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ADSORPTION CHARACTERISTICS OF CU (II) ONTO BLUE GREEN ALGAE - MODELING AND APPLICABILITY OF VARIOUS ISOTHERMS

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ABSTRACT Adsorption of Cu (II) onto blue green algae (BGA) is studied in this investigation under batch mode at room temperature. It is aimed to determine the maximum adsorption capacity of BGA by varying the initial metal ion concentration from 25ppm to 250ppm under the optimum pH of 6, 2g of biomass loading, 120 rpm of agitation rate and 24 hrs of contact time. To identify the adsorption mechanism and to establish the characteristic parameters for process design, the experimental data are tested with various isotherm models. In this context; One, Two, Three, Four and Five parameter isotherm models are analysed with experimental data. The experimental data infers that the isotherm is L shape which indicates, no strong competition between solvent and Cu (II) to occupy the active sites of BGA. Also it indicates that the BGA has a limited sorption capacity for adsorption of Cu (II). Through modeling studies, it is inferred that the Fritz-Schlunder-V isotherm model is highly significant followed by Freundlich and Langmuir model in establishing the mechanism of adsorption of Cu (II) under the conditions employed in this investigation. The qmax obtained by Fritz-Schlunder-V model indicates its relevance more precisely for adsorption of Cu (II) onto BGA (isotherm qmax = 34.55 mg/g and experimental qmax = 35.79 mg/g). The concurrence of experimental data with Vieth-Sladek isotherm model indicates that the adsorption of Cu (II) onto BGA is influenced both by van der Waals and ionic forces for the entire range of concentration employed in this investigation.

KEYWORDS : -Adsorption, Copper, Isotherms, Blue Green Algae, Modeling.

1. INTRODUCTION

Water contamination by heavy metals is a main problem in the current world. Considerable attention has to be paid to the methods of metal removal from industrial wastewaters because they pose serious environmental problems and are dangerous to human health and aquatic life [1]. Several million gallons of water containing toxic heavy metals are discharged into the environment by natural or human activities [2]. Mining, smelting, steel plants, metal refineries, electrolytic zinc plating etc is the major sources of heavy metal disposal onto the environment [3].

Cu, the metal considered in this study, is a widely used material. It occurs mostly in the form of oxides and sulphides in nature [4]. Metal plating, electronic and electrical device manufacturing, mining, manufacture of computer heat sinks, Cu plumbing, ceramic glazing and glass colourings are the main sources for Cu metal contamination in the environment [5]. Unfortunately, Cu is a bio accumulative and toxic chemical that does not readily break down in the environment and also not easily metabolized. It may accumulate in the ecological food chain through consumption [6]. Cu content in drinking water higher than normal level results in liver and kidney damage, stomach cramp, vomiting, diarrhea and nausea [7]. Prolonged oral administration of excessive quantities of copper may result in liver damage and chromic poisoning [8]. 1.5 to 2.0 mg/L is the suggested safe level of Cu in drinking water for humans [9, 10]. Hence, removal of copper from water and wastewater is of high importance.

Ion exchange, membrane separation, dialysis and electro dialysis reduction followed by chemical precipitation, electro coagulation and adsorption/filtration are the conventional treatment technologies to remove Cu from water and wastewater [11, 12]. Among these, adsorption is documented as the most efficient, promising and widely used fundamental technique. It is simple and cost effective for recovering heavy metal ions from dilute solutions [13, 14].

It is a surface phenomenon in which one or more components present in a multi-component fluid (gas or liquid) mixture is attracted onto the surface of solid adsorbents via physical or chemical bonds [15, 16, 17].

Insight knowledge on adsorption mechanism provides proper understanding and interpretation on the phenomena of adsorption of metal ions on the surface of adsorbents. This enables to improvise the adsorption pathways to facilitate effective design of adsorption. The presence of metal ions in aqueous media and subsequent development of pollution measures have resulted in the success of adsorption process. Studies with various bio sorbents are abundant in literature which includes seaweeds, moulds, yeast, bacteria, crab shells, agricultural products and so on [18,19,20]. Marine macro-algae are harvested or cultivated in many parts of the world and hence readily available in large quantities for the development of highly effective bio sorbent materials [13]. The microalgae which exist in the freshwater environment and in the oceans are important in global ecology, extremely efficient, and taxonomically diverse [21, 22].

The investigation of adsorption capacities of various adsorbents for the removal of Cu (II) metal ion has been made conventionally with study of two parameter models. Extensive investigation have been made by various researchers in evaluating the characteristics of specific adsorbent-adsorbate systems and evaluating the degree of applicability of two parameter models for the systems concerned specifically. The mechanism of Cu (II) metal ion adsorption from relevant sources with three, four and five parameter models in literature is very limited [23,24]. Hence it is essential to formulate the adsorption phenomena with well-designed models describing adsorption isotherms. High parameter models may provide clear and apt information about the adsorption process under equilibrium condition than the applicability of one and two parameter isotherm models [25, 26]. The high parameter model can overcome the limitations of the simple one and two-parameter models [27, 28]. The objectives of the present research are to (i) investigate the biosorption capacity of BGA for the removal of Cu (II) metal ions from synthetic solutions, (ii) analyze the isotherm data with one, two, three, four and five parameter models.

2. MATERIALS AND METHODS

The BGA is collected from coastal area around Chidambaram, Tamil Nadu, India. It is washed with distilled water and dried at room temperature. It is powdered to a uniform size of 150-200 microns

[29]. Fourier Transform Infrared (FT-IR) spectrometer (BRUKER FT-IR, ALPHA - T, GERMANY) is used for IR spectral (4000 cm-1 - 400 cm-1) studies of dried biomass and Cu (II) sorbed biomass.

Analytical grade salt Copper (II) sulfate pentahydrate (CuSO4 5H2O) is used to prepare the synthetic Cu (II) solution. 3.9290 g of CuSO4 5H2O is made to one litre with double distilled water to prepare stock solution of 1000 ppm. This stock solution is further diluted to obtain desired concentration in the range of 25 -250 ppm. The batch adsorption study is carried out in a 500 ml conical flask. The initial metal ion concentrations are taken as 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 ppm. The pH of each solution is adjusted 2 to 7. The pH adjustments are made by using 0.1N nitric acid and 0.1N sodium hydroxide solutions. The sorbent dosage is varied from 0.5 to 2.5g (0.5, 1.0, 1.5, 2.0 and 2.5 g). The flasks are kept in a rotary shaker for agitation at a rate of 120 rpm. 24 hours of contact (shaking) time is provided which is sufficient to achieve equilibrium. Double beam Atomic Adsorption Spectrophotometer (AAS SL176-Elico Limited India) is used to find the metal ion concentrations. The percentage removal of metal ions is calculated from the initial (Cin) and equilibrium concentration (Ceq) according to Equation 1.

$$\% \text{ Removal} = \frac{C_{in} - C_{eq}}{C_{in}} \times 100 \quad (1)$$

The equilibrium metal uptake, qeq is calculated from the initial concentration (Cin) and equilibrium concentration (Ceq) of the metal ion solution according to the following Equation 2.

$$q_{eq} = \frac{V}{M} \left(C_{in} - C_{eq} \right) \quad (2)$$

Where V is the volume of liquid sample (l) and M is the weight of adsorbent (g). Experiments are repeated for concordant values to achieve optimum conditions.

One parameter model (Henry's law), Two parameter models (Henry's law with intercept, Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Hill-de Boer, Fowler-Guggenheim, Flory-Huggins, Halsey, Harkin-Jura, Jovanovic, Elovich and Kiselev), Three parameter models (Hill, Redlich - Peterson, Sips, Langmuir-Freundlich, Fritz - Schlunder - III, Radke-Prausnits - I, Radke-Prausnits - II, Radke-Prausnits - III, Toth, Khan, Koble-Corrigan, Jossens, Jovanovic–Freundlich, Brouers–Sotolongo, Vieth–Sladek, Unilan, Holl–Krich and Langmuir–Jovanovic), Four parameter models (Fritz–Schlunder-IV, Baudu Weber–van Vliet and Marczewski-Jaroniec) and Five parameter model (Fritz - Schlunder - 5) are used to analyse the experimental data to find out the applicability. This is accomplished using cftool kit available in MATLAB R2010a software. This enables to compute the fit and model parameters. The applicability of model are test using the r2, SSE and RMSE values

3. ISOTHERM MODELS - THEORETICAL KNOWLEDGE
The adsorption isotherms indicate the distribution of molecules between the liquid and solid phase when the adsorption process reaches equilibrium. It is employed to establish the maximum sorption capacity of adsorbents and expressed in terms of quantity of metal adsorbed per unit mass of adsorbent used [30,31].

3.1 ONE PARAMETER MODEL
3.1.1 Henry's law Isotherm Model
This is the simplest adsorption isotherm in which the amount of solute adsorbed is related linearly to the equilibrium effluent concentration [31]. This model describes the mechanism of adsorption appreciably only at low solute concentration. The model is given in Equation 3.

$$q_{eq} = K\, C_{eq} \quad (3)$$

3.2 TWO PARAMETER MODELS
3.2.1 Henry's law with intercept Isotherm Model

This model is developed with the aim of eliminating the discrepancy raised in the one parameter model and to apply over a wide range of metal ion concentration [31]. In this model, all the terms used have the same connotation as that in one parameter model. The model is given in Equation 4.

$$q_{eq} = K\, C_{eq} + C \quad (4)$$

3.2.2 Langmuir Isotherm Model
The Langmuir model (Equation 5) assumes the surface available for adsorption as homogeneous. This model indicates that the adsorption sites have equal sorbate affinity. Also the adsorption at one site does not affect sorption at the adjacent site. The development of monolayer coverage of the adsorbate at the outer surface of the adsorbent is well explained by this model. It depicts the surface coverage by estimating the rate of adsorption and rate of desorption under equilibrium condition. The rate of adsorption in this model is proportional to the fraction of the adsorbent surface that is open and the rate of desorption is proportional to the fraction of the adsorbent surface that is covered [32, 33].

$$q_{eq} = \frac{q_{max} b_L C_{eq}}{1 + b_L C_{eq}} \quad (5)$$

The Langmuir constant bL is used to narrate to adsorption capacity (mg/g) by correlating the variation of the suitable area and porosity of the adsorbent. The Langmuir separation factor RL (dimensionless constant), used to explain the important feature of the Langmuir isotherm. The value of RL is calculated from Equation 6 using the bL and q_{max}. .

$$R_L = \frac{1}{1 + b_L q_{max}} \quad (6)$$

R_L values indicate the adsorption to be unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable when $0 < R_L < 1$, and irreversible when $R_L = 0$.

3.2.3. Freundlich Isotherm Model
The Freundlich adsorption isotherm model (Equation 7) indicates the extent of heterogeneity of the adsorbent surface. The adsorptive sites are made up of small heterogeneous adsorption sites each of which is homogeneous [34].

$$q_{eq} = a_F C_{eq}^{\frac{1}{n_F}} \quad (7)$$

aF is Freundlich adsorption capacity. nF is adsorption intensity used to indicate the relative distribution of the energy and the heterogeneity of the adsorbate sites. The larger the value of the adsorption capacity aF, higher the adsorption capacity is. The magnitude of 1/nF ranges between 0 and 1 and an indicative of favourable adsorption, becoming more heterogeneous as its value tends to zero [35, 36].

3.2.4. Dubinin-Radushkevich Isotherm Model
This empirical model assumes a multilayer character involving Van Der Waal's forces applicable for physical adsorption processes. It is often used to estimate the characteristic porosity in addition to the apparent free energy of adsorption [37]. This model is suitable to distinguish the physical and chemical adsorption of metal ions with its mean free energy. Another unique feature of the Dubinin-Radushkevich isotherm is that it is temperature dependent. The adsorption mechanism is explained with Gaussian energy distribution onto a heterogeneous surface [38]. Due to unrealistic asymptotic behaviour, this Dubinin-Radushkevich isotherm model is appropriate only for intermediate range of adsorbate concentrations. Also it does not obey Henry's law at low pressure [39, 40]. Dubinin-Radushkevich isotherm model is given as.

$$q_{eq} = K_{DR} \exp[-B_{DR}\,(\varepsilon)^2] \quad (8)$$

Where

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_{eq}} \right] \quad (9)$$

ε is called as Polanyi Potential shown in Equation 9. Equation 10 is used to calculate the energy of activation or mean free energy E (kJ/mol).

$$E = \frac{1}{\sqrt{2K_{DR}}} \qquad (10)$$

The value of E is used to predict whether an adsorption is physisorption or chemisorptions.

Less than 8 KJ/mol of E value is the indication of physical adsorption and between 8 to 16 KJ/mol is the indication of chemical adsorption [41].

3.2.5. Temkin Isotherm Model
Temkin adsorption isotherm model is highly suitable for predicting the gas phase adsorption equilibrium. On the other hand, complex adsorption systems including the liquid-phase adsorption isotherms are usually not suitable to be described. Moreover Temkin isotherm model is valid only for an intermediate range of ion concentrations. It illustrates the effects of indirect adsorbate/adsorbate interactions on the adsorption process. The main assumption in this model is the heat of adsorption decreases linearly with increasing coverage and the adsorption is characterized by a uniform distribution of binding energies [42, 43]. The Temkin adsorption isotherm model is given in Equation 11.

$$q_{eq} = \frac{RT}{b_T} \ln\left[A_T \; C_{eq}\right] \qquad (11)$$

The term RT/b_T is related to heat of adsorption and A_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy.

3.2.6. Hill - de Boer Isotherm Model
In Hill - de Boer isotherm model (Equation 12) the mobile adsorptions as well as lateral interaction among adsorbed molecules are well described [44,45].

$$K_1 C_{eq} = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \frac{K_2\,\theta}{R\,T}\right) \quad (12)$$

Positive value of K2 indicates the attraction between adsorbed species and the negative value of K2 is the indication of repulsion. If K2 is equal to zero, it indicates no interaction between adsorbed molecules and it reduces to the Volmer equation [46].

3.2.7 Fowler-Guggenheim Isotherm Model
Fowler-Guggenheim adsorption isotherm model details the lateral interaction of the adsorbed molecules. This is the simplest model allowing for the lateral interaction and it indicates that the heat of adsorption varies linearly with loading. Fowler-Guggenheim adsorption isotherm model is given in Equation 13.

$$K_{FG} \; C_{eq} = \frac{\theta}{1-\theta} \exp\left[\frac{2\theta W}{RT}\right] \qquad (13)$$

Positive W is the indication of interaction between the adsorbed molecules is attractive. The interaction among adsorbed molecules is repulsive when W is equal to zero. The model is valid when the surface coverage θ is less than 0.6 [47, 48].

3.2.8. Flory-Huggins Isotherm Model
Flory-Huggins isotherm model (Equation 14) discusses the degree of surface coverage of the adsorbate onto the adsorbent. This model is well appropriate to find the feasibility and spontaneous nature of an adsorption process [24, 25, 49, 50].

$$\frac{\theta}{C_{in}} = K_{FH} \left[1 - \theta\right]^{n_{FH}} \qquad (14)$$

K_{FH} is used to calculate the spontaneity of the sorption.

3.2.9. Halsey Isotherm Model
Halsey adsorption isotherm model (Equation 15) is appropriate to

multilayer adsorption at a relatively large distance from the surface. The model applies to adsorbents of heteroporous nature [51].

$$q_{eq} = \mathrm{Exp}\left[\frac{\ln K_{Ha} - \ln C_{eq}}{n_{Ha}}\right] \qquad (15)$$

3.2.10. Harkins-Jura Isotherm Model
Hurkins - Jura adsorption isotherm model (Equation 16) accounts for the multilayer adsorption on the surface of absorbents having heterogeneous pore distribution. The existence of a heterogeneous pore distribution can be well explained by this model [52].

$$q_{eq} = \sqrt{\frac{A_{HJ}}{B_{HJ} - \ln C_{eq}}} \qquad (16)$$

3.2.11. Jovanovic Isotherm Model
Jovanovic adsorption isotherm model (Equation 17) is similar to that of Langmuir model with the approximation of monolayer localized adsorption without lateral interactions. Additionally the possibility of mechanical contacts between the adsorbent and desorbing molecules are incorporated [53].

$$q_{eq} = q_{max}\left[1 - e^{-(K_J\,C_{eq})}\right] \qquad (17)$$

At high concentrations of adsorbate, it becomes the Langmuir isotherm, however does not follow the Henry's law.

3.2.12. Elovich Isotherm Model
The Elovich isotherm model (Equation 18) assumes that the adsorption sites grow exponentially with adsorption, indicating a multilayer adsorption. It is highly useful in describing chemisorption on highly heterogeneous adsorbents. This model is often valid for systems in which the adsorbing surface is heterogeneous [54].

$$\frac{q_{eq}}{q_{max}} = K_E C_{eq} \exp^{\frac{q_{eq}}{q_{max}}} \qquad (18)$$

3.2.13. Kiselev Isotherm Model
The Kiselev adsorption isotherm model is also known as localized monomolecular layer model [55]. This model is valid only for surface coverage > 0.68. The Kiselev adsorption isotherm model is given by Equation 19.

$$K_{eqK} \; C_{eq} = \frac{\theta}{(1-\theta)\,(1 + K_{nK}\,\theta)} \qquad (19)$$

3.3. THREE PARAMETER MODELS
3.3.1. Hill Isotherm Model
The Hill isotherm model (Equation 20) describes the adherence of different species onto homogeneous substrates. The assumption in this model is, the adsorbate adhered on the surface of the adsorbent would influence the binding sites on the same adsorbent for adsorption [56]. Hill adsorption isotherm model is given in Equation 20.

$$q_{eq} = \frac{q_{max}\,C_{eq}^{n_H}}{K_H + C_{eq}^{n_H}} \qquad (20)$$

If nH is greater than 1, this isotherm indicates positive co-operativity in binding, nH is equal to 1, it indicates non–cooperative or hyperbolic binding and nH is less than 1 is the indication of negative co-operativity in binding.

3.3.2. Redlich-Peterson Isotherm Model
The Redlich-Peterson isotherm model is developed based on the principles of Langmuir and Freundlich models. Consequently the mechanism of adsorption does not follow ideal monolayer adsorption [57]. This Redlich-Peterson isotherm model is given in Equation 21.

$$q_{eq} = \frac{A_{RP}\, C_{eq}}{1 + B_{RP} C_{eq}^{\beta_{RP}}} \qquad (21)$$

This model is applicable over a wide concentration range; the model has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be applied either in homogeneous or heterogeneous systems due to its adaptability. At high liquid-phase concentrations of the adsorbate, Redlich-Peterson isotherm model reduces to the Freundlich model. This model approaches Henrys Law model when the liquid phase concentration is low. The exponent, βRP, generally ranges between 0 and 1. While βRP = 0, this model approaches Langmuir model.

3.3.3. Sips Isotherm Model
Sips adsorption isotherm model described mainly the localized adsorption without adsorbate-adsorbate interactions [58]. This model is a combination of Langmuir and Freundlich expressions developed to predict the heterogeneous adsorption systems. The limitation of increased adsorbate concentration normally associated with the Freundlich isotherm is neglected in this model. At low adsorbate concentrations, it is transformed to Freundlich isotherm. At high adsorbate concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm [59]. Sips adsorption isotherm model is given in Equation 22.

$$q_{eq} = \frac{q_{max} K_s C_{eq}^{\beta_S}}{1 + K_s C_{eq}^{\beta_S}} \qquad (22)$$

When βS equal to 1 this isotherm approaches Langmuir isotherm.

3.3.4. Langmuir-Freundlich Isotherm Model
Langmuir-Freundlich isotherm model depicts the adsorption on heterogeneous surfaces. This model elucidates the distribution of adsorption energy onto heterogeneous surface. When the adsorbate concentration is low, this model becomes the Freundlich isotherm model, contradictorily when the adsorbate concentration is high; this model becomes the Langmuir isotherm [32, 33]. Langmuir-Freundlich isotherm model is given in Equation 23.

$$q_{eq} = \frac{q_{max} \left(K_{LF} C_{eq} \right)^{m_{LF}}}{1 + \left(K_{LF} C_{eq} \right)^{m_{LF}}} \qquad (23)$$

mLF is heterogeneous parameter and it lies between 0 and 1. This parameter increases with decreasing degree of surface heterogeneity. For mLF is equal to 1, this model covert to Langmuir model.

3.3.5. Fritz-Schlunder-III Isotherm Model
Fritz - Schlunder three parameter isotherm model is developed to fit over an extensive range of experimental results because of huge number of coefficients in their isotherm [60].

This expression is given in Equation 24.

$$q_{eq} = \frac{q_{max} K_{FS3} C_{eq}}{1 + q_{max} C_{eq}^{m_{FS3}}} \qquad (24)$$

If mFS3 is equal to 1, the Fritz–Schlunder–III model becomes the Langmuir model but for high concentrations of adsorbate, the Fritz–Schlunder–III reduces to the Freundlich model.

3.3.6. Radke-Prausnits Isotherm Model
The Radke-Prausnits isotherm model has several important properties which makes it more preferred in most adsorption systems at low adsorbate concentration. This isotherm is applicable over a wide range of adsorbate concentration. This isotherm model reduces to a linear isotherm (Henrys Model) when the adsorbate concentration is low. This model becomes the Freundlich isotherm when the adsorbate concentration is high. When Radke-Prausnits model exponent mRaP3 is equal to zero, this model becomes the Langmuir isotherm [61]. Radke-Prausnits isotherm models are given

in Equation 25 to 27.

Model 1 $\qquad q_{eq} = \dfrac{q_{max}\, K_{RaP1} C_{eq}}{\left[1 + K_{RP1} C_{eq}\right]^{m_{RaP1}}}$ $\qquad (25)$

Model 2 $\qquad q_{eq} = \dfrac{q_{max}\, K_{RaP2} C_{eq}}{1 + K_{RP2} C_{eq}^{\,m_{RaP2}}}$ $\qquad (26)$

Model 3 $\qquad q_{eq} = \dfrac{q_{max}\, K_{RaP3} C_{eq}^{m_{RaP3}}}{1 + K_{RP3} C_{eq}^{\,m_{RaP3}-1}}$ $\qquad (27)$

If the value of both mRaP1 and mRaP2 is equal to 1, the Radke–Prausnitz 1, 2 models reduce to the Langmuir model but at low concentrations, the model becomes Henry's law; but for high adsorbate concentration, the Radke–Prausnitz 1 and 2 models becomes the Freundlich model. But the Radke–Prausnitz–3 equation reduces to Henry's law while the exponent mRaP3 is equal to 1 and become Langmuir isotherm when the exponent mRaP3 is equal to 0.

3.3.7. Toth Isotherm Model
The development of Toth model is aimed to explain the heterogeneous adsorption nature in the whole range of solute concentration. This model is the modified form of Langmuir isotherm with the intension of rectifying the error between experimental and predicted data [62]. The Toth isotherm model is given Equation 28.

$$q_{eq} = \frac{q_{max} C_{eq}}{\left(\dfrac{1}{K_T} + C_{eq}^{n_T} \right)^{\frac{1}{n_T}}} \qquad (28)$$

It is clear that when n =1, this equation reduces to Langmuir isotherm equation, the process approaches onto the homogeneous surface. Therefore the parameter n characterizes the heterogeneity of the adsorption system. If it deviates further away from unity, then the system is said to be heterogeneous. This isotherm model is suitable for the modelling of several multilayer and heterogeneous adsorption systems.

3.3.8. Khan Isotherm Model
The Khan Isotherm model is developed for adsorption of bi-adsorbate from pure dilute equations solutions. This isotherm is applicable on both limits of Freundlich and Langmuir. [63]. Kahn isotherm model is given in Equation 29.

$$q_{eq} = \frac{q_{max} b_K C_{eq}}{(1 + b_K C_{eq})^{a_K}} \qquad (29)$$

While aK is equal to 1, Toth model approaches the Langmuir isotherm model and at higher values of concentration, Toth model reduces to the Freundlich isotherm model.

3.3.9. Koble-Corrigan Isotherm Model
Koble-Corrigan isotherm model is the resemblance of Sips isotherm model. This model incorporates both Langmuir and Freundlich isotherm [64]. Koble-Corrigan isotherm model is given in Equation 30.

$$q_{eq} = \frac{A_{KC}\, C_{eq}^{n_{KC}}}{1 + B_{KC} C_{eq}^{\,n_{KC}}} \qquad (30)$$

Koble-Corrigan isotherm model is applicable when the constant n is greater than or equal to 1. If not this model is unfit to define the experimental data even with high concentration coefficient or low error value.

3.3.10. Jossens Isotherm Model
The Jossens isotherm model is developed on the basis of energy distribution of adsorbate-adsorbent interactions at adsorption sites [65]. At low concentrations this model is reduced to Henry's law model. Jossens isotherm model is given in Equation 31.

$$q_{eq} = \frac{K_J C_{eq}}{1 + J\, C_{eq}^{b_J}} \qquad (31)$$

J corresponds to Henry's constant at low capacities. bJ is Jossens isotherm constant and it is characteristic of the adsorbent irrespective of temperature and the nature of adsorbents.

3.3.11. Jovanovic–Freundlich Isotherm Model
Single-component adsorption equilibrium on heterogeneous surfaces is well described by this Jovanovic–Freundlich isotherm model. Assumption made in this model is the rate of decrease of the fraction of the surface unoccupied by the adsorbate molecules is proportional to a certain power of the partial pressure of the adsorbate.

When the surface becomes homogeneous this model reduced to the Jovanovic equation. At low pressures, the equation reduces to the Freundlich isotherm but at high pressures, monolayer coverage is achieved. As in the case of Jovanovic model, the Jovanovic-Freundlich model presumes the possibility of some mechanical contacts between the adsorbing and desorbing molecules. Furthermore, this isotherm is utilized for heterogeneous surfaces without lateral interactions [66]. Jovanovic–Freundlich isotherm model is given in Equation 32.

$$q_{eq} = q_{max} \left[1 - e^{-(K_{JF} C_{eq}{}^{n_{JF}})} \right] \qquad (32)$$

3.3.12. Brouers–Sotolongo Isotherm Model
This isotherm is designed in the form of deformed exponential function for adsorption onto the heterogeneous surface mainly because of Langmuir who has recommended the extension of the simple Langmuir isotherm to non–uniform adsorbent surfaces. The assumption made in this isotherm is the surface of adsorbent consists of a fixed number of patches of active sites of equal energy [67]. Brouers–Sotolongo model is given in Equation 33.

$$q_{eq} = q_{max} \left[1 - exp^{\left(-K_{BS} C_{eq}^{\alpha_{BS}} \right)} \right] \qquad (33)$$

The parameter BS is related with distribution of adsorption energy and the energy of heterogeneity of the adsorbent surfaces at the given temperature [68].

3.3.13. Vieth–Sladek Isotherm Model
This model incorporates two distinct sections to calculate the diffusion rates in solid adsorbents for transient adsorption. The first one is defined by a linear section (Henry's law) and second one is non–linear section (Langmuir isotherm).

The linear section depicts the physisorption of gas molecules onto the amorphous adsorbent surfaces and the non–linear section explains the adherence of gas molecules to sites on the porous adsorbent surfaces [69]. Vieth–Sladek isotherm model is given in Equation 34.

$$q_{eq} = K_{VS}C_{eq} + \frac{q_{max}\beta_{VS}C_{eq}}{1 + \beta_{VS}C_{eq}} \qquad (34)$$

3.3.14. Unilan Isotherm Model
Unilan isotherm model presumes the application of the local Langmuir isotherm and uniform energy distribution. This equation is restricted to Henry's law, thus it is valid at extremely low adsorbate concentrations. It is frequently used for adsorption of gas phase onto a heterogeneous adsorbent surface [70]. Unilan isotherm model is given in Equation 35.

$$q_{eq} = \frac{q_{max}}{2\beta_U} Ln \left[\frac{1 + K_U C_{eq} e^{\beta_U}}{1 + K_U C_{eq} e^{-\beta_U}} \right] \qquad (35)$$

The higher the model exponent βU, the more is the heterogeneity of the system. If βU is equal to 0, the Unilan isotherm model becomes the classical Langmuir model as the range of energy distribution is zero in this limit [65, 71, 72].

3.3.15. Holl–Krich Isotherm Model
Holl–Krich Isotherm Model is a modified form of Langmuir isotherm [73]. This model becomes the Freundlich isotherm at low concentrations. The capacity reaches a finite capacity more leisurely

than the Langmuir isotherm at high concentrations [37]. Holl–Krich Isotherm Model is given in Equation 36.

$$q_{eq} = \frac{q_{max}K_{HK}C_{eq}^{n_{HK}}}{1 + K_{HK}C_{eq}^{n_{HK}}} \qquad (36)$$

3.3.16. Langmuir–Jovanovic Isotherm Model
This empirical model is the combined form of both Langmuir and Jovanovic isotherm [74]. The Langmuir–Jovanovic model is given in Equation 37.

$$q_{eq} = \frac{q_{max}C_{eq} \left[1 - exp^{\left(K_{LJ}C_{eq}^{n_{LJ}} \right)} \right]}{1 + C_{eq}} \qquad (37)$$

3.4. FOUR PARAMETER MODELS
3.4.1. Fritz–Schlunder-IV Isotherm Model
Fritz–Schlunder IV model is another model comprised of four-parameter with combined features of Langmuir–Freundlich isotherm [60]. The model is given in Equation 38.

$$q_{eq} = \frac{A_{FS5} \, C_{eq}^{\alpha_{FS5}}}{1 + B_{FS5}C_{eq}^{\beta_{FS5}}} \qquad (38)$$

This isotherm is valid when the values of FS5 and βFS5 are less than or equal to 1. At high adsorbate concentration, Fritz–Schlunder–IV isotherm becomes Freundlich equation. Conversely if the value of both FS5 and βFS5 equal to 1, this isotherm reduces to Langmuir isotherm. At high concentrations of the adsorbate in the liquid–phase this isotherm model becomes the Freundlich.

3.4.2. Baudu Isotherm Model
Baudu isotherm model has been developed mainly due to the discrepancy in calculating Langmuir constant and coefficient from slope and tangent over a broad range of concentrations [75]. Baudu isotherm model is the transformed form of the Langmuir isotherm. It is given in Equation 39

$$q_{eq} = \frac{q_{max} \, b_o \, C_{eq}^{(1+x+y)}}{1 + b_o C_{eq}^{(1+x)}} \qquad (39)$$

This model is applicable in the range of (1+x+y) < 1 and (1+x) < 1.

3.4.3. Weber–van Vliet Isotherm Model
Weber and van Vliet isotherm model is used to describe equilibrium adsorption data with four parameters [77, 78]. The model is given in Equation 40.

$$C_{eq} = P_1 \, q_{eq}^{\left(P_2 q_{eq}^{P_3} + P_4 \right)} \qquad (40)$$

3.4.4. Marczewski-Jaroniec Isotherm Model
The Marczewski-Jaroniec isotherm model is the resemblance of Langmuir isotherm model. It is developed on the basis of the supposition of local Langmuir isotherm and adsorption energies distribution in the active sites on adsorbent [78, 79]. The Marczewski-Jaroniec isotherm model is given in Equation 41.

$$q_{eq} = q_{max} \left[\frac{\left(K_{MJ}C_{eq} \right)^{n_{MJ}}}{1 + \left(K_{MJ}C_{eq} \right)^{n_{MJ}}} \right] \qquad (41)$$

KMJ describes the spreading of distribution in the path of higher adsorption energy. nMJ describes the spreading in the path of lesser adsorption energies. The isotherm reduces to Langmuir isotherm when nMJ and KMJ are equal to unity.

3.5. FIVE PARAMETER MODEL
3.5.1. Fritz-Schlunder-V Isotherm Model
Fritz-Schlunder adsorption isotherm model is developed with the aim of simulating the model variations more precisely for application over a wide range of equilibrium data [60]. Fritz-

Schlunder adsorption isotherm model is given in Equation 42.

$$q_{eq} = \frac{q_{max} K_{1FS5} C_{eq}^{\alpha_{FS5}}}{1 + K_{2FS5} C_{eq}^{\beta_{FS5}}} \qquad (42)$$

4. RESULTS AND DISCUSSION

Blue Green Algae (BGA) is used as an adsorbent for removal of Cu (II) from aqueous solution. In terms of availability, accessibility and cost, the BGA can be considered as a potential adsorbent. The maximum adsorption capacity of BGA is found to be 35.79 mg/g under the optimum experimental condition of pH 6 and 2 g biomass dosage.

4.1 BGA- Biomass characterization

Figure 1 and Figure 2 shows the results of FTIR analysis of unloaded and copper-loaded BGA respectively at pH 6. The shift of wave number form 3414.83 cm-1 (BGA unloaded) to 3410.66 cm-1 (BGA Cu loaded) indicates that surface -OH and -NH groups are responsible for adsorption. Also the wave numbers 2927.52 cm-1, 2519.85 cm-1 and 2363.49 cm-1 (BGA unloaded) are shifted to 2927.12 cm-1, 2521.18 cm-1 and 2359.85 cm-1 (BGA Cu loaded) due to the -CH2 stretching responsible for Cu(II) adsorption. The broad adsorption bands 1643.81 cm-1 and 1427.97 cm-1 (BGA unloaded) shifted to 1642.96 cm-1 and 1427.39 cm-1 indicates an interaction between Cu(II) and C=O group of carboxylic at the surface of the BGA. 1427.97 cm-1 indicates the S=O stretching which is slightly shifted to 1427.39 cm-1. 1039.87 cm^{-1} indicates the –C–O stretching of alcohol that is shifted to 1040.13 cm-1. 916.77 cm^{-1} indicates the S=O stretching which is shifted to 917.25 cm-1. The shifting and broadening of the bands located at 400 - 900 cm-1 is due to the loading effect of Cu (II) metal ions. The main functional groups that are responsible for the metal uptake onto algal biomass are carboxyl, amines, and hydroxyl. In these figures, the significant changes in the vibrational frequencies indicate that carboxyl, amines and hydroxyl groups bind with copper ions through ion exchange and complex reactions [80, 81].
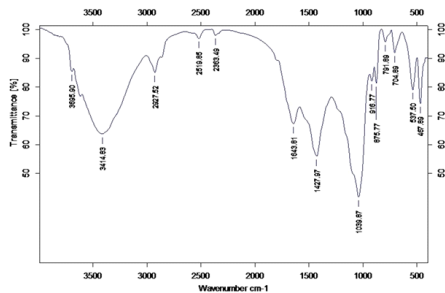

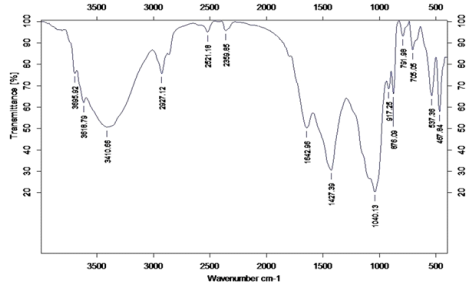**Figure 1: FTIR spectra of BGA biomass before adsorption of Cu (II)**

Figure 2: FTIR spectra of BGA biomass after adsorption of Cu (II)

4.2 BGA - Maximum adsorption capacity

To validate the value of maximum adsorption capacity of BGA, the finding is compared with several authors who have reported their results of investigation on adsorption of Cu (II) from aqueous solution using different sorbents. Mustapha and Djafri[82] studied adsorption of Cu(II) from wastewater by using low cost montmorillonite (natural clay) and kaolinite (treated clay) as adsorbents and reported the maximum adsorption capacity of 15.40 and 12.22 mg/g respectively at pH 6.5. Putra et al., [83] made investigation with three different sorbents viz., coconut tree sawdust (CTS), eggshell (ES) and sugarcane bagasse (SB) as low-cost bio sorbents for the removal of Cu (II) from aqueous solutions and reported that the maximum adsorption capacity is 3.89 mg/g for CTS, 34.48, mg/g for ES, and 3.65, mg/g for SB respectively at pH 6.0. Sadeghalvad et al., [84] studied the removal of Cu (II) from aqueous solution using bentonite as adsorbent and reported its maximum equilibrium adsorption capacity as 21.10 to 22.17 mg/g at a normal pH 7. Similarly, Muslim et al., [85] studied the adsorption of Cu (II) from aqueous solution by using Areca catechu shell (ACS) as adsorbent and reports that its maximum adsorption capacity is 1.33 mg/g at normal pH 7. The comparisons show that BGA is superior to the other sorbents in recovering Cu.

However, Xin et al., [86] synthesized diethylene triamine penta acetic acid (DTPA)-modified magnetic graphene oxide (MGO) for removal of Cu (II) from acidic aqueous solutions and reported 131.4 mg/g of metal uptake at pH 3. Though the qmax is higher than the present investigation, their sorbent are found to be more effective at a low pH which is highly acidic. Such acidic environments are tedious, hazardous and also uneconomical on industrial scale. Similarly, Tulin et al., [87] utilized a novel adsorbent Fe3O4 /Ni/NixB nano composite for the adsorption of copper along with the natural adsorbents carob and grape seeds and reported maximum adsorption capacity of 106.4, 15.6, and 15.9 mg/g in pH 8.4, 6.0, and 5.6, respectively. However the sorbent is made synthetically hence it is comparatively inferior to naturally occurring BGA in terms of availability, accessibility and cost.
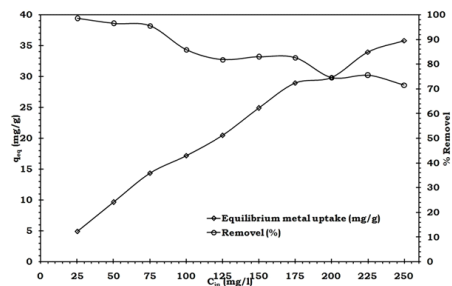

Figure 3: Effect of initial metal ion concentration on equilibrium metal uptake and % removal for adsorption of Cu (II) onto BGA.
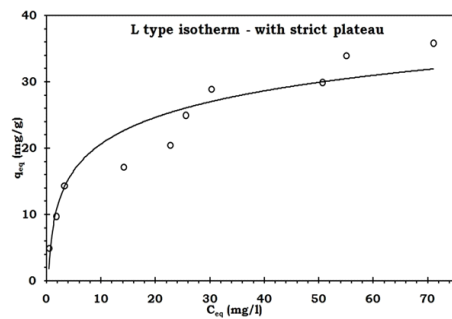
Figure 4: Experimental results of adsorption of Cu (II) onto BGA.

4.3 Effect of initial Cu (II) metal ion concentration on equilibrium metal uptake and percentage removal

The variations of equilibrium metal uptake and percentage removal with the changes in initial metal ion concentration is shown graphically in Figure 3. It is observed that the % removal of Cu (II) metal ions decreases with increase in initial metal ion concentration. This is because; at lower concentration the ratio of the initial number of metal ions to the fixed number of active site is low. For a fixed number of active sites (remaining constant), the number of

substrate metal ions accommodated in the interlayer space, is increased. However increase in initial metal ion concentration increases the equilibrium metal uptake (qeq) due to the decreasing ionic strength. At low initial metal ion concentration, the ionic strength of Cu ions is more which suppresses the amount of metal uptake. Also the electrostatic attraction is another reason which is severely affected by increased ionic strength.

4.4 Adsorption Isotherms

Predicting the mechanism of adsorption strengthens the area of adsorption by modeling the experimental data. The shape of the adsorption isotherms aids to classify the nature of the phenomena of adsorption of Cu (II) onto BGA. The experimental adsorption nature of Cu (II) from its synthetic aqueous solutions onto BGA is shown in Figure 4 which is useful to perceive the shape of the isotherm [24, 88]. Giles et al., [89] classified the isotherms as L, S, H, and C based on the shape of curve. In accordance with this, the isotherm of Cu (II) onto BGA is of L, which indicates that no strong competition between solvent and adsorbate to occupy the adsorbent surface sites exists [90]. Figure 4 shows concavity curve which indicates that the ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases. It reveals the progressive saturation of the solid. Limousine et al., [90] details further, two sub-groups of L shaped isotherms: (i) the curve reaches a strict asymptotic plateau (the solid has a limited sorption capacity), and (ii) the curve does not reach any plateau (the solid does not show clearly a limited sorption capacity). Figure 4 portrays that BGA has a limited sorption capacity for adsorption of Cu (II) under the conditions employed in this investigation.

4.4.1 One Parameter Model

The Henry's law (one parameter) model is applied to the experimental data obtained for the adsorption of Cu (II) onto BGA. The parameter values and regression coefficient R2 are provided in Table 1. Since the R2 value is insignificant, the model fails to fit the experimental data under equilibrium condition.

Table: 1 Parameter values of one parameter adsorption isotherm model for adsorption of Cu (II) onto BGA

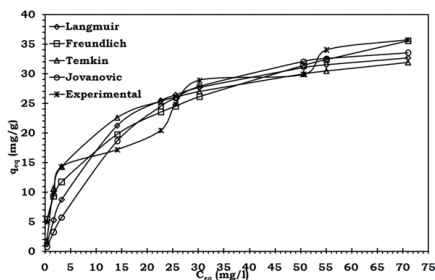| S.No	Models	Parameter	Value	SSE	R2	RMSE
1	Henry's law Isotherm Model	K	0.6346	612.6	0.3755	8.25

Figure 5: Comparison of experimental values of equilibrium uptake of Cu (II) with two parameter model values
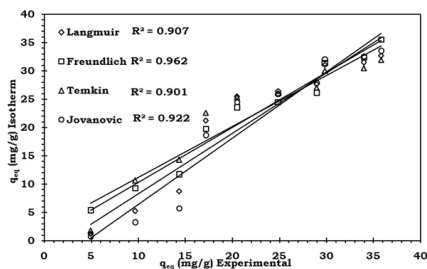
Figure 6: Concurrence of two parameter model values of equilibrium uptake of Cu (II) with experimental values

4.4.2 Two Parameter Models

The values of parameters and regression coefficient R2 of two parameter adsorption isotherm models for adsorption of Cu (II) onto BGA are given in Table 2. Dubinin-Radushkevich, Hill - de Boer, Halsey, Harkin-Jura, Elovich, and Kiselev are eliminated from the running discussion due to the poor and negative R-square values.

The results of Henry's law with intercept model, indicates that the linear relationship between qeq and Ceq is slightly improved due to the introduction of intercept term. However, due to less R2 value, the discussion is needless to extend.

Though significant R2 values are noticed in both Fowler-Guggenheim and Flory-Huggins models than Henry's law with intercept model, the parameter values obtained in both models (W and nFH) are negative which is not physically realizable. Hence both models are not valid. Similarly Temkin model is also invalid due to the high bT value which is not possible. Only three models viz. Freundlich, Jovanovic and Langmuir are taken to execute the further discussion. A plot of Ceq (mg/l) against qeq (mg/g) for the three models along with experimental qeq is shown in Figure 5.

Among the three models, Freundlich isotherm model shows greater accuracy with experimental data (R2 = 0.9628). It indicates the extent of heterogeneity of the BGA surface for adsorption. Due to this, the adsorptive surfaces of BGA are expected to be made up of small heterogeneous adsorption sites which are homogeneous in themselves. Through the surface exchange mechanism, adsorption sites are activated which results in increased adsorption. Since the value of nF is in the range of 1–10, it infers that the adsorption of Cu (II) from its synthetic solution onto BGA is a favourable one. The value of 1/nF is calculated as 0.3631 which is closer to zero ensures that the active sites of BGA for adsorption of Cu (II) onto its surface are more heterogeneous.

Followed by the Freundlich, Jovanovic isotherm model provides better agreement with experimental adsorption data. The high R2 value (R2=0.9019) infers that the recovery of Cu (II) metal ion from aqueous solution onto BGA is monolayer localized adsorption without lateral interaction. Also it ensures that this model sorption does not follow Henry's law. The maximum metal uptake predicted by this model (34.16 mg/g) shows greater coincidence with experimental value under equilibrium condition.

Subsequent to Freundlich and Jovanovic models, the results of Langmuir model indicates its applicability to explain the mechanism of adsorption of Cu (II) metal ion onto BGA. The R2 value of Langmuir model is also significant (R2 = 0.9072). It suggests the applicability of the Langmuir adsorption isotherm and indicates monolayer coverage of the sorbate at the outer surface of the sorbent. The value of Langmuir adsorption equilibrium constant bL is 0.0908 mL/g which shows quantitatively the affinity between Cu (II) and BGA. The calculated value of RL is in between 0 - 1, which ensures that the adsorption of Cu (II) onto BGA is favourable. Based on Langmuir isotherm model, the maximum adsorption capacity of BGA for Cu (II) is found to be 37.8 mg/g and it indicates the concurrence of Langmuir isotherm model with experimental data of adsorption of Cu (II) onto BGA is appreciable.

Since the R^2 values of the three models are high and give good agreement with the experimental data mathematically, a struggle raise to conclude the mechanism of adsorption. Figure 6 ensures the same and shows the comparison and extent of concurrence of the three models with experimental equilibrium metal uptake. It cannot be claimed that the entire three mechanisms suit for adsorption of Cu (II) onto BGA for the entire range of concentration employed in this investigation. Based on the R2, SSE and RMSE values, Freundlich isotherm mechanism obviously shows maximum satisfaction with the equilibrium experimental data. Hence it can be concluded that the BGA surface is highly heterogeneous and through the surface exchange mechanism, adsorption sites are activated which results in increased adsorption.

Table: 2 Parameter values of two parameter adsorption isotherm models for adsorption of Cu (II) onto BGA

S.N	Models	Parameter	Value	SSE	R2	RMSE
1	Henry's law Isotherm	K	0.4016	111.3	0.8865	3.73
		m	10.97			
2	Langmuir Isotherm Model	bL	0.09081	126.3	0.9072	3.974
		qmax	37.8			
		RL	0.2256			
3	Freundlich Isotherm Model	aF (mg/g)	7.567	36.53	0.9628	2.137
		nF	2.754			
4	Dubinin-Radushkevich Model	BDR	1.13×10^{-6}	299.3	0.6948	6.117
		KDR	27.54			
5	Temkin Isotherm Model	AT	3.592	96.45	0.9017	3.472
		bT	437.5			
6	Hill - de Boer Isotherm Model	K1	2.024×10^{4}	1.294×10^{4}	-1.401	40.22
		K2	1.535×10^{5}			
7	Fowler-Guggenheim Isotherm Model	KFG	4.692×10^{-8}	559.2	0.8963	8.36
		W	-0.2574			
8	Flory-Huggins Isotherm Model	KFH	0.0008136	5092	0.9012	25.23
		nFH	-1.067			
9	Halsey Isotherm	KHa	2.524×10^{4}	3740	-2.813	21.62
		nHa	3.479			
10	Harkin-Jura Isotherm Model	AHJ	3.576	23	-3.13	32
		BHJ	2.754			
11	Jovanovic Isotherm Model	KJ	0.05582	166	0.9229	4.555
		qmax	34.16			
12	Elovich Isotherm Model	KE	3.668×10^{-5}	615.2	0.3728	8.769
		qmax	1.724×10^{4}			
13	Kiselev Isotherm Model	KeqK	0.005766	1.262×10^{4}	-1.341	39.71
		KnK	733.9			

4.4.3 Three Parameter Models

Table 3 provides the parameter values for three parameter adsorption isotherm models for adsorption of Cu (II) onto BGA. Similar to the two parameter models, Redlich - Peterson, Langmuir-Freundlich, Fritz - Schlunder - III, Radke-Prausnits -II and Jossens Isotherm Models are eliminated due to their poor R^2 values. In addition, though Hill, Sips, Radke-Prausnits, Radke-Prausnits-III, Toth, Khan, Koble-Corrigan, Jovanovic–Freundlich, Brouers–Sotolongo, Unilan, Holl–Krich and Langmuir–Jovanovic Isotherm Models have significant R^2 values, their parameter and qmax values obtained are either negative or too high which are not physically realizable.

Vieth-Sladek isotherm model shows an admirable concurrence with experimental data points. Its R^2 value is highly significant (R^2 = 0.9630). Figure 7 shows the plot of Ceq (mg/l) against qeq (mg/g) for the Vieth-Sladek isotherm model against experiential data. Hence it is arrived that the adsorption of Cu (II) onto BGA is influenced by both van der waals forces (physical adsorption) and ionic forces (chemical adsorption) for the entire range of concentration employed in this investigation. However a conflict of interest arises upon the lower qmax value of 22.94 mg/g when compared with experimental qmax. Figure 8 shows the comparison and extent of concurrence of Vieth-Sladek isotherm model with experimental equilibrium uptake.
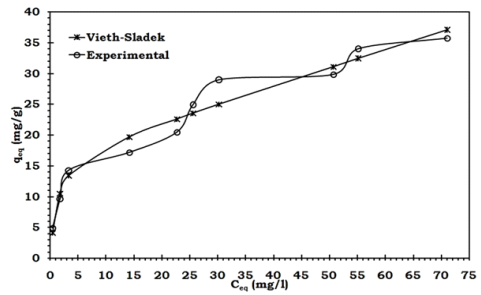

Figure 7: Comparison of experimental values of equilibrium uptake of Cu (II) with three parameter model values
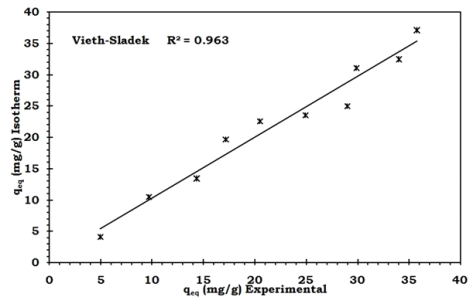

Figure 8: Concurrence of three parameter model values of equilibrium uptake of Cu (II) with experimental values

Table: 3 Parameter values of three parameter adsorption isotherm models for adsorption of Cu (II) onto BGA

S.No	Model	Parameter	Value	SSE	R2	RMSE
1	Hill Isotherm Model	KH	1812	38.32	0.9609	2.34
		nH	0.3421			
		qmax	1.486×10^{4}			
2	Redlich - Peterson Isotherm Model	ARP	9139	521.3	0.4685	8.63
		BRP	1.076×10^{4}			
		β	0.07902			
3	Sips Isotherm Model	KS	0.004063	37.39	0.9619	2.311
		qmax	1959			
		β	0.3529			
4	Langmuir-Freundlich Model	KLF	47.23	1613	0.07953	15.18
		mLF	0.3657			
		qmax	26.28			
5	Fritz - Schlunder - III Isotherm Model	KFS3	61.11	613.2	0.3749	9.359
		MFS3	-3.644			
		qmax	0.01038			
6	Radke-Prausnits Isotherm Model-I	KRaP1	502.9	100.2	0.8979	3.783
		MRaP1	0.482			
		qmax	0.1694			
	Radke-Prausnits Isotherm Model-II	KRaP2	0.02588	614.2	0.3738	9.367
		MRaP2	-4.595			
		qmax	24.512			
	Radke-Prausnits Isotherm	KRaP3	0.004082	43.71	0.9554	2.499
		MRaP3	0.4099			
		qmax	1566			
7	Toth Isotherm Model	KT	2.016	53.92	0.945	2.775
		nT	0.05782			
		qmax	9727			

S.No	Model	Parameter	Value	SSE	R2	RMSE
8	Khan Isotherm Model	aK	0.4839	99.08	0.899	3.762
		bK	539.3			
		qmax	0.1659			
9	Koble-Corrigan Isotherm Model	AKC	7.3	34.93	0.9644	2.234
		BKC	-0.09518			
		nKC	0.2848			
10	Jossens Isotherm Model	KJ	180.1	621.1	0.3668	9.42
		J	295.5			
		nJ	-0.003295			
11	Jovanovic–Freundlich Isotherm Model	KJF	0.006809	37.05	0.9622	2.301
		nJF	0.3559			
		qmax	1155			
12	Brouers–Sotolongo Isotherm Model	KBS	0.007144	37.06	0.9622	2.301
		BS	0.3561			
		qmax	1100			
13	Vieth–Sladek Isotherm Model	KVS	0.286	17.04	0.963	2.278
		βVS	0.8183			
		qmax	22.94			
14	Unilan Isotherm Model	KU	17.56	83.23	0.9151	3.448
		βU	-5.096			
		qmax	-0.004091			
15	Holl–Krich Isotherm Model	KHK	0.003768	37.03	0.9623	2.3
		nHK	0.3569			
		qmax	2081			
16	Langmuir–Jovanovic Isotherm Model	KLJ	-0.009047	60.53	0.9383	2.941
		nLJ	0.2664			
		qmax	1244			

4	Marczewski-Jaroniec Isotherm Model	KMJ	2.443×105	131.3	0.8662	4.677
		mMJ	11.27			
		nMJ	0.2624			
		qmax	51.21			

4.4.5 Five Parameter Model
Table 5 provides the parameter values of Fritz-Schlunder-V parameter model. R2 value gives the significance of this model. Figure 9 shows the comparison of experimental Cu (II) metal uptake against Fritz-Schlunder-V model under equilibrium condition. A significant concurrence of model data with experimental data is observed. Figure 10 shows that the equilibrium experimental metal uptake conforms to the Fritz-Schlunder-V adsorption isotherm model data. The qmax value of this isotherm model 34.55 mg/g is almost equal to the experimental qmax value. Hence the mechanism of adsorption of Cu (II) metal ion from synthetic aqueous solution follows the Fritz-Schlunder-V isotherm model.

Table: 5 Parameter values of five parameter adsorption isotherm model for adsorption of Cu (II) onto BGA

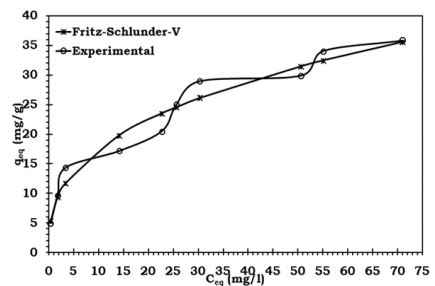| S.No	Model	Parameter	Value	SSE	R2	RMSE
1	Fritz - Schlunder - 5 Isotherm Model	K1FS5	2.144	36.53	0.9628	2.703
		K2FS5	8.795			
		FS5	0.3632			
		$\beta FS5$	0.00004455			
		qmax	34.55			

Figure 9: Comparison of experimental values of equilibrium uptake of Cu (II) with five parameter model values
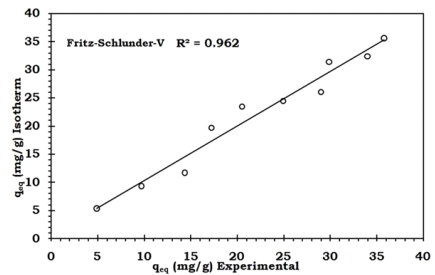

Figure 10: Concurrence of five parameter model values of equilibrium uptake of Cu (II) with experimental values.

5. CONCLUSION
The maximum adsorption capacity of BGA is found to be 35.79 mg/g at pH of 6 and 2 g of biomass loading and 120 rpm agitation speed. An increase in initial Cu (II) metal ion concentration results in the decrease of percentage removal and an increase in metal uptake (q_{eq}) due to the decrease in the ionic strength. The equilibrium experimental data infers that the isotherm is L shape which is and the indication of weak competition between solvent and Cu (II) to occupy the active sites of BGA. Also it indicates that the BGA has a limited sorption capacity for adsorption of Cu (II).

It is obvious that the Fritz-Schlunder-V isotherm model is highly significant in establishing the mechanism of adsorption of Cu (II) under the conditions employed in this investigation followed by Freundlich and Langmuir. The q_{max} 34.55 mg/g obtained by this

4.4.4 Four Parameter Models
Table 4 provides the parameter values of four parameter adsorption isotherm models. Among the four models, Baudu and Weber–van Vliet shows significant R2 value than Fritz–Schlunder-IV and Marczewski-Jaroniec models. However they are not applicable due to the inconsistent parameter values. Hence it can be concluded that all the four parameter models fail to explain the mechanism of adsorption.

Table:4 Parameter values of four parameter adsorption models for adsorption of Cu (II) onto BGA

S.No	Model	Parameter	Value	SSE	R2	RMSE
1	Fritz–Schlunder-IV Isotherm Model	AFS5	5403	490.7	0.4997	9.044
		BFS5	5743			
		FS5	0.3799			
		$\beta FS5$	-0.516			
2	Baudu Isotherm Model	x	-0.7413	39.07	0.9602	2.552
		y	0.2296			
		bo	0.4425			
		qmax	23.21			
3	Weber–van Vliet Isotherm Model	P1	14.56	34.94	0.9644	2.413
		P2	0.1764			
		P3	0.08377			
		P4	-0.453			

model indicates its relevance more precisely. The concurrence of experimental data with Vieth-Sladek isotherm model indicates that the adsorption of Cu (II) onto BGA is influenced both by van der waals forces and ionic forces for the entire range of concentration employed in this investigation.

CONFLICTS OF INTEREST
The authors declare that there are no conflicts of interest regarding the publication of this paper.

NOMENCLATURE
A   Fritz–Schlunder parameter
a_F Freundlich adsorption capacity
A_{HJ} Harkin-Jura isotherm constant
a_K Kahn isotherm model exponent
A_{KC} Koble - Corrigan's isotherm constant
A_{RP} Redlich-Peterson isotherm constant (L/g)
A_T Temkin equilibrium binding constant corresponding to the maximum binding energy
B   Fritz–Schlunder parameter BGAblue green algae
b   Langmuir constant related to adsorption capacity (L/mg)
b_0 Langmuir isotherm equilibrium constant,
B_{DR} Dubinin–Radushkevich model constant.
B_{HJ} Harkin-Jura isotherm constant
b_J Jossens isotherm model parameter
b_K Khan isotherm model constant
B_{KC} Koble - Corrigan's isotherm constant
b_L Langmuir constant related to adsorption capacity (mg/g)
B_{RP} Redlich-Peterson isotherm constant (L/mg),
b_T Temkin constant which is related to the heat of sorption (J/mol)
C   Henry's law models intercept
C_{eq} concentration of adsorbate in bulk solution at equilibrium (mg/L)
C_{in} initial adsorbate concentration (mg/L)
J   Jossens isotherm model parameter
K   Henry's constant
K_1 Hill - de Boer constant (L/mg),
K_{1FS5} Fritz–Schlunder-V parameter
K_2 energetic constant of the interaction between adsorbed molecules (kJ/mol)
K_{2FS5} Fritz–Schlunder-V parameter
K_{BS} Brouers–Sotolongo model isotherm parameter
K_{DR} Dubinin–Radushkevich model uptake capacity
K_E Elovich constant (L/mg)
K_{FG} Fowler–Guggenheim equilibrium constant (L/mg),
K_{FH} Flory-Huggins equilibrium constant (L/mol)
K_{FS3} Fritz–Schlunder III equilibrium constant (L/mg)
K_H Hill isotherm constant
K_{Ha} Halsey isotherm constant
K_{He} Henry's constant
K_{HK} Holl–Krich Isotherm Model parameter
K_J Jossens isotherm model parameter
K_J Jovanovic constant
K_{JF} Jovanovic- Freundlich isotherm equilibrium constant
K_K Kiselev equilibrium constant (L/mg)
K_{LF} Langmuir-Freundlich equilibrium constant for heterogeneous solid
K_{LJ} Langmuir–Jovanovic model parameter
K_{MJ} Marczewski-Jaroniec isotherm model parameter that characterize the heterogeneity of the adsorbent surface
K_{nK} equilibrium constant of the formation of complex between adsorbed molecules
K_{RaP} Radke-Prausnits equilibrium constant
K_S Sips isotherm model constant (L/mg)
K_T Toth isotherm constant (mg/g)
K_U Unilan isotherm model parameter
K_{VS} Vieth–Sladek isotherm model parameter related to Henry's law
m_{FS3} Fritz–Schlunder III model exponent
m_{LF} Langmuir-Freundlich heterogeneity parameter
m_{RaP} Radke-Prausnits model exponent
n_F Freundlich adsorption intensity
n_{FH} number of adsorbate occupying adsorption sites

n_H exponent of Hill adsorption model
n_{Ha} Halsey isotherm exponent
n_{HK} Holl–Krich Isotherm Model exponent
n_{JF} Jovanovic- Freundlich isotherm exponent
n_{KC} Koble - Corrigan's isotherm constant
n_{LJ} Langmuir–Jovanovic model exponent
n_{MJ} Marczewski-Jaroniec isotherm model parameter that characterize the heterogeneity of the adsorbent surface
n_T Toth isotherm exponent
P_1 Weber and van Vliet isotherm model parameter
P_2 Weber and van Vliet isotherm model parameter
P_3 Weber and van Vliet isotherm model parameter
P_4 Weber and van Vliet isotherm model parameter
q_{eq} amount of adsorbate in adsorbent at equilibrium (mg/g)
q_{max} maximum quantity of solute adsorbed by the adsorbent (mg/g)
R   gas constant (8.314 J/mol K)
R_L Langmuir separation factor
R_L Langmuir separation factor
T   absolute temperature (K)
W   interaction energy between adsorbed molecules (kJ/mol)
x   Baudu isotherm model parameter
y   Baudu isotherm model parameter

Greek letters
θ   fractional surface coverage
$β_{RP}$ Redlich-Peterson isotherm exponent
$β_S$ Sips isotherm exponent
$β_{BS}$ Brouers–Sotolongo model isotherm parameter is related to adsorption energy
$β_{VS}$ Vieth–Sladek isotherm model parameter related to Langmuir
$β_U$ Unilan isotherm model exponent
$β_{FS5}$ Fritz–Schlunder-V parameter
$β_{2FS5}$ Fritz–Schlunder-V parameter

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