Thermodynamic study on adsorption of Copper (II) ions in aqueous solution by Chitosan blended with Cellulose & cross linked by Formaldehyde, Chitosan immobilised on Red Soil, Chitosan reinforced by Banana stem fibre

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ABSTRACT
The effective and economic removal of heavy metals from industrial effluents is one of the important issues globally. Batch adsorption experiments were carried to fix the adsorption dosage and also to find the optimum pH. A thermodynamic study was made on the adsorption of Cu^{2+} ions in aqueous solution distinctly by the adsorbents such as Chitosan blended with Cellulose and cross linked by Formaldehyde, Chitosan immobilised on Red Soil and Chitosan reinforced by Banana stem fibre. The adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads increased slightly when temperature was raised up to 45 °C and then decreased largely when the temperature was further raised. The adsorption of Cu^{2+} ions by Chitosan-Banana stem fibre beads increased a little when temperature was raised up to 40 °C and then decreased largely for the further raise in temperature. The thermodynamic study revealed that adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads and by Chitosan-Banana stem fibre beads were spontaneous and by Chitosan-Red Soil beads were non-spontaneous. Also the thermodynamic study showed that the adsorption of Copper (II) ions by the above three adsorbents were physical and exothermic.

Index: Heavy metal removal, Gibbs free energy, Spontaneous adsorption, Non-spontaneous adsorption, Exothermic, Randomness, Cross linked Chitosan-Cellulose, Chitosan-Red Soil, Chitosan-Banana stem fibre

I. INTRODUCTION
Heavy metal contamination is an environmental threat as serious as global warming. Heavy metals are metals and metal compounds that may harm human health when absorbed or inhaled. In very small amounts, some heavy metals support life. But when taken in large amounts, they can become toxic. Examples of heavy metals include arsenic, cadmium, chromium, copper, lead, mercury and zinc. Generally, heavy metals have densities above 5 g/cm³. Copper is an essential trace nutrient that is required in small amounts (1-1.5 mg per day in food) by humans, other mammals, fish and shell fish for the synthesis of haemoglobin, carbohydrate metabolism and the functioning of more than 30 enzymes. Although Copper can be an essential trace element, it could be harmful when it exceeds the tolerance limit. Copper is extensively used in the manufacture of fungicides, anti-fouling paints and also in electrical industries. Copper fume causes irritation of the eyes, nose, and throat, headaches, stomach aches, dizziness, vomiting and diarrhoea and an illness called metal fume fever. High uptakes of copper may cause liver and kidney damage and even death. When copper ends up in soil, it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water, Copper can travel great distances, either suspended on sludge particles or as free ions. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On Copper-rich soils, only a limited number of plants have the chance of survival and hence there is not much plant diversity near copper disposing factories [1].

Many materials of biological origin (e.g., fungi, yeast, bacteria, Chitosan, seeds of papaya, moringa oleifera and tamarind, peels of orange, banana and pomegranate and agricultural wastes) have been recognised as adsorbents for heavy metal ions.
Chitosan is the second most abundant bio polymer in earth after cellulose. Chitosan has been recognised as a biopolymer with significant potential for use as biosorbent for removal of metal ions from wastewater. Chitosan is commercially produced by the deacetylation of Chitin which is found in the outer skeleton of shrimp, crab, lobster and crayfish shells. Chitosan offers a lot of promising benefits for wastewater treatment applications today. Cost of Chitosan is much lower than activated carbon and it has excellent binding capacity [2]. Chitosan has the characteristic feature of having amine groups in which nitrogen is a donor of electron pair that is attractive to most heavy metals and OH groups also take part in the adsorption [3]. Chitosan and its blends exist in various physical forms including resins, microspheres, hydrogels, membranes and fibers. The selection of one particular physical form depends mainly on the system configuration to be used for particular applications. The process of shaping chitosan blends into desired physical form starts from mixing the blend components in the liquid form and applying the appropriate shaping method [4].

II. MATERIALS AND METHODS

II.1 Materials
Chitosan flakes with a deacetylation degree of 85 % were acquired from Pelican Biotech & Chemicals Labs Pvt. Ltd., Kuthiathode, Kerala, India. The chemicals used in this study such as Acetic acid, Cellulose powder, Formaldehyde solution, Hydrochloric acid, Sodium hydroxide pellets were in AR grade and manufactured by SD Fine Chem Limited, Mumbai, India. The AR grade of Cupric Sulphate penta hydrate (CuSO₄·5H₂O) was used for the preparation of Cu⁺² ions. Red Soil has been collected from the college campus itself. Banana stem fibres have been obtained by mechanically crushing the fresh Banana stems and the extracted fibres were dried for 48 hours. Then they were cut in to very small particles (less than 0.3 mm).

In this research work, adsorption of Copper (II) ions in aqueous solution has been analysed by (i) Chitosan blended with Cellulose and cross linked by Formaldehyde; (ii) Chitosan immobilised on Red Soil; (iii) Chitosan reinforced by Banana stem fibre.

The adsorbents were made in the form of small beads. The distinct addition of Cellulose, Red Soil and Banana stem fibre were not only to strengthen the adsorbent beads and also to enhance the adsorption capacity since Cellulose, Red Soil and Banana stem fibre have the unique metal binding capacity.

II.1.1 Cellulose
Cellulose constitutes the most abundant and renewable polymer resource available worldwide. It is estimated that by photosynthesis, 10¹¹–10¹² tons of cellulose are synthesised annually in a relatively pure form [5].

There are three mechanisms for metal ions to bind to cellulose:

a. Hydrated alkali ions present in aqueous systems swell the cellulose by penetration into it and also an exchange of hydrated shell with OH groups of cellulose can occur.

b. Electrostatic interaction between metal ions and cellulose occurs in the absence of ligand in the solution. Carboxylic groups of cellulose exchange cations, i.e. hydrogen leaves carboxylic group and metal ions attaches instead.

c. Metal ion and co-ligand (e.g., ethylene-diamine, ammonia, tartaric acid, etc) form complexes in solution. In the presence of cellulose which acts as ligand, competition for the metal ion occurs between ligand and co-ligand. When the stability of metal ion and co-ligand complex is sufficient weak, cellulose complexes with the metal ion are formed and the co-ligand is released [6].

II.1.2 Red Soil
Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing mineral particles (sand, silt and clay), soil organic matter (SOM) and fluid phases (the soil water and the soil air), which interact with each other and ions entering the soil system [7]. Generally, the interaction between heavy metal ions and soil can occur mainly in the following four ways:

a. Ion exchange
b. Adsorption
c. Complexation and
d. Precipitation.

The Exchange Capacity of soil is a measure of its ability to hold and release various elements and compounds. Cation-exchange capacity is defined as the degree to which a soil can absorb and exchange cations. It is based
on the availability of negatively charged sites in soil. We are mostly concerned with the ability of soil to hold and release plant nutrients, obviously. Specifically here today, we are concerned with the ability of soil to hold and release positively charged nutrients. There are two types of cations, acidic or acid-forming cations, and basic or alkaline-forming cations. Both types of cations may be adsorbed onto either a clay particle or soil organic matter (SOM). All of the nutrients in the soil need to be held there somehow, or they will just wash away when you water the garden or get a good rainstorm. Clay particles almost always have a negative charge, so they attract and hold positively charged nutrients and non-nutrients. Soil organic matter (SOM) has both positive and negative charges, so it can hold on to both cations and anions [8].

II.1.3 Banana stems fibre

Lignocellulosic materials are mainly composed of Cellulose, Hemicellulose and Lignin. Banana stem fibre is one of the lignocellulosic materials. It consists of Cellulose (32 %), Hemicellulose (16 %) and Lignin (16 %). Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. One cubic inch of a lignocellulosic material, for example, with a specific gravity of 0.4, has a surface area of 15 square feet. Even when the lignocellulosic material is ground, the adsorptive surface increases only slightly. Thus, the sorption of heavy metal ions by lignocellulosic materials does not depend on particle size. Lignocellulosic materials are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicellulose and lignin. Thus, through absorption and adsorption, aqueous solutions come into contact with a very large surface area of different cell wall components. Lignocellulosic materials have ion exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations. Lignocellulosic resources all contain, as a common property, poly phenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations [9].

II.2 Methods of Preparation of Adsorbents

II.2.1 Preparation of Chitosan-Cellulose beads

2 g of Chitosan were dissolved in 200 ml of 1% Acetic acid and stirred for 3 hours to make a Chitosan gel. Then 2 g of Cellulose powder was added and stirred for 3 hours for uniform mixing. Formaldehyde solution (10% v/v) was added for the cross linking of polymer chain and stirring continued for another 3 hours. Then the Chitosan - Cellulose gel was injected through a syringe (without needle) over the surface of 1 M NaOH solution in a wide glass tray. The Chitosan - Cellulose beads were obtained on the surface of NaOH solution and they were allowed to stay in it for 12 hours. Then the beads were carefully separated from NaOH solution, cautiously washed many times with distilled water and allowed to be dried for 48 hours at room temperature.

II.2.2 Preparation of Chitosan-Red Soil beads

95 g of Red Soil (size less than 0.296 mm) was thoroughly mixed with 300 ml of 5% Hydrochloric acid and 5 g of Chitosan was added to the semi-solid mixture (Chitosan : Red Soil ratio = 5 : 95) and then stirred for 7 hours to make a Chitosan-Red Soil gel. Then the Chitosan – Red Soil gel was injected through a syringe (without needle) over the surface of 1 M NaOH solution in a wide glass tray. The Chitosan – Red Soil beads were obtained on the surface of NaOH solution and they were allowed to stay in it for 12 hours. Then the beads were carefully separated from NaOH solution, cautiously washed many times with distilled water and allowed to be dried for 48 hours at room temperature.

II.2.3 Preparation of Chitosan-Banana stem fibre beads

3 g of Chitosan were dissolved in 200 ml of 1% Acetic acid and stirred for 5 hours to make a Chitosan gel. Then 3 g of Banana stem fibre was added and stirred for 1 hour for uniform mixing. Then the Chitosan – Banana stem fibre gel was injected through a syringe (without needle) over the surface of 1 M NaOH solution in a wide glass tray. The Chitosan – Banana stem fibre beads were obtained on the surface of NaOH solution and they were allowed to stay in it for 12 hours. Then the beads were carefully separated from NaOH solution, cautiously washed many times with distilled water and allowed to be dried for 48 hours at room temperature. The ratio of Chitosan: Banana stem fibre in the absorbent beads was 50: 50

II.3 Adsorption experiments
Adsorption of Cu$^{2+}$ ions was carried out in batch process with initial concentration ranged from 100 ppm to 500 ppm. Cu$^{2+}$ solutions of necessary concentrations were prepared by dissolving Cupric Sulphate penta hydrate (CuSO$_4$.5H$_2$O) in distilled water. Batch adsorption experiments were carried out in 250 ml glass beakers filled with 100 ml of solution. Beads of adsorbent were added in the beaker and stirred by mechanical stirrer at 250 rpm. The concentration of Cu$^{2+}$ ions after various adsorption processes were analysed by UV-Vis Spectrophotometer under visible lamp range with a wave length of 820 nm.

Equilibrium adsorption capacity

\[ q_e = \frac{(C_0 - C_e)}{W} * V \]

Where, \( C_o \) and \( C_e \) are the initial and final Cu$^{2+}$ concentrations (mg/L) of the solution in each adsorption experiment. \( V \) is the volume of the Copper solution in litres, \( W \) is the weight of adsorbent in each beaker in grams and \( q_e \) is in mg/g.

In the adsorption experiments, Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads turned into blue colour after Cu$^{2+}$ adsorption. In the case of Chitosan-Red Soil beads, typical blue colour got stuck on the beads after Cu$^{2+}$ adsorption. In all cases it had been visually shown that Copper ions were chelated.

### III. RESULTS AND DISCUSSION

#### III.1 Optimum dosage of Adsorbent

Adsorbent dosage had strongly affected the sorption capacity. With the fixed metal ions concentration, the percentage removal of metal ions increased with increasing weight of the adsorbents. This was due to more availability of active sites or surface area at higher concentration of adsorbent. Adsorption experiments of various dosages of each adsorbent starting from 0.05 g to 0.5 g were distinctly carried out at room temperature (28$^\circ$C) in separate 250 ml beakers and each beaker contained 100 ml of 100 ppm concentration. The pH of the solution was 5.2 The samples were tested in every 15 minutes time interval. From the experiments, 0.2 g of cross linked Chitosan-Cellulose beads, 0.5 g of Chitosan-Red Soil beads and 0.2 g of Chitosan-Banana stem fibre beads were found effective and they derived 100 % adsorption of Copper in 100 ppm solution in 120, 90 and 120 minutes respectively.

#### III.2 Optimum pH

The batch experiments were carried out with a pH range of 2 to 10. 1 M HCl and 1 M NaOH solutions were used to alter pH of the solution. The result showed that there was no adsorption at pH of 2. The adsorption of Copper reached maximum at pH of 5 (optimum pH) and slowly decreased from pH 6 in the case of cross linked Chitosan-Cellulose beads and Chitosan-Red Soil beads. For the Chitosan-Banana stem fibre beads, the maximum adsorption was at pH 6 (optimum pH) and the adsorption slowly decreased from pH of 7. According to Low et al., little sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites [10]. At higher pH range, the Copper ions precipitated as their hydroxides which decreased the adsorption rate and as a result of reduction in the percentage removal of Copper ions.

![To find optimum pH](image)

**Fig. 1** Optimum pH for the adsorption of Copper on to cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads

#### III.3 Effect of Initial metal ion concentration on Adsorption

The metal uptake mechanism depended on the initial metal ion concentration. Metals were absorbed by specific sites at low concentrations. But the adsorption amount did not increase proportionally for higher metal ion concentrations since the active sites were filled and saturated. Hence it was very clear that the percentage removal of metal ion decreased with increase in metal ion concentration.
III.4 Effect of Temperature on Adsorption

A temperature range started from 30\(^\circ\) C in the multiples of 5\(^\circ\) C were analysed up to 55\(^\circ\) C. In the case of adsorption by cross linked Chitosan-Cellulose beads, the adsorption increased slightly (2 \%) between 35\(^\circ\) C and 45\(^\circ\) C and then decreased up to 10 \% when the temperature was further raised. In the case of Chitosan-Banana stem fibre beads, the adsorption increased 4 \% between 35\(^\circ\) C and 45\(^\circ\) C and then decreased up to 9 \% when the temperature was further raised. In the case of Chitosan-Red Soil beads, the adsorption increased 2.5 \% between 30\(^\circ\) C and 40\(^\circ\) C and then decreased up to 10 \% when the temperature was further raised.

![Graph showing effect of temperature on adsorption](image1.png)

**Fig.3** Effect of temperature on the adsorption of Copper on to cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads
III.5 Adsorption Isotherms

Adsorption isotherms describe the interaction of adsorbates with adsorbents. The experimental adsorption data of Copper (II) ions on the cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were analysed by Langmuir, Freundlich and Temkin isotherms.

III.5.1 Langmuir Isotherm

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes. The adsorption isotherm data were analysed by the Langmuir isotherm model in the linearised form,

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{(b \ q_{\text{max}})}$$

Where $q_e$ is the equilibrium adsorption capacity of the adsorbent (mg/g), $C_e$ is the equilibrium Cu concentration in solution (mg/l), $q_{\text{max}}$ is the maximum amount of Cu that could be adsorbed on the adsorbent (mg/g) and $b$ is the Langmuir adsorption equilibrium constant (L/mg).

III.5.2 Freundlich Isotherm

The Freundlich model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The experimental data were analysed by Freundlich isotherm model in the linearised form,

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$

where $K_F$ is the Freundlich adsorption constant and it is the maximum adsorption capacity of metal ions (mg/g) and $n$ is the constant illustrates the adsorption intensity (dimensionless).

III.5.3 Temkin Isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied in the Freundlich equation. The adsorption experiment data were analysed by Temkin isotherm model in the linearised form,

$$q_e = B \ln C_e + B \ln A$$

where $B = \frac{RT}{b}$, $b$ is the Temkin constant related to heat of sorption (J/mol), $A$ is the equilibrium binding constant corresponding to the maximum binding energy (L/g), $R$ is the gas constant (8.314 J/mol K), and $T$ is the absolute temperature (K).

The estimated values of the constants of the Langmuir, Freundlich and Temkin Isotherm models for the adsorption of Copper by the Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads have been given in the tables below.

| Table.1 Table of estimated values of constants of Isotherms for cross linked Chitosan-Cellulose beads |
|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Langmuir Isotherm | Freundlich Isotherm | Temkin Isotherm |
| $R^2$ | $q_{\text{max}}$ (mg/g) | $b$ (L/mg) | $K_F$ (mg/g) | $1/n$ | $R^2$ | $b$ (J/mol) | $A$ (L/g) |
| 0.9 | 111.95 | 0.09 | 99 | 43.95 | 49 | 0.9 | 18.9 | 7.4 |
| 0.9 | 11 | 18 | 0.9 | 99 | 49 | 0.9 | 18.9 | 7.4 |

Based on the linear regression values ($R^2 > 0.99$) which are considered as a measure of the goodness-of-fit of data, the experimental data followed the order:

Freundlich > Temkin > Langmuir.

| Table.2 Table of estimated values of constants of Isotherms for Chitosan-Red Soil beads |
|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Langmuir Isotherm | Freundlich Isotherm | Temkin Isotherm |
| $R^2$ | $q_{\text{max}}$ (mg/g) | $b$ (L/mg) | $K_F$ (mg/g) | $1/n$ | $R^2$ | $b$ (J/mol) | $A$ (L/g) |
| 0.9 | 34.90 | 0.0 | 0.9 | 77 | 12.94 | 61 | 0.9 | 18.9 | 7.4 |
| 0.9 | 48 | 659 | 0.9 | 77 | 12.94 | 61 | 0.9 | 18.9 | 7.4 |

Based on the linear regression values ($R^2 > 0.99$) which are considered as a measure of the goodness-of-fit of data, the experimental data follow the order:

Temkin > Langmuir > Freundlich.
Table 3 Table of estimated values of constants of Isotherms for Chitosan-Banana stem fibre beads

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>$R^2$</th>
<th>$q_{ma}$ (mg/g)</th>
<th>b (L/mg)</th>
<th>$R^2$</th>
<th>$K_F$ (mg/g)</th>
<th>$1/n$</th>
<th>$R^2$</th>
<th>b (L/mol)</th>
<th>A (L/g)</th>
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</thead>
<tbody>
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<td>Langmuir</td>
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<td>142</td>
<td>0.0</td>
<td>0.8</td>
<td>32</td>
<td>0.2</td>
<td>0.8</td>
<td>94</td>
<td>0.5</td>
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<tr>
<td>Freundlich</td>
<td>0.8</td>
<td>489</td>
<td>62</td>
<td>14</td>
<td>52</td>
<td>14</td>
<td>43</td>
<td>297</td>
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<tr>
<td>Temkin</td>
<td>0.5</td>
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</table>

Based on the linear regression values ($R^2 > 0.99$) which are considered as a measure of the goodness-of-fit of data, the experimental data follow the order, Langmuir > Freundlich > Temkin

### III.6 Adsorption Thermodynamics

The thermodynamic parameters for the adsorption of Cu (II) ions by Chitosan-Cellulose beads were determined using the following equations:

$$K_D = \frac{q_e}{C_e}$$

$$G^o = -RT \ln K_D$$

$$\ln K_D = \left( \frac{S^o}{R} \right) - \left( \frac{H^o}{RT} \right)$$

where $K_D$ is the distribution coefficient for the adsorption in g/L, $G^o$ is the Gibbs free energy in J/mol, R is the universal gas constant in J/mol K, T is the absolute temperature in K, $S^o$ is the entropy change in J/mol K and $H^o$ is the enthalpy change in kJ/mol [11].

The values of Gibbs free energy ($G^o$) for various temperatures were calculated from the experimental data. The values of enthalpy change ($H^o$) and entropy change ($S^o$) were estimated from the slope and intercept of the plot of $\ln K_D$ vs 1/T. The estimated thermodynamic parameters were tabulated and shown.
Table 4 Table of estimated thermodynamic parameters for the sorption of Copper by cross linked Chitosan-Cellulose beads

<table>
<thead>
<tr>
<th>S.No</th>
<th>T (K)</th>
<th>(\Delta G^o) (J/mol)</th>
<th>(\Delta H^o) (kJ/mol)</th>
<th>(\Delta S^o) (J/mol K)</th>
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<td>2</td>
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<td>6</td>
<td>328</td>
<td>-291.70</td>
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</tr>
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Table 5 Table of estimated thermodynamic parameters for the adsorption of Copper by Chitosan-Red Soil beads

<table>
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<tr>
<th>S.No</th>
<th>T (K)</th>
<th>(\Delta G^o) (J/mol)</th>
<th>(\Delta H^o) (kJ/mol)</th>
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Table 6 Table of estimated thermodynamic parameters for the adsorption of Copper by Chitosan-Red Soil beads

<table>
<thead>
<tr>
<th>S.No</th>
<th>T (K)</th>
<th>(\Delta G^o) (J/mol)</th>
<th>(\Delta H^o) (kJ/mol)</th>
<th>(\Delta S^o) (J/mol K)</th>
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The negative values of Gibbs free energy change (\(\Delta G^o\)) obtained for the adsorption of Cu (II) ions by cross linked Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads at various temperatures had shown the spontaneous nature of the adsorption processes which did not require an external energy source for the system. But the positive values of Gibbs free energy change (\(\Delta G^o\)) obtained for the adsorption of Cu (II) ions by Chitosan-Red Soil beads at various temperatures had shown the non-spontaneous nature of the adsorption process.

The negative values of enthalpy change (\(\Delta H^o\)) obtained for the adsorption of Cu (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads at various temperatures indicated that the adsorption reactions were exothermic. The negative values of entropy change (\(\Delta S^o\)) for the adsorption of Cu (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads at various temperatures showed the decreased randomness at solid-liquid interphase during the sorption processes of Cu\(^{2+}\) ions on the adsorbent beads. This is a direct consequence of (i) opening up of structure of adsorbent beads (ii) enhancing the mobility and extent of penetration within the adsorbent beads and (iii) overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion [12].

The adsorption of Copper (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads slightly increased when temperature was raised up to 45 °C and the adsorption by Chitosan-Banana stem fibre beads increased a little when temperature was raised up to 40 °C. It might be due to the generation of new active sites on the adsorbent surface and also due to the increased rate of pore diffusion. But when the temperature was further raised, adsorption processes had decreased largely. It showed that the adsorption processes of Cu\(^{2+}\) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads were exothermic reactions and physical in nature which involved the weak forces of attraction between the sorbate-sorbent molecules.

IV CONCLUSION

The study explored the effective application of cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads as adsorbents for the removal of Copper (II) ions from aqueous solution. The adsorption processes of Cu\(^{2+}\) ions by the above three adsorbents were found to be dependent on pH, initial metal ion concentration and temperature. The effect of temperature on the adsorption of Copper (II) ions by cross linked Chitosan-Cellulose
beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads showed that the processes were physical in nature. Gibbs free energy change ($\Delta G^\circ$), entropy change ($\Delta S^\circ$) and enthalpy change ($\Delta H^\circ$) were calculated to analyse thermodynamic feasibility, spontaneity and thermal effects of sorption. The Gibbs free energy change ($\Delta G^\circ$) estimated for the adsorption of Cu$^{+2}$ ions by the cross linked Chitosan-Cellulose beads and Chitosan-Banana stem fibre beads showed that the adsorption processes were spontaneous and the adsorption of Cu$^{+2}$ ions by Chitosan-Red Soil beads showed the non-spontaneous nature of the adsorption process. The entropy change ($\Delta S^\circ$) for the adsorption of Cu (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads at various temperatures showed the decreased randomness at the solid-liquid interphase during the sorption processes. The enthalpy change ($\Delta H^\circ$) for the adsorption of Cu (II) ions by cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads at various temperatures indicated that the adsorption reactions were exothermic. The results obtained would be useful for the effective application of cross linked Chitosan-Cellulose beads, Chitosan-Red Soil beads and Chitosan-Banana stem fibre beads as adsorbents to treat industrial effluents.

REFERENCES