ADSORPTION OF CADMIUM USING BLUE GREEN ALGAE: APPLICABILITY OF ISOTHERMS AND MODELING

Engineering

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ABSTRACT

The maximum adsorption capacity of blue green algae (BGA) is investigated through adsorption of Cd (II) from aqueous solution at optimum experimental conditions by varying the initial Cd (II) ion concentration. the maximum adsorption capacity of BGA is found to be 19.9 mg/g at the optimum experimental condition of pH is 6, 2 gm biomass loading, 120 rpm agitation speed and 24 hrs of contact time. The experimental data infers that the isotherm is L shape which indicates, no strong competition between solvent and Cd (II) to occupy the active sites of BGA. One, Two, Three, Four and Five parameter isotherm models are analysed with experimental data to identify the adsorption mechanism. Langmuir isotherm model is found to highly significant. The qmax value of Langmuir model 20.09 mg/g which is very much closer to the experimental qmax value. The Redlich-Peterson βRP is found to be 0.8354 which is close to 1. Hence Redlich-Peterson isotherm model approaches to Langmuir model. This implication is highly supported to arrive that the mechanism of adsorption of Cd (II) by BGA is governed by Langmuir model.

KEYWORDS

Cadmium, Adsorption, Blue Green Algae, Isotherms, Modeling.

INTRODUCTION

The quality of our environment is worsening gradually by the continuous release of untreated or partially treated industrial effluents (Coelho et al., 2018). Plating, photography, nuclear power plants petrochemical industries are main sources for the release of effluents with heavy metal contamination (Lixia et al., 2018). Heavy metals are high atomic weight and a density at least 5 times greater than that of water. Most of the metals including cadmium, chromium, copper, lead, mercury, nickel, selenium, silver and zinc are identified as toxic to human health and the environment (Hatairat et al., 2014). Continuous application of these heavy metals have led to their wide distribution in the environment; raising concerns over potential effects on human physical condition and the environment. Cadmium, even at low concentrations pose serious threats to living organisms and it has been reported in many countries to be the cause of serious health risks (Ehsan et al., 2018). The toxicity depends on several factors including dose, route of exposure, chemical species, age, gender, genetics, and nutritional status of exposed individuals. The permissible limit for cadmium in waste water as prescribed by the World Health Organization (WHO) is 0.003 mg/L. Industries are the main sources for employment and revenue to any country. There is no specific intention to release these toxic effluents into the environment. The only thing is the lack of suitable process and mechanism of treatment. Development of cheap and green remediation technology has become inevitable. The conventional techniques for the removal of heavy metals from water/waste water are chemical precipitation, electrochemical treatment, ion exchange, membrane separation, etc (Taher et al., 2018). However these technologies have certain constraints i.e., expensive, laborious, time-consuming etc., in real time operation. At the same time, these constrains can be overcome with adsorption mechanism. High efficiency, low cost, minimization of chemical or biological sludge, regeneration of sorbent and the possibility of metal recovery are the main advantages of adsorption process (Fu and Wang, 2011).

The mechanisms of adsorption may involve chemisorption, adsorption on surface, diffusion through pores, ion exchange, etc. Adsorption of metal ions is accomplished through electrostatic attraction between metal cations and negatively charged sites on the biosorbent surface such as, carboxyl, phosphoryl, phosphate, amino, amido, acetamido, sulfate and hydroxyl groups. Adsorption with low cost sorbent is the need of the hour in industrial effluent treatment. Hence it is still essential to develop a low-cost, easily available, high adsorption capacity material for heavy metal sorption that can rectify the pollution related environmental issues. Biosorption onto living or non-living biomass, such as fungi, bacteria, yeast, moss, aquatic plants and algae can be a feasible method for removal of heavy metals from their source (Laura et al., 2010; Dumitru and Laura, 2013). Existence of marine algae in coastal areas is important in global ecology, extremely efficient, and taxonomically diverse. Marine macro-algae are harvested or cultivated in many parts of the world and are therefore readily available in large quantities for the development of highly effective bio sorbent materials. In this investigation, it is aimed to use Blue Green Algae (BGA) as adsorbent to remove the Cd (II) metal ions from synthetic aqueous solution. The mechanism of Cd (II) adsorption from relevant sources with three, four and five parameter models in literature is very limited. The high parameter models would overcome the limitations of the simple, one and two-parameter models. Description with high parameter models may provide very clear and apt information about the adsorption process under equilibrium condition. The objectives of the present investigation are, (i) To study the biosorption capacity of BGA for the removal of Cd (II) metal ions from the synthetically prepared stock solution and (ii) To analysis of experimental data using various one, two, three, four and five parameter isotherm models for modeling.

2. MATERIALS AND METHODS

Cd (II) metal ion is adsorbed from synthetic aqueous solution. Blue Green Algae (BGA) is used as potent sorbent. Pre-treatment and preparation of adsorbent, preparation of synthetic stock solution and determination optimum experimental parameters viz., pH, temperature and adsorbent dosage under batch condition are provided. Also the effect initial metal ion concentration of equilibrium metal uptake is discussed. Investigation of effluent concentration to determine the equilibrium metal uptake experimentally and theoretically with isotherm models is discussed.

2.1. Adsorbent - BGA

BGA is collected from ponds in and around Chidambaram town and Veeranam Lake. The algae is washed with distilled water and dried at room temperature (above 30°C). After that it is powdered with a uniform size of 150-200 microns. The dried and powered algae is immobilized on silica gel using standard methods for continuous adsorption (Mahan and Holcombe, 1992) which involves wetting a mixture of silica gel and biomass with ultra pure water followed by drying at 150°C for 20 mins.

2.2. Adsorbate – Cd (II)

Cd $(NO_3)_2$ $4H_2O$ was used as the source of cadmium metal ions. The stock solution of Cd (II) is prepared by dissolving a pre calculated quantity of respective salt in double distilled water. This stock solutions are further diluted to obtain desired concentration in the range of 25 -250 ppm. The pH of each solution is adjusted 2 to 7. The pH adjustments are done by using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH) solutions. Double distilled water was used throughout the experiments for preparing aqueous solutions.

2.3. Analysis

The batch adsorption study is carried out in a 500 ml conical flask. The initial metal ion concentrations are varied to 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 ppm. The pH adjustments are done by using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH) solutions. The biomass to be added to the conical flask is varied from 0.5, 1.0, 1.5, 2.0 and 2.5 g. All the experiments are performed at the room temperature. The flasks are kept in a rotary shaker at rpm of 120 for 24 hours. This is more than sufficient for adsorption equilibrium. The samples are taken regularly with predetermined time intervals. The percentage removal and specific uptake of metal is then calculated.

The adsorption of Cd (II) metal ions from its respective synthetic solutions by the BGA is performed under shaking conditions in rotary shaker (REMI-12, India). The experiments are performed under batch operation mode. To each 400 ml of metal solution a desired quantity of the blue green microalgae is added in 500 ml conical flasks. The mixture is agitated in the rotary shaker at the room temperature and at 120 rpm for predetermined time intervals.

The initial and final concentrations of metal solutions are predicted by double beam Atomic Adsorption Spectrophotometer (AAS SL176-Elico Limited India). The percentage removal of metal ions is calculated from the initial concentration (C_i) and the analyzed final concentration (C_{eq}) of the metal ion solution according to the following Equation 1.

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

The equilibrium metal uptake is calculated from the initial concentration (Ci) and the analyzed final concentration (Ceq) of the metal ion solution according to the following Equation 2

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

Where V is the volume of liquid sample in litre and M is the weight of adsorbent. The same procedure is repeated for another initial metal ion concentration of 50 ppm, 75 ppm, 100 ppm, 125 ppm, 150 ppm, 175 ppm, 200 ppm, 225 ppm and 250 ppm of all the metals. The experimental variables namely pH and biomass loading are optimized and at these optimized conditions the effect of Initial metal ion concentration on percentage removal and specific uptake of metal ions are studied.

2.4. Equilibrium Adsorption Isotherms

One parameter model (Henry's Law), Two parameter models (Henry's Law with constant, Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Hill-de Boer, Fowler-Guggenheim, Flory-Huggins, Halsey, Harkin-Jura, Jovanovic and Elovich, 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 equilibrium adsorption data.

2.5. Cftool and Goodness-of-Fit Statistics

Applicability of these models to fit the experimental data in predicting the mechanism of adsorption is accomplished using cftool kit available in MATLAB R2010a software. This toolkit aids in estimating the model parameters along with the non-linear Regression coefficient (R^2), Adj R^2, Sum of Squares due to Error (SSE) and Root Mean Squared Error (RMSE).

3. ISOTHERM MODELS - THEORETICAL KNOWLEDGE

The isotherms of adsorption indicate the distribution of molecules between the liquid and solid phase when the adsorption process reaches equilibrium. It is employed to establish the maximum capacity of adsorption of metals on adsorbents, expressed in terms of quantity of metal adsorbed per unit mass of adsorbent used (mg/g). 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 (Foust and Aly, 1981; Ruthven, 1984).

3.1 ONE PARAMETER MODEL

The basic adsorption isotherm model contains only one parameter to explain the mechanism of adsorption is experienced here. This is the simplest adsorption isotherm in which the amount of solute adsorbed is related linearly with the equilibrium effluent concentration (Russo et al., 2005). This model describes the mechanism of adsorption appreciably only at low solute concentration. The model is given in Equation 3.

$$q_{eq} = \frac{q_{max} b_L C_{eq}}{1 + b_L C_{eq}} \quad (3)$$

bL is Langmuir constant related to adsorption capacity (mg/g), which correlates the variation of the suitable area and porosity of the adsorbent. The features of the Langmuir isotherm can be explained by a dimensionless constant called the Langmuir separation factor RL which is calculated as Equation 4.

$$R_L = \frac{1}{1 + b_L q_{max}} \quad (4)$$

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

3.1.2. Freundlich Isotherm Model

The Freundlich adsorption isotherm model 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 (Baroni et al., 2008). The model is given in Equation 5.

$$q_{eq} = a_F C_{eq}^{\frac{1}{n_F}} \quad (5)$$

a_F is Freundlich adsorption capacity (L/mg) and n_F is adsorption intensity. Relative distribution of the energy and the heterogeneity of the adsorbate sites are well indicated by this model. The larger the value of the adsorption capacity a_F, the higher the adsorption capacity is. The magnitude of $1/n_F$ ranges between 0 and 1 is an indicative of favourable adsorption, becoming more heterogeneous as its value tends to zero (Freundlich, 1906; Traybal, 1981).

3.1.3. 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 (Dubinin and Radushkevich, 1947). This empirical model is initially conceived for the adsorption of subcritical vapours onto micro pore solids following a pore filling mechanism. This model provides insight knowledge on the adsorption of gases and vapours on micro porous sorbents (Radushkevich, 1949).

This isotherm is applicable for intermediate range of adsorbate concentrations because it exhibits unrealistic asymptotic behaviour and does not predict Henry's laws at low pressure. Also it 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 the fact that it is temperature dependent (Dubinin, 1960; 1965). Dubinin-Radushkevich isotherm model is given in Equation 6.

$$q_{eq} = K_{DR} \exp\left[-B_{DR} \left(RT \ln(1 + \frac{1}{C_{eq}})\right)^2\right] \quad (6)$$

$$\varepsilon = RT \, Ln \left[\frac{1}{C_{eq}}\right] \quad (7)$$

ε is called as Polanyi Potential shown in Equation 7. Polanyi Potential is the energy of activation or mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution. It can be calculated by the Equation 8.

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (8)$$

The value of E is used to predict whether an adsorption is physisorption or chemisorptions. If E< 8 KJ/mol, the adsorption is physisorption and if E = 8-16 KJ/mol, the adsorption is chemisorptions in nature (Ozcan et al., 2005).

3.1.4. 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 (Temkin and Pyzhev, 1940; Temkin, 1941). The Temkin adsorption isotherm model is given in Equation 9.

$$q_{eq} = \frac{RT}{b_T} \left(\ln A_T \, C_{eq} \right) \qquad (9)$$

The term RT/b$_T$ correlates the heat of adsorption. A$_T$ is the equilibrium binding constant (L/mg) equivalent to the maximum binding energy.

3.1.5. Hill - de Boer Isotherm Model
Mobile adsorption as well as lateral interaction among adsorbed molecules is well described by this Hill - Deboer isotherm model (Hill, 1946; 1952). The Hill - Deboer isotherm model is given in Equation 10.

$$K_1 C_{eq} = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta} - \frac{K_2 \, \theta}{R \, T} \right) \quad (10)$$

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 (De Boer, 1953).

3.1.6 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 11.

$$K_{FG} \, C_{eq} = \frac{\theta}{1 - \theta} \exp\left[\frac{2\theta W}{RT} \right] \qquad (11)$$

Positive W indicates that the interaction between the adsorbed molecules is attractive. Negative W value is the indication of the interaction among adsorbed molecules is repulsive. If W is equal to zero, there is no interaction between adsorbed molecules and this model reduced to the Langmuir (Kumara et al., 2010; Sampranpiboon et al., 2014). This model simply relates the interaction between the adsorbed molecules and heat of adsorption. If the interaction between the adsorbed molecules is attractive it results an increase in heat of adsorption. Similarly if the interaction between the adsorbed molecules is repulsive, it results a decrease in heat of adsorption.

3.1.7. Flory-Huggins Isotherm Model
Flory-Huggins isotherm discusses the degree of surface coverage characteristics of the adsorbate onto the adsorbent. This model is well appropriate to find the feasibility and spontaneous nature of an adsorption process (Hamdaoui and Naffrechoux, 2007; Amin et al., 2015; Ayawei et al., 2017; Ebelegi et al., 2017). Flory-Huggins adsorption isotherm model is given in Equation 12.

$$\frac{\theta}{C_{in}} = K_{FH} \left[1 - \theta \right]^{n_{FH}} \qquad (12)$$

KFH is used to calculate the spontaneity Gibbs free energy.
3.1.8. Halsey Isotherm Model

Halsey adsorption isotherm model is appropriate to discuss the multilayer adsorption at a relatively large distance from the surface. The fitting of the experimental data to this equation prove to the heteroporous nature of the adsorbent (Fowler and Guggenheim, 1939). Halsey adsorption isotherm model is given in Equation 13.

$$q_{eq} = Exp\left[\frac{Ln \, K_{Ha} - Ln \, C_{eq}}{n_{Ha}} \right] \qquad (13)$$

3.1.9. Harkin-Jura Isotherm Model
Hurkin-Jura adsorption isotherm accounts for 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 (Foo and Hameed, 2010). Hurkin-Jura adsorption isotherm model is given in Equation 14.

$$q_{eq} = \sqrt{\frac{A_{HJ}}{B_{HJ} - Log \, C_{eq}}} \qquad (14)$$

3.1.10. Jovanovic Isotherm Model
Jovanovic adsorption isotherm model is similar to that of Langmuir model with the approximation of monolayer localized adsorption without lateral interactions. The assumptions in this model are same in the Langmuir model in addition with the possibility of some mechanical contacts between the adsorption and desorbing molecules (Jovanovic, 1969). Jovanovic adsorption isotherm model is given in Equation 15. At high concentrations of adsorbate, it becomes the Langmuir isotherm.

$$q_{eq} = q_{max} \left[1 - e^{-(K_J \, C_{eq})} \right] \qquad (15)$$

At high concentrations of adsorbate, it becomes the Langmuir isotherm.

3.1.11. Elovich Isotherm Model
The Elovich isotherm model 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 (Elovich and Larinov, 1962). The Elovich adsorption isotherm model is given in Equation 16.

$$\frac{q_{eq}}{q_{max}} = K_E C_{eq} \, exp^{\frac{q_{eq}}{q_{max}}} \qquad (16)$$

3.1.12. Kiselev Isotherm Model
The Kiselev adsorption isotherm model explains the localized monomolecular layer formation of adsorbate on adsorbents (Kiselev, 1958). This model is valid when surface coverage θ is greater than 0.68. The Kiselev adsorption isotherm model is given in Equation 17.

$$K_{eqK} \, C_{eq} = \frac{\theta}{(1 - \theta)(1 + K_{nK} \, \theta)} \qquad (17)$$

3.2. THREE PARAMETER MODELS
Models containing three parameters to explain the mechanism of adsorption are discussed using sixteen models viz., Hill, Redlich-Peterson, Sips, Langmuir-Freundlich, Fritz-Schlunder-III, Radke-Prausnits, Toth, Khan, Koble-Corrigan, Jossens, Jovanovic–Freundlich, Brouers–Sotolongo, Vieth–Sladek, Unilan, Holl–Krich and Langmuir–Jovanovic.

3.2.1. Hill Isotherm Model
The Hill isotherm model is derived to describe the adherence of different species onto homogeneous substrates. An assumption is made in this model is adsorption is a cooperative phenomena. It indicates that the adsorbate at one site of the adsorbent would influence the other sites on the same adsorbent (Hill, 1910). Hill adsorption isotherm model is given in Equation 18.

$$q_{eq} = \frac{q_{max} \, C_{eq}^{n_H}}{K_H + C_{eq}^{n_H}} \qquad (18)$$

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, indicating negative co-operativity in binding.

3.2.2. Redlich-Peterson Isotherm Model
The Redlich-Peterson isotherm model is derived with hybrid features of Langmuir and Freundlich isotherms. Consequently the mechanism of adsorption is a hybrid one and it does not follow ideal monolayer adsorption (Redlich and Peterson, 1959). This Redlich-Peterson isotherm model is given in Equation 19.

$$q_{eq} = \frac{A_{RP} \, C_{eq}}{1 + B_{RP} C_{eq}^{\beta}} \qquad (19)$$

This model is applicable with wide concentration range; the model has a linear dependence on concentration in the numerator and an exponential function in the denominator. It is applicable for both homogeneous and heterogeneous systems. 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 = 1 this model approaches Langmuir model and βRP = 0 this isotherm approaches to Freundlich model.

3.2.3. Sips Isotherm Model
Sips adsorption isotherm model described mainly the localized

adsorption without adsorbate-adsorbate interactions (Sips, 1948). This model is a combined 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 (Valenzuela and Myers, 1989). Sips adsorption isotherm model is given in Equation 20.

$$q_{eq} = \frac{q_m K_s C_{eq}^{\beta_s}}{1 + K_s C_{eq}^{\beta_s}} \qquad (20)$$

When β_S equal to 1 this isotherm approaches Langmuir isotherm and β_S equal to 0, this isotherm approaches Freundlich isotherm.

3.2.4. Langmuir-Freundlich Isotherm Model
Langmuir-Freundlich isotherm model describes the adsorption in heterogeneous surfaces. It explains the distribution of adsorption energy of the adsorbent 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 (Langmuir, 1916). Langmuir-Freundlich isotherm model is given in Equation 21.

$$q_{eq} = \frac{q_{max} \left(K_{LF} C_{eq} \right)^{m_{LF}}}{1 + \left(K_{LF} C_{eq} \right)^{m_{LF}}} \qquad (21)$$

m_{LF} is heterogeneous parameter and it lies between 0 and 1. m_{LF} would increase with a decrease in degree of surface heterogeneity. For mLF is equal to 1, this model covert to Langmuir model.

3.2.5. Fritz-Schlunder-III Isotherm Model
Fritz - Schlunder three parameter isotherm models is developed to fit over an extensive range of experimental results because of huge number of coefficients in their isotherm (Fritz and Schlunder, 1974). This expression is given in Equation 22.

$$q_{eq} = \frac{q_{max} K_{FS3} C_{eq}}{1 + q_{max} C_{eq}^{m_{FS3}}} \qquad (22)$$

If m_{FS3} 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.

3.2.6. 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 m_{RaP3} is equal to zero, this model becomes the Langmuir isotherm (Radke and Prausnitz, 1972). Radke-Prausnits isotherm models are given in Equations 23 to 25.

Model 1 $q_{eq} = \dfrac{q_{max} \ K_{RaP1} C_{eq}}{\left[1 + K_{RP1} C_{eq}\right]^{m_{RaP1}}} \qquad (23)$

Model 2 $q_{eq} = \dfrac{q_{max} \ K_{RaP2} C_{eq}}{1 + K_{RP2} C_{eq}^{m_{RaP2}}} \qquad (24)$

Model 3 $q_{eq} = \dfrac{q_{max} \ K_{RaP3} C_{eq}^{m_{RaP3}}}{1 + K_{RP3} C_{eq}^{m_{RaP3}-1}} \qquad (25)$

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 models become 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.

3.2.7. Toth Isotherm Model
Toth adsorption isotherm model is developed to describe the heterogeneous adsorption systems which satisfy both low and high end boundary of adsorbate concentration. This model is the modified form of Langmuir isotherm with the intension of rectifying the error between experimental and predicted data (Toth, 1971). The Toth isotherm model is given Equation 26.

$$q_{eq} = \frac{q_{max} C_{eq}}{\left(\frac{1}{K_T} + C_{eq}^{n_T} \right)^{\frac{1}{n_T}}} \qquad (26)$$

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.

3.2.8. Khan Isotherm Model
The Kahn isotherm model is developed for adsorption of bi-adsorbate from pure dilute equations solutions. This isotherm has applicable on both limits Freundlich on one end and Langmuir isotherm on the other end (Khan et al., 1997). Kahn isotherm model is given in Equation 27.

$$q_{eq} = \frac{q_m b_K C_{eq}}{(1 + b_K C_{eq})^{a_K}} \qquad (27)$$

While a_K 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.

3.2.9. Koble-Corrigan Isotherm Model
Koble-Corrigan isotherm model is the resemblance of Sips isotherm model. This model incorporates both Langmuir and Freundlich isotherm (Koble and Corrigan, 1952). Koble-Corrigan isotherm model is given in Equation 28.

$$q_{eq} = \frac{A_{KC} C_{eq}^{n_{KC}}}{1 + B_{KC} C_{eq}^{n_{KC}}} \qquad (28)$$

This model reduces to Freundlich at high adsorbate concentrations. It is only valid when the constant n is greater than or equal to 1. When n is less than unity, it signifies that the model is incapable of defining the experimental data despite high concentration coefficient or low error value.

3.2.10. Jossens Isotherm Model
The Jossens isotherm model is developed on the basis of energy distribution of adsorbate-adsorbent interactions at adsorption sites. An assumption is made in this model is the adsorbent has heterogeneous surface with respect to the interactions it has with the adsorbate (Jossens et al., 1978). At low concentrations this model is reduced to Henry's law model. Jossens isotherm model is given in Equation 29.

$$q_{eq} = \frac{K_J C_{eq}}{1 + J \, C_{eq}^{b_J}} \qquad (29)$$

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

3.2.11. Jovanovic–Freundlich Isotherm Model
Jovanovic–Freundlich isotherm model is developed to describe single-component adsorption equilibrium on heterogeneous surfaces. An assumption is 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. If the adsorbent surface is homogeneous, this model reduced to Jovanovic. 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 regard as the possibility of some mechanical contacts between the adsorbing and desorbing molecules. Furthermore, this isotherm was utilized for heterogeneous surfaces without lateral interactions (Quinones and Guiochon, 1996). Jovanovic–Freundlich isotherm model is given in Equation 30.

$$q_{eq} = q_{max} \left[1 - e^{-(K_{JF} C_{eq}^{n_{JF}})} \right] \qquad (30)$$

3.2.12. 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 (Brouers et al., 2005). Brouers–Sotolongo model is given in Equation 31.

$$q_{eq} = q_{max} \left[1 - e^{\left(- K_{BS} C_{eq}^{\alpha_{BS}} \right)} \right] \qquad (31)$$

The parameter $_{BS}$ is related with distribution of adsorption energy and the energy of heterogeneity of the adsorbent surfaces at the given temperature (Ncibi et al., 2008).

3.2.13. Vieth–Sladek Isotherm Model
This model incorporates two distinct sections to calculate the diffusion rates in solid adsorbents from 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 clarifies 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 (Vieth and Sladek, 1965). Vieth–Sladek isotherm model is given in Equation 32.

$$q_{eq} = K_{VS}C_{eq} + \frac{q_{max}\beta_{VS}C_{eq}}{1 + \beta_{VS}C_{eq}} \qquad (32)$$

3.2.14. Unilan Isotherm Model
Unilan isotherm model is presumed 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 [42]. Unilan isotherm model is given in Equation 33.

$$q_{eq} = \frac{q_{max}}{2\beta_U} Ln \left[\frac{1 + K_U C_{eq} e^{\beta_U}}{1 + K_U C_{eq} e^{-\beta_U}} \right] \qquad (33)$$

The higher the model exponent βU, the system is more heterogeneous. 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 (Jossens et al., 1978; Chem and Wu, 2001; Hadi et al., 2012).

3.2.15. Holl–Krich Isotherm Model
Holl–Krich Isotherm Model is a modified form of Langmuir isotherm (Parker, 1995). This model becomes the Freundlich isotherm at low concentrations. The capacity reaches a finite capacity more leisurely than the Langmuir isotherm at high concentrations. Holl–Krich Isotherm Model is given in Equation 34.

$$q_{eq} = \frac{q_{max}K_{HK}C_{eq}^{n_{HK}}}{1 + K_{HK}C_{eq}^{n_{HK}}} \qquad (34)$$

3.2.16. Langmuir–Jovanovic Isotherm Model
This empirical model is the combined form of both Langmuir and Jovanovic isotherm (Shahbeig et al., 2013). The Langmuir–Jovanovic model is given in Equation 35.

$$q_{eq} = \frac{q_{max}C_{eq}\left[1 - e^{\left(K_{LJ}C_{eq}^{n_{LJ}}\right)}\right]}{1 + C_{eq}} \qquad (35)$$

3.3. FOUR PARAMETER MODELS
The four parameter models discussed in this study are Fritz–Schlunder-IV, Baudu, Weber–van Vliet and Marczewski-Jaroniec models.

3.3.1. Fritz–Schlunder-IV Isotherm Model
Fritz–Schlunder IV model is another model comprised of four-parameter with combine features of Langmuir–Freundlich isotherm (Fritz and Schlunder, 1974). The model is given in Equation 36.

$$q_{eq} = \frac{A_{FS5} C_{eq}^{\alpha_{FS5}}}{1 + B_{FS5}C_{eq}^{\beta_{FS5}}} \qquad (36)$$

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.

3.3.2. Baudu Isotherm Model
Baudu isotherm model has been developed mainly due to arise of discrepancy in calculating Langmuir constant and coefficient from slope a tangent over a broad range of concentrations (Baudu, 1990). Baudu isotherm model is the transformed form of the Langmuir isotherm. It is given in Equation 37.

$$q_{eq} = \frac{q_{max}\ b_o\ C_{eq}^{(1+x+y)}}{1 + b_o C_{eq}^{(1+x)}} \qquad (37)$$

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

For lower surface coverage, Baudu model reduces to the Freundlich equation (McKay et al., 2014). It is given in Equation 38.

$$q_{eq} = \frac{q_{m0}\ b_o\ C_{eq}^{(1+x+y)}}{1 + b_0} \qquad (38)$$

3.3.3. Weber–van Vliet Isotherm Model
Weber and van Vliet isotherm model is to describe equilibrium adsorption data with four parameters (van Vliet et al., 1980). The model is given in Equation 39.

$$C_{eq} = P_1\ q_{eq}^{\left(P_2 q_{eq}^{P_3} + P_4\right)} \qquad (39)$$

The isotherm parameters P1, P2, P3 and P4 can be defined by multiple nonlinear curve fitting techniques which is predicated on the minimization of sum of square of residual.

3.3.4. 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 (Parker, 1995; Sivarajasekar and Baskar, 2014). The Marczewski-Jaroniec isotherm model is given in Equation 40.

$$q_{eq} = q_{max} \left[\frac{(K_{MJ}C_{eq})^{n_{MJ}}}{1 + (K_{MJ}C_{eq})^{n_{MJ}}} \right] \qquad (40)$$

K_{MJ} describes the spreading of distribution in the path of higher adsorption energy. n_{MJ} describes the spreading in the path of lesser adsorption energies. The isotherm reduces to Langmuir isotherm when n_{MJ} and K_{MJ} are equal to unity. The isotherm reduces to Langmuir-Freundlich model when n_{MJ} equal to KMJ.

3.4. FIVE PARAMETER MODEL
Accounting the high parameter models certainly provides clear information on mechanism of adsorption under equilibrium condition. In this section, only one, five parameter model i.e., Fritz-Schlunder-V isotherm model is applied.

3.4.1. 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 (Fritz and Schlunder, 1974). Fritz-Schlunder adsorption isotherm model is given in Equation 41.

$$q_{eq} = \frac{q_{max}K_{1FS5}C_{eq}^{\alpha_{FS5}}}{1 + K_{2FS5}C_{eq}^{\beta_{FS5}}} \qquad (41)$$

4. RESULTS AND DISCUSSION
Adsorption of Cd (II) metal ion from its respective aqueous solution is studied with BGA as an adsorbent. In this present investigation the maximum adsorption capacity of BGA is found to be 19.9 mg/g at the optimum experimental condition of pH is 6, 2 gm biomass loading, 120 rpm agitation speed and 24 hrs of contact time. All the experiments are performed at room temperature $28 \pm 1^{\circ}C$.

4.1 BGA- Biomass characterization
The analysis of unloaded and Cd (II) loaded BGA is shown in Figure 1 and Figure 2 respectively. The shift of wave number from 3420.08 cm-1 [BGA-unloaded] to 3418.92 cm-1 [BGA-Cd (II) loaded] indicates that surface -OH and -NH groups are responsible for adsorption. Also the wave numbers 2926.42 cm-1 and 2518.50 cm-1 [BGA-unloaded] are shifted to 2927.70 cm-1 and 2521.67 cm-1 [BGA-Cd (II) loaded] due to the -CH$_2$ stretching responsible for Cd (II) adsorption. The broad adsorption bands 1633.83 cm^{-1} and 1428.48 cm-1 (BGA unloaded) shifted to 1631.77 cm-1 and 1428.57 cm-1 indicates an interaction between Cd (II) and C=O group of carboxylic at the surface of the BGA. 1104.71 cm^{-1} indicates the S=O stretching which is slightly shifted to 1105.82 cm^{-1}. The shifting and broadening of the bands located at 400 - 900 cm^{-1} is due to the loading effect of Cd (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 Cd (II) ions through ion exchange and complex reactions (Sivarajasekar and Baskar, 2014; Lei et al., 2017).
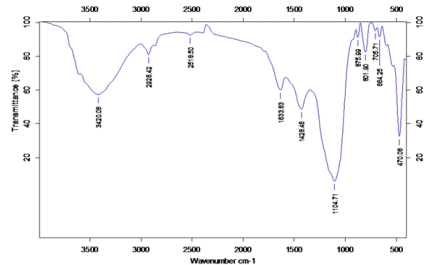
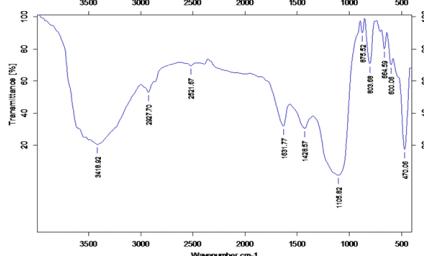**Figure 1 FTIR spectra of BGA biomass after adsorption of Cd (II)**

Figure 2 FTIR spectra of BGA biomass before adsorption of Cd (II)

4.2 BGA - Maximum adsorption capacity

The predicted value of maximum adsorption capacity of BGA is compared with earlier investigation done on the adsorption of Cd (II) form aqueous solution with different adsorbent for validation. (Lei et al., 2017) studied the adsorption of Cd (II) from aqueous solution by modified biomass ash and found the maximum adsorption capacity of 23.95 mg/g in a pH 5. Though the q_{max} is relatively slightly higher than the present investigation, their sorbent are found to be more effective at a low pH which is highly acidic. However such acidic environments are tedious, hazardous and also uneconomical to industrial scale. Aylin at al., (2012) studied the adsorption of Cd (II) from aqueous solution using manganoxide mineral as potent sorbent and reported its maximum adsorption capacity of 6.8 mg/g at the optimum pH of 6. Giwa et al., (2013) investigated the removal of Ca (II) from waste-water using husk of melon *(Citrullus lanatus)* Seed as potent sorbent and detailed its maximum adsorption capacity of 7.81 mg/g at the optimum pH of 6. Abhishek et at., (2015) studied the adsorption of Cd (II) from aqueous solution using Coffee Grounds and Wheat Straw as an adsorbent and found the maximum adsorption capacity of coffee grounds and wheat straw as 16.2 and 31.6 mg/g respectively at the optimum pH of 4.5. Maria et al., (2017) studied Cd (II) removal from aqueous solution using spent coffee grounds as adsorbent and reported that the maximum adsorption capacity is 4.48 mg/g at 10 °C and normal pH of 7. Based on the above said earlier investigations done on adsorption of Cd (II), it is obvious that the selected adsorbent BGA can be considered potent adsorbent in terms of availability, accessibility and cost.
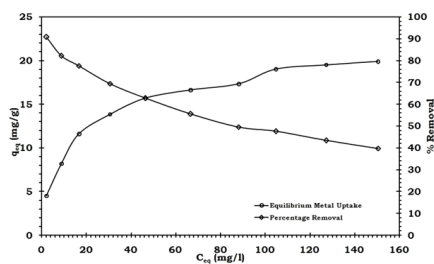

Figure 3 Effect of initial metal ion concentration on equilibrium metal uptake and % removal for adsorption of Cd (II) onto BGA
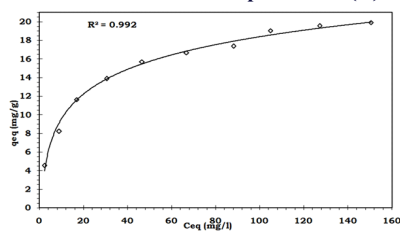

Figure 4 Sorption isotherm for adsorption of Cd (II) by BGA

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

The effect of initial Cd (II) solution concentration on equilibrium metal uptake and percentage removal is shown graphically in Figure 3. It is understandable that the % removal of Cd (II) metal ion decreases with an increase in initial metal ion solution 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, an increase in initial metal ion concentration increases the equilibrium metal uptake (q_{eq}) due to the decreasing ionic strength. At low initial metal ion concentration, the ionic strength of Cd (II) ions is more which smother the amount of metal uptake. Also the electrostatic attraction is another reason which is severely affected by increased ionic strength.

4.4 Adsorption Isotherms

Figure 4 is a plot of equilibrium concentration of Cd (II) solution against equilibrium Cd (II) metal uptake which is very much useful to perceive the shape of the isotherm (Schay, 1982; Hamdaouia and Naffrechoux, 2007). The shape of the adsorption isotherm helps to identify the nature of the adsorption phenomena of Cd (II) onto BGA. Giles et al., (1960) classified the isotherms according to their shapes and grouped as L, S, H, and C. Based on the above classification, the isotherm of Cd (II) onto BGA confirms the L curve pattern. The L shape is the indication of no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites (Limousin et al., 2007). Also the concavity nature of the curve in Figure 1 is designated 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. Further, there are two sub-groups of L shaped isotherms according to Limousine et al., (2017): (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). Based on Limousine et al., (2007), it is observed that (Figure 1) BGA has a limited sorption capacity for adsorption of Cd (II) under the conditions employed in this investigation.

4.4.1 One Parameter Model

The experimental data obtained for the adsorption of Cd (II) onto BGA is applied to Henry's law (one parameter) model for analysis. The parameter values and regression coefficient R^2 are provided in Table 1. Since the R^2 value is negative, the model fails to fit the experimental data under equilibrium condition.

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

S. No	Models	Parameter	Value	SSE	R2	Adj R2	RMSE
1	Henry's law Isotherm Model	K	0.1763	345	-0.4589	-0.4589	6.191

4.3 Two Parameter Models

Table 2 provides the parameters and R^2 values of two parameter adsorption isotherm models for adsorption of Cd (II) onto BGA. Dubinin-Radushkevich, Hill - de Boer, Fowler-Guggenheim, Halsey, Harkin-Jura, Henry's law model with constant, Flory-Huggins, Elovich, and Kiselev are eliminated from the discussion due to their irrelevant R^2 values. The order of the fit of remaining four models is Langmuir, Freundlich, Jovanovic and Temkin. Langmuir model alone considered for discussion due to its superior R^2 value than Freundlich, Jovanovic and Temkin models. Figure 5 helps to a great extent from which it is obvious that the concurrence of Langmuir isotherm mechanism with experimental data is much closer than Freundlich, Freundlich, Jovanovic and Temkin models for the entire range of initial concentration of Cd (II) solution.

Langmuir model shows best fit with R^2 value of 0.9781. The paramount agreement with experimental adsorption data is ensured by Langmuir isotherm model. It implies that the formation of monolayer coverage of the sorbate at the outer surface of the sorbent. The value of Langmuir constant R_L is 0.3972 mL/g which shows quantitatively the affinity between Cd (II) and BGA. Since the calculated value of R_L is in between 0 - 1, it ensures that the BGA is favourable adsorbent for adsorption of Cd (II). The q_{max} value of Langmuir model 20.09 mg/g which is very much closer to the experimental q_{max} value of 19.9 mg/g.

The SSE and RMSE values of Langmuir model are found to be 5.181 and 0.8048. Hence the Langmuir isotherm model described suitably

about the mechanism of adsorption of Cd (II) by BGA from its synthetic solution.

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

S.No	Models	Parameter	Value	SSE	R^2	Adj R^2	RMSE
1	Henry's law Isotherm Model	K	0.08834	47.28	0.8	0.775	2.431
		m	8.9710				
2	Langmuir Isotherm Model	b_L	0.07239	5.181	0.9781	0.9753	0.8048
		q_{max}	20.96				
		R_L	0.3972				
3	Freundlich Isotherm Model	a_F (mg/g)	4.701	6.522	0.9724	0.9690	0.9029
		n_F	3.371				
4	Dubinin-Radushkevich Model	B_{DR}	0.7431	2382	-9.075	-10.33	17.26
		K_{DR}	0.3922				
5	Temkin Isotherm Model	A_T	1.273	1.864	0.9222	0.9212	0.8804
		b_T	6.425				
6	Hill - de Boer Isotherm Model	K_1	749.9	2382	-9.075	-10.33	17.26
		K_2	820.8				
7	Fowler-Guggenheim Isotherm Model	K_{FG}	1176	2382	-9.075	-10.33	17.26
		W	-1496				
8	Flory-Huggins Isotherm Model	K_{FH}	4376	189.1	0.2002	0.1002	4.862
		n_{FH}	-0.0002685				
9	Halsey Isotherm Model	K_{Ha}	6.843×10^{11}	482.6	-1.041	-1.296	7.767
		n_{Ha}	9.179				
10	Harkin-Jura Isotherm Model	A_{HJ}	Complex value computed by model function, fitting cannot continue				
		B_{HJ}					
11	Jovanovic Isotherm Model	K_J	0.05564	16.37	0.9308	0.9221	1.43
		q_{max}	18.4				
12	Elovich Isotherm Model	K_E	-0.006278	55.58	0.7649	0.7355	2.636
		q_{max}	-92.86				
13	Kiselev Isotherm Model	K_{eqK}	-0.1133	219	0.0737	-0.0420	5.232
		K_{nK}	-0.004098				

4.3 Three Parameter Models

Table 2 provides the values of parameters and regression coefficient R^2 of three parameter adsorption isotherm models for adsorption of Cd (II) onto BGA. As in the case of two parameter models, Sips, Langmuir-Freundlich, Toth, Vieth–Sladek, Unilan, Holl–Krich and Langmuir–Jovanovic isotherm model are eliminated from the running discussion in the initial stage itself due to its poor R^2 values. Though Hill, Fritz - Schlunder – III, Radke-Prausnits Isotherm model-I, model-II and model-III and Khan isotherm models have significant R^2 values, the qmax values obtained in each of these models are either negative or low or high which are not physically realizable. Hence these models are also eliminated from the running discussion. Koble-Corrigan isotherm model shows the best concurrence with experimental data points. Its R^2 value is equal to 0.9950. Though the R^2 value gives good mathematical agreement, the n_{KC} is 0.6482 shows that it cannot be physically realizable.

The order of the fit of remaining four models is Redlich - Peterson,

Koble-Corrigan, Jossens, Jovanovic–Freundlich and Brouers–Sotolongo. Though it is difficult to justify the best fit from Figure 6, Redlich- Peterson model is alone considered for discussion due to its superior R^2 value than Koble-Corrigan, Jossens, Jovanovic–Freundlich and Brouers–Sotolongo models. Figure 6 shows the plot of C_{eq} (mg/l) against q_{eq} (mg/g) for the four models such as Redlich-Peterson, Jossens, Jovanovic–Freundlich and Brouers–Sotolongo isotherm models along with experiential values.

Redlich-Peterson isotherm model gives the R^2 value of 0.9946. It's SSE and RMSE values are found to be 1.28 and 0.4276 respectively. It ensures that the mechanism of adsorption of Cd (II) by BGA from its synthetic aqueous solution is hybrid features of Langmuir and Freundlich isotherms. The β_{RP} is found to be 0.8354 and it is close to 1. Hence Redlich-Peterson isotherm model approaches to Langmuir model. This implication is highly supported with the discussion in the two parameter model.

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

S.No	Model	Parameter	Value	SSE	R2	Adj R2	RMSE
1	Hill Isotherm Model	KH	8.423	1.189	0.995	0.9935	0.4121
		nH	0.6482				
		qmax	26.37				
2	Redlich - Peterson Isotherm Model	ARP	3.0412	1.28	0.9946	0.993	0.4276
		BRP	0.3309				
		β	0.8354				
3	Sips Isotherm Model	KS	41.87	231	0.02311	-0.256	5.744
		qmax	14.77				
		β	0.392				
4	Langmuir-Freundlich Model	KLF	Complex value computed by model function, fitting cannot continue				
		mLF					
		qmax					
5	Fritz - Schlunder - III Isotherm Model	KFS3	4.701	6.523	0.9724	0.9645	0.9653
		MFS3	0.7033				
		qmax	-1.202×10^4				
6	Radke-Prausnits Isotherm Model-I	KRaP1	0.2512	1.386	0.9941	0.9925	0.445
		MRaP1	0.8111				
		qmax	10.33				

|							
	Radke-Prausnits Isotherm Model-II	KRaP2	-2.035×10^4	6.523	0.9724	0.9645	0.9653
		MRaP2	0.7033				
		qmax	4.701				
	Radke-Prausnits Isotherm Model-III	KRaP3	3.022	1.28	0.9946	0.993	0.4276
		MRaP3	0.1646				
		qmax	3.041				
7	Toth Isotherm Model	KT	0.9619	2382	-9.075	-11.95	18.45
		nT	0.004634				
		qmax	0.7749				
8	Khan Isotherm Model	aK	0.8111	1.386	0.9941	0.9925	0.445
		bK	0.2512				
		qmax	10.33				
9	Koble-Corrigan Isotherm Model	AKC	3.13	1.189	0.995	0.9935	0.4121
		BKC	0.1187				
		nKC	0.6482				
10	Jossens Isotherm Model	KJ	3.041	1.28	0.9946	0.993	0.4276
		J	0.3309				
		nJ	0.8354				
11	Jovanovic–Freundlich Isotherm Model	KJF	0.1509	1.37	0.9942	0.9925	0.4424
		nJF	0.5486				
		qmax	21.85				
12	Brouers–Sotolongo Isotherm Model	KBS	0.1509	1.37	0.9942	0.9925	0.4424
		BS	0.5486				
		qmax	21.85				
13	Vieth–Sladek Isotherm Model	KVS	0.0883	47.28	0.8	0.7429	2.599
		βVS	-2.049×10^4				
		qmax	8.971				
14	Unilan Isotherm Model	KU	21.61	178.7	0.2444	0.0284	5.052
		βU	-3.541				
		qmax	-0.0073				
15	Holl–Krich Isotherm Model	KHK	13.42	220.1	0.0692	-0.1967	5.607
		nHK	0.4263				
		qmax	15.01				
16	Langmuir–Jovanovic Isotherm Model	KLJ	-4.911	138.8	0.4131	0.2454	4.453
		nLJ	3.805				
		qmax	15.8				
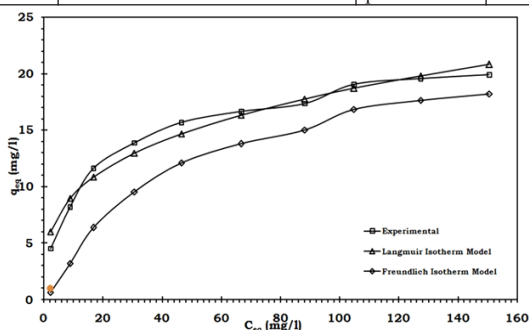
Figure 5 Comparison of experimental values of equilibrium uptake of Cd (II) with two parameter model values
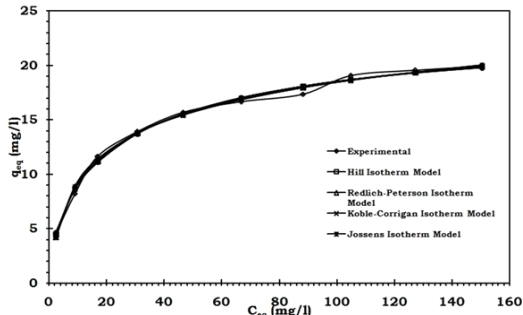

Figure 6 Comparison of experimental values of equilibrium uptake of Cd (II) with three parameter model values

4.4 Four Parameter Models

Among the four – four parameter isotherm models none is suitable to describe the mechanism of adsorption of Cd (II) by BGA due to the poor R-square values and negative parameter values. Table 4 provides the parameter values of four parameter adsorption isotherm models for adsorption of Cd (II) onto BGA.

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

S. No	Model	Parameter	Value	SSE	R2	Adj R2	RMSE
1	Fritz–Schlunder-IV Isotherm Model	AFS5	-1.539×10^6	94.28	0.6012	0.4019	3.964
		BFS5	-1.127×10^6				
		FS5	20.64				
		βFS5	20.07				
2	Baudu Isotherm Model	x	-1	41.63	0.8239	0.7359	2.634
		y	0.6406				
		bo	-1				
		qmax	5.539×10^{-7}				
3	Weber–van Vliet Isotherm Model	P1	1.446	1.177	0.995	0.9925	0.4429
		P2	0.9798				
		P3	-0.1312				
		P4	1.003				
4	Marczewski-Jaroniec Isotherm Model	KMJ	Complex value computed by model function, fitting cannot continue				
		mMJ					
		nMJ					
		qmax					

4.5 Five Parameter Model

Similar to the discussion in four parameter values, Fritz - Schlunder - 5 isotherm model is unable to fit the mechanism of adsorption of Cd (II) by BGA from its synthetic aqueous solution due to the negative parameter value and low q_{max} value. Table 5 gives the parameter values of five parameter adsorption isotherm model for adsorption of Cd (II) onto BGA.

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

S. No	Model	Parameter	Value	SSE	R2	Adj R2	RMSE
1	Fritz - Schlunder - 5 Isotherm Model	K1FS5	2.634	2.085	0.9912	0.9841	0.6457
		K2FS5	1.944				
		FS5	0.2143				
		βFS5	-0.7948				
		qmax	2.737				

5. CONCLUSION

The maximum adsorption capacity of BGA is found to be 19.9 mg/g under the optimum experimental condition of pH 6, 2 g biomass dosage and 120 rpm of agitation rate. The adsorption of Cd (II) onto BGA is found to be L shape. It indicates that no strong competition between solvent and the active sites of BGA exists. BGA has a limited sorption capacity for adsorption of Cd (II) under the conditions employed in this investigation. Adsorption isotherms of Cd (II) metal ion on BGA is studied and modeled using different isotherm models. More emphasis is given to analyze the isotherm data with one, two, three, four and five parameter models to identify the mechanism of adsorption of Cd (II) onto BGA.

Among the various isotherms tested, Langmuir adsorption isotherm model shows its best agreement with experimental results. Since the Langmuir constant R_L lies between 0 and 1, it ensures that the adsorption of Cd (II) onto BGA is favourable. From the Redlich-Peterson isotherm model data, it is confirmed that the mechanism of adsorption of Cd (II) by BGA is governed by Langmuir model.

CONFLICTS OF INTEREST

The authors (Ramadoss Ramsenthil and Subramaniam Dhanasekaran) declare that there are no conflicts of interest regarding the publication of this paper.

SIGNIFICANCE OF THIS RESEARCH WORK

This study realizes the modeling of adsorption isotherms for removal of Cd (II) from aqueous solutions using Blue Green Algae. The application of various isotherm models is essential in design of real time operations in industrial scale. Isotherm modeling in adsorption studies is important in identifying or predicting the mechanism of adsorption processes. Hence in this present investigation, various one, two, three, four and five parameter adsorption isotherm models have been tested.

This study will help the researchers to expose the critical areas of modeling in adsorption that many researchers were not able to explore. Thus this article comprises of critical review of the models with experimental data which would help the readers in acquiring complete knowledge on adsorption mechanisms.

NOMENCLATURE

A   Fritz–Schlunder parameter
a_F Freundlich adsorption capacity (L/mg)
A_{HJ} Harkin-Jura isotherm constant
a_K Kahn isotherm model exponent
A_{KC} Koble - Carrigan'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
BGA Blue 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 - Carrigan'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_{eq} concentration of adsorbate in bulk solution at equilibrium (mg/L)
C_{in} initial adsorbate concentration (mg/L)
J   Jossens isotherm model parameter
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
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 adsorbates 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 - Carrigan's isotherm constant
n_{LJ} Langmuir–Jovanovic model exponent
n_{MJ} Marczewski-Jaroniec isotherm model parameter
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
$_{BS}$ 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
$_{FS5}$ Fritz–Schlunder-V parameter
$β_{2FS5}$ Fritz–Schlunder-V parameter.

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