Characterization and adsorptive behaviour of snail shell-rice husk (SS-RH) calcined particles (CPs) towards cationic dye

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Abstract

In this study, a low-cost composite adsorbent was prepared from snail shell and rice husk (SS-RH) through calcination for brilliant green dye (BGD) adsorption from aqueous solution. Six two-parameter and three three-parameter isotherm models were used to fit the experimental data by both linear and non-linear regression methods using ten error functions. Linear and non-linear regression analysis coupled with linear and non-linear fit error functions all revealed Langmuir and Sip as two- and three-parameter isotherm models well-fitted for BGD uptake from aqueous solution using calcined particles (CPs) of SS-RH. Chi-square ($\chi^2$) error function proved to be the best applicable predictive error function for the two-parameter isotherm study while sum of absolute error (EABS), hybrid functional error (HYBRID) and normalized standard deviation (NSD) are the best error functions for non-linear Redlich-Peterson, Sips and Toth three-parameter isotherm models respectively. Irregular surface texture was observed for the calcined particles of SS-RH as revealed by SEM with BGD filling the opening pores after adsorption. FTIR revealed shift in spectrum broad peaks after adsorption. EDS exhibited active mixed metal oxides formation before adsorption with the observance of weight percent change after adsorption.
1. Introduction

Modern records have revealed worsening of ecosystems resulting from adverse effects of neo-industrial activities causing great threat to human health and the environment in which he lives. Among these is the continuous rise in the pollution of water bodies resulting from discharge of brilliant green dye from textile, printing, pharmaceutical, pulp and paper, carpet, kraft bleaching and tannery industries (Gupta et al., 1992) being assisted by the exponential rise in the world population (Foo and Hameed, 2010). Brilliant green dye (BGD) is a synthesized cationic dye with mutagenic, carcinogenic and toxic attributes causing havoc to different microbiological species (Nandi and Patel, 2017). Thus, a proficient technique is required in the removal of BGD pollutants from water bodies as it is estimated that about 30% of dye used remains unfixed (Lakshmi et al., 2009) due to their high stability and resistance to biodegradation (El-Qada et al., 2008). A broad range of methods such as electrochemical technique (Lin and Peng, 1994), nanofiltration membranes (Ahmad et al., 2008), advanced oxidation and microfiltration (Jana et al., 2010), ultrasonic technique (Gürses et al., 2006), photocatalytic degradation (Mahalakshmi and Arabindoo, 2007), coagulation (Klimiuk et al., 1999), membrane separation (Purkait et al., 2003), merged photo-Fenton and biological oxidation (Martin and Perez, 2008), ozonation (Maldonado et al., 2006), bioremediation (Abd El-Rahim et al., 2009), aerobic degradation (Murthy and Manonmani, 2007), photodegradation (Lodha et al., 2011) and adsorption (Nandi et al., 2009) have been proposed in treatment of waste water contaminated with dyes. However, their respective advantages and shortcomings had been presented in literatures (Can et al., 2006; Mohan et al., 2007; Basha et al., 2008; Daneshvar and Ashassi Sorkhabi Kasiri, 2004; Bayramoglu et al., 2004; Liang et al., 2009) with adsorption being considered as an outstanding method of contaminated waste water treatment (Meghea and Rehner, 1998; Panahi et al., 2008) due to its simplicity, availability, low cost, technically viable, high performance and socially satisfactory features (Nouri et al., 2007; Gottipati and Mishra, 2010).

Numerous adsorbents synthesized from low-cost natural materials such as wheat shell (Bulut and Aydin, 2006), eggshell (Akazdam et al., 2017), saw dust (Zafar et al., 2008), clay (Amin et al., 2015), bamboo charcoal (Zhu et al., 2009), guava leaf powder (Ponnusami et al., 2008), pinang frond (Ahmad and Alrozi, 2011) and so on had been used for the removal of coloured dyes from aqueous solution. In recent developments, nanocomposite iron-based adsorbent had been used for methylene blue and malachite green dyes (Alqadami et al., 2018), brown macroalga for methylene blue dye (Daneshvar et al., 2017), starch/poly(alginic acid-
acrylamide) nanohydrogel for coomassie brilliant blue R-250 dye (Sharma et al., 2017), amberlite IRA-938 resin for rose Bengal dye (Naushad et al., 2016), polyaniline Zr(IV) selenotungstophosphate nanocomposite for methylene blue and malachite green dyes (Pathania et al., 2015), potassium hydroxide-treated palm kernel shell for methyl violet dye (Ming-Twanga et al., 2017) and nanostructured TiO2/polyaniline nanocomposite for methyl orange and methylene blue dyes (Gnanasekaran et al., 2018) removal from aqueous solution.

In general, information obtained from simulation results of equilibrium isotherms of adsorption using experimental data is very imperative. Adsorption isotherms explain pollutants interaction with the used adsorbent at constant temperature. Parameters obtained from this are very crucial as they are applicable for (1) adsorption mechanism pathways optimization (2) adsorption systems effective design purposes and (3) surface properties and adsorbents capacities expression (El-Khaiary, 2008; Thompson et al., 2001). To achieve these, the use of error analyses is required for accurate and consistent adsorption parameters prediction to enable adequate adsorption equilibrium correlations establishment (Srivastava et al., 2006). Nevertheless, data obtained from series of batch adsorption experiments have discrepancies resulting from measurement error which in return affect data accuracy. Thus, statistical error functions are effective tools to tackle great challenges of data errors to affirm accurate measurement results and better fitness of equation to experimental data.

Recently, rice husk was used as adsorbents for acidic dye removal from aqueous solution (Edokpayi et al., 2018). However, this novel study reveals the effectiveness of composite snail shell-rice husk as adsorbent for brilliant green dye uptake from aqueous solution which is a cheaply available low-cost adsorbent that could be beneficial to small scale industries for waste water treatment before disposal. Also, this research work exhibits not only best-fit isotherm model for the obtained experimental data but also best error function that gives highest efficiency of experimental data. These will be of immeasurable benefits to prospective researchers in the fields of equipment design (adsorption column) for waste water treatment and material science with specialization on generating useful materials from dumped wastes such that new theories and innovations can be developed in these areas of research.

In this study, a low-cost composite adsorbent prepared from snail shell and rice husk (SS-RH) was used for the adsorption of brilliant green dye (BGD) from aqueous solution. Two-parameters (Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Harkin-Jura and Halsey) and three-parameters (Redlich-Peterson, Sips and Toth) isotherm models were used to fit the experimental data. Because of the main shortcomings of linear regression method in fitting model and its parameters evaluation which include: (1) error changes discrepancy (Kumar and Sivanesan, 2006) and (2) unsuitability for models with more than two parameters (Kumar 2007), both linear and non-linear regression methods were used to test the fitness of these models.

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and their parameters evaluation using nonlinear chi-square test ($\chi^2$), sum of squares of the errors (SSE), average relative error (ARE), residual root mean square error (RMSE), coefficient of determination ($R^2$), standard deviation of relative errors ($S_{RE}$), Marquardt’s percent standard deviation (MPSD), normalized standard deviation (NSD), hybrid functional error (HYBRID), sum of absolute error (EABS) and Spearman’s correlation coefficient ($r_s$) error functions. These error functions were minimized while $R^2$ was maximized simultaneously over examined concentration range to obtain best experimental data fitness and estimation of models coefficients using Microsoft Excel® solver Add-Ins.

2. Materials and methods

2.1. Preparation of calcined particles of SS-RH composite

The rice husk and snail shell were obtained as wastes from Lafenwa market, Abeokuta, Ogun State and Bodija international market, Ibadan, Oyo State, Nigeria respectively. The snail shell was soaked for some hours and unwanted materials were removed after which it was washed with distilled water for purification. The rice husk was sieved and handpicked to remove dirt and unnecessary materials. Both raw materials were oven dried at 100 °C for 24 hours. Mechanical grinder and sieve were used to obtain less than 0.4 mm particle size. The powder form of each of the raw materials was kept in separate clean polythene bag to avoid moisture contamination and placed in a covered bucket. A mixture of snail shell-rice husk was prepared at a ratio of 2.61 with the addition of 100 ml distilled water in a beaker to form a suspension. The mixture was filtered after being homogenised on a hot plate for 1 hour while the residue was placed in an oven to eliminate excess water for 2 hours at a temperature of 130 °C. The mixture was calcined at 681.10 °C for 2.61 hour in a muffle furnace (Carbolite, ELF11/6B, S/N 21-403009, United Kingdom) to obtain the composite adsorbent.

2.2. Preparation of brilliant green dye solution

The adsorbate (brilliant green dye) used in this work was purchased from TopJay Scientific Laboratory, Ajilosun, Ado-Ekiti, Ekiti State with the following physico-chemical properties: chemical formulae $C_{27}H_{33}N_2.HO_4S$, molar mass 482.64 g/mol, melting point 210 °C, maximum wavelength 625 nm and solubility in water to be 100 g/L at 20 °C. 1 g of brilliant green dye powder was dissolved in 1 Litre of distilled water (1000 mg/L) to make a stock solution.

2.3. Equilibrium studies of batch adsorption

The batch adsorption process was executed using a temperature-controlled magnetic heat stirrer (Stuart heat-stirrer, SB162). UV-visible spectrophotometer (Spectrumlab
752s) was used to measure filtrate absorbance at maximum wavelength of 625 nm. A calibration curve was prepared by plotting absorbance measured at different initial concentrations of 20, 40, 60 and 80 mg/L of BGD against each other to determine adsorbate concentration. The adsorption capacity of the adsorbent, $q_e$ (mg/g) at equilibrium is measured using Eq. (1).

$$q_e = \frac{(C_o - C_e) V}{W}$$

where $C_o$ and $C_e$ are initial and final concentrations of the BGD (mg/L), $V$ is the volume of solution (L) and $W$ is the weight of adsorbent (g).

### 2.4. Characterization of calcined particles of SS-RH composite

The calcined particles of snail shell-rice husk used as adsorbent for BGD adsorption was characterized before and after the process using scanning electron microscopy (SEM-JEOL-JSM 7600F) to study its surface morphology and textural structure. The active functional groups present in the adsorbent enhancing its adsorptive characteristic for BGD uptake from aqueous solution was characterized by Fourier transform infrared (FTIR) spectrometer (Nicolet iS10 FT-IR Spectrometer).

### 2.5. Isotherm models for adsorption equilibrium studies

Adsorption isotherms explain adsorbed molecules distribution between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Table 1 summarizes all the isotherm and kinetic models used. The isotherm models used to fit the experimental data include two-parameters (Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Harkin-Jura and Halsey) and three-parameters (Redlich-Peterson, Sips and Toth) isotherm models. Pseudo-first and pseudo-second order kinetic models were used to study the progress of the reaction.

### 2.6. Error functions for isotherm parameters prediction

The list of error functions (non-linear chi-square test, sum of squares of the errors, average relative error, residual root mean square error, coefficient of determination, standard deviation of relative errors, Marquardt’s percent standard deviation, normalized standard deviation, hybrid functional error, sum of absolute error and Spearman’s correlation coefficient) used for this study is presented in Table 2. Non-linear chi-square test is calculated via summation of squares differences between experimental and calculated data with each squared difference divided by its corresponding value. Sum of squares of the errors is obtained by summing the squares of the difference between experimental and calculated value for the number of data points considered. The residual root mean square error is used to judge equilibrium model with optimal magnitude. The coefficient of determination, $R^2$, gives
| Models | Linear models | Non-linear models | Plot | Slope and intercept | References |
|--------|---------------|-------------------|------|---------------------|------------|
| **Two-parameter isotherms** | | | | | |
| Freundlich | \[ \log q_e = \log K_F + \frac{1}{n} \log C_e \] | \[ q_e = K_F C_e^n \] | \[ \log q_e \text{ vs } \log C_e \] | Slope = \(1/n\), Intercept = \(\log K_F\) | Piccin et al. (2011) |
| Langmuir | \[ C_e = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \] | \[ q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \] | \[ C_e \text{ vs } C_e \] | Slope = \(\frac{1}{q_{\text{max}}}\), Intercept = \(\frac{1}{(K_L q_{\text{max}})}\) | Langmuir (1918) |
| Temkin | \[ q_e = b_T \ln A_T + b_T \ln C_e \] | \[ q_e = \frac{RT}{b_T} \ln A_T C_e \] | \[ q_e \text{ vs } \ln C_e \] | Slope = \(b_T\), Intercept = \(\frac{b_T \ln A_T}{C_e}\) | Temkin and Pyzhev (1940) |
| Dubinin-Radushkevich | \( E = \frac{1}{\sqrt{(-2B_D)}} \) | \[ q_e = (q_{\text{m}}) \exp(-B_D e^2) \] | \[ q_e \text{ vs } \ln \left(1 + \frac{1}{C_e}\right)^2 \] | Slope = \(-B_D(RT)^2\), Intercept = \(\ln (q_{\text{m}})\) | Dubinin (1960), Hobson (1969) |
| Harkin-Jura | \[ q_e = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \] | \[ q_e = \left(\frac{A_H}{B_H - \log C_e}\right)^{\frac{1}{2}} \] | \[ q_e \text{ vs } \log C_e \] | Slope = \(-\frac{1}{A_H}\), Intercept = \(\frac{B_H}{A_H}\) | Almeida et al. (2009) |
| Halsey | \[ q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_e \] | \[ q_e = \exp\left(\frac{\ln K_H - \ln C_e}{n_H}\right) \] | \[ q_e \text{ vs } \ln C_e \] | Slope = \(-\frac{1}{n_H}\), Intercept = \(\frac{1}{n_H} \ln K_H\) | Tahir et al. (2010) |

| **Three-parameter isotherms** | | | | | |
| Redlich-Peterson | \[ \ln \left(\frac{K_{RP} C_e}{q_e} - 1\right) = \beta_{RP} \ln C_e + \ln \sigma_{RP} \] | \[ q_e = \frac{K_{RP} C_e}{1 + \beta_{RP} C_e^\sigma} \] | \[ \ln \left(\frac{K_{RP} C_e}{q_e} - 1\right) \text{ vs } ln C_e \] | Slope = \(\beta_{RP}\), Intercept = \(\ln \sigma_{RP}\) | Redlich and Peterson (1959) |

(continued on next page)
### Table 1. (Continued)

| Models         | Linear models                                      | Non-linear models                          | Plot                                      | Slope and intercept | References |
|----------------|----------------------------------------------------|--------------------------------------------|------------------------------------------|---------------------|------------|
| Sips           | [In \( \frac{q_e}{q_m - q_e} \)] = \( \frac{1}{n} \) \( \ln(C_e) + \ln(b) \frac{1}{n} \) \( q_e = \frac{1}{q_m b_n C_e^n} \) \( \ln(\frac{q_e}{q_m - q_e}) \) vs \( \ln(C_e) \) | Slope = \( \frac{1}{n} \) \( \frac{1}{1 + b(C_e^n)^n} \) | Intercept = \( \ln(b) \frac{1}{n} \) | Sips (1948) |
| Toth           | [In \( \frac{q_e^p}{q_m^p - q_e^p} \)] = \( n_i \ln(C_e) + n_i \ln(K_i) \) \( q_e = \frac{q_m K_i C_e}{(1 + (K_i C_e)^n)^n} \) \( \ln(\frac{q_e^p}{q_m^p - q_e^p}) \) vs \( \ln(C_e) \) | Slope = \( n_i \) \( \ln(C_e) \) | Intercept = \( n_i \ln(K_i) \) | Toth (1971) |

**Kinetic models**

| Pseudo-first-Order | \( \ln(q_e - q_t) = \ln(q_e) - k_1 t \) | \( \ln(q_e - q_t) \) vs t | Slope = \( -k_1 \) \( \ln(q_e) \) | Lagergren (1898) |
| Pseudo-second-Order | \( \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \) | \( \ln(q_e - q_t) \) vs t | Slope = \( \frac{1}{q_e} \) \( \ln(q_e) \) | Cheung et al. (2001) |

\( q_e \) (mg g\(^{-1}\)): experimental adsorption capacity of SS-RH adsorbent at equilibrium, \( K_F \) (mg\(^{1-1/n}\) L\(^{1/n}\) g\(^{-1}\)): Freundlich isotherm constant related to the sorption capacity, \( C_e \) (mg L\(^{-1}\)): BGD adsorbate equilibrium concentration, \( n \): a constant which gives an idea of the grade of heterogeneity, \( K_L \) (L mg\(^{-1}\)): Langmuir constant related to the affinity of the binding sites and the energy of adsorption, \( C_0 \) (mg L\(^{-1}\)): highest initial adsorbate concentration, \( R_L \): dimensionless Langmuir equilibrium parameter, \( q_m \) (mg g\(^{-1}\)): maximum monolayer adsorption capacity of the SS-RH adsorbent, \( R (8.314 J mol^{-1} K^{-1}) \): universal gas constant, \( T (K) \): absolute temperature, \( b_T \) (J mol\(^{-1}\)): Temkin constant related to heat of adsorption, \( A_T \) (L mg\(^{-1}\)): equilibrium binding constant corresponding to the maximum binding energy, \( B_D \) (mol\(^2\) J K\(^{-1}\)): Dubinin-Radushkevich constant of adsorption energy, \( \varepsilon \): Polanyi potential related to the equilibrium concentration, \( E (kJ mol^{-1}) \): mean free energy of adsorption, \( A_HJ \) and \( B_HJ \): Harkin-Jurah adsorption constants; \( K_H \) and \( n_H \): Halsey isotherm constants; \( K_RP \) (L/g): Redlich–Peterson isotherm constant, \( a_{RP} \) (L/mg): Redlich–Peterson isotherm constant, \( b \): Redlich–Peterson exponent which lies between 0 and 1, \( b_S \): Sips isotherm constant related to energy of adsorption, \( K_t \): Toth model adsorption isotherm constant, \( n_t \): Toth model exponent, \( q_t \) (mg g\(^{-1}\)): equilibrium adsorption uptake at time, \( t \) \( k_1 \) (min\(^{-1}\)): pseudo-first-order rate constant of adsorption, \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)): pseudo-second-order rate constant of adsorption.
Table 2. List of error functions.

| Error function                          | Abbreviation | Model                                      | Reference                      |
|-----------------------------------------|--------------|--------------------------------------------|--------------------------------|
| Nonlinear chi-square test               | $\chi^2$     | $\chi^2 = \sum_{i=1}^{n} \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)^2$ | Ho et al. (2002), Boulinguez et al. (2008) |
| Sum of squares of the errors            | $SSE$        | $SSE = \sum_{i=1}^{n} (q_{e,exp} - q_{e,calc})^2$ | Kumar and Sivanesan (2006)      |
| Average relative error                  | $ARE$        | $ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right|$ | Subramanyam and Das (2014)       |
| Residual root mean square error         | $RMSE$       | $RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (q_{e,exp} - q_{e,calc})^2}$ | Vijayaraghavan et al. (2006)    |
| Coefficient of determination            | $R^2$        | $R^2 = \frac{\sum (q_{e,exp} - \bar{q}_{e,calc})^2}{\sum (q_{e,exp} - \bar{q}_{e,exp})^2}$ | Marquardt (1963)                |
| Standard deviation of relative errors   | $S_{RE}$     | $S_{RE} = \sqrt{\frac{\sum_{i=1}^{n} (q_{e,exp} - q_{e,calc}) - ARE^2}{n-1}}$ | Marquardt (1963)                |
| Marquardt’s percent standard deviation  | $MPSD$       | $MPSD = \frac{1}{100} \sum_{i=1}^{n} \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)^2$ | Marquardt (1963)                |
| Normalized standard deviation           | $NSD$        | $NSD = \Delta q(\%) = \frac{100}{n-p} \sum_{i=1}^{n-p} \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)^2$ | Wang et al. (2010)              |
| Hybrid functional error                 | $HYBRID$     | $HYBRID = \frac{100}{n-1} \sum_{i=1}^{n} \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)^2$ | Ng et al. (2002)                |
| Sum of absolute error                   | $EABS$       | $EABS = \sum_{i=1}^{n} |q_{e,exp} - q_{e,calc}|$ | Ng et al. (2003)                |

The proportion of one variable variance that is predictable from the other variable and its measure allows validating the certainty of predictions made from a certain model. Hybrid functional error was developed as an improvement on sum of squares errors ($SSE$) at low concentrations obtained by dividing $SSE$ value with the experimental solid-phase concentration with an inclusive divisor in the system as a term for the number of degrees of freedom (data points number minus the number of parameters within the isotherm equation). The algorithms for the simulation of linear and nonlinear isotherm models using error functions with aide of Microsoft Excel® solver Add-Ins are presented as Figs. 1 and 2 respectively.

2.7. Adsorption operation parameters effect

The effects of pH (3, 5, 7 and 9), brilliant green dye initial concentration (50, 100, 150 and 200 mg/L), contact time (10, 20, 30, 40, 50 and 60 mins) and adsorbent mass (0.1, 0.2, 0.3 and 0.4 g) were investigated with the aid of a temperature controlled heat magnetic stirrer (Stuart heat-stirrer, SB162) placed at rotational speed...
of 140 rpm. The required acidity and alkalinity were achieved using 0.1M HCl and/or 0.1M NaOH with the aid of a pH meter (OAKION, S/N 2202625, Eutech Instruments, Singapore). Initial concentration of BGD, contact time and reaction temperature were 50 mg/L, 30 mins and 50 °C respectively to study the effects of pH and mass dosage while BGD initial concentration and contact time effects were studied at constant adsorbent mass dosage of 0.2 g with unadjusted pH.

3. Results and discussion

3.1. Linear regression analysis of isotherm models

3.1.1. Linear regression of two-parameter isotherm models

Two-parameter adsorption isotherm constants and correlation coefficients are presented in Table 3 for BGD uptake on SS-RH at 50 °C. Previous study has shown

![Algorithm for linear isotherm models regression using error functions.](https://doi.org/10.1016/j.heliyon.2019.e01153)
Fig. 2. Algorithm for non-linear isotherm models regression using error functions.
this temperature as favourable for dye adsorption from solution (Achmad et al., 2012). Among the investigated two-parameter isotherms, a value of 0.9995 obtained for R² by Langmuir isotherm proved it to be well-fitted for the BGD uptake onto SS-RH. Freundlich, Temkin, Dubinin-Radushkevich, Harkin-Jura and Halsey isotherms have R² values of 0.9519, 0.9892, 0.9451, 0.8419 and 0.9519 respectively. In support of this, maximum monolayer adsorbent capacity (qmax) value of 129.87 mg g⁻¹ was predicted by Langmuir model. Recent studies also found Langmuir model to be well-fitted for adsorption process over others (Alqadami et al., 2017; Naushad et al., 2017). The linear plots for all the linearized two-parameter isotherm models are presented in Fig. 3.

**Table 3.** Linearized and non-linearized two- and three-parameter adsorption isotherm constants and R² values for BGD uptake on SS-RH at 50 °C.

| Isotherm models                  | Constants | Linearized | Non-linearized |
|----------------------------------|-----------|------------|----------------|
| **Two-parameter isotherm models** |           |            |                |
| Freundlich                       | K_F (mg⁻¹L⁻¹mg g⁻¹) | 13.216     | 13.0406        |
|                                  | 1/n       | 0.417      | 0.4180         |
|                                  | R²        | 0.9519     | 0.9365         |
| Langmuir                         | q_max (mg g⁻¹) | 129.870    | 131.1093       |
|                                  | K_L (L mg⁻¹) | 0.027      | 0.0260         |
|                                  | R_L       | 0.085      | -              |
|                                  | R²        | 0.9995     | 0.9983         |
| Temkin                           | b_f (kJ mol⁻¹) | 28.886    | 85.4446        |
|                                  | A_f (L mg⁻¹) | 0.248      | 0.2046         |
|                                  | R²        | 0.9892     | 0.9802         |
| Dubinin-Radushkevich            | q_max (mg g⁻¹) | 97.701     | 97.8204        |
|                                  | B_p × 10⁻³ (mol⁻¹kJ⁻²) | 4.210      | 4.3274         |
|                                  | E (kJ mol⁻¹) | 108.985    | -              |
|                                  | R²        | 0.9451     | 0.9157         |
| Harkin-Jura                      | A_HJ      | 2000.0     | 2948.771       |
|                                  | B_HJ      | 2.2        | 2.5227         |
|                                  | R²        | 0.8419     | 0.0895         |
| Halsey                           | n_H       | -2.397     | 10.0805        |
|                                  | K_H       | 0.002      | 1 × 10⁻¹⁰     |
|                                  | R²        | 0.9519     | 0.4257         |
| **Three-parameter isotherm models** |           |            |                |
| Redlich-Peterson                 | K_RP (L/g) | 63.7292    | 3.0366         |
|                                  | a_RP (L/mg) | 7.0104     | 0.0149         |
|                                  | b_RP      | 0.5905     | 1.0892         |
|                                  | R²        | 0.9755     | 0.9996         |
| Sips                            | 1/n       | 1.1265     | 1.1432         |
|                                  | b_s (L/g) | 0.0301     | 0.0185         |
|                                  | q_m (mg g⁻¹) | 123.30     | 122.1850       |
|                                  | R²        | 1.000      | 0.9999         |
| Toth                            | n_t       | 1.2267     | 1.2584         |
|                                  | K_t       | 0.0475     | 0.0240         |
|                                  | q_m (mg g⁻¹) | 109.38     | 120.1149       |
|                                  | R²        | 0.9503     | 0.9999         |
Table 3 presents three-parameter adsorption isotherm constants and correlation coefficients for BGD uptake on SS-RH at 50 °C. The Sip isotherm fitted well for the adsorption of BGD using SS-RH with \( R^2 \) value of 1.000. The \( R^2 \) values for Redlich-Peterson and Toth isotherms were 0.9755 and 0.9503 respectively. Sips isotherm had been shown by previous studies to be the most fitted three-parameter isotherm model for adsorption process. The linear plots for all the linearized three-parameter isotherm models are presented in Fig. 4.

**3.1.2. Linear regression of three-parameter isotherm models**

Table 3 presents three-parameter adsorption isotherm constants and correlation coefficients for BGD uptake on SS-RH at 50 °C. The Sip isotherm fitted well for the adsorption of BGD using SS-RH with \( R^2 \) value of 1.000. The \( R^2 \) values for Redlich-Peterson and Toth isotherms were 0.9755 and 0.9503 respectively. Sips isotherm had been shown by previous studies to be the most fitted three-parameter isotherm model for adsorption process. The linear plots for all the linearized three-parameter isotherm models are presented in Fig. 4.
3.2. Non-linear regression analysis of isotherm models

3.2.1. Non-linear regression of two-parameter isotherm models

The best fit was chosen based on sum of normalized error (SNE) with minimum value. Table 3 presents the values of isotherm constants and R² values obtained for each two-parameter isotherm models. The values were then used to calculate adsorption capacity of SS-RH adsorbent at equilibrium ($q_e$) plotted against BGD adsorbate equilibrium concentration ($C_e$) presented as Fig. 5. The R² values revealed Langmuir to be two-parameter isotherm model that best describes adsorption of BGD onto SS-RH. The increasing order of best fit is Langmuir > Temkin > Freundlich > Dubinin-Radushkevich > Halsey > Harkin-Jura with R² values of 0.9983 > 0.9802 > 0.9365 > 0.9157 > 0.4257 > 0.0895 which is the same as that obtained for the linear regression. Nevertheless, values of isotherm constants obtained for the non-linear regression are very close to those of linear regression which shows the efficacy of the non-linear isotherm models. The quantity of adsorbed BGD onto SS-RH increases with the initial concentration of BGD as shown in Fig. 5. This is an indication of the existence of greater affinity for BGD by the calcined SS-RH particles (Nandi et al., 2009). However, the Halsey plot revealed a reverse order as the
amount of BGD adsorbed decreases with increase in initial concentration of the BGD which suggests that an increase in dye concentration increases number of BGD ions present in solution with limited number of active sites (Gottipati and Mishra, 2010). Nevertheless, a poor R² value of 0.4257 obtained for Halsey does not make this exhibition to be justifiable in driving at this conclusion.

### 3.2.2. Non-linear regression of three-parameter isotherm models

The sum of normalized error with minimum value was also used here in selecting the best fit for the non-linear regression of three-parameter isotherm models. The values of isotherm constants and R² values obtained are presented in Table 3 while the plots of adsorbed quantity of BGD by calcined SS-RH particles (qₑ) with initial BGD concentrations (Cₑ) for all the three-parameter isotherm models are shown in Fig. 6. The R² values being very close to unity proved all the three-parameter isotherm models to be best fit for the BGD adsorption using SS-RH. However, Sips and Toth are the best fit with R² value of 0.9999. The linear regression revealed only Sips to be the best three-parameter isotherm model with R² value of 1.0000 with very close values of isotherm constants as obtained for the non-linear regression. In all the plots shown in Fig. 6, L-type shape was obtained indicating that adsorbed quantity of BGD onto SS-RH increases with BGD initial concentration (Giles et al., 1974). Nevertheless, it shows the efficacy of the calcined SS-RH adsorbent to adsorb BGD even at higher initial concentrations. This is also supported by increased in driving force for mass transfer at higher concentrations (Tehrani-Bagha et al., 2011).
3.3. Error analysis

3.3.1. Results of error functions for linear fit

In order to obtain an isotherm model that best describes the equilibrium relationship of BGD removal from aqueous solution using SS-RH, the use of error functions for the linearized isotherm models for best fit determination is imperative. Though linearized form of isotherm models have been attributed with some anomalies of error deviation, they are needed for comparative purposes with the non-linear types (Subramanyam and Das, 2009). Table 4 presents the values obtained from the simulation of error functions using linearized isotherm models of two- and three parameters. The result revealed Langmuir isotherm model to be the best two-parameter model fit for BGD uptake from aqueous solution using SS-RH having highest $R^2$ value of 0.9984 and lowest values for the error functions while Sips is the best three-parameter isotherm model that best describes the adsorption process with highest $R^2$ value of 0.9999 and lowest error functions values. The order of best fit for two-parameter isotherm models is Langmuir > Temkin > Freundlich > Halsey > D-R > H-J while the order is Sips > Toth > R-P for three-parameter models. Nevertheless, of all the error functions used, chi-square was the best error method that can accurately determine isotherm model parameters as it gave the lowest error value of 0.0770 and 0.0028 for two- and three-parameter isotherm models respectively (Ncibi, 2008). The error functions results obtained also corroborate with the linear regression analysis for the isotherm models (shown in Table 3) as both Langmuir and Sips were revealed to be the best model describing BGD adsorption from aqueous solution using SS-RH composite adsorbents. Previous studies have also presented similar results [(Bera et al., 2013), (Hamdaoui and Naffrechoux, 2007)].
Table 4. Error functions for linear regression.

| Model               | Error functions                  |
|---------------------|----------------------------------|
|                     | $R^2$  | $\chi^2$ | SSE       | ARE   | RMSE  | $s_{RE}$ | MPSD  | NSD  | HYBRID | EABS  |
| Two-parameters isotherm models |
| Freundlich          | 0.9362 | 2.0628    | 175.9846  | 7.8095 | 9.3804 | 11.8105  | 11.4960 | 9.3865 | 15.6190 | 24.5745 |
| Langmuir            | 0.9984 | 0.0770    | 4.1280    | 1.5594 | 1.4367 | 2.3216   | 2.8354  | 2.3151 | 3.1188  | 3.7698  |
| Temkin              | 0.9893 | 0.3743    | 27.9383   | 3.6273 | 3.7375 | 5.2184   | 5.3996  | 4.4088 | 7.2547  | 10.4705 |
| D-R                 | 0.9143 | 2.7626    | 241.9271  | 7.0652 | 10.9983| 11.7803  | 12.7627 | 10.4207| 14.1305 | 24.2266 |
| H-J                 | 0.8617 | 5.0446    | 422.7903  | 12.5909| 14.5394| 21.8056  | 18.1083 | 14.7854| 25.1818 | 39.4935 |
| Halsey              | 0.9325 | 2.1602    | 186.9215  | 7.9017 | 9.6675 | 12.8670  | 11.8114 | 9.6439 | 15.8033 | 24.5931 |
| Three-parameters isotherm models |
| R-P                 | 0.7039 | 38.4831   | 3347.598  | 34.0905 | 40.9121| 13.0308  | 68.9862 | 39.8292| 136.3618| 109.808 |
| Sips                | 0.9999 | 0.0028    | 0.2185    | 0.2892 | 0.3306 | 0.5713   | 0.6549  | 0.3781 | 1.1566  | 0.8494  |
| Toth                | 0.8752 | 8.0441    | 389.1901  | 14.6936| 13.9497| 19.0037  | 42.1909 | 24.3589| 58.7745 | 32.1797 |

Bolded values indicate justification for isotherm model best fit.
3.3.2. Error functions results for non-linear fit

The results of different error functions used for the non-linear regression of two- and three-parameter isotherm models are presented in Table 5. It was observed that different error functions have different lowest sum of normalized error (SNE) values for different isotherm models. Among the two-parameter isotherm models studied, chi-square ($\chi^2$) error function revealed parameter set with minimum SNE in three out of the six models investigated. HYBRID error function produced parameter set with lowest and highest SNE values of 3.309937 and 7.575291 respectively occurring in two out of the six two-parameter models examined. Thus, $\chi^2$ proved to be the best applicable predictive error function for the two-parameter isotherm study of BGD adsorption onto SS-RH. However, highest $R^2$ value of 0.9984 obtained revealed non-linear Langmuir isotherm model to be the best fit for the adsorption process. The order of $R^2$ values obtained is 0.9984 > 0.9893 > 0.9510 > 0.9183 > 0.9162 > 0.5000 for non-linear Langmuir, Temkin, Freundlich, Dubinin-Radushkevich, Harkin-Jura and Halsey isotherms respectively. The results of the error functions for linear fit also revealed Langmuir isotherm model to be the best fit with same $R^2$ value of 0.9984. Nevertheless, almost same order was obtained for the remaining two-parameter isotherm models. In support of these, the predicted values for maximum monolayer adsorption capacity of the SS-RH adsorbent ($q_{max}$) and Langmuir constant ($K_L$) by the non-linear Langmuir isotherm model with highest $R^2$ value were 130.1184 mg g$^{-1}$ and 0.0267 L mg$^{-1}$ respectively. The results of the linear experimental plot of Langmuir isotherm (presented in Table 3) revealed approximately same results of 129.870 mg g$^{-1}$ and 0.027 L mg$^{-1}$ for $q_{max}$ and $K_L$ respectively. Ghaffari et al. (2017) also presented similar results revealing same isotherm parameter values for both linear and non-linear Langmuir isotherm as the best fit. This affirms linear and non-linear Langmuir isotherm model to be the best fit of all the two-parameter isotherm models. Also, the values of isotherm parameters obtained by non-linear regression are consistent and similar to the linear transform values.

For the non-linear three-parameter isotherm models, the result (presented in Table 5) revealed EABS, HYBRID and NSD as best error function for non-linear Redlich-Peterson, Sips and Toth isotherm models respectively with respective lowest SNE values of 2.047518, 6.311617 and 3.647134. However, all the values obtained for the error functions of the linear regression of isotherm models were higher than those of the non-linear regression showing that using linear isotherm transformation is not an appropriate method in selecting a model for BGD sorption equilibria using SS-RH. However, the $R^2$ error function results revealed non-linear Sips isotherm model as the most appropriate three-parameter isotherm model to represent BGD adsorption using SS-RH with excellent and highest value of 1.000 as compared with non-linear Redlich-Peterson and Toth isotherm models having $R^2$ values of...
Table 5. Error functions for non-linear regression.

### Non-linear Freundlich isotherm (two-parameters)

|          | $R^2$ | $\chi^2$ | SSE      | ARE   | RMSE | $S_{RE}$ | MPSD | NSD  | HYBRID | EABS |
|----------|-------|----------|----------|-------|------|----------|------|------|--------|------|
| $K_F$    | 16.8110 | 14.6012  | 16.8044  | 14.5942 | 16.8043 | 12.7044 | 13.0406 | 13.0405 | 16.8000 | 16.8101 |
| $1/n$    | 0.3636 | 0.3934  | 0.3637  | 0.3824 | 0.3637 | 0.4052 | 0.4180 | 0.4180 | 0.3555 | 0.3553 |
| $R^2$    | 0.9510 | 0.9465  | 0.9510  | 0.9250 | 0.9510 | 0.8887 | 0.9365 | 0.9365 | 0.9376 | 0.9376 |
| $\chi^2$ | 2.1612 | 1.9236  | 2.1595  | 2.6788 | 2.1595 | 4.1356 | 2.0641 | 2.0642 | 2.4844 | 2.4848 |
| SSE      | 132.9008 | 145.8949 | 132.9002 | 215.2372 | 132.9002 | 348.1372 | 175.1534 | 175.1561 | 173.6063 | 173.4964 |
| ARE      | 8.6888 | 8.1153  | 8.6865  | 7.8935 | 8.6865 | 8.2587 | 7.7272 | 7.7272 | 8.5183 | 8.5212 |
| RMSE     | 8.1517 | 8.5409  | 8.1517  | 10.3739 | 8.1517 | 13.1935 | 9.3582 | 9.3583 | 9.3168 | 9.3139 |
| $S_{RE}$ | 12.2647 | 11.2266 | 12.2510  | 8.0277 | 12.2510 | 7.1501 | 11.0980 | 11.0981 | 9.7000  | 9.7086 |
| MPSD     | 14.2800 | 11.9961 | 14.2685  | 13.2703 | 14.2685 | 15.7961 | 11.4238 | 11.4239 | 14.2102 | 14.2189 |
| NSD      | 11.6596 | 9.7948  | 11.6502  | 10.8351 | 11.6502 | 12.8975 | 9.3275 | 9.3275 | 11.6026 | 11.6097 |
| HYBRID   | 17.3777 | 16.2306 | 17.3731  | 8.2302 | 17.3731 | 16.5175 | 1.3052 | 1.3053 | 17.0367 | 2.4828 |
| EABS     | 22.7673 | 23.7201 | 22.7690  | 23.3701 | 22.7690 | 28.3091 | 24.6054 | 24.6056 | 22.5702 | 22.5670 |

|          | $q_{max}$ | 130.1184 | 131.1093 | 130.1183 | 134.0179 | 130.1183 | 130.0548 | 132.0671 | 132.0671 | 132.0671 | 127.6149 |
|----------|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| $K_L$    | 0.0267    | 0.0260   | 0.0267   | 0.0245   | 0.0267   | 0.0256   | 0.0254   | 0.0254   | 0.0250   | 0.0288   |
| $R^2$    | 0.9984    | 0.9983   | 0.9984   | 0.9965   | 0.9984   | 0.9960   | 0.9979   | 0.9979   | 0.9972   | 0.9972   |
| $\chi^2$ | 0.0697    | 0.0620   | 0.0697   | 0.0988   | 0.0697   | 0.1275   | 0.0669   | 0.0669   | 0.0893   | 0.1710   |
| SSE      | 4.0577    | 4.4853   | 4.0577   | 9.0354   | 4.0577   | 10.2702  | 5.5016   | 5.5016   | 7.2620   | 7.2526   |
| ARE      | 1.5180    | 1.4061   | 1.5180   | 1.1774   | 1.5180   | 1.3674   | 1.3175   | 1.3175   | 1.2432   | 1.8453   |

(continued on next page)
Table 5. (Continued)

**Non-linear Freundlich isotherm (two-parameters)**

|        | $R^2$   | $\chi^2$ | SSE      | ARE      | RMSE   | $S_{RE}$ | MPSD | NSD | HYBRID | EABS  |
|--------|---------|----------|----------|----------|--------|----------|------|-----|--------|-------|
| RMSE   | 1.4244  | 1.4975   | 1.4244   | 2.1255   | 1.4244 | 2.2661   | 1.6586 | 1.6586 | 1.9055 | 1.9043 |
| $S_{RE}$ | 2.1886  | 2.0182   | 2.1884   | 2.2732   | 2.1884 | 1.3348   | 2.0077 | 2.0077 | 1.6754 | 3.0114 |
| MPSD   | 2.6067  | 2.1981   | 2.6066   | 2.3610   | 2.6066 | 2.8297   | 2.0904 | 2.0904 | 2.3643 | 4.5319 |
| NSD    | 2.1284  | 1.7947   | 2.1283   | 1.9277   | 2.1283 | 2.3105   | 1.7068 | 1.9304 | 3.7003 |
| HYBRID | 3.0359  | 2.8122   | 3.0359   | 2.3548   | 3.0359 | 2.7347   | 2.6349 | 2.6349 | 2.4864 | 3.6907 |
| EABS   | 3.8292  | 3.9651   | 3.8293   | 4.2383   | 3.8293 | 4.5356   | 4.0697 | 4.0697 | 4.2683 | 3.5045 |
| SNE    | 6.797889| 6.498436 | 6.797796 | 7.400936 | 6.79796| 7.917252 | 6.572740| 6.572740| 6.957199| 9.317985|

|        | $R^2$   | $\chi^2$ | SSE      | ARE      | RMSE   | $S_{RE}$ | MPSD | NSD | HYBRID | EABS  |
|--------|---------|----------|----------|----------|--------|----------|------|-----|--------|-------|
| Non-linear Temkin isotherm (two-parameters) |

|        | $b_T$   | $\chi^2$ | SSE      | ARE      | RMSE   | $S_{RE}$ | MPSD | NSD | HYBRID | EABS  |
|--------|---------|----------|----------|----------|--------|----------|------|-----|--------|-------|
| RMSE   | 92.9657 | 90.6904  | 92.9657  | 86.2552  | 92.9658| 94.1191  | 89.0458| 89.0458| 89.0458| 85.4446|
| $A_T$  | 0.2477  | 0.2307   | 0.2477   | 0.2107   | 0.2477 | 0.2335   | 0.2206| 0.2206| 0.2161| 0.2046|
| $R^2$  | 0.9893  | 0.9887   | 0.9893   | 0.9814   | 0.9893 | 0.9788   | 0.9874| 0.9874| 0.9869| 0.9802|
| $\chi^2$ | 0.3727  | 0.3417   | 0.3727   | 0.4828   | 0.3728 | 0.6732   | 0.3560| 0.3560| 0.3824| 0.5110|
| SSE    | 27.9323 | 29.5691  | 27.9323  | 49.1090  | 27.9323| 56.5742  | 32.8848| 32.8848| 34.2220| 52.1184|
| ARE    | 3.6174  | 3.1797   | 3.6174   | 2.6284   | 3.6175 | 3.1506   | 2.8956| 2.8956| 2.7411| 2.4217|
| RMSE   | 3.7371  | 3.8451   | 3.7371   | 4.9553   | 3.7371 | 5.3186   | 4.0549| 4.0549| 4.1366| 5.1048|
| $S_{RE}$ | 5.1728  | 4.7553   | 5.1728   | 5.8280   | 5.1730 | 3.1244   | 4.7331| 4.7331| 4.1463| 5.6542|
| MPSD   | 5.3694  | 4.6310   | 5.3694   | 4.9408   | 5.3696 | 6.3775   | 4.4894| 4.4894| 4.6869| 5.0500|
| NSD    | 4.3841  | 3.7812   | 4.3841   | 4.0341   | 4.3843 | 5.2072   | 3.6655| 3.6655| 3.8268| 4.1233|
| HYBRID | 7.2349  | 6.3593   | 7.2349   | 5.2567   | 7.2350 | 6.3011   | 5.7912| 5.7912| 5.4821| 4.8434|
| EABS   | 10.4704 | 10.1401  | 10.4704  | 9.4461   | 10.4704| 10.6318  | 9.8908| 9.8908| 9.8908| 9.3114|

(continued on next page)
| Table 5. (Continued) |
|----------------------|
| **Non-linear Freundlich isotherm (two-parameters)** |
| $R^2$ | $\chi^2$ | SSE | ARE | RMSE | $S_{RE}$ | MPSD | NSD | HYBRID | EABS |
| SNE | 8.306214 | 7.732511 | 8.306214 | 8.399985 | 8.306508 | 9.267340 | 7.621757 | 7.621757 | **7.575291** | 8.399462 |

| **Non-linear Dubinin-Radushkevich isotherm (two-parameters)** |
| $R^2$ | $\chi^2$ | SSE | ARE | RMSE | $S_{RE}$ | MPSD | NSD | HYBRID | EABS |
| $q_{max}$ | 99.5280 | 97.8204 | 99.5280 | 99.3553 | 99.5239 | 99.3553 | 99.3553 | 99.3553 | **99.3553** | 101.2865 |
| $B_D \times 10^{-5}$ | 4.6418 | 4.3274 | 4.6337 | 4.2021 | 4.6385 | 4.1411 | 4.1395 | 4.2025 | 4.2959 |
| $R^2$ | **0.9183** | 0.9157 | 0.9183 | 0.9144 | 0.9183 | 0.8090 | 0.9093 | 0.9091 | 0.9144 | 0.9110 |
| $\chi^2$ | 2.8724 | **2.7410** | 2.8675 | 2.8937 | 2.8702 | 8.6404 | 2.8220 | 2.8247 | 2.8939 | 3.1665 |
| SSE | 229.5278 | 237.8142 | 229.5287 | 241.9766 | **229.5272** | 726.1105 | 258.3910 | 258.8829 | 254.0987 |
| ARE | 8.1621 | 7.5395 | 8.1281 | 6.3413 | 8.1498 | 14.7114 | 7.4425 | 7.4501 | **6.3370** | 6.8173 |
| RMSE | 10.7128 | 10.9045 | 10.7128 | 10.9995 | **10.7128** | 19.0540 | 11.3664 | 11.3772 | 10.9958 | 11.2716 |
| $S_{RE}$ | 12.6733 | 11.8799 | 12.6706 | 12.2446 | 12.6744 | 9.6877 | 11.3916 | 11.3841 | 12.2209 | 13.6736 |
| MPSD | 13.8847 | 12.8393 | 13.8592 | 13.3145 | 13.8784 | 24.9099 | **12.6253** | 12.6253 | 13.2998 | 14.1616 |
| NSD | 11.3368 | 10.4833 | 11.3160 | 10.8712 | 11.3317 | 20.3388 | 10.3085 | **10.3085** | 10.8592 | 11.5629 |
| HYBRID | 0.7330 | **0.4259** | 0.6305 | 12.6827 | 16.2996 | 29.4229 | 14.8850 | 14.9001 | 12.6739 | 13.63461 |
| EABS | 24.3343 | 24.8338 | 24.2748 | **21.7691** | 24.3104 | 24.5320 | 26.0971 | 26.1367 | 21.7852 | 23.0323 |

| **Non-linear Harkin-Jura isotherm (two-parameters)** |
| $R^2$ | $\chi^2$ | SSE | ARE | RMSE | $S_{RE}$ | MPSD | NSD | HYBRID | EABS |
| SNE | 5.378589 | 5.198526 | 5.368649 | 5.556628 | 5.905602 | 9.589472 | 5.713813 | 5.716522 | 5.552557 | 5.881071 |

(continued on next page)
Table 5. (Continued)

### Non-linear Freundlich isotherm (two-parameters)

|       | $R^2$   | $\chi^2$ | SSE     | ARE    | RMSE    | $S_{RE}$ | MPSD   | NSD    | HYBRID | EABS   |
|-------|---------|---------|---------|--------|---------|----------|--------|--------|--------|--------|
| $R^2$ | 0.9162  | 0.0840  | 0.9162  | 0.0863 | 0.9162  | 0.1165   | 0.0857 | 0.0857 | 0.0895 | 0.0895 |
| $\chi^2$ | 319.6541 | 7.0599  | 319.6541 | 7.5564 | 319.6541 | 18.9849  | 7.8099 | 7.8099 | 8.5318 | 8.5318 |
| SSE   | 2580.495| 28267.95| 2580.490| 28267.89| 2580.491| 28267.94 | 2580.491| 28267.89| 28267.93| 28267.93|
| ARE   | 99.8399 | 15.5107 | 99.8399 | 14.7480 | 99.8399 | 18.9476  | 15.7140| 15.7140| 14.6957| 14.6957|
| RMSE  | 35.9200 | 118.8864| 35.9199 | 118.8864| 35.9199 | 118.8864 | 118.8864| 118.8864| 118.8864| 118.8864|
| $S_{RE}$ | 37.1976 | 20.1313 | 37.1976 | 16.8878 | 37.1976 | 13.6110  | 19.0463| 19.0463| 15.5278| 15.5278|
| MPSD  | 141.1950| 24.7931 | 141.1950| 24.5544 | 141.1950| 33.0002  | 23.4050| 23.4050| 24.0559| 24.0559|
| NSD   | 115.2853| 20.2435 | 115.2853| 20.0486 | 115.2853| 26.9445  | 19.1101| 19.1101| 19.6416| 19.6416|
| HYBRID| 199.6799| 31.0213 | 199.6799| 29.4960 | 199.6799| 31.4280  | 29.3914| 29.3914| 24.5692| 24.5692|
| EABS  | 320.1002| 41.8594 | 320.1002| 39.5225 | 320.1002| 46.7383  | 46.7383| 46.7383| 42.5692| 42.5692|
| SNE   | 8.393424| 3.447638| 8.393423| 3.338546| 8.393423| 3.610912 | 3.422323| 3.422323| 3.30937| 3.30937|

### Non-linear Halsey isotherm (two-parameters)

|       | $n_H$    | $K_H$    | $R^2$    | $\chi^2$ | SSE     | ARE    | RMSE    | $S_{RE}$ | MPSD   | NSD    | HYBRID | EABS   |
|-------|----------|----------|---------|----------|---------|--------|---------|----------|--------|--------|--------|--------|
| $n_H$ | $5.41 \times 10^8$ | $10.0805$ | $9.6941$ | $9.7544$ | $9.6660$ | $12.2371$ | $10.5503$ | $10.5503$ | $9.7544$ | $9.7544$ |
| $K_H$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ | $1 \times 10^{20}$ |
| $R^2$ | 0.500    | 0.4257   | 0.3852  | 0.4544  | 0.3826  | 0.4907  | 0.4589  | 0.4589  | 0.3913  | 0.3913  |
| $\chi^2$ | 312.6043 | 62.0665  | 70.5855 | 67.8975 | 72.0597 | 132.3204 | 69.5309 | 69.5309 | 67.8975 | 67.8975 |
| SSE   | 27630.97 | 4890.040| 4254.551| 4286.399| 4250.795| 12815.26 | 6475.502| 6475.502| 4286.399| 4286.399|
| ARE   | 98.5672 | 43.3621  | 43.866  | 42.6491 | 44.522 | 54.7047  | 44.2178 | 44.2178 | 42.6491 | 42.6491|
| RMSE  | 117.5393 | 49.4472  | 46.1224 | 46.2947 | 46.1020 | 80.0477  | 56.9012 | 56.9012 | 46.2947 | 46.2947|
| $S_{RE}$ | 36.9262 | 47.6276  | 58.6866 | 55.7017 | 60.1522 | 32.4637  | 39.7980 | 39.7980 | 55.7017 | 55.7017|

(continued on next page)
Table 5. (Continued)

Non-linear Freundlich isotherm (two-parameters)

|        | R²    | χ²   | SSE  | ARE  | RMSE | S<sub>RE</sub> | MPSD  | NSD   | HYBRID | EABS  |
|--------|-------|------|------|------|------|---------------|-------|-------|--------|-------|
| MPSD   | 139.3976 | 69.2279 | 83.7700 | 80.7604 | 85.2771 | 83.6452 | 64.1482 | 64.1482 | 80.7603 | 80.7603 |
| NSD    | 113.8177 | 56.5244 | 68.3979 | 65.9406 | 69.6285 | 68.2960 | 52.3768 | 52.3768 | 65.9405 | 65.9405 |
| HYBRID | 197.1344 | 10.2201 | 87.7323 | 85.2983 | 88.9043 | 109.4093 | 88.4355 | 88.4355 | 85.2983 | 85.2983 |
| EABS   | 316.5470 | 127.3641 | 112.2073 | 111.4226 | 112.5861 | 197.6429 | 145.5357 | 145.5357 | 111.4226 | 111.4226 |
| SNE    | 9.613880 | **4.326761** | 4.964644 | 4.977089 | 5.022927 | 6.023670 | 4.797641 | 4.797641 | 4.850888 | 4.850888 |

Non-linear Redlich-Peterson isotherm (three-parameters)

|        | R²    | χ²   | SSE  | ARE  | RMSE | S<sub>RE</sub> | MPSD  | NSD   | HYBRID | EABS  |
|--------|-------|------|------|------|------|---------------|-------|-------|--------|-------|
| K<sub>Rp</sub> | 3.0873 | 3.0583 | 3.0873 | 3.4778 | 3.0876 | 3.0704 | 3.0396 | 3.0395 | 3.0363 | 3.0366 |
| a<sub>Rp</sub> | 0.0154 | 0.0147 | 0.0154 | 0.0356 | 0.0154 | 0.0154 | 0.0142 | 0.0142 | 0.0143 | 0.0149 |
| b<sub>Rp</sub> | 1.0804 | 1.0868 | 1.0804 | 0.9367 | 1.0804 | 1.0791 | 1.0918 | 1.0918 | 1.0893 | 1.0892 |
| R²     | **0.9998** | 0.9998 | 0.9998 | 0.9883 | 0.9998 | 0.9996 | 0.9998 | 0.9998 | 0.9998 | 0.9996 |
| χ²     | 0.0058 | **0.0054** | 0.0058 | 0.3183 | 0.0058 | 0.0114 | 0.0056 | 0.0056 | 0.0067 | 0.0066 |
| SSE    | 0.4403 | 0.4646 | **0.4403** | 30.4853 | 0.4403 | 0.9410 | 0.5116 | 0.5120 | 0.6110 | 0.6118 |
| ARE    | 0.4305 | 0.3821 | 0.4304 | 2.1645 | 0.4310 | 0.3953 | 0.3581 | 0.3579 | 0.3077 | **0.3068** |
| RMSE   | 0.4692 | 0.4820 | 0.4692 | 3.9042 | **0.4692** | 0.6859 | 0.5058 | 0.5060 | 0.5527 | 0.5529 |
| S<sub>RE</sub> | 0.6393 | 0.5898 | 0.6391 | 4.3220 | 0.6410 | **0.4122** | 0.5820 | 0.5821 | 0.6325 | 0.6334 |
| MPSD   | 0.9238 | 0.8133 | 0.9232 | 5.8540 | 0.9257 | 1.1842 | **0.7936** | 0.7936 | 0.8653 | 0.8659 |
| NSD    | 0.5333 | 0.4696 | 0.5330 | 3.3798 | 0.5345 | 0.6837 | 0.4582 | **0.4582** | 0.4996 | 0.4989 |
| HYBRID | 1.7220 | 1.5283 | 1.7216 | 8.6580 | 1.7239 | 1.5813 | 1.4325 | 1.4314 | **1.2308** | 1.2316 |
| EABS   | 1.2464 | 1.2296 | 1.2465 | 7.7766 | 1.2459 | 1.3527 | 1.2386 | 1.2383 | 1.0878 | **1.0827** |

(continued on next page)
## Table 5. (Continued)

### Non-linear Freundlich isotherm (two-parameters)

|          | $R^2$ | $\chi^2$ | SSE     | ARE     | RMSE    | $S_{RE}$ | MPSD    | NSD     | HYBRID  | EABS    |
|----------|-------|----------|---------|---------|---------|----------|---------|---------|---------|---------|
| SNE      | 2.174416 | 2.081165 | 2.174099 | 9.988498 | 2.175875 | 2.059893 | 2.059722 | 2.048831 | 2.047518 |

### Non-linear Sips isotherm (three-parameters)

|          | $R^2$ | $\chi^2$ | SSE     | ARE     | RMSE    | $S_{RE}$ | MPSD    | NSD     | HYBRID  | EABS    |
|----------|-------|----------|---------|---------|---------|----------|---------|---------|---------|---------|
| $1/n$    | 1.1395 | 1.1416   | 1.1395  | 1.1395  | 1.1395  | 1.1385   | 1.1432  | 1.1432  | 1.1432  | 1.1395  |
| $b_s$    | 0.0187 | 0.0186   | 0.0187  | 0.0187  | 0.0187  | 0.0187   | 0.0185  | 0.0185  | 0.0185  | 0.0187  |
| $q_m$    | 122.3609 | 122.2639 | 122.3605 | 122.3605 | 122.2555 | 122.1850 | 122.1850 | 122.1850 | 122.3606 |
| $R^2$    | **1.0000** | 0.9999   | 0.9999  | 0.9999  | 1.0000  | 0.9999   | 0.9999  | 0.9999  | 0.9999  | 0.9999  |
| $\chi^2$ | 0.000423 | **0.000408** | 0.000463 | 0.000423 | 0.000423 | 0.001148 | 0.000415 | 0.000415 | 0.000417 | 0.000463 |
| SSE      | 0.0371 | 0.0381   | **0.0371** | 0.0405  | 0.0371  | 0.0990   | 0.0399  | 0.0399  | 0.0399  | 0.0405  |
| ARE      | 0.1079 | 0.0963   | 0.1079  | 0.0965  | 0.1079  | 0.1471   | 0.0905  | 0.0905  | 0.0905  | 0.0965  |
| RMSE     | 0.1363 | 0.1379   | 0.1363  | 0.1423  | **0.1363** | 0.2225   | 0.1413  | 0.1413  | 0.1413  | 0.1423  |
| $S_{RE}$ | 0.1683 | 0.1582   | 0.1682  | 0.1382  | 0.1682  | **0.1227** | 0.1555  | 0.1555  | 0.1555  | 0.1382  |
| MPSD     | 0.2257 | 0.2117   | 0.2256  | 0.2327  | 0.2256  | 0.3729   | **0.2092** | 0.2092  | 0.2092  | 0.2327  |
| NSD      | 0.1303 | 0.1222   | 0.1303  | 0.1344  | 0.1303  | 0.2153   | 0.1208  | **0.1208** | 0.1208  | 0.1344  |
| HYBRID   | 0.4317 | 0.3853   | 0.4315  | 0.3860  | 0.4317  | 0.3685   | 0.3618  | 0.3618  | **0.3529** | 0.3860  |
| EABS     | 0.3508 | 0.3377   | 0.3507  | 0.3442  | 0.3508  | 0.4774   | 0.3325  | 0.3325  | **0.3313** | 0.3442  |
| SNE      | 1.0000 | 0.9999   | 0.9999  | 1.0000  | 0.9999  | 0.9999   | 0.9999  | 0.9999  | 0.9999  | 0.9999  |

### Non-linear Toth isotherm (three-parameters)

|          | $R^2$ | $\chi^2$ | SSE     | ARE     | RMSE    | $S_{RE}$ | MPSD    | NSD     | HYBRID  | EABS    |
|----------|-------|----------|---------|---------|---------|----------|---------|---------|---------|---------|
| $n_t$    | 1.2435 | 1.2521   | 1.2435  | 1.2687  | 1.2435  | 1.2392   | 1.2584  | 1.2584  | 1.2063  | 1.2286  |

(continued on next page)
| R²    | $\chi^2$ | SSE  | ARE  | RMSE | S_{RE} | MPSD | NSD | HYBRID | EABS |
|-------|--------|------|------|------|--------|------|-----|--------|------|
| K₀    | 0.0242 | 0.0241 | 0.0242 | 0.0239 | 0.0242 | 0.0240 | 0.0240 | 0.0239 | 0.0241 |
| q_{m} | 120.5514 | 120.3080 | 120.5517 | 120.0994 | 120.5515 | 120.4588 | 120.1148 | 120.1149 | 123.0771 | 121.0800 |
| R²    | 0.9999 | 0.9999 | 0.9999 | 0.9998 | 0.9999 | 0.9999 | 0.9999 | 0.9999 | 0.9999 |
| $\chi^2$ | 0.001565 | 0.001486 | 0.001565 | 0.002666 | 0.001565 | 0.003033 | 0.001521 | 0.001521 | 0.012901 | 0.002588 |
| SSE   | 0.1308 | 0.1353 | 0.1308 | 0.2581 | 0.1308 | 0.2596 | 0.1442 | 0.1442 | 1.2939 | 0.2013 |
| ARE   | 0.2166 | 0.1913 | 0.2164 | 0.1314 | 0.2166 | 0.2164 | 0.1785 | 0.1785 | 0.4791 | 0.1946 |
| RMSE  | 0.2557 | 0.2601 | 0.2557 | 0.3592 | 0.2557 | 0.3603 | 0.2685 | 0.2685 | 0.8043 | 0.3172 |
| S_{RE} | 0.3297 | 0.3061 | 0.3296 | 0.3919 | 0.3297 | 0.2281 | 0.3002 | 0.3002 | 1.0611 | 0.2627 |
| MPSD  | 0.4504 | 0.4108 | 0.4502 | 0.5248 | 0.4504 | 0.6035 | 0.4040 | 0.4039 | 1.1407 | 0.5790 |
| NSD   | 0.2600 | 0.2372 | 0.2599 | 0.3030 | 0.2600 | 0.3485 | 0.2332 | 0.2332 | 0.6586 | 0.3343 |
| HYBRID | 0.8662 | 0.7650 | 0.8657 | 0.5256 | 0.8662 | 0.8654 | 0.7141 | 0.7140 | 1.9162 | 0.7782 |
| EABS  | 0.6732 | 0.6504 | 0.6730 | 0.5087 | 0.6732 | 0.7570 | 0.6433 | 0.6432 | 1.8499 | 0.6426 |
| SNE   | 3.908702 | 3.702006 | 3.907494 | 3.965639 | 3.908702 | 4.469293 | 3.647328 | 3.647134 | 9.999599 | 4.172974 |

NB: The bolded values are the lowest values of respective error functions. Only R² have highest values.
0.9998 and 0.9999 respectively. The values of non-linear Sips isotherm parameters obtained were 1.1395, 0.0187 L/g and 122.3609 mg g$^{-1}$ respectively for inverse of constant $(1/n)$, Sips constant $(b_s)$ and $q_{max}$ respectively which are almost the same as 1.1265, 0.0301 L/g and 123.30 mg g$^{-1}$ obtained respectively for the linear plot of the Sips model (presented in Table 3). This affirms the consistency of the non-linear Sips isotherm model with the linear form. Similar studies have shown non-linear Langmuir and Sip isotherm models using parameter set obtained from MPSD error as the best overall model for all two- and three-parameter models (Ho et al., 2002; Chen, 2015).

### 3.4. Adsorption operational parameters effect

The adsorption capacity of calcined particles of snail shell-rice husk increases from 37.342 to 88.625 mg/g as the solution pH increases from 3 to 9 (Fig. 7a). Lower adsorption capacity at lower pH resulted from the presence of positively charged ion generated via calcination on adsorbent surface competing with the hydrogen ions present in the solution. 

![Graph (a)](image1.png)

![Graph (b)](image2.png)

![Graph (c)](image3.png)

**Fig. 7.** Adsorption operation parameters effects for (a) BGD solution pH (b) adsorbent mass dosage (c) contact time and BGD initial concentration.
ion of the BGD. However, presence of strong electrostatic and weak van der Waals forces between the adsorbate negatively charged ions (OH\(^-\)) and adsorbent positively charged ion (H\(^+\)) accounted for higher adsorption capacity at higher pH value. This observation was also revealed by previous study (Rahman and Sathasivam, 2015).

The adsorbent adsorption capacity increases from 57.237 to 125.618 mg/g as the adsorbent mass dosage increases from 0.1 to 0.4 g (Fig. 7b). This could be attributed to formation of additional surface area for BGD removal from aqueous solution which subsequently increases the number of active sites. Similar results have been reported elsewhere (Venckatesh et al., 2010; Shirmardi et al., 2012).

As the adsorption contact time increases coupled with increase in the BGD initial concentration, the adsorption capacity also increases rapidly at the first 20 minutes of each experimental run while equilibrium was attained after 40 minutes (Fig. 7c). The adsorption process was favoured by increase in concentration gradient; and electrostatic forces between molecules of BGD and atoms on adsorbent surface. Attainment of equilibrium after 40 minutes could be attributed to decrease in active sites on adsorbent surface due to its pores being occupied by BGD causing reduction in internal diffusion. Similar studies have also reported almost same results (Ramuthai et al., 2009; Aljebori and Alshirifi, 2017).

### 3.5. Kinetic studies

Table 6 presents parameters obtained for the pseudo-first-order and pseudo-second-order kinetic studies of BGD uptake from aqueous solution using calcined particles of SS-RH. First order rate constant \(k_1\) and corresponding theoretical equilibrium adsorption capacity \(q_{e,\text{cal}}\) were respectively obtained from the intercept and slope of \(\ln(q_e - q_t)\) against time. Second order rate constant \(k_2\) and corresponding theoretical equilibrium adsorption capacity \(q_{e,\text{cal}}\) were respectively obtained from the intercept and slope of \(t/q_t\) against time. The \(R^2\) values of pseudo-first-order kinetic model ranging between 0.9746 and 0.9979 for all BGD initial concentrations coupled with close margin between values of theoretical \(q_{e,\text{cal}}\) and experimental

| \(C_0\) (mg/L) | \(q_{\text{exp}}\) (mg/g) | Pseudo-first-order | Pseudo-second-order |
|---------------|-----------------|-------------------|-------------------|
|               | \(k_1\) (min\(^{-1}\)) | \(q_{e,\text{cal}}\) (mg/g) | \(R^2\) | \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) | \(q_{e,\text{cal}}\) (mg/g) | \(R^2\) |
| 50            | 37.643          | 5.41*10\(^{-2}\)   | 36.146 0.9944    | 1.43*10\(^{-2}\) | 29.281 0.9691 |
| 100           | 73.094          | 7.12*10\(^{-2}\)   | 74.935 0.9979    | 1.78*10\(^{-2}\) | 57.144 0.9492 |
| 150           | 91.210          | 3.33*10\(^{-2}\)   | 89.985 0.9831    | 2.52*10\(^{-2}\) | 75.081 0.9205 |
| 200           | 108.291         | 2.87*10\(^{-2}\)   | 107.914 0.9746   | 2.88*10\(^{-2}\) | 90.150 0.9879 |
qe,exp adsorption capacities at equilibrium suggest it as being the best to describe BGD adsorption onto calcined particles of SS-RH. The reaction rate was controlled by chemisorptions due to electrons exchange between BGD ions and SS-RH functional groups (Hameed et al., 2009). Also, physi-sorption of SS-RH towards BGD dye was observed to an extent (Idan et al., 2018). Previous studies have also reported similar results (Shelke et al., 2010; Amin et al., 2015). However, contrary result was presented elsewhere (Alqadami et al., 2017).

3.6. Material characterization

3.6.1. SEM images

The SEM images obtained before and after the adsorption of BGD onto calcined particles of SS-RH are presented as Fig. 8(a) and (b) respectively. Fig. 8a revealed an irregular surface texture with creation of pores resulting from the calcination of the raw composite adsorbent coupled with water liberation which allows uptake of BGD onto the surface and the pores. The SEM image shown as Fig. 8b revealed the adsorption of BGD onto the surface and opening pores of the SS-RH. Nearly all the available pores created were filled up with the BGD after the adsorption process with noticeable change in the colour of the calcined particles of SS-RH.

3.6.2. FT-IR analysis

Table 7 summarizes the values of broad peaks wavelengths with respective suggestions revealed by FT-IR spectra (Fig. 9) of the composite SS-RH adsorbent before and after the uptake of BGD respectively recorded in the range of 350–4400 nm. Observed sharp broad peaks suggested complex nature of the calcined particles of SS-RH adsorbent with the availability of active functional groups enhancing BGD adsorption onto the adsorbent surface and pores. A shift in the broad peaks of the spectrum after adsorption and the stated observations suggests functional groups presence on the SS-RH surface (Amin et al., 2015); and interaction between the
BGD molecules and the functional groups during adsorption respectively (Kooh et al., 2016).

3.6.3. Energy dispersive spectroscopy (EDS) analysis

Table 8 presents the energy dispersive spectroscopy (EDS) results revealing formation of active mixed metal oxides (Al-O, Na-O, Fe-O, Ca-O, Si-O, S-O) with different weight percent due to calcination of the SS-RH particles at higher temperature. Changes in the respective weight of the active mixed metal oxides after adsorption revealed their positive influence on the BGD adsorption on the active

| IR band | FT-IR wavelength (cm⁻¹) for SS-RH Before adsorption | FT-IR wavelength (cm⁻¹) for SS-RH After adsorption | Observations/suggestions |
|---------|-----------------------------------------------------|----------------------------------------------------|--------------------------|
| 1       | 3844.71                                             | -                                                  | Stretching vibration of H₂O molecules |
| 2       | 3402.00                                             | 3496.23                                           | -OH and -NH functional groups vibration |
| 3       | 2971.22                                             | 3007.62                                           | Asymmetric stretching vibrations of the C-H bonds of the aliphatic groups |
| 4       | 2799.27                                             | 2816.01                                           | Symmetric Stretching of C-H bond |
| 5       | 2549.14                                             | 2549.47                                           | Bending vibration of C-H bond in methylene group |
| 6       | 1794.62                                             | 1797.84                                           | Stretching vibration of -C=O of carboxylate groups |
| 7       | 1427.63                                             | 1427.00                                           | symmetric stretching vibration group of COO⁻ and aromatic rings vibrational stretching |
| 8       | 878.86                                              | 878.98                                            | S=O stretching bands of -SO₃⁻ bonds in sulfonate groups |
| 9       | 703.72                                              | 703.79                                            | Out-of-plane bending of C-O |
| 10      | -                                                   | 368.38                                            | Bending vibration of Al—O—Si present in the rice husk |

Fig. 9. Ftlr spectra before and after BGD adsorption.

BGD molecules and the functional groups during adsorption respectively (Kooh et al., 2016).

3.6.3. Energy dispersive spectroscopy (EDS) analysis

Table 8 presents the energy dispersive spectroscopy (EDS) results revealing formation of active mixed metal oxides (Al-O, Na-O, Fe-O, Ca-O, Si-O, S-O) with different weight percent due to calcination of the SS-RH particles at higher temperature. Changes in the respective weight of the active mixed metal oxides after adsorption revealed their positive influence on the BGD adsorption on the active
sites of calcined SS-RH particles. A study also revealed silicon and calcium composition to be 32.2 and 10.21 wt% whose sources were from rice husk and snail shell respectively (Korotkova et al., 2016). Reduction in wt% of active oxides of Si, Al and S in the calcined SS-RH particles suggested their strong affinity to adsorb BGD from aqueous solution. Though a study presented by Kumar et al. (2010) synthesized active mixed metal oxides from only rice husk for adsorption of cadmium from aqueous solution, similar weight percent were observed before and after the process.

### 3.7. Proposed adsorption mechanism of brilliant green dye onto calcined particles of snail shell-rice husk

The reaction mechanism of BGD adsorption onto CPs of SS-RH is a function of electrostatic attractive force existing between negatively charged surface of the adsorbent and positively charged BGD dye. The functional groups present on the CPs of SS-RH surface and pH reliance of BGD adsorption from aqueous solution onto CPs of SS-RH are instruments for the explanation of these electrostatic attractive forces. The existence of hydroxyl (OH\(^{-}\)) and carboxyl (COO\(^{-}\)) groups on CPs of SS-RH were revealed by FTIR (Table 7) at wavelengths 3496.23 cm\(^{-1}\) and 1427.63 cm\(^{-1}\) respectively. The ionization of OH\(^{-}\) and COO\(^{-}\) groups is a function BGD solution pH which causes electrical charge on CPs of adsorbent surface. These groups on adsorbent surface can either lose or gain a proton which results to surface charge that varies with changes in BGD solution pH.

At low solution pH, protonation reaction occurs at the active sites present on CPs of SS-RH surface. Thus, the adsorbent surface is positively charged due to reaction between H\(^{+}\) in solution and groups (OH\(^{-}\) and COO\(^{-}\)) on its surface as shown in Eqs. (2) and (3) below.

\[
\text{SS-RH} - \text{OH} + \text{H}^{+} \rightarrow \text{SS-RH} - \text{OH}_2^{+}
\]
SS-RH − COOH + H⁺ → SS-RH − COOH₂⁺  

Deprotonation reaction occurs at high solution pH and the active sites on CPs of SS-RH surface are negatively charged as a result of reaction between OH⁻ and groups (OH⁻ and COO⁻) on its surface as shown in Eqs. (4) and (5) below.

SS-RH − OH + OH⁻ → SS-RH − O⁻ + H₂O  

SS-RH − COOH + OH⁻ → SS-RH − COO⁻ + H₂O  

Eqs. (4) and (5) revealed that electrostatic attractive forces enhanced BGD adsorption onto CPs of SS-RH at high solution pH. Thus, the proposed mechanism of adsorption process can be represented as Eqs. (6) and (7).

SS-RH − O⁻ + BGD⁺ → SS-RH − O⁻⋅BDG  

SS-RH − COO⁻ + BGD⁺ → SS-RH − COO⁻⋅BDG  

4. Conclusion

Linear and non-linear regression of two- and three-parameter isotherm models have been investigated using different error functions for BGD removal from aqueous solution using snail shell-rice husk. Langmuir and Sip fitted well for BGD uptake from aqueous solution using SS-RH. Chi-square (χ²) predicted well for non-linear Langmuir model while EABS, HYBRID and NSD predicted well for non-linear R-P, Sips and Toth isotherm models for BGD adsorption onto SS-RH. The SEM images before and after adsorption revealed formation of irregular surface texture and adsorption of BGD onto the surface of calcined particles of SS-RH opening pores respectively. FTIR analysis exhibited shift in the spectrum broad peaks after adsorption suggesting the presence and interaction of active functional groups on SS-RH surface with BGD molecules. EDS analysis showed the formation of active mixed metal oxides before adsorption while changes in their respective weight percent was observed after adsorption.

Declarations

Author contribution statement

Lekan T. Popoola: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
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Additional information

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