $1429.25\text{ cm}^{-1}$  ascribed to CN stretching. Similar spectra of acrylamide are presented in the literature<sup>17</sup>. A band of graft copolymer is recorded at  $3392.78\text{ cm}^{-1}$ , corresponding to the overlapping of asymmetrical OH and NH stretching (Fig. 1c). The signal depicted at  $3217.13\text{ cm}^{-1}$  is related to symmetric stretching of the NH bond. A peak representing CH bond stretching is seen at  $2935.65\text{ cm}^{-1}$ , while an intense peak, associated with superimposition of the amide carbonyl stretching of acrylamide and asymmetrical stretching of carboxylate C=O appears at  $1668.42\text{ cm}^{-1}$ . The signal observed at  $1611.25\text{ cm}^{-1}$  corresponds to amide N-H bending. Band at  $1450.46\text{ cm}^{-1}$  represent CN stretching. The graft copolymer spectrum presented a combination of the bands found in spectra of locust bean gum and acrylamide.



Scheme 1—Mechanism of formation of graft copolymer

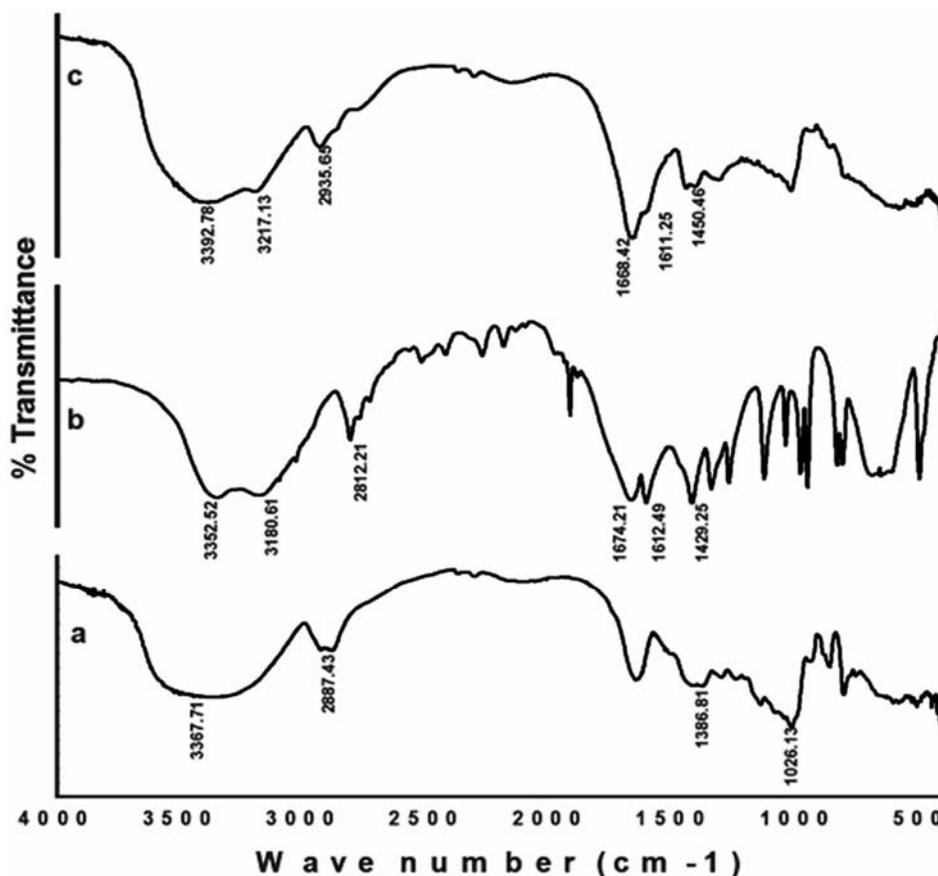


Fig. 1—FTIR spectra of (a) locust bean gum, (b) acrylamide, (c) grafted copolymer

The X-ray diffractogram of acrylamide showed the crystalline nature of acrylamide with the characteristics peak of acrylamide appearing at  $2\theta$  range of  $0-60^\circ$  (Fig. 2A.a)<sup>18</sup>. The X-ray diffractogram of locust bean gum shows amorphous structure, as there is no characteristic peak of crystallinity was observed (Fig. 2A.b). Similarly, the locust bean gum grafted acrylamide shows amorphous structure as demonstrated by broad halo (Fig. 2A.c). The crystallinity of acrylamide was disappeared. This phenomenon was due to the strong interaction (formation of covalent bond) between locust bean gum and acrylamide.

Acrylamide is characterized by crystalline structure (Fig. 2B.a)<sup>18</sup>. The locust bean gum was fibrous in nature (Fig. 2B.b)<sup>16</sup>. The SEM images of graft copolymer show that the grafting of acrylamide onto locust bean gum changes the shape and size of the locust bean gum particles (Fig. 2B.c).

#### Confirmation of adsorption

In the loaded copolymer (Fig. 3A.b) the OH stretching and NH stretching peaks are seen

shifted to  $3361.92\text{ cm}^{-1}$  and  $3213.13\text{ cm}^{-1}$  indicating complexation between the zinc species and the hydroxyl and  $\text{NH}_2$  group of the copolymer. A change in position of CH stretching peak was also observed after zinc sorption which further confirmed the loading of zinc.

The SEM picture showed that graft copolymer before (Fig. 3B.a) and after (Fig. 3B.b) zinc loading had significantly different morphologies. The morphology of the biopolymer surfaces showed small deposition of the zinc species at the copolymer surface after zinc biosorption.

#### Determination of optimum reaction conditions

Reaction parameters like exposure time, reaction temperature, monomer concentration, polymer concentration, and initiator concentration were optimized keeping the total reaction volume fixed.

#### Effect of initiator concentration

The concentration of APS was varied from  $0.1 \times 10^{-3}$  to  $10 \times 10^{-3}\text{ mol/L}$  (Fig. 4a). The grafting parameter increase with increase in the initiator concentration and reaches a maximum value at  $0.5 \times 10^{-3}\text{ mol/L}$ . The

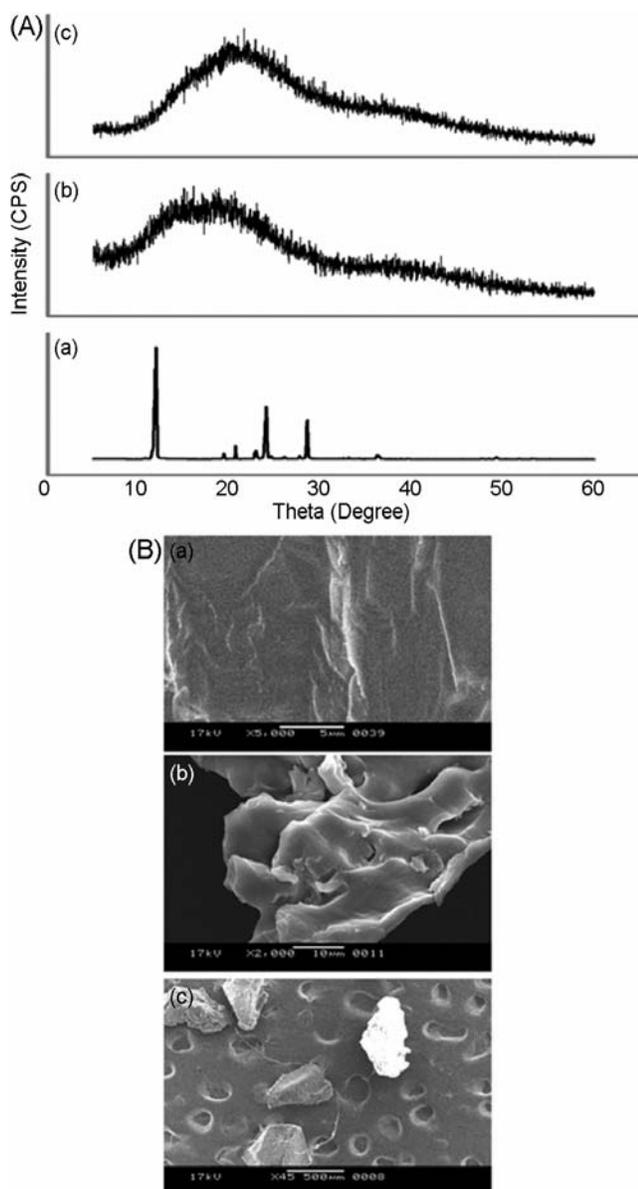


Fig. 2—A) XRD spectrum of (a) acrylamide, (b) locust bean gum, (c) grafted copolymer B) Scanning electron micrograph of (a) acrylamide, (b) locust bean gum, (c) grafted copolymer

increment in grafting parameters may be due to the generation of free radicals which produce more number of active sites on polymeric backbone where monomer addition takes place. Grafting parameters decreases at relatively high concentration of the initiator due to increase in the number of LBG free radicals terminated prior to acrylamide addition. Similar observation was reported by other authors<sup>19</sup>.

#### Effect of monomer concentration

The concentration of acrylamide was varied from 10 to 30 g/L (Fig. 4b). Grafting parameters increase

on increasing the concentration of acrylamide and reaches maximum value at 20 g/L thereafter decreases. Increase of monomer concentration leads to the accumulation of monomer molecules in close proximity to the polymer backbone. The monomer molecules that are in immediate vicinity of reaction sites, become acceptors of LBG macroradicals resulting in chain initiation. However, beyond 20 g/L grafting parameters decrease due to formation of homopolymer. These homopolymers successfully hinder the rate of penetration of monomer molecules resulting in decrease in grafting parameters. Similar observation was reported by other authors<sup>20</sup>.

#### Effect of reaction time

The grafting of acrylamide on to LBG was studied as a function of time (Fig. 4c). It was found that there is an increase in grafting parameters and reaches maximum value at 60 min. Increasing the time period further resulted in a decrease of the grafting parameters. There may be an addition of a greater number of monomer molecules to the growing grafted chain. The decrement in the parameters is observed after maximum value which might be due to termination of growing grafted chains. Similar result was observed for graft copolymerization of 2-acrylamidoglycolic acid on to partially carboxymethylated guar gum<sup>21</sup>.

#### Effect of reaction temperature

The effect of temperature on grafting parameters has been studied from 40 to 80 °C (Fig.4d). As the temperature is increased from 40 to 60°C, there is an increment in value of grafting parameters. The increase in grafting parameters with increasing temperature was due to the increased diffusion rate of monomer and initiator<sup>22</sup>. However, beyond 60°C there is decrement in grafting parameters due to the premature termination of growing grafted chains by excess free radicals at higher temperature. Similar results were observed in graft copolymerization of acrylamide onto xanthan gum<sup>23</sup>.

#### Effect of polymer concentration

The concentration of polymer was varied from 10 to 25 g/L (Fig. 4e). As the concentration of LBG increased from 10 to 15 g/L, the grafting parameters have been found to increase due to availability of more grafting sites with increasing concentration of LBG. As the concentration of LBG further increases the viscosity of the reaction medium increases, which hinders the movement of free radicals, thereby

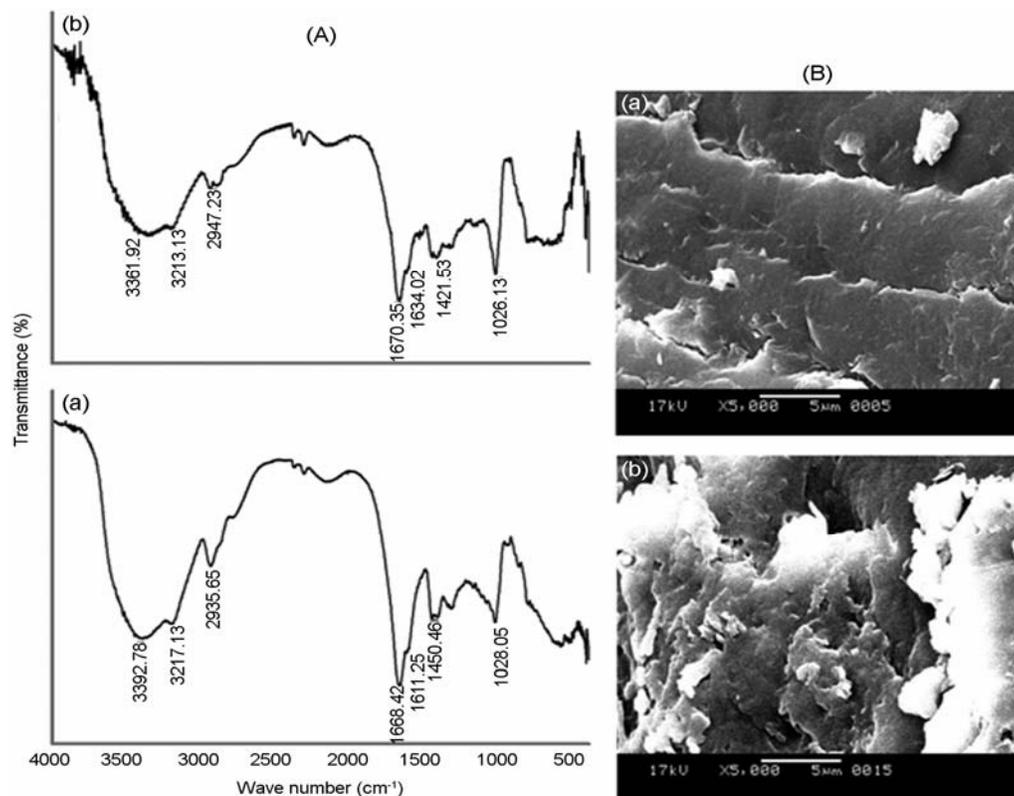


Fig. 3—A) FTIR analysis of grafted copolymer (a) before Zn<sup>2+</sup> biosorption and (b) after Zn<sup>2+</sup> biosorption B) Scanning electron microscopic spectra of graft copolymer (a) before zinc metal ions loading and (b) after zinc ions loading.

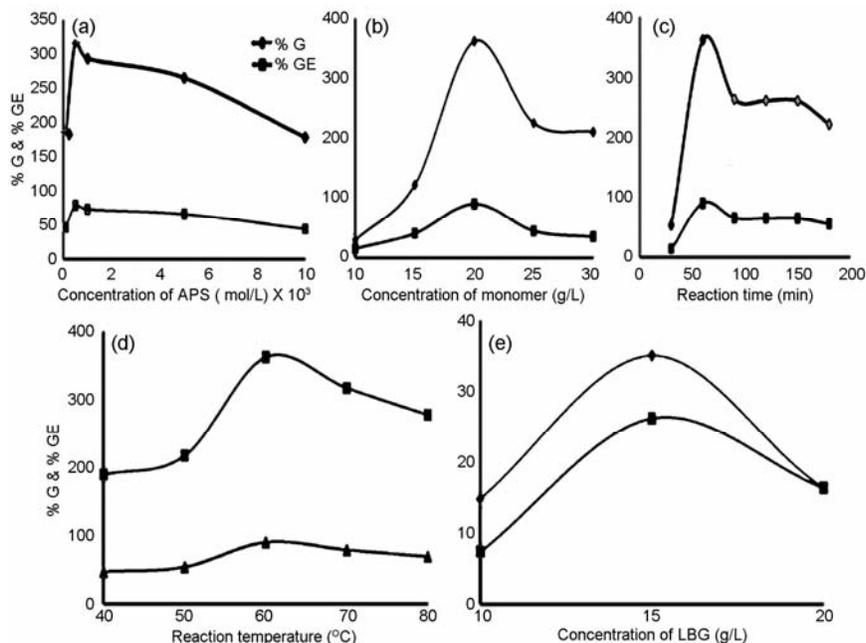


Fig. 4—Optimization of reaction parameter (a) effect of initiator concentration at LBG=5g/L, AAm=20g/L, temperature= 60°C, reaction volume= 50 mL, time = 60 min (b) effect of monomer concentration at LBG=5g/L, AAm=20g/L, APS=0.5×10<sup>-3</sup> mol/L, temperature= 60°C, reaction volume= 50 ml, time = 60 min (c) effect of reaction time at LBG=5g/L, AAm=20g/L, APS=0.5×10<sup>-3</sup> mol/L, temperature= 60°C, reaction volume= 50 ml (d) effect of temperature at LBG=5g/L, AAm=20g/L, APS=0.5×10<sup>-3</sup> mol/L, reaction volume= 50 ml (e) effect of LBG concentration at AAm=20g/L, APS=0.5×10<sup>-3</sup> mol/L, temperature= 60°C, reaction volume= 50 ml

decreasing the grafting parameters. Similar observation was made by other authors<sup>24</sup>.

#### Zinc ion adsorption

The adsorption of zinc ion on the graft copolymer was investigated as a function of contact time, pH, initial zinc ion concentration, adsorbent dose, and temperature.

#### Effect of contact time

The adsorption of zinc ions versus contact time are shown in the Fig. 5a. The increase in contact time from 0 to 15 min is accompanied by an increase in the adsorption of zinc ions. This was due to the availability of sufficient vacant adsorbing sites in presence of higher zinc ions concentration. Further increase in contact time beyond 15 min did not increase the adsorption due to deposition of zinc ions on the available adsorption sites.

#### Effect of pH

The effect of pH on the adsorption of zinc ions onto graft copolymer was studied at pH 1 to 8 for

initial metal ion concentration of 100 mg/L (Fig. 5b). The adsorption of zinc ions increased up to pH 6 and then decreased. The increment in the metal adsorption up to pH 6 is due to the amino group of graft copolymer that deprotonated and offer site for binding the ions. However, beyond pH 6 the protonation of the sorbent surface decreases leading to reduction in the electrostatic attraction between the zinc species and the sorbent surface. Moreover, at higher pH zinc could be suffering hydrolysis forming  $Zn(OH)^+$  species, which promotes a reduction of the adsorption capacity, due to the reduction of the formal charge of the metallic ion.

#### Effect of initial metal ion concentration

Adsorption of zinc ions by graft copolymer on initial concentration of zinc is shown in Fig. 5c. The adsorption of zinc by the graft copolymer increased rapidly with increase in the zinc concentration in the range of 25 to 100 mg/L. However, adsorption of zinc ions increased slowly

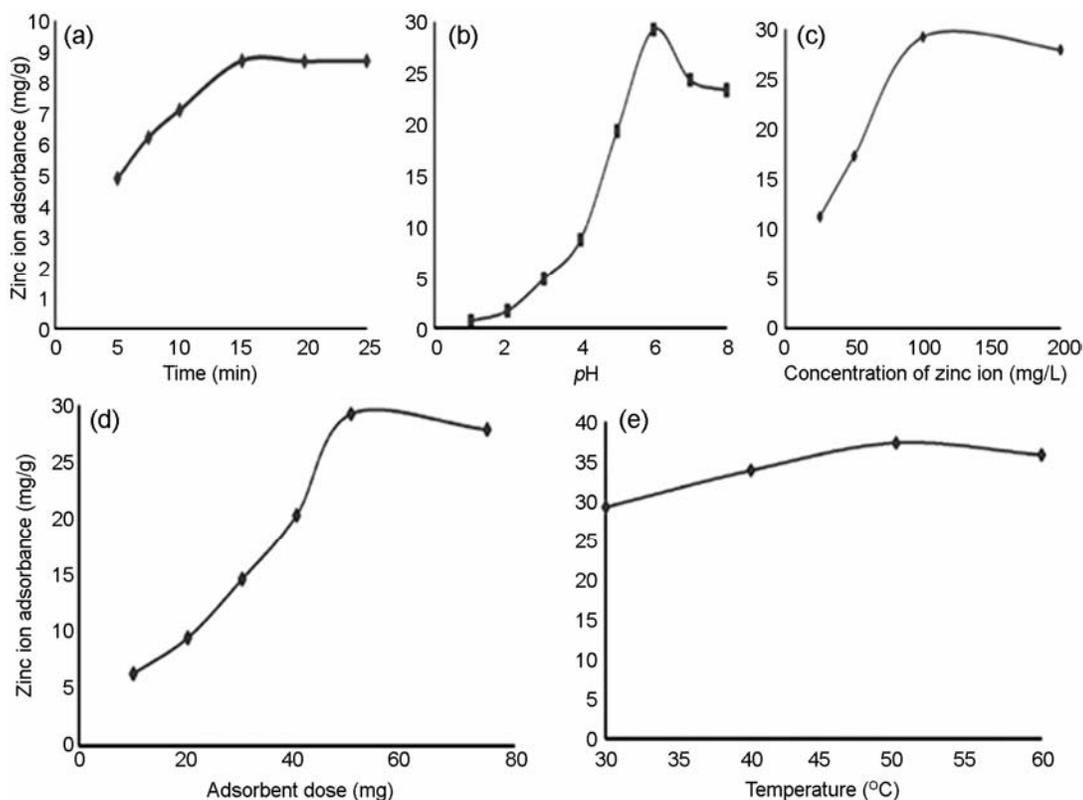


Fig. 5—Optimization of  $Zn^{++}$  adsorption (a) effect of contact time at fixed concentration of  $Zn^{++}$  100 mg/L, pH 5.0, adsorbent dose 50 mg/L, temperature 30°C (b) effect of pH at fixed concentration of  $Zn^{++}$  100 mg/L, adsorbent dose 50 mg/L, contact time 15 min, temperature 30°C (c) effect of initial metal ion concentration at fixed pH 6.0, adsorbent dose 50 mg/L, contact time 15 min, temperature 30°C. (d) effect of adsorbent dose at fixed concentration of  $Zn^{++}$  100 mg/L, pH 6.0, contact time 15 min, temperature 30°C (e) effect of temperature at fixed concentration of  $Zn^{++}$  100 mg/L, pH 6.0, adsorbent dose 50 mg/L, contact time 15 min

as the ion concentration was higher than 100 mg/L. The initial concentration provided an important driving force to overcome all mass transfer resistances of all molecules between the aqueous phase and the adsorbent<sup>25,26</sup>. More zinc was left unabsorbed in solution due to the saturation of binding sites at higher concentrations.

#### Effect of adsorbent dose

The adsorption of zinc ions increased from 6.35 to 29.23 mg/g with an increase in the adsorbent dose from 10 to 50 mg as the number of binding sites would be increased. However, the amount of zinc ions adsorbed decreased beyond adsorbent dose 50 mg (Fig. 5d). The addition of extra adsorbent was left unutilized once the interaction of zinc-graft copolymer reached equilibrium. These unutilized graft copolymer leading to reduction of adsorption value.

#### Temperature

The adsorption of zinc ions from the solution increased as the temperature increased from 30 to 50°C (Fig. 5e) was due to the increase in active surface centers available for sorption with temperature. Further increase in the temperature decreased the sorption indicated some desorption was taking place at higher temperatures.

#### Adsorption isotherms

The Langmuir and Freundlich isotherm are used to describe the adsorption data. The expression for the Langmuir isotherm is:

$$\frac{C_e}{q_e} = \left[ \frac{1}{bq_m} \right] + \left[ \frac{C_e}{q_m} \right] \quad \dots (4)$$

where  $q_e$  and  $C_e$  are the adsorption capacity (mg/g) and the equilibrium concentration of the adsorbate (mg/L), respectively, while  $q_m$  represents the maximum adsorption capacity of adsorbents (mg/g) and  $b$  is the Langmuir constant (L/mg) related to the affinity of binding sites and is a measure of the energy of adsorption<sup>27</sup>.

The essential feature of the Langmuir adsorption can be expressed by means of  $R_L$ , a dimensionless constant referred to as separation factor for predicting whether an adsorption system is favorable or unfavorable.  $R_L$  is calculated using the following equation.

$$R_L = \frac{1}{(1 + bC_o)} \quad \dots (5)$$

where  $C_o$  is the initial Zn (II) concentration (mg/L). If  $R_L$  values lies between 0 and 1, the adsorption is favorable.

The Freundlich isotherm represented by the following equation.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots (6)$$

where  $C_e$  (mg/L) is the equilibrium concentration,  $q_e$  (mg/g) is the amounts adsorbed per specific amount of adsorbent at equilibrium,  $K_F$  (mg/g) and  $n$  are constants which are adsorption capacity and intensity of adsorption, respectively<sup>28</sup>.

A plot of  $C_e/q_e$  versus  $C_e$  gives straight line as shown in Fig. 6A.a. The correlation coefficient ( $R^2$ ) value was found to be 0.989.  $Q_{max}$  and  $b$  were determined from slope and intercept of the plot and were found to be 30.30 mg/g and 0.1823, respectively (Table 1). It is clear from Table 2 that all  $R_L$  values lie between 0 and 1 indicating the favorable sorption of  $Zn^{++}$  by the graft copolymer.

Freundlich isotherm of  $Zn^{++}$  ion adsorption by the graft copolymer is shown in Fig. 6A.b. The values of Freundlich constants  $K_F$  and  $n$  were calculated and found to be 9.04 and 3.73 respectively. The value of  $n$  (3.73) for  $Zn^{++}$  ion adsorption by graft copolymer ( $>1$ ) indicates that the sorption of  $Zn^{++}$  ion by the graft copolymer is favorable<sup>29</sup>. The correlation coefficient value was found to 0.927. According to the correlation coefficient it can be observed that the  $Zn^{++}$  adsorption experimental data was better fitted to the Langmuir model than that of the Freundlich isotherm model.

Some of the reported zinc adsorbents have been compared with the present sorbent in Table 3. Present sorbent proved more efficient than most of the previously reported ones.

#### Sorption kinetics

The rate constants were calculated by using first order Lagergren and pseudo-second order kinetic models and the rate controlling step was determined by intra-particle diffusion model.

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first order equation. The non-linear form of the pseudo-first order equation is described as under

$$\frac{dq_t}{dt} = K_L(q_e - q_t) \quad \dots (7)$$

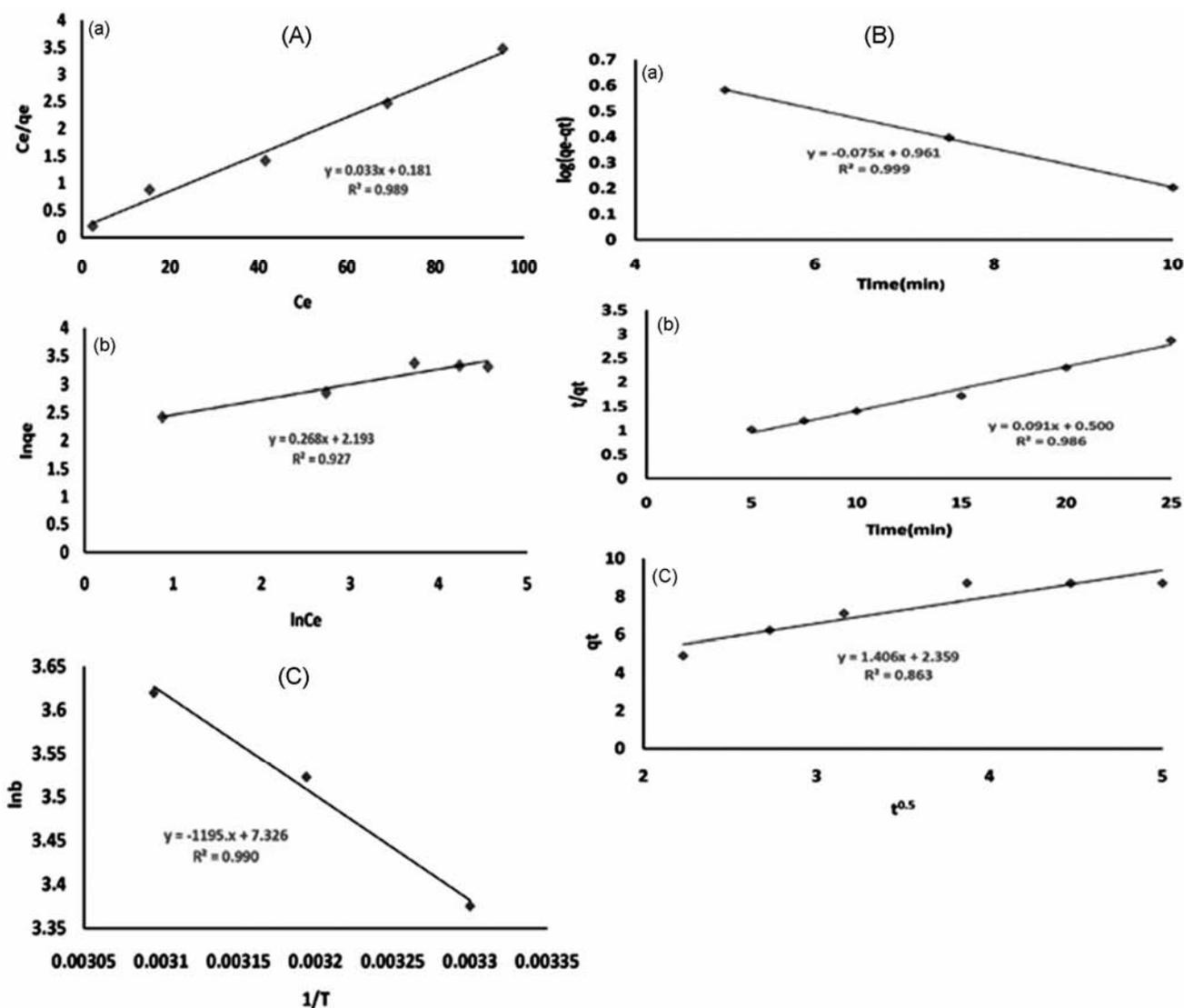


Fig. 6—A) Langmuir (a) and Freundlich (b) isotherms for  $Zn^{++}$  sorption by graft copolymer B) Lagergren first order (a), pseudo second order (b), and intraparticle diffusion model (c), for the adsorption of  $Zn^{++}$  ions by graft copolymer C) Plot of  $\ln b$  versus  $1/T$  for removal of  $Zn^{++}$  by graft copolymer

Table 1 — Langmuir and Freundlich constants for the adsorption of  $Zn^{++}$  by graft copolymer

Langmuir isotherm			Freundlich isotherm		
$Q_{max}$ ( $mg\ g^{-1}$ )	$b$ ( $L\ mg^{-1}$ )	$R^2$	$n$	$K_F$ ( $mg\ g^{-1}$ )	$R^2$
30.30	0.1823	0.989	3.73	9.04	0.927

Table 2 —  $R_L$  values based on Langmuir equation for  $Zn^{++}$  sorption by the graft copolymer

Pb(II) concentration ( $mg\ L^{-1}$ )	$R_L$ value
25	0.1799
50	0.0980
100	0.0520
125	0.0420
150	0.0352

Table 3 — Comparison of  $Zn^{++}$  adsorption capacity of graft copolymer with other sorbents

Biosorbent	$Q_{max}$ ( $mg/g$ )	Reference
Black locust	5	30
Rice husk ash	14.30	31
Oak saw dust	6.9	30
Activated alumina	13.69	31
Saw dust	14.1	32
Neem Bark	13.3	32
Low grade phosphate	10.31	33
Sugar beat pulp	17.7	34

Table 4 — Sorption kinetics of the Zn<sup>++</sup> adsorption by graft copolymer

Pseudo second order		Lagergren		Intra particle diffusion	
R <sup>2</sup>	K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	K <sub>L</sub> (min <sup>-1</sup> mg g <sup>-1</sup> )	R <sup>2</sup>	K <sub>id</sub> (m <sup>2</sup> g <sup>-1</sup> min <sup>-0.5</sup> )
0.986	1.65×10 <sup>-2</sup>	0.999	7.5×10 <sup>-2</sup>	0.863	1.406

where  $q_e$  and  $q_t$  are the amounts of zinc adsorbed (m<sup>2</sup>g<sup>-1</sup>) at equilibrium time and at any time  $t$ , respectively,  $K_L$  (min<sup>-1</sup>) is the rate constant of the pseudo-first order sorption. The integrated rate law after application of the initial condition of  $q_t = 0$  at  $t = 0$ , becomes a linear equation as given by equation as under

$$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303} \times t \quad \dots (8)$$

The plot of  $\log(q_e - q_t)$  versus  $t$  gives a straight line for the pseudo-first order adsorption kinetics, from the adsorption rate constant,  $K_L$ , is estimated<sup>35</sup>.

The pseudo second order model expressed as following<sup>36</sup>.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad \dots (9)$$

where  $K_2$  is the equilibrium rate constant of the second order biosorption (g<sup>2</sup>m<sup>2</sup>g<sup>-2</sup>min<sup>-1</sup>).

Intraparticle diffusion model is assumed that the rate of adsorption is not limited by mass transfer from the bulk liquid to particle external surface. The rate determining step may be intraparticle diffusion. The intraparticle diffusion model expressed as following.

$$q_t = K_{id} \times t^{0.5} + C \quad \dots (10)$$

where  $q_t$ (m<sup>2</sup>g<sup>-1</sup>) is amount of zinc adsorbed at time  $t$ ,  $C$ (m<sup>2</sup>g<sup>-1</sup>) is intercept and  $K_{id}$  (m<sup>2</sup>g<sup>-1</sup> min<sup>-0.5</sup>) is intraparticle diffusion constant<sup>37</sup>.

The linear plot of  $\log(q_e - q_t)$  versus  $t$  (Fig. 6B.a) shows that the sorption obeyed Lagergren kinetic model ( $R^2 > 0.99$ ). Kinetic data of Zn<sup>++</sup> adsorption by the graft copolymer also fitted into pseudo second order kinetic model, where linear plot of  $t/q_t$  versus  $t$  was obtained (Figure 6B.b). The correlation coefficient and rate constants were 0.986 and 1.65×10<sup>-2</sup>, respectively (Table 4). Plot of  $q_t$  versus  $t^{0.5}$  has poor linear regression coefficient ( $R^2 = 0.863$ ) indicating the inapplicability of this model (Fig. 6B.c). It is clear that Lagergren kinetic model proved to be a better mathematical fit for equilibrium data than pseudo second order kinetic model, based on the higher  $R^2$  value.

Table 5 — Thermodynamic parameters of the adsorption by the graft copolymer

Temperature (°K)	$\Delta G^\circ$ (KJmol <sup>-1</sup> )	$\Delta H^\circ$ (KJmol <sup>-1</sup> )	$\Delta S^\circ$ (KJmol <sup>-1</sup> K <sup>-1</sup> )
303	-8.502	+9.935	+0.00609
313	-9.167		
323	-9.720		

#### Adsorption Thermodynamics

The values of thermodynamic parameters are relevant for the practical application of adsorption process. Isotherm data related to adsorption at various temperatures were analyzed to obtain the values of thermodynamic parameters. The values of thermodynamic function  $\Delta S_o$  and  $\Delta H_o$  were evaluated using Vant Hoff's equation which is given by:

$$\ln b = \frac{\Delta S_o}{R} - \frac{\Delta H_o}{RT} \quad \dots (11)$$

$$\Delta G_o = \Delta H_o - T\Delta S_o \quad \dots (12)$$

where  $\Delta G_o$  is the Gibbs free energy (Jmol<sup>-1</sup>),  $R$  is the universal gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>),  $T$  is the absolute temperature (K), and  $b$  is the Langmuir equilibrium constant. By plotting the values of  $\ln b$  versus  $1/T$  (Fig. 6C), the values of entropy change ( $\Delta H_o$ ) (Jmol<sup>-1</sup>) and enthalpy change ( $\Delta S_o$ ) (Jmol<sup>-1</sup>K<sup>-1</sup>) were calculated from the slope and intercept, respectively.

The negative value of Gibbs free energy change ( $\Delta G_o$ ) indicates that the adsorption process for the metal ion is feasible and spontaneous. It was observed that the values become more negative with increase in temperature (Table 5). Thus adsorption of Zn<sup>++</sup> onto the graft copolymer was increased at higher temperature. The positive value of enthalpy change ( $\Delta H_o$ ) established the endothermic nature of the adsorption process. Positive values of  $\Delta S_o$  suggested excellent affinity of the metal ion toward the adsorbent.

#### Conclusion

The experimental investigations conclude the capacity of graft copolymer to biosorb the Zn<sup>++</sup> ions. The biosorption of Zn<sup>++</sup> ion was influenced by contact

time,  $pH$  of the medium, initial concentration of the metal ions, temperature, and biopolymer content. The sorption data was found to obey both Langmuir and Freundlich sorption isotherms but Langmuir isotherm proved to be a better mathematical fit for equilibrium data than Freundlich model. The negative value of the Gibbs free energy change indicated that the thermodynamically spontaneous nature of  $Zn^{++}$  ions biosorption onto graft copolymer.

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