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Isotherms, kinetic and thermodynamic studies of methylene blue adsorption on chitosan flakes derived from African giant snail shell

Olaosebikan Abidoye Olafadehan1*, Victor Ehigimetor Bello1, Kehinde Olawale Amoo2 and Adebukola Morufat Bello1

1Department of Chemical and Petroleum Engineering, University of Lagos, Akoka-Yaba, Lagos 101017, Nigeria.
2Department of Chemical Engineering, Lagos State University, Epe, Lagos State, Nigeria.

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In the present study, modeling of 19 adsorption isotherms, 8 kinetic models and thermodynamics of methylene blue (MB) adsorption on chitosan flakes synthesized using Archachatina marginata shell wastes was investigated in a batch mode. The operational parameters’ effects on the MB adsorption were studied. The model parameters were statistically analyzed using 10 error functions. The choices of the best fitted adsorption and kinetic models were based on the comparison of the sum of normalized error (SNE) and two statistical tools of information-based criteria. The 5-p Fritz-Schlünder isotherm best fitted the experimental adsorption data of MB on chitosan flakes based on SNE whereby maximum adsorption capacity, $q_{\text{max}}$, of 143.6660 mg/g was obtained. The adsorption rate of MB on chitosan flakes was kinetically described by pseudo second-order model at all initial concentrations of MB investigated, with film diffusion being the rate-controlling step and the adsorption process chemisorption-influenced. The calculated thermodynamic parameters, $\Delta H^\circ = 4.23$ kJ/mol, $\Delta S^\circ = 0.4563$ kJ/(mol K), negative $\Delta G^\circ$ values revealed that the adsorption of MB onto chitosan flakes was physical, endothermic, spontaneous, energetically favorable and exergonic. The reaction mechanism of the adsorption of MB onto chitosan flakes was proposed taking cognizance of the electrostatic force of attraction between the negatively charged surface of the chitosan (biosorbent) and the positively charged MB.

Key words: chitosan, dye adsorption, isotherm, kinetics, thermodynamics, information-based criteria.

INTRODUCTION

The use of dyes in dyeing and printing processes is quite enormous, which is evident in many industries globally (Afroze et al., 2015). The perennial discharges of wastewater containing dyes from textile, dyeing, pharmaceutical, food, cosmetics and healthcare, paper and leather industries, amongst others, into the water
bodies are worrisome and of great concern (Derakhshan et al., 2013) owing to their potent obstinately color and great amount of biochemical oxygen demand that is non-aesthetical to the environment (Annadurai and Krishnan, 1997). Many of these dye wastes pose serious hazards to aquatic living organisms for reason of their toxicity and even carcinogenicity and mutagenic influence on human beings. Equally, there is a reduced penetration of light as a result of their presence in water bodies thereby preventing the aqueous fauna and flora photosynthesis (Elizalde-González and Hernández-Montoya, 2009). A typical example of such dyes is methylene blue (a heterocyclic aromatic chemical compound), which is reported to be responsible for a number of health issues such as eye burn, regurgitation, shock, blue discoloration of the skin (that is, cyanosis), yellowness of the eyes, skin and urine (that is, icterus), high heart rate, among others, with much acute exposure. Consequently, environmental regulations have been enacted by many governments concerning the quality of colored effluents and thus the dye-industries have been compelled to decolorize these colored effluents before they are being discharged into the environment. Hence, much attention should be given to the treatment of dyes before discharge. However, dye producers and users generate dyestuff that is somewhat not easy to degrade after utilization. Attempt to remove them from industrial wastewater by employing the conventional treatment technologies such as trickling filter, liquid-liquid extraction, membrane filtration, chemical coagulation, activated sludge, carbon adsorption and photodegradation, whose extensive review has been provided by Vandevivere et al. (1998), is financially demanding due to their resistant biodegradable complex structure (Afroz et al., 2015; Khodaie et al., 2013). Among these treatment techniques, adsorption is highly employed owing to its flexibility, ease of operation, high performance and relatively inexpensive use, efficient regeneration and eco-friendly operating system (Vakili et al., 2014). It can equally manage quite high flow rates. Hence, during the photodegradation of wastewater-containing dyes using ultra-violet light, the generation of obnoxious substances, such as free radicals and ozone, is mitigated so that high-quality effluent results (Wang et al., 2013). Moreover, adsorption process is still a relevant and comparatively simple, viable and less expensive among other unit operations. However, its effectiveness depends largely on the adsorbents applied and the operating conditions of the process.

Many investigators have reported dyes adsorption on different adsorbents such as peat (Poots et al., 1976), wood (Poots et al., 1976; Asfour et al., 1985a; 1985b; El-Geundi, 1991), pith (McKay, 1987), activated carbon (Walker and Weatherley, 1997; Namasivayam et al., 2001a; Namasivayam and Kavitha, 2002), waste red mud (Namasivayam and Arasi, 1997; Namasivayam et al., 2001b; Namasivayam et al., 2002), fuller’s earth (Atun et al., 2003), bottom ash and de-oiled soya (Mittal et al., 2010), copper oxide nanoparticle modified activated carbon (Nekouei et al., 2015), and synthesized novel adsorbent of ZnO-NR-activated carbon (Di et al., 2016). Other commercially-potentially adsorbents employed to treat industrial wastewater containing dyes are agricultural byproducts (Namasivayam and Kavitha, 2002; Marshall and Champagne, 1995; Marshall and Johns, 1996), miswak leaves (Elmorsi, 2011), titanium (IV) oxide surface (Gupta et al., 2011), multi-walled carbon nanotubes and titanium (IV) oxide (Saleh and Gupta, 2014). Equally, mercury-doped zinc (II) oxide nanorods (Saravanan et al., 2013a), ZnO/CuO nanocomposites (Saravanan et al., 2013b), CeO2, V2O5, CuO and nanocomposite of CeO2/V2O5 and CeO2/Cu (Saravanan et al., 2013c) and zinc (II) oxide/silver nanocomposite (Saravanan et al., 2013d) have been applied for the adsorption of dyes. Also, adsorbents for the treatment of dye contaminated aqueous solution include Fe3O4 nanoparticles (Ghaedi et al., 2015), zinc (II) oxide/silver/Mn3O4 nanocomposite (Saravanan et al., 2015), carbonaceous material (Gupta et al., 2016), ZnO/Co3O4 nanoparticles (Saravanan et al., 2016), commercially used bast fibers under the names of flax, ramie and kenaf (Kyzas et al., 2018) and activated carbon coated with zinc oxide (Pourali et al., 2020). In particular, adsorbents that have been utilized for methylene blue adsorption from aqueous solution include jute fiber carbon (Senthilkumaran et al., 2005), unburned carbon (Wang et al., 2005), cedar sawdust and crushed brick (Hamdaoui, 2006), bamboo activated carbon (Hameed et al., 2007), garlic peel (Hameed and Ahmad, 2009), bentonite (Hong et al., 2009) and carbon nanotube (Yao et al., 2010). Nevertheless, some of these adsorbents showed a low-level property of methylene adsorption and have the drawbacks of inefficacious extraction of MB (Sun et al., 2011). Moreover, almost all of them become problematic with regard to recycling and reuse. Thus, a high-performance, inexpensive and easily-regenerated adsorbent is highly preferred.

In general, non-synthetic and sustainable materials are being used as cost-effective adsorbents in the process of adsorption. Biosorbents have gained wide attention owing to their somewhat plenteousness and non-toxic nature (Tran et al., 2015). Natural polymer biosorbents (such as polysaccharides, that is, chitosan and its precursor, chitin) have been favorably utilized in adsorption studies (Sarode et al., 2019). The second naturally available biopolymer after cellulose is chitin. The application of chitosan typically those derived from crustacean sources are presently considered as a good replacement for charcoal due to their high adsorption capacities under favorable conditions. However, the application of chitin on a commercial scale is limited owing to its poor solubility. Hence, soluble chitosan has been obtained from chitin by an alkaline deacetylation process (Hameed et al., 2016; Muxika et al., 2017). Chitosan is
an efficacious biosorbent for the removal of a number of contaminants owing to its reactive functional groups, amine and hydroxyl groups, enriched-structure (Sharififard et al., 2018). Thus, for reason of their intrinsic characteristics, the non-synthetic polymers are usually deployed as effective biosorbents for the removal or the recovery of hazardous dyes, proteins, heavy metals, amongst others (Fan et al., 2012). So, the evaluation of adsorption capacity of chitosan from diverse sources is an area of great interest to many researchers. Chitosan has been applied in the literature (Annadurai et al., 1999; Hu et al., 2006; Annadurai et al., 2008; Hasan, 2008; Wan Ngaha et al., 2011; Fan et al., 2013; Periolatto and Ferrero, 2013; Li et al., 2014; Sheshmani et al., 2014; Shajahan et al., 2017; Ahmed et al., 2020; da Silva Alves et al., 2021) as an adsorbent for the removal of dyes from aqueous solution. However, to the best of our knowledge, none of these studies carried out an extensive investigation on the modeling of the equilibrium data of the adsorption of methylene blue on chitosan flakes from Archachatina marginata shell powder using 19 isotherms and 8 kinetic models coupled with statistical criteria and sum of normalized error (SNE) to select the best models. Hence, the present study reports comprehensively the adsorption of methylene blue (MB) on the prepared chitosan from A. marginata shell powder. The effects of operational parameters such as adsorbent dosage, pH of methylene blue solution, initial concentration of MB solution, contact time and temperature on the % removal of MB and adsorption capacity of the chitosan flakes were investigated. The fit of the experimental equilibrium adsorption data of MB to seven 2-p, eight 3-p, three 4-p and one 5-p isotherms were exhaustively carried out in this study, wherein the inherent parameters in the 19 isotherms were evaluated using linear and non-linear methods, as the case may be, to convincingly reflect the surface properties and by extension the adsorption capacity of the chitosan flakes from A. marginata shell powder. The kinetics of the adsorption of MB on chitosan flakes was investigated using 8 kinetic models. Moreover, sum of normalized error (SNE) was used to opt the most superior models amongst the isotherms and kinetic models for the adsorption of MB on chitosan flakes since SNE has been reported as a way or criterion for selecting the best fitted isotherm/kinetic model (Anirudhan and Radhakrishnan, 2009; Yanev et al., 2013; Popoola, 2019). Equally, in this study, Akaike information criteria (AIC) and model selection criterion (MSC) were used to select the best fitted isotherm and kinetic models for the MB adsorption on the prepared chitosan flakes. Thermodynamic parameters such as activation energy, \( E_a \), changes in enthalpy, \( \Delta H^\circ \), entropy, \( \Delta S^\circ \) and Gibbs free energy, \( \Delta G^\circ \), were evaluated. The data reported in this study can be of beneficial use for the design and fabrication of an economically viable treatment process using batch reactor for MB adsorption on a biosorbent and for diluting industrial effluents.

**MATERIALS AND METHODS**

The analytical grade chemical reagents used in this study included NaOH pellet (99.8% purity), obtained from Merck, India and methylene blue (\( C_{16}H_{18}N_3SCl \)), whose molecular weight and purity are 319.85 g/mol and 98.7%, respectively, procured from Loba Chemie Pvt Limited, India, ethanol (absolute 98%), hydrochloric acid (36.5-38%, specific gravity=1.18) and acetone, \( \text{CH}_2\text{C}=\text{O} \) (≥ 99.5% ACS), which were procured from BDH Laboratories Supplies, England. These chemicals were used without additional treatment.

**Production of biosorbent**

The production of the biosorbent (chitosan) used in this study from the shell wastes of A. marginata (African giant snail) was performed by washing the shell, drying, pulverization and following the processes of demineralization, deproteinization, deacetylation and decolorization as detailed in the works of Amoo et al. (2019), Olafadegan et al. (2020; 2021) and Bello and Olafadegan (2021).

**Characterization of biosorbent**

The characterization of the resulting flakes of chitosan was extensively carried out and reported elsewhere (Bello and Olafadegan, 2021). In this study, the surface point of zero charge of the prepared chitosan flakes from A. marginata shell was performed using the pH drift method as adopted by Banerjee and Chattopadhyaya (2013) with slight modification. 0.1 M NaCl solution was freshly prepared and 50 mL was placed in a series of 250 mL Erlenmeyer flasks and various values of pH between 2 and 12 were initiated using 0.1 M HCl and 0.1 M NaOH solutions monitored by a sensitive pH meter. 0.1 g of the chitosan flakes was discharged into the solution, which was allowed to reach equilibrium in 24 h. The solutions were filtered and the difference between the initial pH values \( (pH_i) \) and final pH values, \( (pH_f) \) was evaluated to obtain change in pH values, \( \Delta(pH) \). The \( \Delta(pH) \) values were plotted against \( (pH_i) \) values. The point of intersection of the curve with the abscissa, \( (pH)_{zpc} \), gives the zero-point charge value, \( pH_{zpc} \).

**Preparation of methylene blue solution**

A stock solution of 1000 mg/L of methylene blue (MB) was prepared by dissolving a weighed portion of 1 g of it in 1000 cm\(^3\) (or 1 L), from which various concentrations were obtained by serial dilution.

**Batch adsorption experiment**

The batch adsorption experiment considered the operational effects of adsorbent dosage, pH of MB solution, initial concentration of MB solution, contact time and temperature on the methylene blue adsorption on the prepared chitosan flakes. Each 50 mL sample of methylene blue solution was put in 250 mL capacity of Erlenmeyer flasks at specific or certain conditions. The effect of adsorbent dosage on the % removal of MB and adsorption capacity of the chitosan was studied by using the mass of the biosorbent between 0.1 and 2 g. The influence of pH was investigated in acidic and
alkaline medium by varying pH values using 0.1 M HCl and 0.1 M NaOH measured by a pH meter. The effect of initial concentration of MB solution on the % removal of methylene blue (MB) was investigated by using 10 to 60 mL with a fixed amount of 0.1 g of biosorbent (chitosan) at contact time of 30 min, agitated using a mechanical orbit shaker set at 120 rev/min and ambient temperature of 30 ± 2°C. The impact of contact time was carried out within 4 h durations at a fixed mass of 0.1 g chitosan and room temperature of 30 ± 2°C. The thermodynamics study, which is hinged on the effect of variation of temperature, was carried out in water bath within the temperature ranges of 30 to 90°C at a fixed adsorbent amount of 0.1 g.

At the end of each adsorption operational batch experiments, chitosan flake particles were filtered from the suspension and the final concentration was measured by ultra-visible spectrophotometer at maximum wavelength of 650 nm.

**Adsorption equilibrium isotherms**

An adsorption isotherm is an empirical equation that solely gives an insight of the mechanism or phenomenon that revolves round the retention or release of a liquid phase (adsorbate) on a solid phase (adsorbent) at constant temperature (Deng and Chen, 2019). The adsorption process is said to have attained equilibrium when the adsorbate and adsorbent have been sufficiently contacted and adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Magdy et al., 2018). This present study uses two-, three-, four- and five- parameter isotherms to model the equilibrium sorption data of methylene blue on chitosan flakes using linear and non-linear regression methods, where appropriate.

**2-p Freundlich isotherm**

The 2-p Freundlich isotherm assumes a reversible adsorption that is not limited to the formation of monolayer, non-uniform distribution of heat of adsorption, heterogeneous adsorbate surface without lateral interaction and initial stronger binding sites, which reduce with increase of coverage. The empirical equation of Freundlich isotherm is of the form (Freundlich, 1906):

\[ q_e = k_F c_e^{1/N} \]  

where \( q_e \) is the weight of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), \( c_e \) the residual concentration of the solute (mg/L) and \( k_F \) is a constant depending on the adsorbate and the adsorbent: it indicates the Freundlich adsorption capacity (Benzaouei et al., 2018) and the parameter, \( N \), characterizes the homogeneity of the system (that is, the favorability of adsorption). A larger \( N \) value is an indication that the system is more heterogeneous that usually results in the non-linearity of the adsorption isotherm.

Taking natural logarithms of Equation 1, we have:

\[ \ln q_e = \ln k_F + \frac{1}{N} \ln c_e \]  

The linear plot of \( \ln q_e \) against \( \ln c_e \) is used to test the fitness of equilibrium data to the Freundlich isotherm provided \( N > 1 \) and a high correlation coefficient, \( R^2 \), close to unity is obtained. Thus, the Freundlich isotherm parameters, \( N \) and \( k_F \), can be determined from the slope \((= 1/N)\) and intercept on \( \ln q_e \) axis \((= \ln k_F)\), respectively. The values of \( N \) between 1 and 10 are used to assess the adsorbent-adsorbate interaction (Kumar et al., 2012). The magnitude of the exponent, \( 1/N \), is a measure of the nature of the adsorption process. When \( 1/N = 0 \), the adsorption is irreversible. The adsorption is favorable (that is, indicative of chemisorption) when \( 0 < 1/N < 1 \). It is also indicative of chemisorption and unfavourability when \( 1/N > 1 \). Hence, if \( 1 < N \), favorable (or cooperative) adsorption results (Pandey and Mishra, 2011). The empirical constant, \( N \), which indicates adsorption intensity, depends on the temperature and properties of the adsorbate and the adsorbent.

**2-p Langmuir isotherm**

Langmuir (1918) proposed an empirical model, which assumes complete monolayer adsorption, limited number of active sites, voidance of lateral interaction, homogeneous adsorbent surface with identical adsorption sites and constant heat of adsorption for all sites. The 2-p Langmuir isotherm, when applied to liquid phase adsorption, is given by:

\[ q_e = \frac{q_{max} K_L c_e}{1 + K_L c_e} \]  

where \( q_{max} \) is the Langmuir constant related to the adsorption capacity (that is, maximum adsorption capacity for the solid phase loading) (mg/g) and \( K_L \) the energy constant related to the heat of adsorption (L/mg). \( q_{max} \) can be correlated with the variation of the suitable area and porosity of the adsorbent. Hence, large surface area and pore volume result in higher adsorption capacity of the adsorbent (Olafadehan, 2021).

Five different linear forms can result from Equation 3. One of such forms used in this study is given by:

\[ \frac{c_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} \frac{1}{c_e} \]  

The linear plot of \( (c_e/q_e) \) against \( c_e \) should yield a straight line with a high coefficient of regression, \( R^2 \), being close to unity if the adsorption process was described by the model. The inherent parameters, \( q_{max} \) and \( K_L \), in the 2-p Langmuir isotherm can thus be determined from the slope \((= 1/q_{max})\) and intercept on \( (c_e/q_e) \) axis \((= 1/(q_{max} K_L))\) respectively.

Hall et al. (1966), Weber and Chakkravortic (1974) and Malik (2004) described the essential attributes of the Langmuir model using a dimensionless constant referred to as separation factor or equilibrium parameter, \( R_L \), given by Mahmoud et al. (2016) thus:
\[ R_L = \frac{1}{1 + K_L c_0} \]  

The factor, \( R_L \), describes the nature of adsorption within a certain limit as either irreversible for \( R_L < 1 \), favorable for \( 0 < R_L < 1 \), linear for \( R_L = 1 \) and unfavorable for \( R_L > 1 \) (Zhai et al., 2004).

2-p Temkin isotherm

The Temkin isotherm assumes that the heat of adsorption, \( \Delta H_{ads} \), of the molecules at the surface of the adsorbent decreases linearly rather than logarithmically with coverage \( \theta \), that is, \( \Delta H_{ads} = (\Delta H_{ads})_0 (1 - \theta) \); homogeneous distribution of binding energies of the adsorbent surface and it takes cognizance of the adsorbate-adsorbent surface interaction (Temkin and Pyzhev, 1940). The 2-p Temkin isotherm is given by:

\[ q_e = \frac{RT}{b_T} \ln(A_T c_e) = \frac{RT}{b_T} (\ln A_T + \ln c_e) \]  

where \( b_T \) is Temkin constant, which is related to the heat of adsorption (J/mol) and \( A_T \) the Temkin isotherm constant (L/g). A plot of \( q_e \) against \( \ln c_e \) should be a straight line with slope equals \( RT/b_T \) and intercept on \( q_e \) axis = \( RT \ln A_T / b_T \). Hence, the two parameters, \( b_T \) and \( A_T \), of the isotherm can be determined at the temperature of adsorption.

2-p Dubinin-Radushkevich (D-R) isotherm

The mechanism for adsorption can be expressed with a Gaussian energy distribution onto a heterogeneous surface using the 2-p Dubinin-Radushkevich model (Celebi et al., 2007; Gunay et al., 2007). It assumes a multilayer physical adsorption process that involves van der Waal’s forces and is a fundamental equation that is used qualitatively for the description of the adsorption of gases and vapors onto microporous sorbents (Israel and Eduok, 2012). The 2-p Dubinin-Radushkevich isotherm is expressed as:

\[ q_e = q_{DR} \exp(-\beta \varepsilon^2) \]  

In linear form, Equation 7 becomes:

\[ \ln q_e = \ln q_{DR} - \beta \varepsilon^2 \]  

The approach was often applied to distinguish between the physisorption and chemisorption of metal ions (Dubinin, 1960; Vijayaraghavan et al., 2006), with its mean free energy, \( E \), per molecule of adsorbate (for removing a molecule from its location in the adsorption space to infinity) given by:

\[ E = 1/\sqrt{2\beta} \]  

The Polanyi potential, \( \varepsilon \), is given by:

\[ \varepsilon = RT \ln \left(1 + c_e^{-1}\right) \]  

Using Equation 10 in Equation 8, a linear plot can be made to determine the relevant constants inherent in Dubinin-Radushkevich isotherm.

2-p Harkins-Jura (H-J) isotherm

The 2-p Harkins-Jura model accounts for the adsorption of multilayer on the surface of adsorbents having heterogeneous pore distribution. The non-linear relationship of Harkins-Jura isotherm is given by:

\[ q_e = \sqrt{\frac{A_{HJ}}{B_{HJ}} - \log c_e} \]  

where \( A_{HJ} \) and \( B_{HJ} \) are the isotherm constant parameters. On linearization of Equation 11, we have:

\[ \frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \log c_e \]  

Therefore, a straight line should be obtained from the plot of \( 1/q_e^2 \) against \( \log c_e \), which is adequate to determine the isotherm parameters, \( A_{HJ} \) and \( B_{HJ} \), from slope = \( 1/A_{HJ} \) and intercept on vertical axis = \( B_{HJ} / A_{HJ} \).

2-p Frenkel-Halsey-Hill (F-H-H) isotherm

The 2-p Frenkel-Halsey-Hill assumes a multilayer adsorption on a heterogenous adsorbent surface. Its non-linear form is expressed as:

\[ q_e = \exp \left( \frac{\ln K_{FHH} - \ln c_e}{n_{FHH}} \right) \]  

whose linear form is given by:

\[ \ln q_e = \frac{1}{n_{FHH}} \ln K_{FHH} - \frac{1}{n_{FHH}} \ln c_e \]  

Therefore, a straight line should be obtained from the plot of \( \ln q_e \) against \( \ln c_e \), which suffices to determine the isotherm parameters, \( n_{FHH} \) and \( K_{FHH} \), from slope = \( 1/n_{FHH} \) and intercept on the vertical axis = \( \ln K_{FHH} / n_{FHH} \).

Brunauer-Emmett-Teller (BET) isotherm

The Brunauer-Emmett-Teller (BET) model is a notable representation of multilayer adsorption. It assumes that the adsorbate-adsorbent surface interaction is much larger than
between neighboring molecules, the possession of homogeneous chemical properties by the adsorbent and it is applied generally for estimating the surface area of porous media (Chen et al., 2017). The non-linear form of BET isotherm is expressed as (Olafadéhan, 2021):

\[
q_e = \frac{q_s c_{BET} c_e}{(c_s - c_e)[1 + (c_s/c_e - 1]^\frac{1}{c_s}]}
\]  

(15)

where \(c_s\) is the adsorbate monolayer saturation concentration, \(q_s\) the amount of solute adsorbed in forming a complete monolayer (mg/g) and \(c_{BET}\) indicates a constant that explains the energy of interaction with the surface.

The linearized form of Equation 15 is given thus:

\[
\frac{c_e}{q_e(c_s - c_e)} = \frac{1}{q_s c_{BET}} + \frac{(c_s/c_e - 1)}{q_s c_{BET}} c_e
\]  

(16)

Equation 16 serves as a two-parameter BET isotherm (designated as BET1 in this current study) if the monolayer saturation concentration, \(c_s\), was considered as a constant value (Agarwal et al., 2014; Rahimi et al., 2018; Gupta and Kumar, 2019; Sabar et al., 2020) and a three-parameter BET isotherm as a curve fitting value (designated as BET2 in this study). According to Ebadi et al. (2009), to eliminate the discrepancies associated with the value of monolayer saturation concentration widely reported, a new or modified 3-parameter BET equation was developed (designated as BET3 in this study), represented as:

\[
q_e = \frac{q_m K_s c_e}{(1 - K_L c_e)(1 - K_L c_e + K_s c_e)}
\]  

(17)

where \(K_L\) is the equilibrium constant of adsorption of upper layers in BET3 isotherm (L/mg) and \(K_s\) the equilibrium constant of adsorption for the first layer in Langmuir and BET isotherms (L/mg).

3-p Redlich-Peterson isotherm

The 3-p Redlich-Peterson isotherm, given in Equation 18, fuses the Langmuir and Freundlich isotherms into a single equation (Redlich and Peterson, 1959).

\[
q_e = \frac{k_{RP} c_e}{1 + \alpha_{RP} c_e^{\beta_{RP}}}
\]  

(18)

where \(k_{RP}\) and \(\alpha_{RP}\) are the Redlich-Peterson isotherm constant parameters of units L/g and L/mg, respectively and \(0 < \beta_{RP} < 1\).

For \(\beta_{RP} = 0\) and \(\beta_{RP} = 1\), Equation 18 reduces to Henry’s law (or linear adsorption) and Langmuir isotherm, respectively.

Rearranging and linearizing Equation 18, we have:

\[
\frac{c_e}{q_e} = \frac{1}{k_{RP}} + \left(\frac{\alpha_{RP}}{k_{RP}}\right)^{\beta_{RP}}
\]  

(19)

The inherent parameters in the Redlich-Peterson isotherm are determined by minimizing the sum of squares of errors between the \((q_e)^{exp}\) and \((q_e)^{pred}\) values using \(0 < \beta_{RP} < 1\) when a plot of \((c_e/q_e)\) versus \(c_e\) is made with slope \((\alpha_{RP}/k_{RP})\) and intercept on vertical \((1/k_{RP})\).

3-p Tóth isotherm

The 3-p Tóth model arises from the potential theory and is mainly appropriate to describe heterogeneous adsorption systems that satisfy both low- and high-end boundaries of adsorbate concentration (Padmesh et al., 2014). It is hinged on the presupposition of possession of a quasi-Gaussian energy distribution of the adsorbent sites, that is, the sites predominantly have adsorption energies lower than the maximum adsorption (Tóth, 1971; Padmesh et al., 2006). The non-linear form of Tóth isotherm is represented thus:

\[
q_e = \frac{q_m K_T c_e}{(1 + (K_T c_e)^{\beta_T})^{\beta_T}}
\]  

(20)

where \(K_T\) and \(\beta_T\) are the Tóth isotherm constants, which are both expressed in (mg/g). The heterogeneity of the adsorption system is characterized by the parameter, \(\beta_T\) (Behbahani and Behbahani, 2014). The adsorption system is said to be heterogeneous if \(\beta_T\) is not close to 1. The parameters, \(q_m\), \(K_T\) and \(\beta_T\), of the Tóth isotherm can be estimated by non-linear regression analysis.

3-sips isotherm

The 3-p Sips isotherm model assumes localized adsorption void of interactions between adsorbates and fuses the Langmuir and Freundlich expressions patterned to predict the behavior of heterogeneous adsorption systems. This model eradicates the Freundlich model limitation at high concentration of adsorbate but rather gives the prediction of a monomolecular layer adsorption capacity of Langmuir isotherm and is uniquely transformed to the isotherm of Freundlich at low adsorbate concentration. The non-linear Sips isotherm is expressed thus:

\[
q_e = \frac{q_{SP} K_{SP} c_e^{\beta_s}}{1 + K_{SP} c_e^{\beta_s}}
\]  

(21)

where \(q_{SP}\) and \(K_{SP}\) are the Sips isotherm model constant and \(\beta_s (=1/N)\) is the Sips isotherm exponent. These isotherm parameters are determined using non-linear regression analysis.

3-p Khan isotherm

The 3-p Khan model, which was developed originally for bi-
adsorbate from simulated or pure dilute solutions, combines the features of Langmuir and Freundlich isotherms. The non-linear Kahn isotherm is given by (Amrhar et al., 2015a, b):

\[ q_e = \frac{q_{max} b_K c_e}{a_K (1 + b_K c_e)} \]  

(22)

where \( q_{max} \) is the Kahn isotherm maximum adsorption capacity (mg/g), \( a_K \) the Kahn isotherm exponent and \( b_K \) the Kahn isotherm constant.

Linearizing Equation 22, we have:

\[ \frac{1}{q_e} = \left( \frac{a_K}{q_{max} b_K} \right) \frac{1}{c_e} + \frac{a_K}{q_{max}} \]  

(23)

Therefore, a straight line should be obtained from the plot of \( 1/q_e \) against \( 1/c_e \), with slope \( = a_K / (q_{max} b_K) \) and intercept \( = a_K / q_{max} \). Thus, the general expression for the Kahn isotherm can be obtained using Equation 22. However, non-linear regression method is employed to determine the three Kahn isotherm model parameters, \( q_{max} \), \( a_K \) and \( b_K \).

3-p Radke-Prausnitz isotherm

The 3-p Radke-Prausnitz model is basically applied for broad range of concentration and is widely used for adsorption systems at low concentration (Ramadoss and Subramaniam, 2018). It is expressed as:

\[ q_e = \frac{q_{max} K_{RPI} c_e}{(1 + K_{RPI} c_e)^{\alpha_{RPI}}} \]  

(24)

where \( q_{max} \) is the Radke-Prausnitz maximum adsorption capacity (mg/g), \( K_{RPI} \) the Radke-Prausnitz equilibrium constant and \( \alpha_{RPI} \) the Radke-Prausnitz model exponent. The Radke-Prausnitz model parameters, \( q_{max} \), \( K_{RPI} \) and \( \alpha_{RPI} \) can be obtained by non-linear statistical fit of experimental data.

3-p Fritz-Schlünder isotherm

The 3-p Fritz-Schlünder isotherm is a model that incorporates the features of Langmuir and Freundlich isotherms and it utilizes three parameters that fit a wide range of experimental data. It is expressed as (Ramadoss and Subramaniam, 2018):

\[ q_e = \frac{(q_m)_{FS} K_{FS} c_e}{1 + (K_{FS} c_e)^{\alpha_{FS}}} \]  

(25)

where \( (q_m)_{FS} \) is Fritz-Schlünder maximum adsorption capacity, \( K_{FS} \) the Fritz-Schlünder equilibrium constant and \( \alpha_{FS} \) the Fritz-Schlünder isotherm exponent. The 3-p Fritz-Schlünder isotherm parameters can be determined by non-linear regression analysis.

4-p Fritz-Schlünder isotherm

The 4-p Fritz-Schlünder is an empirical model that integrates the Langmuir and Freundlich isotherms and is given thus (Hamdaoui and Naffrechoux, 2007):

\[ q_e = \frac{A_{FS} c_e^{\alpha_{FS}}}{1 + B_{FS} c_e^{\beta_{FS}}} \]  

(26)

The model is valid only when \( \Phi_{FS} \) and \( \beta_{FS} \leq 1 \). The 4-p Fritz-Schlünder isotherm parameters can be determined by non-linear regression analysis.

4-p Bauder isotherm

The 4-p Bauder model was born out of the need to accurately account for the differences in the course of calculating Langmuir constant and coefficient over a wide range of certain specifications linked to its parameters. It is given by:

\[ q_e = \frac{(q_m)_B b_0 c_e^{1+x+y}}{1 + b_0 c_e^{1+x}} \]  

(27)

where \( (q_m)_B \) is Bauder maximum adsorption capacity, \( b_0 \) the Bauder equilibrium constant, \( x \) and \( y \) are the Bauder isotherm parameters. Owing to the inherent bias resulting from linearization, the 4-p Bauder isotherm parameters can be obtained by non-linear regression analysis. However, its application must satisfy the conditions of \( (1 + x + y) < 1 \) and \( (1 + x) < 1 \).

4-p Marczewski-Jaroniec isotherm

The 4-p Marczewski-Jaroniec model considers the local Langmuir isotherm and takes into cognizance the distribution of adsorption energies associated with the active sites of adsorbent for low and high value cases of the process. It is expressed as (Ayawei et al., 2017):

\[ q_e = \left( q_m \right)_{MJ} \frac{\left( K_{MJ} c_e^{\alpha_{MJ}} \right)^{\beta_{MJ}}}{1 + \left( K_{MJ} c_e^{\alpha_{MJ}} \right)^{\beta_{MJ}}} \]  

(28)

where \( (q_m)_{MJ} \) is Marczewski-Jaroniec maximum adsorption capacity, \( K_{MJ} \) the Marczewski-Jaroniec equilibrium constant, the heterogeneity of the adsorbent surface is characterized by the Marczewski-Jaroniec isotherm parameters, \( \alpha_{MJ} \) and \( \beta_{MJ} \). \( \alpha_{MJ} \) and \( \beta_{MJ} \) give the description of the spreading of distribution in the path of less and higher adsorption energies respectively. The 4-p Marczewski-Jaroniec isotherm parameters, \( (q_m)_{MJ} \), \( K_{MJ} \), \( \alpha_{MJ} \) and \( \beta_{MJ} \)
and $\beta_{MI}$, are obtained by non-linear regression analysis.

5-p Fritz-Schlünder isotherm

The 5-p Fritz-Schlünder isotherm was proposed to simulate accurately variations in isothermic model such that it can be applied over a large range of equilibrium data. It is given by:

$$q_e = \frac{(q_m)_{FS5} K_{FS5} c^{\alpha_{FS5}}}{1 + \Phi_{FS5} c^{\beta_{FS5}}}$$  \hspace{1cm} (29)$$

where $(q_m)_{FS5}$ is Fritz-Schlünder maximum adsorption capacity.

The 5-p Fritz-Schlünder isotherm parameters, $(q_m)_{FS5}, K_{FS5}, \Phi_{FS5}, \alpha_{FS5}$ and $\beta_{FS5}$, are estimated by non-linear regression analysis.

Batch reactor design

The aim of the prototype is to determine the mass of the prepared chitosan flakes (adsorbent), $m$, required to remove the adsorbate (methylene blue) from solution of volume, $V$, at near real environmental initial concentration of $c_0$ to relatively allowable levels of concentration, $c_e$. However, the design of single solute batch adsorption systems can be facilitated by adsorption isotherms and equilibrium data. Based on the applicable adsorption isotherm, the mass of adsorbent required to realize specified percentage removal efficiency, $R$, from aqueous solution of volume $V$ for a known initial concentration of the adsorbate, except for 100% removal efficiency, is derived in this study. The adsorption percentage, $R$, adsorption capacity values at equilibrium, $q_e$, and at time $t$, $q_t$, are determined using Equations 30 to 32, respectively:

$$R = \left( \frac{c_0 - c_e}{c_0} \right) \times 100$$  \hspace{1cm} (30)$$

where $c_0$ is initial concentration of methylene blue solution (adsorbate), and $c_e$ the concentration of adsorbate at equilibrium, both of units, mg/L.

$$q_e = \left( \frac{c_0 - c_e}{m} \right) V$$  \hspace{1cm} (31)$$

$$q_t = \left( \frac{c_0 - c_t}{m} \right) V$$  \hspace{1cm} (32)$$

where $c_t$ is the concentration of adsorbate at time $t$, expressed in mg/L, $m$ the mass of adsorbent (g), $V$ volume of aqueous solution in contact with the adsorbent (L).

From Equation 30, we obtain:

$$c_e = c_0 \left( 1 - \frac{R}{100} \right)$$  \hspace{1cm} (33)$$

Combining Equations 30 and 31, we have:

$$q_e = R V c_0 / 100 m$$  \hspace{1cm} (34)$$

Equations 33 and 34 can now be used in the isotherm that correlates the equilibrium adsorption data to determine the mass of adsorbent required to achieve certain percentage removal of adsorbate from solutions of varied volumes (say, 1-20 L) at ambient temperature in a mono-solute batch reactor system. Olafadehan (2021) obtained Equation 35 assuming the adsorption equilibrium data are correlated using Langmuir isotherm.

$$m = \frac{V \times R \times c_0 \left[ 1 + K_L \left( c_0 \left[ 1 - \left( \frac{R}{100} \right) \right] \right) \right]}{100 q_{max} K_L \left( c_0 \left[ 1 - \left( \frac{R}{100} \right) \right] \right)}$$  \hspace{1cm} (35)$$

Adsorption kinetics

The adsorption kinetics describes rate of uptake of the solute, which, in turn, influences the residence time of the uptake of the adsorbate at the solid-solution interface. Thus, it is imperative to understand the reaction mechanism for the sorption process in a bid to design appropriately the sorption treatment plants. So, the adsorption kinetics is a major issue in the design of a treatment system using adsorbent. Moreover, it is used to establish the controlling step in an adsorption process. Adsorption kinetics provides information to relational industry operators and planners that can be used to effectively treat the contaminated wastewater by adsorption since rapid adsorption of the solute in an adsorption system is desirable and beneficial for actual or industrial applications. The kinetic parameter, which aids the prediction of the rate of adsorption and equilibrium time, gives significant information for designing and modeling the adsorption processes (Sivarajasekar and Baskar, 2014). The adsorption kinetics investigated in this study are illustrated in the following.

Fractional power model

The fractional power model can be expressed in the form of Freundlich equation, which indicates that the uptake of the adsorbate (or solute) increases exponentially with time. It is given by:

$$q_t = k_f t^v$$  \hspace{1cm} (36)$$

where $q_t$ is the amount of solute adsorbed per weight of adsorbent at time $t$ (mg/g); $v$ the fractional order, $k_f$ is the fractional power kinetic model constant (mg/g min$^v$) and $t$ time of adsorption (min).

Taking natural logarithms of Equation 36 gives:

$$\ln q_t = \ln k_f + v \ln t$$  \hspace{1cm} (37)$$

Therefore, a plot of $\ln q_t$ against $\ln t$ can be made to determine the parameters, $v$ and $k_f$, from the slope and intercept on the vertical axis, respectively.
Lagrgren pseudo first-order kinetic model

The Lagergren pseudo first-order kinetic model, expressed in Equation 38, describes the adsorption of solutes onto adsorbents following the first-order mechanism (Ho, 2004):

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]  

(38)

where \( k_1 \) the Lagergren pseudo first-order rate constant (min\(^{-1}\)).

The integral of Equation 38 from \( t=0 \), \( q_t=0 \) to \( t=t \), \( q_t=q_e \) yields the non-linear form:

\[
q_t = q_e \left(1 - e^{-k_1 t}\right)
\]

(39)

The linearized form of Equation 39 is:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

(40)

Therefore, a straight line should be obtained from the plot of \( \ln (q_e - q_t) \) against \( t \), which is adequate to determine \( k_1 \).

Pseudo second-order kinetic model

The pseudo second-order kinetic model assumes the adsorption of solutes onto adsorbents follows the second-order mechanism and is given by:

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]

(41)

where \( k_2 \) is the specific reaction rate constant for the pseudo second-order kinetics (g/(mg min)), which can be used to calculate the initial sorption rate, \( h \) [= mg/(g min)] thus:

\[
h = k_2 q_e^2
\]

(42)

When integrated, Equation 41 yields:

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}
\]

(43)

Linearization of Equation 43 yields different forms. One of such linear forms employed in this study is:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(44)

Therefore, a straight line should be obtained from the plot of \( (t/q_t) \) against \( t \), which is adequate to determine \( k_2 \).

Elovich kinetic model

The Elovich kinetic model describes adsorption process in a non-ideal state and on chemisorption phenomena (Gupta and Kumar, 2019) and is given by:

\[
\frac{dq_t}{dt} = \alpha \exp\left(- \beta q_t\right)
\]

(45)

where \( \alpha \) and \( \beta \) are constants during an experiment. As \( q_t \to 0 \), \( dq_t/dt \to \alpha \). Hence, \( \alpha \) is regarded as the initial rate of adsorption. Equation 45, when integrated using the conditions \( t=0 \), \( q_t=0 \) and \( t=t \), \( q_t=q_e \), yields:

\[
q_t = \frac{1}{\beta} \left[\ln (t + \Phi) - \ln \Phi\right]
\]

(46)

where \( \Phi = 1/\alpha \beta \). If \( t \gg \Phi \), Equation 46 simplifies to:

\[
q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t
\]

(47)

Therefore, a straight line should be obtained from the plot of \( q_t \) against \( \ln t \) to check if \( t \gg \Phi \) for the coefficient of determination, \( R^2 \), should be greater than 1. This allows the determination of \( \beta \) (g/mg) and \( \alpha \) (mg/(g min)) from the slope and intercept on vertical axis respectively.

Avrami kinetic model

The Avrami kinetic model, also known as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, was first derived by Kolmogorov et al. (1937) and popularized by Avrami (1939, 1940, 1941). The Avrami kinetic model assumes random nucleation sites across the reaction surface of the adsorbent and it evaluates changes in kinetic parameters as function of reaction time and temperature. The non-linear form of the expression is given as (Ahmad et al., 2014; Yoro et al., 2017):

\[
q_t = q_e \left[1 - \exp\left(- k_{AV} t^{n_{AV}}\right)\right]
\]

(48)

where \( k_{AV} \) is the Avrami rate constant (min\(^{-n_{AV}}\)) and \( n_{AV} \) is a dimensionless constant related to the mechanism of adsorption with regard to temperature and contact time.

Taking the natural logarithms of Equation 48, we have:

\[
-ln \left(1 - \frac{q_t}{q_e}\right) = k_{AV} t^{n_{AV}}
\]

(49)

To enable determination of the inherent kinetic parameters in the Avrami kinetic model, another natural logarithmic approach is applied to Equation 49 to yield:

\[
\ln \left[-\ln \left(1 - \frac{q_t}{q_e}\right)\right] = \ln k_{AV} + n_{AV} \ln t
\]

(50)
which allows the determination of the constants, \( n_{AV} \) and \( k_{AV} \), from a plot of \( \ln \left[ -\ln \left( 1 - \frac{q_t}{q_e} \right) \right] \) against \( \ln t \). If the transformation followed the Avrami equation, this yields a straight line with slope = \( n_{AV} \) and intercept on vertical axis = \( \ln k_{AV} \), from which \( k_{AV} \) can be determined.

Adsorption is largely over when \( \left( q_t / q_e \right) \) reaches values close to 1, which will be at an adsorption time, \( t_a \), defined by \( k_{AV} (t_a)^{n_{AV}} \approx 1 \) as then the exponential term in the above expression for \( \left( q_t / q_e \right) \) will be small. Thus, adsorption takes a time of order:

\[
t_a = 1.01167 \left( k_{AV} \right)^{\frac{1}{n_{AV}}}.
\]  

(51)

Therefore, adsorption takes a time that decreases as one over the one-quarter power of \( k_{AV} \).

**Intraparticle diffusion (IPD) (or Weber-Morris) model**

The intraparticle diffusion (IPD) (or Weber and Morris) model, given in Equation 51, is employed to establish the diffusion mechanism involved in the adsorption process.

\[
q_t = k_{IPD} \sqrt{t} + C
\]

(52)

where \( k_{IPD} \) is the intraparticle diffusion rate constant (mg/(g min\(^{1/2}\))) and \( C \) is a constant (mg/g). The intraparticle diffusion rate constant, \( k_{IPD} \), can be estimated from the slope of \( q_t / \sqrt{t} \) plot, which ought to be a straight line passing through the origin \( (C = 0) \) if IPD model could be employed to describe the kinetics of the adsorption process.

The intraparticle diffusion model has attracted many researchers because of the multi-linearity the plot of Equation 52 gives. Malash and El-Khairy (2010) suggested the use of piecewise regression in expressing adequately the model. The piecewise regression is a special type of linear regression that is used when a single line is insufficient to model a data set marked with multi-linearity. It allows multiple linear models to be fitted to the data for different independent variables. For a two-segment form, the expression is given as:

\[
y_i = \beta_0 + \beta_1 x_{i1} + \beta_2 \left( x_{i1} - x^{(k)} \right) x_k
\]

(53)

where \( x_{i1} \) is the independent variable value, \( x^{(k)} \) the knot value and \( x_k \) the knot dummy variable is expressed as:

\[
x_k = \begin{cases} 
0 & \text{if } x_{i1} \leq x^{(k)} \\
1 & \text{if } x_{i1} > x^{(k)} 
\end{cases}
\]

(54)

In this investigation, Equation 52 is tagged IPD-1 segment and Equation 53 is named IPD-2 segment.

**Boyd model**

Though the Boyd et al. (1947) diffusion model was developed theoretically for ion-exchange kinetics, it had been applied successfully to adsorption studies (Morrison and Boyd, 2004; Castillejos et al., 2011; El-Khairy and Malash, 2011; Olafadehan et al., 2018) to establish the exact rate-limiting step involved in the adsorption process due to the two-mass transfer processes of solute, which are film and pore diffusion. The Boyd model assumes that the boundary layer surrounding the adsorbent has a greater effect on the diffusion of solute. The Boyd’s model is given by:

\[
F_B(t) = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -n^2 Bt \right)
\]

(55)

where \( F_B(t) \) is dimensionless fraction of solute adsorbed at time \( t \), \( B = \pi^2 D/R_p^2 \) : \( D \) the effective intraparticle diffusion coefficient (m\(^2\)/s) and \( R_p \) radius of adsorbent particle (m).

If intraparticle diffusion was the rate-controlling step in the adsorption process, Equation 52 is valid with \( C = 0 \). Reichenberg (1953) obtained approximate expressions given by Equations 56 and 58 via the application of Fourier transform and then integration of Equation 55:

\[
F_B(t) = 1 - \frac{6}{\pi^2} \exp \left( -Bt \right) , \ F_B(t) > 0.85
\]

(56)

That is,

\[
Bt = - \ln \left[ 1 - F_B(t) \right] - 0.4977 , \ F_B(t) > 0.85
\]

(57)

\[
Bt = \left( \sqrt{\pi} - \sqrt{\pi - \frac{2F_B(t)}{3}} \right) , \ F_B(t) \leq 0.85
\]

(58)

The value of \( B \) can be determined using Equation 57 or 58 for each and every value of \( F_B(t) \), depending on the conditions given and the Boyd plots (\( B-t \) constructed (Olafadehan et al., 2018; Ho et al., 2002). The distinction between intraparticle transport-controlled rates of adsorption and the film diffusion (external transport) is revealed by the linearity of the \( B-t \) plots (Olafadehan et al., 2018; Wang et al., 2006). If the adsorption process was controlled by intraparticle diffusion, a straight line passing through the origin would be obtained; otherwise, film diffusion governs the adsorption process (El-Khairy and Malash, 2011; Olafadehan et al., 2018; Mohan and Singh, 2002; Sharma and Das, 2012).

**Diffusion-chemisorption model**

The diffusion-chemisorption model assumes that the adsorption or uptake of adsorbate is under the influences of both diffusion and chemisorption. This model was originally used for the uptake of heavy metals on heterogeneous surface (Sutherland and
Venkobachar, 2010). The non-linear form of the diffusion-chemisorption model is given by:

\[
\frac{q_e^2}{(q_e - q_i)} = k_{DC} \sqrt{t} + q_e
\]  

(59)

where \( k_{DC} \) (mg/(g min\(^{0.5}\))) is the diffusion-chemisorption parameter related to the initial sorption rate, \( k_i \) (mg/(g min)) by assuming a linear region as \( t \to 0 \) using the empirical relationship:

\[
k_i = \frac{k_{DC}^2}{q_e}
\]  

(60)

The linear form of Equation 59 amenable for the determination of \( k_{DC} \) and \( q_e \) by plotting \( \sqrt{t}/q_i \) against \( \sqrt{t} \) is expressed in Equation 61:

\[
\frac{\sqrt{t}}{q_i} = \frac{1}{q_e} + \frac{1}{k_{DC}}
\]  

(61)

**Error functions**

The minimization of the error distribution between the experimental equilibrium data and the predicted isotherms/adsorption kinetics can be determined via error functions’ values. Depending on definition of the error function, the error distribution between the experimental equilibrium data and the predicted values is minimized either by the minimization or maximization of the error function. Thus far, no detailed studies are available to compare the accuracy of the error functions in predicting the isotherm/kinetic parameters and also the optimum isotherm/kinetics. The various error functions used in this study for the comparison of the experimental and predicted equilibrium adsorption data are shown in Table 1 where \( Q_{k, \text{exp}} = \{q_e\}_{k, \text{exp}} \) or \( (q_i)_{k, \text{exp}} \) is the measured adsorption data for run \( k \), \( Q_{k, \text{pred}} = \{q_e\}_{k, \text{pred}} \) or \( (q_i)_{k, \text{pred}} \) the predicted (or calculated) adsorption data for run \( k \), \( N_e \) the number of experimental data points and \( N_p \) the number of model parameters.

**Information-based criteria**

The information-based criteria (IC) are criteria for selecting the best fitted isotherm and kinetic model through the use of statistical tools such as Akaike Information Criterion (AIC), Schwarz Bayesian Information Criterion (SBIC), Khinchin’s law of Iterated Logarithm Criterion (KLIC), among others (Davila-Jimenez et al., 2014). The model selection depends on the sample size. The criteria estimate loss of information that a model records as a measure of distance from the true model (Aliston et al., 2015). The SBIC and KLIC are usually used for large sample data while AIC are used for both large and small sample data. In the present work, only AIC are employed for both the adsorption isotherm and the kinetic studies.

**Akaike information criteria**

The AIC were developed by Akaike (1974). They are statistical tools that have been adopted for selecting the most fitted model amongst competing models with a varying number of parameters (Akpa and Unuabonah, 2011; Turner et al., 2015; Nayak and Pal, 2019). According to Nayak and Pal (2019), with the assumption of independent model errors and normal error distribution, the equation for using AIC is expressed as follows:

\[
A_{IC} = 2N_p - N_e \ln \left( \frac{\text{ERRSQ}}{N_e} \right)
\]  

(62)

Sugiura (1978) and Hurvich and Tsai (1989) modified and advanced the model for a small data in which \( (N_e/N_p < 40) \) as follows (Nayak and Pal, 2019):

\[
(A_{IC})_{mod} = A_{IC} + \left[ \frac{2N_p(N_p + 1)}{N_e - N_p - 1} \right]
\]  

(63)

The use of Akaike weights, \( \lambda_i \), and strength of evidence, \( ER \), gives one greater insight into the relative merits of the competing models (Turner et al., 2015; Wagenmakers and Farrell, 2004; Ibrahim et al., 2018). The Akaike weight, \( \lambda_i \), is expressed as:

\[
\lambda_i = \frac{\exp(-0.5\Delta A_{IC}^i)}{\sum_{k=1}^{i} \exp(-0.5\Delta A_{IC}^k)}
\]  

(64)

\[
(\Delta A_{IC}^i)^k = (A_{IC}^i)^k - (A_{IC}^i)_{k-1}
\]  

(65)

\[
ER = \frac{1}{\exp[-0.5(\Delta A_{IC}^i)]}
\]  

(66)

where \( (\Delta A_{IC}^i)_{k} \) denotes the differences between the value of \( A_{IC}^i \) for the \( k \)-th model and the minimum \( A_{IC}^i \) value of the best ranked model, denoted by \( (\Delta A_{IC}^i)_{k} \).

**Model selection criterion**

The model selection criterion is a statistic that expresses a function for assessing competing models vying for the best fitted model and it is expressed as (Adegunbi et al., 2019):

\[
MSC = \ln \left( \frac{ESS}{SSE} \right) - \frac{2P}{N}
\]  

(67)

\[
ESS = \sum_{k=1}^{N_p} \left( Q_{k, \text{pred}} - \overline{Q}_{k, \text{pred}} \right)^2
\]  

(68)

where \( MSC \) is the model selection criterion, \( ESS \) the sum of squares...
Table 1. Mathematical expressions for error functions.

| S/N | Error functions                        | Model                                                                 | Reference                  |
|-----|----------------------------------------|-----------------------------------------------------------------------|----------------------------|
| 1   | Coefficient of determination, $R^2$    | $R^2 = 1 - \frac{\sum_{k=1}^{N_e} (Q_{e,\text{exp}} - Q_{k,\text{pred}})^2}{\sum_{k=1}^{N_e} (Q_{k,\text{pred}} - Q_e)^2}$ | Olafadehan (2021)         |
| 2   | Average relative error, $ARE$          | $ARE = \frac{100}{N_e} \sum_{k=1}^{N_e} \left| \frac{Q_{e,\text{exp}} - Q_{k,\text{pred}}}{Q_{e,\text{exp}}} \right|$ | Chan et al. (2012)        |
| 3   | Standard deviation of relative errors, $SRE$ | $SRE = \sqrt{\frac{1}{N_e} \sum_{k=1}^{N_e} \left( (Q_{e,\text{exp}} - Q_{k,\text{pred}}) - ARE \right)^2}$ | Popoola (2019)            |
| 4   | Marquardt’s percent standard deviation, $MPSD$ | $MPSD = 100 \sqrt{\frac{1}{N_e - N_p} \sum_{k=1}^{N_e} \left( 1 - \frac{Q_{k,\text{pred}}}{Q_{k,\text{exp}}} \right)^2}$ | Chan et al. (2012)        |
| 5   | Normalized standard deviation, $NSD$   | $NSD = 100 \sqrt{\frac{1}{N_e - 1} \sum_{k=1}^{N_e} \left( \frac{Q_{e,\text{exp}} - Q_{k,\text{pred}}}{Q_{e,\text{exp}}} \right)^2}$ | Ahmad et al. (2014)       |
| 6   | Residual Root Mean Square Error, $RMSE$ | $RMSE = \frac{1}{N_e - 2} \left( \sum_{k=1}^{N_e} (Q_{e,\text{exp}} - Q_{k,\text{pred}})^2 \right)^{1/2}$ | Alston et al. (2015)      |
| 7   | Normalized chi-square test, $\chi^2$  | $\chi^2 = \sum_{k=1}^{N_e} \left( \frac{(Q_{e,\text{exp}} - Q_{k,\text{pred}})^2}{Q_{e,\text{exp}}} \right)$ | Amrhar et al. (2015a, b)  |
| 8   | Sum of squares of the errors, $ERRSQ$  | $ERRSQ = \frac{1}{N_e} \sum_{k=1}^{N_e} (Q_{e,\text{exp}} - Q_{k,\text{pred}})^2$ | Amrhar et al. (2015a, b)  |
Table 1. Contd.

|   |   |   |
|---|---|---|
| 9 | Sum of absolute error, \(EABS\) | \[EABS = \sum_{k=1}^{N_p} (Q_{k,exp} - Q_{k,pred})\] Chan et al. (2012) |
| 10 | Hybrid functional error, \(HYBRID\) | \[HYBRID = \frac{100}{N_e - N_p} \sum_{k=1}^{N_p} \left( \frac{(Q_{k,exp} - Q_{k,pred})^2}{Q_{k,exp}} \right)\] Olafadehan (2021) |

due to regression, that is, the sum of the squares of the difference of the predicted values and the mean value of the response variable and \(Q_{k,pred}\) is the mean of the predicted values.

Thermodynamics studies

The thermodynamic features and parameters (such as change in Gibbs free energy, \(\Delta G^0\), enthalpy change, \(\Delta H^0\), entropy change, \(\Delta S^0\)) of the adsorption of methylene blue on chitosan flakes were determined using Equations 69 and 70 (Erdem et al., 2004; He et al., 2010; Hefni et al., 2019):

\[K_d = \left(\frac{c_0 - c_e}{c_e}\right) \times \frac{V}{M}\] (69)

\[\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K_d\] (70)

where \(K_d\) is the distribution coefficient (mL/g) and \(c_d\) (\(= c_0 - c_e\)) the concentration of MB on chitosan flakes (mg/L). From Equation 70, the linear plot of \(\ln K_d\) against \(T^{-1}\) enables \(\Delta H^0\) and \(\Delta S^0\) to be obtained from the slope \[\frac{\Delta H^0}{R}\] and intercept on vertical axis \[\frac{\Delta S^0}{R}\], respectively.

The modified Arrhenius type equation is used to relate the sticking probability, \(S^*\), to surface coverage, \(\theta\), thus (Najim et al., 2010):

\[S^* = (1 - \theta) \exp \left( -\frac{E_a}{RT} \right)\] (71)

Where

\[\theta = 1 - \frac{c_e}{c_0}\] (72)

The linearized form of Equation 71 is given as:

\[\ln(1 - \theta) \approx \frac{E_a}{RT} + \ln S^*\] (73)

Hence, the linear plot of \(\ln(1 - \theta)\) against \(T^{-1}\) enables the activation energy, \(E_a\), and \(S^*\) to be obtained from the slope and intercept on vertical axis, respectively.

RESULTS AND DISCUSSION

Characterization of chitosan flake

The physicochemical properties of the prepared chitosan flakes from \(A. marginata\) shell powder, which included moisture, ash, fiber and protein contents, average molecular weight and apparent viscosity, were reported in our recent work to be 5.5%, 0.25%, 2.70, (0.85 ± 0.27%), 220 kDa and (85.20 cP at 20°C), respectively (Bello and Olafadehan, 2021). Other properties of the chitosan flakes obtained in this study are particle size =150 µm, bulk density = 0.9 g/cm³, pH = 7.3 and pHpcz = 7.8. Equally, the morphological features of the chitosan flakes were assessed using Scanning Electronic Morphology (SEM) at 10,000 and 11,000 magnifications in our investigation (Bello and Olafadehan, 2021). It was revealed in Bello and Olafadehan (2021) that the surfaces of the shell of \(A. marginata\) and the chitosan flakes possessed cavities, pores and rough surfaces, which are viable characteristics of a typical adsorbent such as chitosan flakes. Also, the Electron Dispersive X-ray Spectroscopy (EDS) spectrum and the distribution of chemical elements in the grated \(A. marginata\) shell waste revealed that the precursor contained the highest weight % of calcium (53.35) and least weight % of iron (0.52) with weight % of oxygen, silica, sodium, magnesium, phosphorus and carbon being 3.20, 1.72, 2.24, 3.32, 13.10 and 2.45, respectively (Bello and Olafadehan, 2021). The X-ray diffraction (XRD) of the prepared chitosan...
flakes indicated the crystalline natures of the biopolymer, where well-defined peaks, conspicuously among others at 2θ = 20 and 26°, were obtained (Bello and Olafadehan, 2021). In addition, the Fourier transform infrared spectroscopy (FT-IR) spectrophotometer (IS10, Thermo Nicolet, USA) in the wave number range of 4000-400 cm\(^{-1}\) with KBr pellet was used to determine the absorption bands and subsequent functional groups for A. marginata shell and the chitosan flakes before and after adsorption of methylene blue (Bello and Olafadehan, 2021). We showed that there was an interaction between methylene blue (MB) and the chitosan flakes and the adsorption was accomplished for reason of the significant differences in absorbance wavelength coupled with an increase in the absorbance wavelength of the amide and hydroxyl groups being responsible for the efficacious adsorption of methylene blue on the prepared chitosan flakes from A. marginata shell powder.

Effects of operational parameters on MB adsorption

Effect of adsorbent dosage

Figure 1 depicts the respective effects of the mass of adsorbent (chitosan flakes), \(M\), on the removal efficiency of the chitosan flakes and the equilibrium adsorption capacity, \(q_e\). It is revealed in the figure that the percentage removal of MB increases appreciably with increase in adsorbent mass owing to the fact that an increase in adsorbent mass leads to an increase in the number of active sites, except for cases of overlapping of adsorption sites or due to the screening effect occasioned by overcrowding of adsorbent where the percentage removal of the target pollutant shows no further increase (Benzaoui et al., 2018).

It was observed in Figure 1 that the adsorption capacity decreases with a corresponding increase in the dosage of the adsorbent. This is as a result of entire exposure of the active sites at low amount of adsorbent dose while a few fractions were exposed at higher dose of the chitosan flakes (Alghamdi et al., 2019).

Effect of solution pH

The influence of pH of methylene blue solution on adsorption capacity, \(q_e\), of the chitosan flakes and % removal of MB was investigated by varying the solution pH values for an initial concentration of MB of 100 mg/L at 303 K. Figure 2 reveals that the pH of solution influences appreciably the percentage of MB molecules adsorbed on the chitosan flakes and the adsorption capacity of the chitosan flakes within a pH range of 2 to 12 considered. The percentage removal of MB increases from 49.82 to 98.95 at solution pHs of 2.4 and 11.8, respectively largely due to the pH of zero point charge (pHzpc) of the adsorbent measured at 7.3. At a solution pH lower than zero-point charge \(pH < pHzpc\), the surface charge of the adsorbent becomes positively charged and initiates the presence of hydrogen ions, which heightened the competition between the MB cations and the hydrogen ions on the active site of the adsorbent. Thus, % removal of MB as well as the adsorption capacity is low. Conversely, at higher solution pH, the surface charge of the adsorbent becomes negatively charged owing to the large presence of hydroxyl ions, which eventually paved way for less competition and facilitates the electrostatic forces of attraction between the cations of MB on the much available active sites (Bernal et al., 2017; Boumediene...
Effect of solution pH on removal of MB on chitosan flakes and adsorption capacity.

Figure 2.

Effect of initial concentration of MB on adsorption capacity and % removal of MB.

Figure 3.

et al., 2018). Thus, a relatively high amount of MB adsorbed on the chitosan flakes as well as adsorption capacity was achieved.

**Effect of initial MB concentration**

The respective effects of the initial methylene blue concentrations on the % removal of MB and adsorption capacity of the chitosan flakes were shown in Figure 3. The percentage removal of MB decreases from 96.49 to 61.11 as the initial concentration of MB increases from 10 to 60 mg/L while the amount of MB adsorbed per unit mass of chitosan flakes increases significantly from 0.9641 to 3.67 mg/L as the initial MB concentration increases from 10 to 60 mg/L as a result of the
Effect of contact time

The contact time is an influential factor and a key parameter for design, management and operation of wastewater treatment. Figure 4 shows the amount of MB adsorbed per unit mass of chitosan flakes and percentage removal of MB against contact time at a temperature of 30°C, pH of 8.2, adsorbent dose of 0.1 g and varying initial MB concentrations, \( c_0 \), of 50, 100 and 150 mg/L. It was observed that the first phase of adsorption of MB on the chitosan flakes, which is characterized by a steeper gradient, depicts an increment in the percentage removal of MB and the amount of MB adsorbed per unit mass of the chitosan flakes as the contact time increases until the second phase, which is recognized as the equilibrium stage, was attained. During the first phase, the enormous number of vacant active sites is available for the adsorption of MB molecules on the chitosan flakes. However, at the second stage in the adsorption process characterized with a plateau, there are no significant observable changes in both the % removal of MB and the adsorption capacity of the chitosan flakes due to the few available sites and possible repulsive forces between MB molecules adsorbed on the chitosan flakes and the solution phase ([Edet and Ifelebuegu, 2020; Slimani et al., 2011]). Equilibrium times were established at 70, 80 and 100 min with % removal of MB of 98.2, 94.7 and 87 at initial concentrations of MB of 50, 100 and 150 mg/L respectively. In a similar fashion, the amount of MB molecules adsorbed per unit mass of the chitosan flakes at the respective established equilibrium times was obtained as 1.96, 2.84 and 4.35 mg/g for 50, 100 and 150 mg/L. These results imply that the higher the initial concentration of MB, the higher the equilibrium time and conversely (Kuang et al., 2020).

Effect of temperature

The respective effects of temperature on the percentage adsorption of MB ions and the adsorption capacity of the chitosan flakes are depicted in Figure 5. It was observed that the percentage removal of MB and adsorption capacity of the chitosan flakes reduce as the temperature increases. These obvious trends lend credence to the fact that the adsorption process is favored at low temperature and inimical at high temperature. From literature, this equally inferred that the process of adsorption is an exothermic one, which is in consonance with the thermodynamics parameters estimated ([Edet and Ifelebuegu, 2020; Horsfall and Spiff, 2005]).

Analysis of 2-p adsorption isotherms

The Gill isotherm classification enables an insight to the specific adsorption process. Figure 6 shows the relationship between \( q_e \) and \( c_e \), wherein an “L” shape is
obtained. This implies that there is no strong competition between the solvent and the adsorbate vying for the occupation of the adsorbent surface sites. It can equally be inferred that the methylene blue molecules are adsorbed flat on the surface of the chitosan flakes because the longitudinal axes of the adsorbed MB molecules are parallel to the adsorbent surface (Hamdaoui and Naffrechoux, 2007).

All the isotherms investigated in this study were attempted to be fitted to the batch equilibrium data of MB adsorption on chitosan flakes as adsorbent at pH=8.2, temperature of 30°C, agitation speed=150 rpm and adsorbent dose of 0.1 g.

From the linear plot of 2-p Freundlich isotherm, expressed in Equation 2, the estimated $R^2$ value is 0.914, the adsorption intensity, $N$, is 3.663 and the measure of adsorption capacity, $k_f = 1.5516$. The calculated value of $1/N (= 0.273)$ is within the range of 0.1 to 1.0. Thus, the adsorption of MB on the prepared chitosan flakes is adjudged to be a good adsorption process (Kuang et al., 2020). From the literature, it was reported that adsorption process is good for $2 \leq N < 10$, moderate difficult for $1 \leq N < 2$ and poor for $N < 1$ (Olafadehan et al., 2018; Razavi et al., 2013; Húmpola et al., 2013; Chen et al., 2010; Tahir and Rauf, 2006). Hence, the 2-p Freundlich isotherm obtained for the
The mean energy of adsorption, $E$ was calculated to be 2.2361 kJ/mol. From the literature, the mean energy of adsorption value indicates physical adsorption for values of 1–8 kJ/mol; ion-exchange for values of 8-16 kJ/mol and 20-40 kJ/mol for chemisorption (Chen et al., 2010; Tahir and Rauf, 2006). This result clearly reflects a physical adsorption process of MB adsorption on chitosan flakes from A. marginata shell powder.

From the linear plot of 2-p Freundlich isotherm, expressed in Equation 12, the isotherm constants, $A_{JJ}$ and $B_{JJ}$ were evaluated to be 2.2894 and 1.3299 g/mg$^2$, respectively with a relatively poor regression coefficient, $R^2=0.7044$.

From the linear plot of 2-p Frenkel-Halsey-Hill isotherm, expressed in Equation (14), the isotherm constants, $n_{FHH}$ and $K_{FHH}$ were evaluated to be -3.6630 and 0.2, respectively with regression coefficient, $R^2=0.914$.

From the linear plot of 2-p Brunauer-Emmett-Teller isotherm, expressed in Equation 16, which is designated as BET1 isotherm in this study, the isotherm constants, $q_s$ and $c_{BET}$ were evaluated to be 99.99 mg/L and 1.00, respectively with a significant high regression coefficient, $R^2=0.9816$ for the saturated concentration, $c_s$, of MB used = 43210 mg/L (Salimi and Roosta, 2019).

The estimated parameter values of the 2-p isotherms using linear regression methods are shown in Table 2.

The decreasing order of the fit of the isotherms to the equilibrium adsorption data of MB on chitosan flakes, as shown in Table 2, is 2-p Langmuir isotherm, 2-p BET1 isotherm > 2-p Temkin isotherm > 2-p Dubinin-Radushkevish isotherm > 2-p Frenkel-Halsey-Hill isotherm > 2-p Harkins-Jura isotherm, 2-p Freundlich isotherm. Hence, 2-p Langmuir and 2-p BET1 isotherms are adjudged to correlate best the adsorption of MB on chitosan flakes.
Table 2. Comparison of linear and non-linear adsorption isotherm parameters.

| Isotherm          | Parameter | Estimated values using linear form | Estimated values using non-linear form |
|-------------------|-----------|------------------------------------|---------------------------------------|
| 2-p Freundlich    | N         | 3.6630                             | 1.6310                                |
|                   | $k_f$ (mg/g) | 1.5516                             | 3.9800                                |
|                   | $R^2$      | 0.9140                             | 1.0                                   |
|                   | $q_{\text{max}}$ (mg/g) | 3.7327                             | 3.4824                                |
| 2-p Langmuir      | $K_L$ (L/mg) | 0.5615                             | 1.1818                                |
|                   | $R^2$      | 0.9816                             | 1.0                                   |
|                   | $R_L$      | $0 < R_L < 1$ | $0 < R_L < 1$ |
| 2-p Temkin        | $b_T$ (J/mol) | 4481.6616                           | 4439.68                               |
|                   | $A_T$ (L/g) | 20.4606                             | 20.4870                                |
|                   | $R^2$      | 0.9533                             | 1.0                                   |
|                   | $\beta$ (mol/J)$^2$ | $1.0 \times 10^{-7}$ | $7.0 \times 10^8$ |
| 2-p Dubinin-Radushkevish | $q_{DR}$ (mg/g) | 3.0213                             | 3.3109                                |
|                   | $R^2$      | 0.9254                             | 0.8331                                 |
|                   | E (kJ/mol) | 2.2361                             | 2.6726                                 |
|                   | $A_{HJ}$   | 2.2894                             | 2.3008                                 |
| 2-p Harkins-Jura  | $B_{HJ}$ (g/mg)$^2$ | 1.3299                             | 1.7079                                |
|                   | $R^2$      | 0.7044                             | 1.0                                   |
|                   | $n_{FHH}$  | -3.6630                            | -3.9763                                |
| 2-p Frenkel-Halsey-Hill | $K_{FHH}$  | 0.2                                | 0.1433                                 |
|                   | $R^2$      | 0.914                              | 1.0                                   |
|                   | $q_S$ (mg/L) | 99.99                              | 3.6313                                 |
| 2-p BET1          | $c_{BET}$  | 1.00                               | 26832                                  |
|                   | $R^2$      | 0.9816                             | 1.0                                   |

Analysis of adsorption isotherms using non-linear regression analysis

For the purpose of adequate modeling of the adsorption process of MB on chitosan flakes and to evaluate the affinity of MB on the chitosan flakes, nineteen different adsorption isotherms were investigated using non-linear method characterized by trial-and-error-procedure aided by the SOLVER ADD-IN obtained in MICROSOFT EXCEL SPREADSHEET and guided by 9 different error functions aside the $R^2$ function shown in Table 1. These involve seven two-parameter isotherms, eight three-parameter isotherms, three four-parameter and one five-parameter isotherms. The algorithm adopted in this work for non-linear evaluation of isotherm and kinetic models’ parameters is the one given by Popoola (2019) with slight modification of the inclusion of statistical evaluation as another criterion for model selection amongst competing models and the process for evaluating sum of normalized errors (SNE) adopted for the isotherm and kinetic models’ parameters is given by Amrhar et al. (2015a, b).

The estimated parameter values of the 3-p, 4-p and 5-p isotherms using non-linear regression methods are summarized in Table 3.
Table 3. Values of three, four and five-parameter isotherms using non-linear method.

| Isotherm                  | Parameter | Estimated value using non-linear method |
|---------------------------|-----------|----------------------------------------|
|                           | $q_s$     | 2.6489                                 |
| 3-p BET2                  | $c_{BET}$ | 160.5411                                |
|                           | $c_s$     | 77.0698                                 |
|                           | $R^2$     | 1.0                                     |
|                           | $q_m$     | 2.6496                                 |
| 3-p BET3                  | $K_s$     | 2.0696                                 |
|                           | $K_L$     | 0.0130                                 |
|                           | $R^2$     | 1.0                                     |
|                           | $k_{RP}$  | 11.7778                                |
| 3-p Redlich-Peterson      | $\alpha_{RP}$ | 6.0082                              |
|                           | $\beta_{RP}$ | 0.8079                        |
|                           | $R^2$     | 1.0                                     |
|                           | $q_m$     | 3.4824                                 |
| 3-p Toth                  | $K_T$     | 1.1818                                 |
|                           | $\beta_T$ | 1.0                                    |
|                           | $R^2$     | 0.9149                                 |
|                           | $q_{SP}$  | 14.4412                                |
| 3-p Sips                  | $K_{SP}$  | 0.1277                                 |
|                           | $\beta_S$ | 3.3306                                |
|                           | $R^2$     | 1.0                                    |
|                           | $q_{max}$ | 1.3364                                 |
| 3-Khan                    | $b_K$     | 6.1178                                 |
|                           | $a_K$     | 0.8023                                 |
|                           | $R^2$     | 1.0                                    |
|                           | $q_{max}$ | 1.3363                                 |
| 3-p Radke-Prausnitz       | $K_{RP}$  | 6.1174                                 |
|                           | $\alpha_{RP}$ | 0.8023                        |
|                           | $R^2$     | 1.0                                    |
A closer examination of the results in Tables 2 and 3 depicts that the non-linear method gives the better fit of the isotherms to the adsorption data of MB on chitosan flakes than the linear method on the basis of high regression coefficient, $R^2$, which almost gave a value of 1 in all cases, except for 2-p Dubinin-Radushkevich and 3-p Toth isotherms with $R^2$ values of 0.8331 and 0.9149, respectively.

### Kinetic study

#### Linearized kinetic models

The necessary linear plot for each of the adsorption kinetics investigated in the current study for the adsorption of MB on chitosan flakes was made to
determine the kinetic parameters inherent in it. Table 4 presents the values of the kinetic parameters in each of the 8 kinetic models investigated for the adsorption of MB on chitosan flakes using the linearized kinetic models.

For the fractional power kinetic model, the exponent, $\nu$, at all initial MB concentrations was found to be less than unity with a good correlation value at initial methylene blue concentrations of 100 and 150 mg/L shown in Table 4. This validates the time-dependence behavior during the adsorption of MB on the chitosan flakes (El-Khairy and Malash, 2011).

At concentrations of MB of 50, 100 and 150 mg/L initially, high regression coefficients, $R^2$, of 0.9529, 0.9726 and 0.9894 were obtained respectively using the Lagergren pseudo first-order kinetic model. As presented in Table 4, higher values of regression coefficient were marginally obtained for the pseudo second-order kinetic model than for the Lagergren pseudo first-order kinetic model and any other kinetic models at all the initial concentrations of MB investigated. It was thus observed that $R^2$ values of 0.9924, 0.9996, 0.9984 at initial MB concentrations of 50, 100 and 150 mg/L, respectively are good representations of the experimental kinetic data of MB adsorption on chitosan flakes.

In Table 4, the Elovich kinetic model equally gave high regression coefficient values, which are good enough to fit the experimental kinetic data of the adsorption of MB on chitosan flakes but not as high as the $R^2$ values obtained using the pseudo second-order model.

For the intra-particle diffusion (IPD) model, reasonably good $R^2$ values were obtained, with straight line not passing through the origin at all initial concentrations of MB considered, as shown in Figure 8. Consequently, the intraparticle diffusion was not the rate-limiting step in the adsorption of MB on the chitosan flakes. The plots of the model had intercepts for all initial concentrations of MB of 50, 100 and 150 mg/L. The value of the intercept increases significantly with initial MB concentrations of 50 to 100 mg/L and then decreases slightly at 150 mg/L. This gives the impression that the boundary layer linked to the intercepts may likely increase with increase in initial concentrations of MB in the range 50 to 100 mg/L.

A closer observation of the graphs in Figure 8 shows a multi-linear one of three distinct phases, especially for the initial concentrations of MB solution under study. The first phase was observed to be relatively fast due to boundary layer or strong electrostatic attraction of MB on the external surface of the chitosan flakes. The second observable phase is a palpable gradual adsorption stage suggested to be influenced or occasioned by intraparticle as the rate-limiting step at this stage, which culminated to the equilibrium phase (that is, the third phase) with high affinity to the chitosan flakes surface active sites (Zbair et al., 2018).

The estimated intra-particle diffusion rate constant, $k_{IPD}$, shows a gradually retrogression from the slopes values of the multi-lines under study. The intercept values, $C$, for each observed stage shows progressive increment in value as the initial concentration of MB increases. This presupposes the boundary effect is taking a toll on the adsorption process. Such increase in boundary layer thickness would pave way for low external mass transfer and high chances of internal mass transfer.

The Boyd model plot in Figure 9 confirms that the intra-particle diffusion step is not the rate-controlling step in the adsorption of MB on chitosan flakes but rather film diffusion (external diffusion) due to the linearity observed to be away from the origin.

In Table 4, the diffusion-chemisorption model equally gave high regression coefficient values, which are good enough to fit the experimental kinetic data but not as high as the pseudo second-order model. Using the diffusion-chemisorption model, the resulting straight line, coupled with high regression coefficient values, shows that the adsorption process is under the influences of both diffusion and chemisorption.

**Results from non-linear kinetic model**

The estimated kinetic parameters for the non-linear kinetic models using non-linear regression method subjected to the error functions used previously are shown in Table 5. Using the values of the coefficient of determination, the non-linear method gave a better fit than the linear method. With the various error functions employed, for MB concentration of 150 mg/L, NSD function fitted 4 kinetic models (fractional power model, pseudo second-order model, Elovich model, intraparticle diffusion, IPD model); EABS fitted 1 model (Lagergren pseudo pseudo first-order model); ARE fitted 1 model (Avrami model) and RSME fitted 1 model (diffusion-chemisorption model). For MB concentration of 100 mg/L, NSD fitted 4 models (fractional power model, Lagergren pseudo first-order, Elovich and IPD models); ARE fitted 1 model (pseudo second-order model); RSME fitted the diffusion-chemisorption model and HYBRID function fitted 1 model (Elovich model). For the case of initial concentration of MB of 50 mg/L, NSD function fitted 3 models (Lagergren pseudo first-order, pseudo second-order and Elovich models); SSE fitted 1 model (IPD model); HYBRID fitted 1 model (Avrami model); RSME fitted 1 model (fractional power law) and SRE function fitted 1 model (diffusion-chemisorption model).

**Isotherm and kinetic models’ selection**

Since the sum of normalized error (SNE) has been reported as a way or criterion for selecting the best fitted isotherm/kinetic model (Anirudhan and Radhakrishnan, 2009; Yanev et al., 2013; Popoola, 2019), the SNE value was used as a yardstick for the model selection in this
Table 4. Values of the parameters in the linearized kinetic models for the adsorption of MB on chitosan flakes.

| Kinetic model                          | Parameter   | Values of the parameters at initial MB concentration |
|----------------------------------------|-------------|------------------------------------------------------|
|                                        |             | 50 mg/L | 100 mg/L | 150 mg/L |
| Fractional power                       | v           | 0.135   | 0.1637   | 0.2363   |
|                                        | $k_f$       | 1.1632  | 1.6900   | 1.5186   |
|                                        | $R^2$       | 0.8760  | 0.9873   | 0.9918   |
| Lagergren pseudo first-order kinetic   | $k_1$ (min$^{-1}$) | 0.0788 | 0.0635   | 0.0345   |
| model                                 | $q_e$ (mg/g) | 1.3620  | 2.150    | 2.5870   |
|                                        | $R^2$       | 0.9529  | 0.9726   | 0.9894   |
|                                        | $k_2$ (g/(mg min)) | 0.0550 | 0.0520   | 0.0220   |
| Pseudo second-order kinetic model      | $q_e$ (mg/g) | 2.3030  | 3.5740   | 4.6707   |
|                                        | $h$ (mg/(g min)) | 0.2917 | 0.6642   | 0.4799   |
|                                        | $R^2$       | 0.9924  | 0.9996   | 0.9984   |
| Elovich kinetic model                  | $\alpha$ (mg/(g min)) | 0.5224 | 8.5724   | 0.6032   |
|                                        | $\beta$ (g/mg) | 2.0593  | 2.1240   | 0.7955   |
|                                        | $R^2$       | 0.9941  | 0.9970   | 0.9029   |
| Avrami kinetic model                   | $n_{AV}$   | 0.3300  | -0.7476  | -0.6277  |
|                                        | $k_{AV}$ (min$^{-n_{AV}}$) | 1.0932 | 0.1825   | 0.1956   |
|                                        | $t_a$ (min) | 0.7722  | 0.1040   | 0.0752   |
|                                        | $R^2$       | 0.9942  | 0.9592   | 0.9776   |
| Intraparticle diffusion (IPD)          | $k_{IPD}$ (mg/(g min$^{0.5}$)) | 0.1914 | 0.1710   | 0.2773   |
|                                        | $C$ (mg/g)  | 0.7186  | 1.9826   | 2.8335   |
|                                        | $R^2$       | 0.8226  | 0.9558   | 0.9724   |
| Boyd model                             | $D$ (m$^2$/s) | $4.4911 \times 10^{-11}$ | $3.6191 \times 10^{-11}$ | $1.9663 \times 10^{-11}$ |
|                                        | $R^2$       | 0.9529  | 0.9726   | 0.9893   |
| Diffusion-chemisorption model          | $k_{DC}$ (mg/(g min$^{0.5}$)) | 1.2979 | 1.7550   | 1.3419   |
|                                        | $q_e$ (mg/g) | 2.5100  | 4.330    | 6.4800   |
|                                        | $k_i$ (mg/(g min)) | 0.6711 | 0.7113   | 0.2779   |
|                                        | $R^2$       | 0.9865  | 0.9994   | 0.9980   |

study. The most fitted model amongst the non-linearized isotherms using the non-linear regression method is the one with the lowest value of SNE. The computed SNE values for the 2-p isotherms, 3-p isotherms, 4-p isotherms.
and 5-p isotherm are shown in Table 6. The 5-p Fritz-Schlünder isotherm gave the lowest SNE value closely followed by the 2-p Temkin isotherm. Thus, the former is the most fitted isotherm using the SNE value as selection. Moreover, the lowest values of Pearson’s chi-squared analysis, Akaike information criterion (AIC), model selection criterion for isotherm models and its associated values for each of the isotherm models investigated are shown in Table 6. Using the SNE for the goodness-of-fit amongst the two-parameter isotherms considered, the 2-p Temkin isotherm fitted best the adsorption equilibrium data of MB on chitosan flakes having a value of 4.7721 with the NSD statistical indicator. For the three-parameter isotherms, Redlish-Peterson isotherm fitted best, which recorded a value of 5.0828 with EABS as error function while Marczewski-Jaroniec isotherm fitted best amongst the four-parameter isotherms having a value of 6.2345 with MPSD as error function. The 5-p Fritz-Schlünder isotherm fitted best overall among all other number of parameters of the isotherm considered having the lowest value of 4.6506 with the NSD error function. The lowest value of SNE with the corresponding error function reflect the optimum isotherm parameter for the various isotherm models considered (Ghaffari et al., 2017; Rahman et al., 2018). In all the 19 isotherm models considered, NSD best fitted for 12 adsorption isotherms, chi-squared best fitted for 4 isotherms while MPSD, EABS and HYBRID best fitted for 1 isotherm each. Also from Table 6, the Pearson’s Chi-squared ($\chi^2$) analysis carried out at the respective degree of freedom, $df$ (difference between the number of experimental data and the number of parameters) shows that all the models have a non-significant lack of normality of the residuals since the calculated value is less than the critical or table value. Statistically, it translates or reveals a high level of acceptance of the models (Mitrevski et al., 2017). In addition, the results projects Bauder isotherm as the best fitted isotherm in terms of normality of residual followed by the 3-p BET2 and 3-p BET3 isotherms in descending order.

The AIC function is a statistical tool well rooted as a yardstick for comparing model equations with varying number of parameters. Its principle of operation is hinged simply on the difference between calculated AIC values over a set of model equation with a likely product of positive or negative value. The ($AIC_{\text{mod}}$) value of a model equation with the lowest value (considering the sign),
The lowest value of evidence ratio (ER) and the highest value of model selection criterion (MSC) amongst the competing equations is adjudged to be the superior equation over others (Akaike, 1974). From the results in Table 6, the 3-p BET2 and 3-p BET3 model equations portrayed the same lowest value of \( (A_\infty)_{\text{mod}} = -16.2878 \) and evidence ratio, \( ER \), of 1. With the highest value obtained for \( MSC \), the 3-p BET3 isotherm is considered the most fitted model for the adsorption of MB on the synthesized chitosan flakes. Similarly, using the information-based criteria for the selection of the best fitted kinetic models for the adsorption of MB on chitosan flakes, the pseudo second-order kinetics recorded the lowest \( (A_\infty)_{\text{mod}} \), lowest evidence ratio and highest \( MSC \) values, amongst all the investigated kinetic models, at all initial concentrations of MB solution under this present study, as revealed in Tables 7 and 8. Hence, the adsorption rate of MB on chitosan flakes can be kinetically described by the pseudo second-order model, with the model satisfying all the criterial used in selecting the best fitted kinetic models.

In the same vein, the Pearson’s chi-squared analysis carried out at the respective degree of freedom shows that all the models have a non-significant lack of normality of the residuals. The same trend was observed in all the criteria as shown in the ranking for the best fitted kinetic models.

The sticking probability, \( S^* \), known as the rate of adsorption per molecular collision with the adsorbent surface, directly expresses the difficulty encountered by a molecule in overcoming the barrier to adsorption. The calculated value of \( S^* \), which is less than unity, indicates that the likelihood of MB ions sticking onto the chitosan surface is very high.

### Thermodynamics study

The effect of temperature in adsorption studies is considered as a fundamental factor in adsorption systems. It gives the thermodynamics parameters: activation energy, sticking probability and changes in entropy, enthalpy and Gibbs free energy. From the results in Table 9 and Figure 10, \( \Delta H^0 \) is positive, which indicates an endothermic process of adsorption of MB on the prepared chitosan flakes from \( A. \ marginata \). This implies that adsorption capacity of the derived chitosan flakes increases with temperature.

The value of \( \Delta H^0 \) is within the range of 1-8 kJ/mol for physisorption (Zarrouk et al., 2011). Also, the positive value of \( \Delta S^0 \) suggests a high degree of randomness at the chitosan-MB interface with appreciable structural changes with the adsorbate species (Saha and Chowdhury, 2011). It is also noteworthy that the negative value of the Gibbs free energy, \( \Delta G^0 \), reflects a high degree of spontaneity of the adsorption process of MB on chitosan flakes and exergonic and energetically favorable adsorption process with increasing negative values occasioned by increases in temperature.

The sticking probability, \( S^* \), known as the rate of adsorption per molecular collision with the adsorbent surface, directly expresses the difficulty encountered by a molecule in overcoming the barrier to adsorption. The calculated value of \( S^* \), which is less than unity, indicates that the likelihood of MB ions sticking onto the chitosan surface is very high.

### Batch reactor design

Figure 11 illustrates briefly the batch reactor design using
Table 5. Estimated values of the parameters in the non-linear kinetic models for the adsorption of MB on chitosan flakes using non-linear regression method.

| Kinetic model                        | Parameter | Values of the parameters at initial MB concentration |
|--------------------------------------|-----------|------------------------------------------------------|
|                                      |           | 50 mg/L | 100 mg/L | 150 mg/L |
| Fractional power                     | \( v \)   | 0.1095  | 0.1360   | 0.2018   |
|                                      | \( k_f \) | 1.2886  | 1.5827   | 1.7335   |
|                                      | \( R^2 \) | 1.0     | 1.0      | 1.0      |
|                                      | \( k_1 \) (min\(^{-1}\)) | 0.1065  | 0.0774   | 0.0910   |
|                                      | \( q_e \)\(_{\text{exp}}\) (mg/g) | 1.9649  | 2.8420   | 4.3509   |
|                                      | \( q_e \) (mg/g) | 1.9575  | 2.7381   | 3.7477   |
|                                      | \( R^2 \) | 1.0     | 1.0      | 1.0      |
| Lagregren pseudo first-order kinetic model | \( k_2 \) (g/(mg min)) | 0.0602  | 0.0287   | 0.0559   |
|                                      | \( q_e \) (mg/g) | 2.2813  | 3.3044   | 4.0516   |
|                                      | \( h \) (mg/(g min)) | 0.3133  | 0.3134   | 0.9176   |
|                                      | \( R^2 \) | 1.0     | 1.0      | 1.0      |
|                                      | \( \alpha \) (mg/(g min)) | 3.9943  | 2.2664   | 1.4534   |
| Pseudo second-order kinetic model    | \( \beta \) (g/mg) | 13.9360 | 4.1265   | 3.4587   |
|                                      | \( R^2 \) | 1.0     | 1.0      | 1.0      |
| Elovich kinetic model                | \( n_{AV} \) | 4.0761  | 4.0761   | 4.0761   |
|                                      | \( k_{AV} \) (min\(^{-n_{AV}}\)) | 2.7060  | 2.7060   | 2.7060   |
| Avrami kinetic model                 | \( q_e \) (mg/g) | 1.9298  | 2.614035 | 3.6491   |
|                                      | \( t_a \) (min) | 0.7924  | 0.7924   | 0.7924   |
|                                      | \( R^2 \) | 0.8534  | 0.8610   | 0.8315   |
|                                      | \( k_{DC} \) (mg/(g min\(^{-0.5}\))) | 0.0990  | 0.2100   | 0.5      |
|                                      | \( q_e \) (mg/g) | 0.0040  | 0.01432  | 0.0612   |
| Diffusion-chemisorption model        | \( k_i \) (mg/(g min)) | 1.0     | 1.0      | 1.0      |

Equation 35. The plots so obtained shows the mass of chitosan flakes to increase with increasing solution volume at a certain % removal of MB using the chitosan flakes prepared from A. marginata shell waste.

Proposed adsorption mechanism of methylene blue onto chitosan flakes

The reaction mechanism of the adsorption of MB onto chitosan (CH) was proposed by noting that the adsorption mechanism is dependent on the electrostatic attractive force between the surface of the chitosan (biosorbent) and the methylene blue, which are negatively and positively charged respectively. The electrostatic force of attraction arises as a result of the functional groups present on the surface of the chitosan and the pH dependence of MB adsorption from aqueous solution onto the chitosan flakes. The presence of hydroxyl (\( OH^- \)) and amide (\( NH_2^- \)) groups on CH was revealed
Table 6. Results of SNE, Pearson’s chi-squared analysis, Akaike information criterion (AIC) and model selection criterion for isotherm models.

| Isotherm                | \( N_p \) | Sum of Normalized Error | \( \chi^2 \) analysis (p<0.05) | Akaike Information Criteria (AIC) | Model selection criterion |
|------------------------|-----------|-------------------------|---------------------------------|-----------------------------------|-------------------------|
|                        |           | EF | Value | RK | df | Calc.value | Table value | RK | \( (AIC)_{mod} \) | \( \lambda_i \) | ER | RK | Value | RK |
| Freundlich             | 2         | NSD | 6.3603 | 8 | 4  | 0.1496     | 9.488 8 | -11.7676 | 0.0354 | 9.5843 | 4   | 2.2651 | 6   |
| Langmuir               | 2         | NSD | 7.5061 | 18 | 4  | 0.1670     | 9.488 10 | -7.0296 | 0.0033 | 102.4258 | 13  | 1.6383 | 14  |
| Temkin                 | 2         | NSD | 4.7721 | 2  | 4  | 0.1026     | 9.488 6 | -12.2426 | 0.0448 | 7.5580 | 3   | 2.3683 | 4   |
| D-R                    | 2         | \( \chi^2 \) | 8.9350 | 19 | 4  | 0.3026     | 9.488 11 | -2.0904 | 0.0003 | 1210.4068 | 15  | 2.0635 | 11  |
| H-J                    | 2         | HYBRID | 5.2870 | 4  | 4  | 0.3525     | 9.488 12 | -7.4073 | 0.0040 | 84.7987 | 11  | 1.5762 | 17  |
| F-H-H                  | 2         | NSD | 7.1578 | 14 | 4  | 0.1496     | 9.488 8 | -11.7676 | 0.0354 | 9.5843 | 4   | 2.2663 | 5   |
| BET1                   | 2         | NSD | 6.9096 | 12 | 4  | 0.1667     | 9.488 9 | -7.0450 | 0.0033 | 101.6406 | 12  | 1.9966 | 13  |
| BET 2                  | 3         | \( \chi^2 \) | 6.8166 | 11 | 3  | 0.0503     | 7.815 2 | -16.2878 | 0.3390 | 1.0000 | 1   | 3.0413 | 2   |
| BET 3                  | 3         | \( \chi^2 \) | 7.0100 | 13 | 3  | 0.0503     | 7.815 2 | -16.2878 | 0.3390 | 1.0000 | 1   | 3.0448 | 1   |
| Redlich-Peterson       | 3         | EABS | 5.0828 | 3  | 3  | 0.1009     | 7.815 13 | -10.7609 | 0.0214 | 15.8547 | 7   | 2.1120 | 10  |
| Toth                   | 3         | NSD | 6.3803 | 9  | 3  | 0.4449     | 7.815 14 | 4.1817 | 1.217 \times 10^{-4} | 27855.4010 | 16  | 0.5768 | 19  |
| Sips                   | 3         | NSD | 6.3063 | 6  | 3  | 0.1296     | 7.815 7 | 0.6508 | 7.12 \times 10^{-5} | 4766.3842 | 17  | 0.5760 | 18  |
| Khan                   | 3         | NSD | 7.2572 | 16 | 3  | 0.0950     | 7.815 3 | -11.0676 | 0.0249 | 13.6007 | 5   | 2.1623 | 8   |
| Radke-Prausnitz        | 3         | NSD | 7.3801 | 17 | 3  | 0.0950     | 7.815 3 | -11.0676 | 0.0249 | 13.6007 | 5   | 2.1624 | 7   |
| Fritz-Schlünder        | 3         | \( \chi^2 \) | 6.3172 | 7  | 3  | 1.0090     | 7.815 4 | -10.7610 | 0.0214 | 15.8537 | 6   | 2.1130 | 9   |
| Fritz-Schlünder        | 4         | NSD | 7.2517 | 15 | 2  | 0.1020     | 5.991 5 | -8.7610 | 0.0079 | 43.0948 | 9   | 1.8945 | 12  |
| Bauder                 | 4         | NSD | 6.7445 | 10 | 2  | 0.0340     | 5.991 1 | -13.5762 | 0.0874 | 3.8800 | 2   | 2.6347 | 3   |
| Marczewski-Jaroniec    | 4         | MPSD | 6.2345 | 5  | 2  | 0.1496     | 5.991 8 | -7.7675 | 0.0048 | 70.8233 | 10  | 1.5873 | 15  |
| Fritz-Schlünder        | 5         | NSD | 4.6506 | 1  | 1  | 0.1604     | 3.841 9 | -6.7246 | 0.0028 | 119.3006 | 14  | 1.5797 | 16  |

EF, RK, \( df \) denote error function, ranking, degree of freedom, respectively.

Table 7. Results of SNE and criterion for kinetic models.

| Kinetic models                        | Sum of normalized error (SNE) | \( \chi^2 \) analysis (p<0.05) |
|---------------------------------------|---------------------------------|---------------------------------|
|                                       | 50 mg/L                         | 100 mg/L                        | 150 mg/L                        | Average calc. value | Table value | RK |
|                                       | EF Value | RK | EF Value | RK | EF Value | RK | EF Value | RK | Value | RK |
| Fractional power model                | RMSE | 6.3819 | 4 | NSD | 4.5572 | 3 | NSD | 3.7526 | 2 | 0.0796 | 21.026 | 4 |
| Lagergren pseudo first-order kinetic model | NSD | 4.7505 | 2 | NSD | 5.3946 | 4 | NSD | 4.1980 | 3 | 0.0606 | 21.026 | 2 |
| Pseudo second-order model             | NSD | 3.9002 | 1 | ARE | 0.8418 | 1 | NSD | 1.6201 | 1 | 0.0200 | 21.026 | 1 |
| Elovich                               | NSD | 5.2056 | 3 | NSD | 3.0317 | 2 | NSD | 4.1980 | 3 | 0.0606 | 21.026 | 2 |
| Avrami                                | HYBRID | 6.7487 | 5 | HYBRID | 5.9436 | 5 | SRE | 5.06358 | 5 | 0.5376 | 21.026 | 5 |
in the FTIR study at wavelengths 3419.79 and 3458.21 cm\(^{-1}\) before and after adsorption of MB respectively (Bello and Olafadehan, 2021). The ionization of these functional groups is a function of the pH of MB solution that causes the surface of CH to be electrically charged. The amide and hydroxyl groups on the surface of the biosorbent can either gain or lose a proton (that is, hydrogen ion), thereby resulting in the variation of surface charge of CH with pH of MB solution.

At low-level of pH of MB solution, protonation takes place on the active centers (that is, sites) of the chitosan flakes. Hence, the surface of the adsorbent (chitosan flakes) acquires a positive charge owing to the reactions between each of \(OH^-\) and \(NH_2^+\) functional groups on the adsorbent surface and the hydrogen ion (\(H^+\)) in solution. These reactions are represented in Equations 74 and 75, respectively:

\[
\text{CH} - \text{OH} + \text{H}^+ \rightarrow \text{CH} - \text{OH}_2^+ \tag{74}
\]

\[
\text{CH} - \text{NH}_3 + \text{H}^+ \rightarrow \text{CH} - \text{NH}_4^+ \tag{75}
\]

Deprotonation occurs at high pH of MB solution and the active sites on the surface of CH acquire a negative charge owing to the reactions between each of \(OH^-\) and \(NH_2^-\) functional groups on the surface of CH and the hydroxyl ion (\(OH^-\)). These reactions are represented in Equations 76 and 77, respectively:

\[
\text{CH} - \text{OH} + \text{OH}^- \rightarrow \text{CH} - \text{O}^- + \text{H}_2\text{O} \tag{76}
\]

\[
\text{CH} - \text{NH}_3 + \text{OH}^- \rightarrow \text{CH} - \text{NH}_2^- + \text{H}_2\text{O} \tag{77}
\]

Hence, Equations 76 and 77 reveal that electrostatic force of attraction enhances MB adsorption onto CH at high-level of MB solution pH. Thus, the reaction mechanism of MB adsorption onto the synthesized chitosan flakes from African giant snail (\(A.\ marginata\)) shell
Conclusion

The capacity of chitosan extracted from African giant snail (*A. marginata*) shell powder in the removal of methylene blue (MB) from aqueous solution and the effects of operational parameters on its adsorption capacity in a batch system were investigated in this study. Equally, modeling of the adsorption equilibrium data using 19 isotherms and 8 kinetic models coupled with statistical criteria of Akaike information criteria (AIC), evidence ratio (ER), model selection criterion (MSC) and sum of normalized error (SNE) to select the best isotherm and kinetic models was carried out. The thermodynamic parameters such as activation energy, $E_a$, changes in enthalpy, $\Delta H^0$, entropy, $\Delta S^0$ and Gibbs free energy, $\Delta G^0$, were evaluated. The most important conclusions...
from this work are summarized thus:

(1) The *A. marginata* shell waste is an abundant and cheaply available precursor for the production of chitosan.

(2) The produced chitosan flake is potentially viable as an adsorbent for the removal of MB from aqueous solution. Consequently, it may be an alternative to costly biosorbents.

(3) The 5-p Fritz-Schlünder isotherm best fitted the experimental equilibrium adsorption data of MB on chitosan flakes based on the sum of normalized error (SNE) and the 3-p BET3 isotherm is the most fitted model for the adsorption of MB on the prepared chitosan flakes based on the lowest values of AIC, lowest ER value and highest value of MSC.

(4) Kinetically, the pseudo-second-order model well represented the adsorption rate of MB on chitosan flakes at all initial concentrations of MB investigated in this study.

(5) The intraparticle diffusion was not found to be the rate-limiting step for the adsorption of MB on the synthesized chitosan flakes but rather film (i.e., external) diffusion and the sorption process was chemisorption-influenced.

(6) The adsorption of MB on the prepared chitosan flakes from *A. marginata* shell powder is a physical and endothermic process with $\Delta H^0 = 4.23 \text{ kJ/mol}$, a high degree of randomness at the chitosan-MB interface ($\Delta S^0 = 0.4563 \text{ kJ/mol}$), high degree of spontaneity (negative $\Delta G^0$ values), energetically favorable and exergonic.

(7) The data reported in this study can be of beneficial use in the conception and construction of a less-costly viable treatment process using batch reactor for MB adsorption on a biosorbent and for diluting industrial effluents.

**CONFLICT OF INTERESTS**

The authors have not declared any conflict of interests.

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