



Modeling of Tartrazine Dye Adsorption onto Treated and Untreated Cocoa Shell by Non-Linear Regression Methods

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ABSTRACT

Tartrazine is a toxic industrial dye, and it is reported to affect water quality and is harmful to human health. The objective of this study is to contribute to elaborate less expensive adsorbents from cocoa shell for the elimination of tartrazine from aqueous solution. The effects of initial pH (2-8), contact time (0-90 min), mass of adsorbent (10-70 mg) and the nature of treatment were evaluated on the adsorption of tartrazine. The optimal conditions for the adsorption of tartrazine on all the substrates are pH=2, contact time=60 min, amount of adsorbent=40 mg. Nonlinear regression analysis showed the best fit for pseudo second order kinetics regardless of material with Chi-square (χ^2) test values of 0.1672, 0.0811 and 0.0366 respectively for CC-H₂O, CC-HNO₃ and CC-H₃PO₄. Equilibrium data were fitted to two-parameter mono-solute models and mono-solute three-parameter models. Adsorption isotherm data were best described by Jovanovic model for water washed substrate, Langmuir model for phosphoric acid treated substrate and Dubinin-Radushkevich model for treated substrate to nitric acid for the 2-parameter isotherms. As for the three-parameter isotherms, it is the Khan model that better describes the data for the substrate washed with water and the substrate treated with phosphoric acid, whereas the Redlich-Peterson model was found for the substrate treated with nitric acid.

Keywords: Adsorbents; Tartrazine yellow dye; Isotherm model; Kinetics; Non-linear regression

INTRODUCTION

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc., to color their products. The dyes are invariably left as the major waste in these industries. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals and, therefore, are difficult to be decolorized once released into the aquatic environment [1,2]. Many of the organic dyes are hazardous and may affect aquatic life and even the food chain. One of them is tartrazine (C.I. Acid Yellow 23, AY23) which is an anionic azo dye whose presence in thousands of foods and drugs has been reported as a possible cause of asthma, urticaria, and angioedema [3,4]. It also has phototoxic potential [3]. The removal of dyes from industrial waste before they are discharged into the water bodies is therefore very important from health and hygiene point of view and for environmental protection. Various techniques have been employed for the removal of dyes

from wastewaters such as, ion exchange, electrolysis, membrane processes, flocculation, Advanced Oxidation Processes (AOP), coagulation, photocatalytic processes, biological treatments and adsorption [5,6]. Conventional physical and chemical methods are either costly, or produce concentrated sludge, or may not be capable of treating large volumes of effluent without the risk of clogging. Natural materials that are available in abundance, or certain waste products from industrial or agricultural operations, may have great potential as an inexpensive sorbent [7, 8]. The linear regression method has long been used to determine the best-fitting models and the least squares method has been used to find the parameters of the models [9-12]. After plotting a linear regression, the parameters are calculated from the slope and the intersection of the line. The adsorption kinetics and isotherm model with the best fit for the adsorption data is selected based on the correlation coefficient (R²) [13]. The most significant disadvantage of linear regression is the non-fixed error distribution [14,15]. Also, in case

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Received: 15-Oct-2022, Manuscript No. MCA-22-18791; **Editor assigned:** 18-Oct-2022, PreQC No. MCA-22-18791 (PQ); **Reviewed:** 02-Dec-2022, QC No. MCA-22-18791; **Revised:** 09-Dec-2022, Manuscript No. MCA-22-1879178 (R); **Published:** 16-Dec-2022, DOI: 10.35248/2329-6798.22.10.383.

Citation: Nemgne MN, Kouteu APN, Tchui fon DRT, Ngakou CS, Nche NAG, Gabche AS (2022) Modeling of Tartrazine Dye Adsorption onto Treated and Untreated Cocoa Shell by Non-Linear Regression Methods. *Modern Chem Appl*.10:383.

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of kinetics and isotherms with more than two parameters, we cannot calculate the value of unknown parameters using linear regression and graphical method [14].

More recently, the non-linear regression method in conjunction with error analysis as an alternative to linear regression has been used to create a model in adsorption studies [16]. Several error analysis methods such as residual Root Mean Square Error (RMSE), nonlinear chi-square test error function (χ^2), coefficient of determination (R²) were introduced for nonlinear analysis [17,18].

Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. In this study, cocoa shell untreated and treated with nitric acid and phosphoric acid were used for the biosorption of tartrazine from water. The optimization of sorption parameters, sorption isotherms and kinetics were investigated in batch mode.

METHODOLOGY

Collection and preparation of adsorbent and adsorbate

Cocoa shell was collected from Kekem, in the Haut-Nkam division, West region of Cameroon. It was washed with tap water, grinded in a mill and sieved (100 μ m). The treatment was made with concentrates phosphoric acid and nitric acid (5.10⁻³ M). In a flask, 10 g of cocoa shell and 100 ml of each acid were put together. After 2 hours of agitation (200 trs/min), the mixture was filtered, and the adsorbent was washed several times with distilled water. It was then dried in an oven at about 80°C to remove moisture and grinded before it was used as adsorbent of tartrazine dye.

Characterization of adsorbents

The three adsorbents were characterized by determining the following parameters: Functional groups, moisture content, loss of mass on ignition, pH and bulk density, the zero-point charge using standard procedures.

Fourier transform infrared: Adsorbents were characterized by Infrared Fourier Transform Spectroscopy to identify the functional groups and chemical bonds of the adsorbents and their participation in tartrazine dye adsorption. The FT-IR was recorded in the wave number range 4000-400 cm^{-1} using a Bruker, Alpha-P Spectrometer in Attenuated Total Reflectance mode.

Moisture contents: It was done by weighing 10 g of each adsorbent into a crucible. This was placed in the oven at constant temperature of 105°C until obtained a constant mass. The sample was then removed and put rapidly into a desiccator to prevent more moisture uptake from atmosphere. The sample was re-weighed. The ratio of the mass lost by the powder to its original mass gave the moisture content of the sample [19].

$$\% \text{Moisture Content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (1)$$

Where W1 is the weight of crucible, W2 is the initial weight of crucible with sample, and W3 is the final weight of crucible with sample.

Bulk density (g/cm³): The bulk density of each of the samples was determined using Archimedes' principle, by weighing a measuring cylinder before and after filling with the samples. The measuring cylinder was then dried, and the sample was packed inside the measuring cylinder, leveled, and weighed. The weight of the sample packed in the measuring cylinder was determined from the

difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation below [20].

$$D = \frac{W_2 - W_1}{V} \quad (2)$$

Where W1 is the weight of empty measuring cylinder, W2 is the weight of cylinder filled with sample, and V is the volume of cylinder.

pH and zero point charge (pH_{ZPC}): pH of zero charge, pH_{ZPC}, corresponds to the pH at which the surface charge is null. pH_{ZPC} of the cocoa shell was estimated according to standard procedure. 15 ml of a decimolar solution of NaCl was introduced each into a reactor each containing 50 mg of cocoa shell to be analyzed. The pH of each solution was adjusted by addition of decimolar solutions of NaOH or HCl (by varying values of pH between 2 and 12). pH_{ZPC} was determined by the intersection point of the representative curves pH (final)=f[pH (initial)] and the first bisector curve. Stirring was maintained at 27°C for 48 hours with the aid of a multi-agitator system. The contents of the reactors were then filtered with Whatman N°4 filter paper after which the pH of the final solutions was measured [21].

Sorption experiment

The dye tartrazine was used without further purification. A stock solution of 500 mg/lit of tartrazine was made by dissolving the required amount of the dye in distilled water. Several standard solutions were made from the stock solution in concentration range 10 to 50 mg/lit and a calibration curve was drawn by measuring the absorbance at $\lambda_{\text{max}}=428$ nm using a JENWAY visible spectrophotometer. The experiments were done adjusting the pH of the solutions with decimolar nitric acid and sodium hydroxide. The batch adsorption was carried in 100 ml conical flasks by mixing a pre-weighed amount of the cocoa shell with 15 ml of aqueous dye solution of a particular concentration. The conical flasks were kept on a shaker and were agitated for a pre-determined time interval at a constant speed 150 trs/min. The system parameters such as pH, agitation time, adsorbent amount, and concentration were controlled during the experiments. After adsorption was over, the mixture was filtered and the residual concentration of the filtrate was analyzed using a spectrophotometer (JENWAY, model 6715). The amount of adsorbed (mg/g) was calculated using the formulae below:

$$Q_e = (C_i - C_f) \frac{V}{m} \quad (3)$$

Where Q_e is the amount of solute adsorbed from the solution, V is the volume of the adsorbate, C_i is the initial concentration of tartrazine, C_f is the concentration after adsorption, and m is the weight in gram of the adsorbent.

The removal efficiency was determined by computing the percentage sorption using the formulae in the Equation (4) below

$$\%_{\text{ads}} = (C_i - C_f) \times \frac{100}{C_i} \quad (4)$$

Effect of initial pH: To determine the effect of the initial pH, 40 mg of the adsorbent was agitated in a 15 ml aqueous solution of 40 mg/lit of tartrazine, in the pH range of 2.0-8.0 pH adjustment was done by adding either HCl or NaOH. After 1 hour, the solution was rapidly filtered, and the residual concentration determined by

spectrophotometer. The amount (Q_t) of tartrazine adsorbed was calculated by using equation (3).

Effect of contact time: The effect of agitation time on the adsorption process was determined by agitating 40 mg of ground adsorbent in a 15 ml solution of tartrazine of initial concentration 40 mg/lit for different time intervals. At each time, the solution was rapidly filtered, and the residual concentration determined by spectrophotometer. The percentage removal (%) of tartrazine was calculated by using Equation (4).

Effect of amount of adsorbent: In this set of experiments, different masses of the adsorbents ranging between 10 to 70 mg were agitated with 15 ml solution of tartrazine of initial concentration 40 mg/lit during the equilibrium time.

Effect of biosorbent treatment: To investigate the effect of biosorbent treatment, adsorption of tartrazine on biosorbent was carried out using 40 mg of biosorbent, 15 ml of solution of concentration 40 mg/lit at initial pH=2, agitation speed 150 rpm at 60 min (equilibrium time).

Batch equilibrium experiments: Isotherm experiments were carried out by agitating 15 ml of tartrazine dye of concentration ranging from 10 to 50 mg/lit with 40 mg of each biosorbent in a 100 ml flask at room temperature at optimum pH of 2 and a constant agitation speed of 150 rpm for 60 minutes. The data collected were fitted to the pseudo-first order kinetic model, pseudo-second order kinetic model, and intraparticle diffusion kinetic models. To determine the best adsorption model, initial concentration and their adsorption capacities were fitted to two kinds of models: Two parameter monosolute model (Langmuir model, Freundlich model, Temkin model, Dubinin-Radushkevich model and Redlich-Peterson model) and Momo-solute three-parameter models (Redlich-Peterson model, Sips model, Toth model, Hill's model and Kahn's model).

The comparison of literature models for adsorption isotherms and reaction kinetics was based on a statistical calculation of several error function among the most used in the literature: Residual moot Mean Square Error (RMSE), nonlinear chi-square test error function (χ^2), Coefficient of determination (R²), Hybrid fractional error function (HYBRID).

Adsorption kinetics

Several kinetics models were tested to determine the best kinetics model of the adsorption of tartrazine on the biosorbents.

Pseudo-first-order model: The pseudo-first order equation is generally expressed in [22].

$$Q_t = Q_e [1 - \exp(-k_1 t)] \quad (5)$$

With K_1 : Adsorption rate constant (g/mg.min); Q_e : quantity adsorbed at equilibrium (mg/g) and Q_t : quantity adsorbed at time t (mg/g).

The pseudo-second-order model: The pseudo-second order chemisorption kinetic equation [23].

$$Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \quad (6)$$

With K_2 : Pseudo-second order adsorption rate constant (g/mg.min); Q_e : quantity adsorbed at equilibrium (mg/g) and Q_t : quantity adsorbed at time t (mg/g).

Elovich's model: The Elovich equation is generally expressed [24].

$$\frac{dq_t}{dt} = \alpha e^{(-\beta q_t)} \quad (7)$$

To simplify the Elovich equation, Chien and Clayton in 1980 assumed that $\alpha\beta \gg \gg 1$ and applying the initial conditions $q_t=0$ to $t=0$ the equation (7) becomes

$$\frac{dq_t}{dt} = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta} \quad (8)$$

With α : The initial adsorption rate (g/mg.min); β : desorption rate constant (g/mg.min) and Q_t : Amount adsorbed at time t (mg/g).

Intraparticle diffusion: The intraparticle diffusion model is expressed as equation (9) [24].

$$Q_t = k_{id} t^{1/2} + C \quad (9)$$

With K_{id} : Weber intraparticle diffusion rate constant in (mg/g min^{1/2}); Q_t : Amount adsorbed at time t (mg/g); C: value of the thickness of the boundary layer.

Adson isotherm

To determine the best adsorption model, initial concentration and their adsorption capacities were fitted to two kinds of models: Two parameter monosolute model and Momo-solute three-parameter models.

Two-parameter mono-solute models

Langmuir model: The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution.

$$Q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \quad (10)$$

With Q_e : Amount adsorbed at equilibrium (mg/g); Q_m : Maximum amount adsorbed at equilibrium (mg/g); C_e : Equilibrium concentration of the adsorbate in solution (mg/lit) and K_L : Langmuir's constant relates to the adsorption energy (Lit/mg).

Freundlich model: Freundlich equation is an equation based on the adsorption onto a heterogeneous surface

$$Q_e = k_f C_e^{1/n} \quad (11)$$

With Q_e : Amount adsorbed at equilibrium (mg/g), C_e : Concentration of adsorbent at equilibrium (mg/L); K_f and n are empirical constants.

Temkin model: Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process.

$$Q_e = \frac{RT}{b} \ln(AC_e) \quad (12)$$

With A: Constant of the Temkin isotherm (Lit/mg); b: Variation in the heat of adsorption (kJ/mol); R: Perfect gas constant (8.314 J/mol.K); C_e : Concentration of the adsorbent at equilibrium (mg/lit); Q_e : quantity adsorbed at equilibrium (mg/g) and T: absolute temperature (K). The adsorption obeys the Temkin model if the determined coefficients are low.

Dubinin-radushkevich model: The model of D-R was developed for the adsorption of substances in trace amounts in aqueous phase onto porous solids.

$$Q_e = Q_m \exp(-K' \varepsilon^2) \quad (13)$$

With Q_e : Amount adsorbed at equilibrium (mg/g); Q_m : Maximum amount adsorbed at equilibrium (mg/g); C_e : Equilibrium concentration of the adsorbate in solution (mg/lit); K' : Constant linked to the adsorption energy (mol³K/J³) and ε : Polanyi potential (kJ/mol) its expression is given by equation (14)

$$\varepsilon RT \ln\left(1 + \frac{1}{C_e}\right) \quad (14)$$

With R: Ideal gas constant (R=8.314 kJ/mol.K) and T: The absolute temperature.

The adsorption energy can be obtained from the value of K' using the following equation [25].

$$E = (-2K')^{-1} \quad (15)$$

Jovanovic model: The Jovanovic model is predicated on the assumptions contained in the Langmuir model, but in addition the possibility of some mechanical contacts between the adsorbate and adsorbent [26].

$$Q_e = Q_m(1 - e^{-K_j C_e}) \quad (16)$$

With Q_e : Amount adsorbed at equilibrium (mg/g); Q_m : maximum amount adsorbed at equilibrium (mg/g); C_e : The adsorbent concentration at equilibrium (mg/lit) and K_j is the Jovanovic constant (Lit/mg).

2-mono-solute three-parameter models

Most of these models are derived from simple Langmuir and Freundlich models. Three parameter models were developed to improve the simulation of adsorption isotherms compared to two-parameter models.

Model of redlich-peterson: It is the most quoted and most used three-parameter model in the literature because it is applicable over a wide concentration range. It is an empirical equation developed by Redlich-Peterson to improve adaptation by the Langmuir and Freundlich equation. It approaches the Freundlich model for high concentrations and the Langmuir equation for low concentrations. It can be applied to both homogeneous and heterogeneous systems [27,28].

The Redlich and Peterson model is given by the following equation:

$$Q_e = \frac{AC_e}{1 + BC_e^\beta} \quad (17)$$

With C_e : equilibrium concentration (mg/L); Q_e : quantity adsorbed at equilibrium (mg/g), A and B are the constants of the Redlich-Peterson model (Lit/mg); β : parameters of the Redlich and Peterson equation with β heterogeneity parameters, between 0 and 1. When the recovery rate is high, the equation can be reduced to the Freundlich equation in the following form [29]:

$$Q_e = \frac{A}{B} C_e^{1-\beta} \quad (18)$$

Hence A/B and (1- β) represents respectively the parameters K_f and 1/n of the Freundlich equation.

Model of sips: Identifying the problem of continuously increasing adsorbed amount with increasing concentration in the Freundlich equation, Sips proposed an equation combining Freundlich and Langmuir isotherms. This produces an expression that has a finite limit at a high enough concentration. This model is valid for predicting heterogeneous adsorption and localized adsorption systems without adsorbate-adsorbate interactions. The Sips model for low concentrations is reduced to the Freundlich model. At high

concentrations, the Sips model predicts the monolayer adsorption capacity, which is specific to the Langmuir isotherm. Also, for $\beta=1$, the Sips equation is reduced to the Langmuir model. The Sips model is expressed by the following equation [30].

$$Q_e = \frac{K_s C_e^{\beta s}}{1 + a_s C_e^{\beta s}} \quad (19)$$

βs : parameter of the Sips equation; a_s : adsorption equilibrium constant (Lit/g) and K_s : constant of the Sips model (L/g); Q_e : amount adsorbed at equilibrium (mg/g) and C_e the adsorbent concentration at equilibrium (mg/lit).

Model of toth: The Toth model was established for adsorption in the gas phase, from the Langmuir isotherm, but considering that the surface of the adsorbent is not energetically homogeneous. In the liquid phase, it is generally used as an adaptation of the Langmuir model, close to the empirical Redlich-Peterson model. The model proposed by Toth is an empirical equation that describes many adsorption systems multilayer and heterogeneous systems. It is valid for low and high concentrations [31].

Toth's equation is given by the following expression:

$$Q_e = \frac{K_T C_e Q_m}{[1 + (K_T C_e)^n]^{\frac{1}{n}}} \quad (20)$$

With K_T and n the Toth isotherm constants (L/g); Q_e : Amount adsorbed at equilibrium (mg/g); Q_m : Maximum amount adsorbed at equilibrium (mg/g) and C_e : the adsorbent concentration at equilibrium (mg/lit)

If n=1, Toth's equation is reduced to Langmuir's equation. If it deviates from unity, the system is said to be heterogeneous [28].

Hill's model: Hill in 1910 proposed an isothermal model from the non-ideal competitive adsorption model to define different adsorbent bonds on a homogeneous adsorbent surface. This isothermal model assumes that adsorption is basically a cooperative manifestation, including the ability to bind the ligand to one site on the macromolecule, influencing various binding sites on the same macromolecule [32,33].

The Hill isotherm can be represented as follows:

$$Q_e = \frac{Q_{SH} C_e^{n_H}}{K_D + C_e^{n_H}} \quad (21)$$

With n_H and K_D the Hill isotherm constants; Q_{SH} : Maximum adsorption capacity of the Hill isotherm (mg/g); Q_e : Amount adsorbed at equilibrium (mg/g) and C_e : equilibrium concentration of the adsorbate in solution (mg/lit).

Kahn's model: Kahn's adsorption isotherm model is a general model for the adsorption of dilute pure solutions [34].

Kahn's model is expressed by the following equation:

$$Q_e = \frac{Q_{\max} b_k C_e}{(1 + b_k C_e)^{a_k}} \quad (22)$$

With a_k and b_k are constants of the Kahn isotherm model, Q_{\max} is the maximum adsorption capacity of the Khan isotherm (mg/g); Q_e : Amount adsorbed at equilibrium (mg/g) and C_e : Equilibrium concentration of the adsorbate in solution (mg/lit).

If equals $a_k=1$, the above equation approximates the Langmuir isotherm and at higher concentration values this model reduces to the Freundlich isotherm.

Error functions

In this study, non-linear regression was applied using Microsoft Excel Solver function from Excel Microsoft 2013 for fitting the curve. The best fit for experimental data was determined from the coefficient of determination (R²), Residual root Mean Square Error (RMSE) and Chi-square test (χ^2). The expressions of the error functions are given as follows [35-37].

$$\chi^2 = \sum_{i=1}^N \frac{(Q_{e,exp} - Q_{e,cal})^2}{Q_{e,cal}^2} \quad (23)$$

$$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^N (Q_{e,exp} - Q_{e,cal})^2} \quad (24)$$

$$R^2 = \frac{\sum_{i=1}^N (Q_{e,cal} - Q_{e,exp})^2}{\sum_{i=1}^N (Q_{e,cal} - Q_{e,exp})^2 + (Q_{e,cal} - Q_{e,exp})^2} \quad (25)$$

Where $Q_{e,exp}$ and $Q_{e,cal}$ (mg/g) are the equilibrium capacity of adsorption obtained from the experiment and by calculating from the model, respectively and N is the number of data points.

RESULTS AND DISCUSSION

Characterization of adsorbents

IR spectra: The Fourier Transform InfraRed (FT-IR) spectroscopy method is used to investigate the presence of certain functional groups in a molecule. The spectra of cocoa shell washed with water and treated with phosphoric acid or nitric acid obtained are shown in Figure 1. Between 3650-3200 cm⁻¹ is the -OH group vibration in the main constituents of lignocellulosic materials: Elongation vibration of the C-H aliphatic bonding in cellulose, hemicellulose, and lignin. Between 3000-2840 cm⁻¹, with a high intensity at 2919 cm⁻¹ meanwhile the adsorption band at 1603 cm⁻¹ is attributed to a carboxylic function (C=O). 1500-1200 cm⁻¹: O-H or -C-O deformation vibration of alcohols and -NO₂ of aromatic nitro compounds; 1200-1000 cm⁻¹: -C-O elongation vibration in carboxylic acids, lactones, esters, or aliphatic amines. Figure 1 shows that, all the spectra have the same peaks. This proves that both biosorbents have identical functional groups on their surfaces.

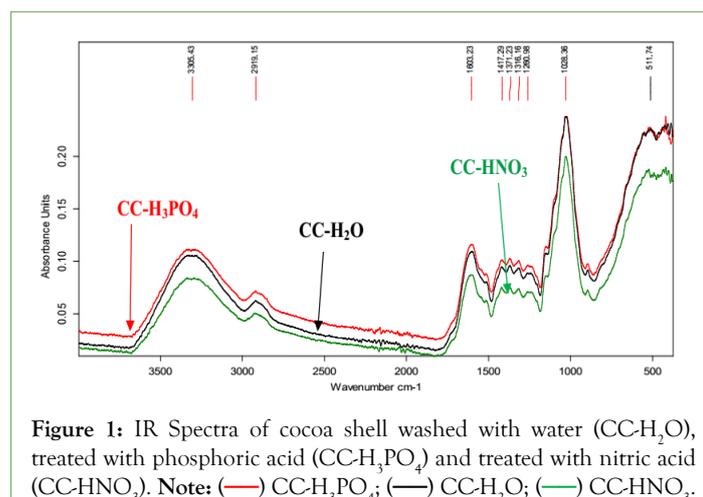


Figure 1: IR Spectra of cocoa shell washed with water (CC-H₂O), treated with phosphoric acid (CC-H₃PO₄) and treated with nitric acid (CC-HNO₃). Note: (—) CC-H₃PO₄; (—) CC-H₂O; (—) CC-HNO₃.

Physicochemical parameters of the adsorbents: The water content of the substrates obtained from the acid treatment (nitric acid and phosphoric acid) varies from 4.48 to 4.55, values higher than that of the substrate washed with water which is 3.88. The bulk densities are not very different with values ranging from 0.35 to 0.37. The pH of the substrates all have acid pHs whatever the treatment used, but the acid treatments lead to the lowest values, 6.31 for the phosphoric acid treatment and 6.25 for the acid treatment nitrate against 6.51

for washing with water. On the other hand, for the pH_{zc} which is an important characteristic illustrating the electrostatic interactions at the level of the surface of the adsorbents as a function of the pH of the medium, a notable difference is observed between that of the substrates treated with acids (6.74) and that washed with water (5.92). These results show that for pH values below 6.74, the surface of acid-treated substrates tends to be positively charged and if the pH is above 6.74, the surface tends to be negatively charged. For the substrate washed with water, the surface tends to be positively charged if the pH is lower than 5.92 and negatively if it is higher than 5.92. The values reported are in the range with those reported in the literature (Table 1) [38].

Table 1: Some physicochemical parameters of the cocoa shell washed with water (CC-H₂O), treated with phosphoric acid (CC-H₃PO₄) and treated with nitric acid (CC-HNO₃).

Properties	CC-H ₂ O	CC-H ₃ PO ₄	CC-HNO ₃
% Moisture content	3.88	4.48	4.55
Bulk density (g/cm ³)	0.37	0.35	0.36
pH	6.51	6.31	6.25
pH _{ZPC}	5.92	6.74	6.74

Biosorption

Effect of initial pH: The adsorption characteristics of Tartrazine by cocoa shell were studied at varying pH range from 2 to 8. The profile concerning pH shows that in the observed pH range the adsorption capacity was much pronounced at lower pH 2, while as the pH increases adsorption decreases. This is attributed to the protonation of the fibers of the adsorbents at low values of pH in which H⁺ ions provide a significantly strong electrostatic attraction between the fibers surface and the dye molecules leading to maximum adsorption. The decrease in the adsorption capacity for the dye was attributed to two mechanisms: firstly, an electrostatic attraction between the protonated amino groups of adsorbents and dyes; and secondly, the chemical interaction between tartrazine and adsorbents [14]. As such all subsequent studies were performed at pH 2, which is the optimum value for adsorption (Figure 2) [39].

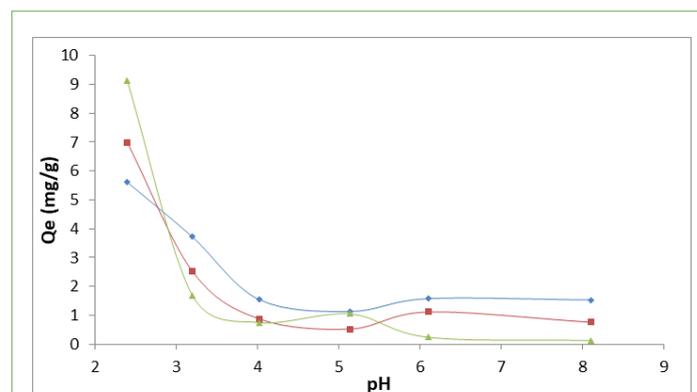
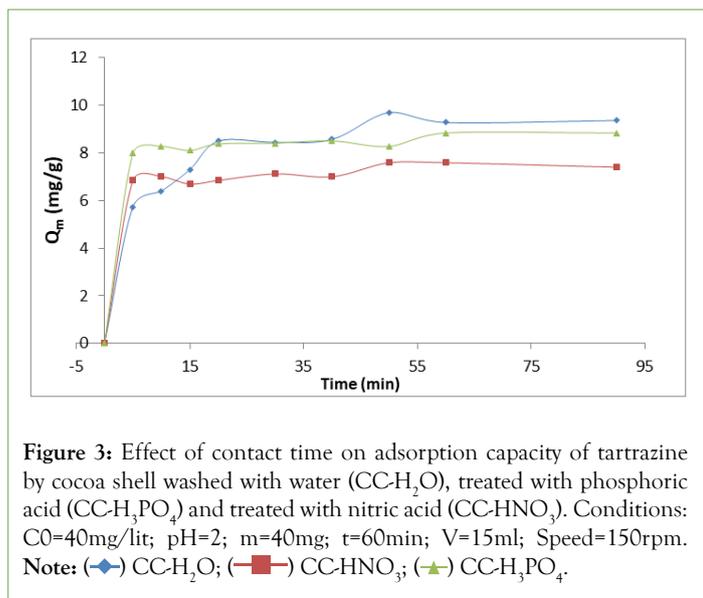


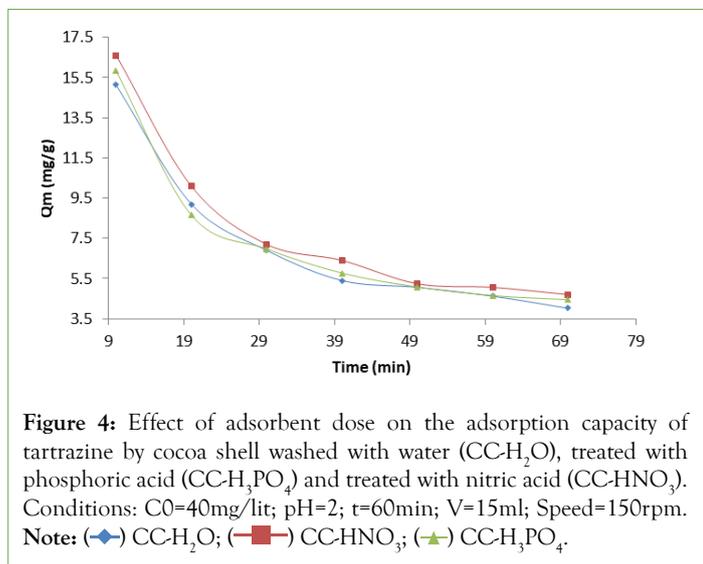
Figure 2: Effect of initial pH on adsorption capacity of tartrazine on cocoa shell washed with water (CC-H₂O), treated with phosphoric acid (CC-H₃PO₄) and treated with nitric acid (CC-HNO₃) in the pH range of 2.0-8.0. Conditions: C₀=40mg/lit; m=40mg; t=60min; V=15ml; Speed=150rpm. Note: (◆) CC-H₂O; (■) CC-HNO₃; (▲) CC-H₃PO₄.

Effect of contact time: The contact time between the adsorbate

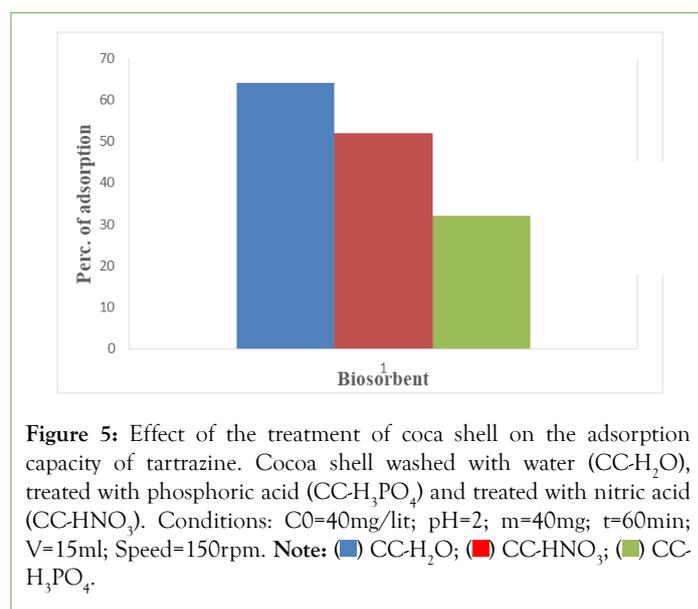
and adsorbent is an important parameter for designed adsorption process. The results show that the adsorption process took place in two phases. The first phase occurred very fast and takes place during the first 10 minutes of adsorption for CC-H₃PO₄ and CC-HNO₃, and 20 minutes for CC-H₂O. This is explained by the great availability of all the adsorption sites of the biosorbent. The second phase that occurred was less fast and takes place within 10-50 minutes for CC-H₂O and 30 min pour CC-HNO₃ and 60 min for CC-H₃PO₄ where the adsorption capacity at the equilibrium point. In this study, the equilibrium time necessary for adsorption was found approximately 60 min for all adsorbents (Figure 3).



Effect of amount of adsorbent: Figure 4 shows the effect of adsorbent dose on the adsorption capacity of tartrazine dye by cocoa shell washed by water and treated by phosphoric acid or nitric acid. It is observed that removal efficiency increases with increase in the biosorbent. This can be mostly attributed to an increase in the adsorptive surface area and the availability of more active adsorption sites. Furthermore, at higher biosorbent dosage, there is a very fast adsorption onto the biosorbent surface. However, with increase in the biosorbent the quantity of dye adsorbed per unit weight of macrophyte gets reduced. A decrease in q_e value with increasing biomass loading may be due to complex interactions of several factors such as availability of solute, interference between binding sites and electrostatic interactions [40].



Effect of biosorbent treatment: The treatment of the biosorbent can be an influence of the behavior of the biosorbent during the adsorption process. Figure 5 shows that the percentage of the dye removed by cocoa shell washed with water (CC-H₂O) is greater than that of the treated materials (CC-H₃PO₄) and (CC-HNO₃). This result can be explained by the fact that during the treatment, some components of the lingo cellulosic materials present before the treatment having great affinity towards amaranth red, has been solubilized or destroyed. However, it was observed that (CC-H₃PO₄) has a higher percentage adsorption than (CC-HNO₃), which explains the fact that (CC-H₃PO₄) has more extractibles than (CC-HNO₃). Moreover (CC-HNO₃) has a better specific surface than (CC-H₃PO₄). This results clearly show that the adsorption of the dye doesn't depend on the surface area but depends on the functional group on the biosorbent [16].



Modeling of kinetic studies

Adsorption kinetics for the removal of tartrazine dye in aqueous solution: To investigate the potential rate controlling step such as the mass transfer or chemical reaction processes, pseudo-first order model, pseudo-second order model, Elovich model and Intraparticle diffusion model were tested on these experimental data.

The pseudo-first-order model is based on multilayer adsorption on the surface of each adsorbent material. This type of adsorption is based on van der Waal type interactions between tartrazine yellow and the different materials. These interactions thus demonstrate physical adsorption between the adsorbate and the adsorbent. Similarly, we also observe a good fit of the results with the pseudo second order model with the values of the coefficient of determination close to unity ($R^2 > 0.98$) thus indicating chemical adsorption. This chemical adsorption is also supported with the adjustment of the Elovich model. The negative value of Q_m obtained from the pseudo-second order model on the adsorption by the CC-H₃PO₄ material indicates that this model cannot be used to describe the results obtained. The negative values of the coefficient of determination obtained whatever the material (CC-HNO₃ and CC-H₃PO₄) indicate that this model cannot be used to describe the process of adsorption on these biomaterials and the low value obtained for the material CC-H₂O indicates that

diffusion is not the limiting step of the adsorption phenomenon that takes place. It emerges from the rest of the models that there is a competition between physisorption and chemisorption for the adsorption of tartrazine yellow on these biomaterials studied (Figure 6 and Table 2).

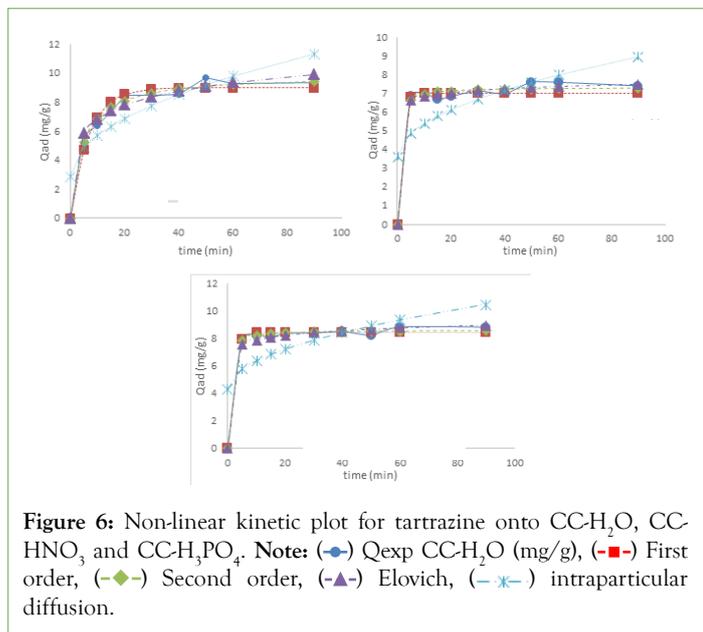


Figure 6: Non-linear kinetic plot for tartrazine onto $CC-H_2O$, $CC-HNO_3$ and $CC-H_3PO_4$. Note: (—●—) Q_{exp} $CC-H_2O$ (mg/g), (—■—) First order, (—◆—) Second order, (—▲—) Elovich, (—*—) intraparticle diffusion.

Table 2: Optimum kinetics parameters and their statistical comparison values onto $CC-H_2O$, $CC-HNO_3$ and $CC-H_3PO_4$.

N°	Models	Constants	Values	R ²	χ ²	RMSE
CC-H₂O						
1	Pseudo first-order	Q _e (mg/g)	9.0065	0.9614	0.4619	1.7178
		K ₁ (1/min)	0.146			
2	Pseudo second order	Q _e (mg/g)	9.8992	0.9832	0.1672	1.116
		K ₂ (g/min.mg)	0.023			
3	Elovich	α (mg/g.min) β (g/mg)	17.5404 0.7079	0.9275	0.1706	1.1946
4	Intraparticle diffusion	K _p (mg/g.min ^{0.5}) C (mg/g)	0.8913 2.8866	0.6825	1.2274	4.247
CC-HNO₃						
1	Pseudo first-order	Q _e (mg/g)	7.0057	0.9778	0.1396	0.989
		K ₁ (1/min)	0.7113			
2	Pseudo second order	Q _e (mg/g)	7.3216	0.9874	0.0811	0.7613
		K ₂ (g/min.mg)	0.2722			
3	Elovich	α (mg/g.min) β (g/mg)	31.15 × 107 3.3758	0.926	0.0533	0.6148
4	Intraparticle diffusion	K _p (mg/g.min ^{0.5}) C (mg/g)	0.566 3.5862	-0.0302	5.4438	4.8579
CC-H₃PO₄						
1	Pseudo first-order	Q _e (mg/g)	8.4592	0.9923	0.058	0.7005
		K ₁ (1/min)	0.5649			
2	Pseudo second order	Q _e (mg/g) K ₂ (g/min.mg)	-8.6238 0.2466	0.9951	0.0366	0.5577

3	Elovich	α (mg/g.min)	43.16 × 104	0.9271	0.0677	0.7397
		β (g/mg)	2.0235			
4	Intraparticle diffusion	K _p (mg/g.min ^{0.5})	0.6528	-0.1065	6.517	5.8072
		C (mg/g)	4.3057			

Batch equilibrium experiments: The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. The study of the isotherms of adsorption is carried out on isotherms with two parameters and those of three well-known parameters [41].

1-isotherm with 2 parameters

For this work, 5 isothermal models namely Langmuir, Freundlich, Temkin and Dubinin-Raduskevich and Jovanovic were used, the plots are in Figure 7 and Table 3 presents the constants obtained, it appears that the Jovanovic model better describes the adsorption of the compound on the $CC-H_2O$ material with the highest value of the coefficient of determination $R^2=0.9912$ and the lowest value of the Chi-test χ^2 of 0.0325. This model is based on the assumptions contained in the model as that of Langmuir, but which gives the possibility of certain mechanisms between the adsorbent and the adsorbate. This model is all the more confirmed as it is followed by the Langmuir model. For the $CC-HNO_3$ material, the Dubinin-Radushkevich model better describes the adsorption. This model with its semi-empirical equation describes adsorption with a pore filling mechanism. This model also assumes multilayer adsorption involving Van der Waals forces, applicable to physical adsorption processes. For the $CC-H_3PO_4$ material, the Langmuir model best describes the adsorption phenomenon, followed by the Temkin model. The Temkin adsorption energies are all positive on the 3 materials, which implies exothermic adsorption. The adsorption energies of the Dubinin-Radushkevich model are: 16.222; 20.412; 19.612 kJ/mol respectively for $CC-H_2O$, $CC-HNO_3$, $CC-H_3PO_4$ materials. All these values above 16 kJ/mol imply that the process is dominated by intraparticle diffusion [42].

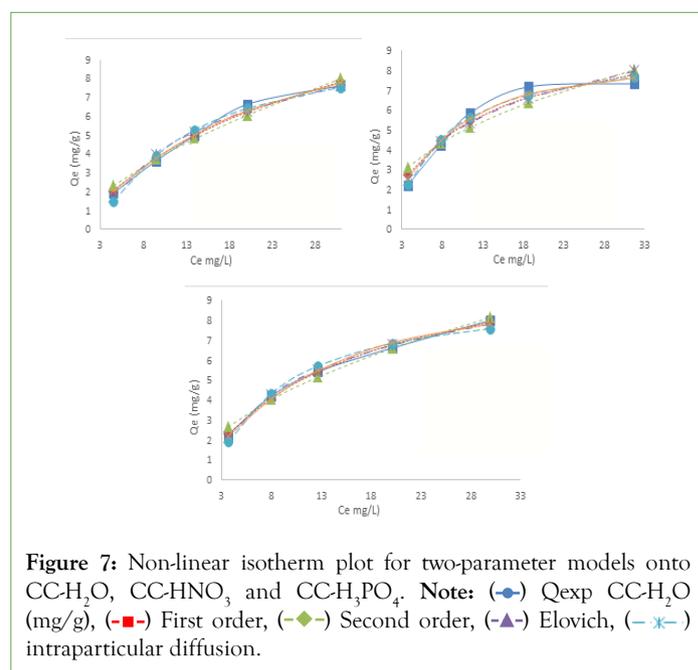


Figure 7: Non-linear isotherm plot for two-parameter models onto $CC-H_2O$, $CC-HNO_3$ and $CC-H_3PO_4$. Note: (—●—) Q_{exp} $CC-H_2O$ (mg/g), (—■—) First order, (—◆—) Second order, (—▲—) Elovich, (—*—) intraparticle diffusion.

Table 3: Optimum isotherm parameters and their statistical comparison values for two-parameter models onto CC-H₂O, CC-HNO₃ and CC-H₃PO₄.

Models	Constants	Values	R ²	χ ²	RMSE
CC-H ₂ O					
Langmuir	Q _{max} (mg.g ⁻¹)	14.8864	0.9872	0.0478	0.4995
	K _L (L.mg ⁻¹)	0.0358			
Freundlich	K _F (L.mg ⁻¹)	0.8761	0.9646	0.1474	0.8196
	n	1.5521			
Temkin	a (L.mg ⁻¹)	0.3838	0.9837	0.0876	0.578
	b (J.mol ⁻¹)	804.1662			
Dubinin-radushkevich	Q _{max} (mg.g ⁻¹)	10.2413	0.9817	0.1669	0.6339
	K (L.mg ⁻¹)	0.0019			
Jovanovic	Q _{max} (mg.g ⁻¹)	9.746	0.9912	0.0325	0.4117
	K _J (L.mg ⁻¹)	-0.0516			
CC-HNO ₃					
Langmuir	Q _{max} (mg.g ⁻¹)	10.4031	0.9353	0.2098	1.0003
	K _L (L.mg ⁻¹)	0.0953			
Freundlich	K _F (L.mg ⁻¹)	1.7511	0.8215	0.5392	1.5988
	n	2.2652			
Temkin	(L.mg ⁻¹)	0.7142	0.9381	0.1833	1.0408
	b (J.mol ⁻¹)	969.0134			
Dubinin-radushkevich	Q _{max} (mg.g ⁻¹)	9.2545	0.976	0.0688	0.6547
	K (L.mg ⁻¹)	0.0012			
Jovanovic	Q _{max} (mg.g ⁻¹)	7.9128	0.9685	0.1103	0.7059
	K _J (L.mg ⁻¹)	-0.1062			
CC-H ₃ PO ₄					
Langmuir	Q _{max} (mg.g ⁻¹)	11.9452	0.9974	0.0087	0.2241
	K _L (L.mg ⁻¹)	0.0656			
Freundlich	K _F (L.mg ⁻¹)	1.3354	0.9844	0.0842	0.5362
	n	1.8783			
Temkin	(L.mg ⁻¹)	0.6132	0.9964	0.132	0.2638
	b (J.mol ⁻¹)	920.8788			
Dubinin-radushkevich	Q _{max} (mg.g ⁻¹)	9.4449	0.9784	0.1127	0.6622
	K (L.mg ⁻¹)	0.0013			
Jovanovic	Q _{max} (mg.g ⁻¹)	8.6267	0.9935	0.023	0.3635
	K _J (L.mg ⁻¹)	-0.0798			

Three parameter adsorption models

The application of models with more than two parameters necessarily implies the use of nonlinear forms because it is almost impossible to obtain three unknowns from a straight line. For these studies of isotherms with three parameters, we have chosen five, namely the models of Redlich-Peterson, Sips, Toth, Hill and Khan. Figure 8 presents the plots obtained for the three materials and table Y gives the constants of these isotherms. Table 4 presents the calculated parameters of these five adsorption isotherms obtained using the nonlinear fit analysis. As indicated in Table 4, all the values of the coefficient of determination whatever the model are

close to unity (R²>0.96) except the Hill model on the CC-HNO₃ material which has a low value of the coefficient of determination R²=0.8706 and a large value of chi-square test χ². The values of β and n obtained respectively from the Redlich-Peterson and Toth models are different from 1, which means that the adsorption of tartrazine yellow by these three materials cannot be reduced to the Langmuir isotherm. The very high R² values (R²>0.96) obtained indicate the suitability of all these models for the adsorption of tartrazine yellow. These models thus highlight the existence of heterogeneous adsorption sites on the surface of these three materials. According to the work of Ho et al., the small values of χ² and RMSE indicate a better adjustment of the model [42,43].

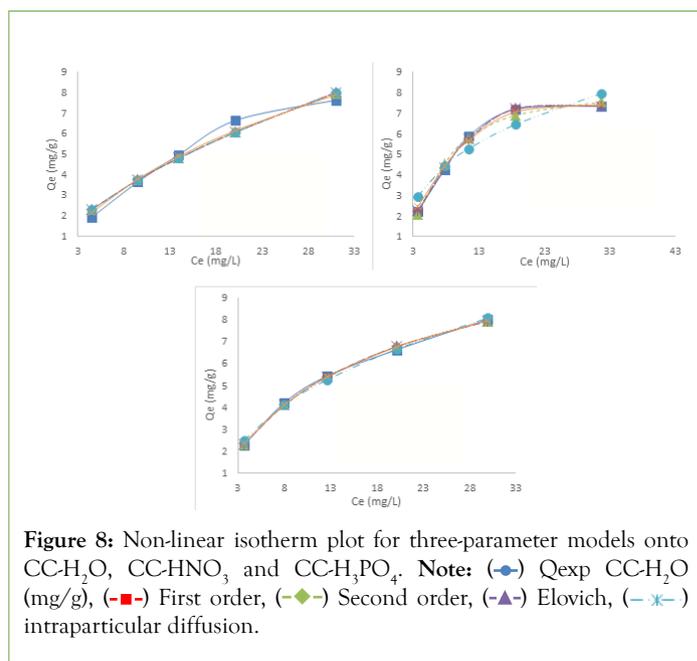


Figure 8: Non-linear isotherm plot for three-parameter models onto CC-H₂O, CC-HNO₃ and CC-H₃PO₄. **Note:** (●) Q_{exp} CC-H₂O (mg/g), (■) First order, (◆) Second order, (▲) Elovich, (×) intraparticle diffusion.

Table 4: Optimum isotherm parameters and their statistical comparison values for three-parameter models onto CC-H₂O, CC-HNO₃ and CC-H₃PO₄.

Models	Constants	Values	R ²	χ ²	RMSE
CC-H ₂ O					
Redlich-peterson	A (L.g ⁻¹)	12.7508	0.965	0.1454	0.8139
	B (L.mg ⁻¹)	13.7765			
	β	0.3659			
Sips	K _s (L.g ⁻¹)	60.0972	0.969	0.1291	0.7611
	a _s (L.g ⁻¹)	0.0138			
	β _s	1.4294			
Toth	Q (mg/g)	0.9349	0.9657	0.1421	0.8058
	K _e	0.2006			
	n (mg/g)	0.6088			
Hill	Q _m (mg/g)	1.0476	0.9651	0.1452	0.8125
	K _H (L.g ⁻¹)	0.2135			
	n _H	0.834			
Khan	Q _m (mg/g)	4.9386	0.9793	0.08	0.6308
	b _k (L.g ⁻¹)	0.1236			
	a _k	0.5548			
CC-HNO ₃					

Redlich-peterson	A (L.g ⁻¹)	0.6164	0.9985	0.0055	0.1685
	B (L.mg ⁻¹)	0.002			
	β	1.9382			
Sips	K _s (L.g ⁻¹)	8.0184	0.987	0.0493	0.494
	a _s (L.g ⁻¹)	0.0332			
	β_s	0.5602			
Toth	Q (mg/g)	1.24 × 10 ⁴	0.998	0.0072	0.1882
	K _c	385.3453			
	n (mg/g)	1.6674			
Hill	Q _m (mg/g)	2.2029	0.8706	0.3962	1.3728
	K _H (L.g ⁻¹)	1.4384			
	n _H	1.813			
Khan	Q _m (mg/g)	1.2 × 10 ³	0.9907	0.0399	0.3918
	b _k (L.g ⁻¹)	0.0006			
	a _k	63.7796			
CC-H ₃ PO ₄					
Redlich-peterson	A (L.g ⁻¹)	0.8508	0.9977	0.0098	0.2104
	B (L.mg ⁻¹)	0.097			
	β	0.919			
Sips	K _s (L.g ⁻¹)	12.4529	0.9975	0.0096	0.2203
	a _s (L.g ⁻¹)	0.0664			
	β_s	1.0381			
Toth	Q (mg/g)	9.7124	0.9976	0.0088	0.2141
	K _c	12.7772			
	n (mg/g)	0.975			
Hill	Q _m (mg.g ⁻¹)	1.6518	0.9947	0.0305	0.3145
	K _H (L.g ⁻¹)	1.5125			
	n _H	1.9819			
Khan	Q _m (mg/g)	8.3125	0.9978	0.0097	0.2039
	b _k (L.g ⁻¹)	0.1009			
	a ^k	0.8258			

CONCLUSION

The present work shows that the quantity of Tartrazine dye adsorbed varied with initial solution pH, biomass dosage, dye concentration and time of contact. The biosorption process achieved better results with the washed cocoa shell (CC-H₂O). Nonlinear regression analysis showed the best fit for pseudo second order kinetics regardless of material with Chi-square (χ^2) test values of 0.1672, 0.0811 and 0.0366 respectively for CC-H₂O, CC-HNO₃ and CC-H₃PO₄. Equilibrium data were fitted to two-parameter mono-solute models and mono-solute three-parameter models. Adsorption isotherm data were best described by Jovanovic model for water washed substrate, Langmuir model for phosphoric acid treated substrate and Dubinin-Radushkevich model for treated substrate to nitric acid for the 2-parameter isotherms. The results indicated cocoa shell constitutes a promising low-cost technology biosorbent for the removal of waste dyes.

DECLARATION OF INTERESTS

The authors declare that there are no conflicts of interest.

ACKNOWLEDGEMENTS

We appreciate the technical assistance of the Researchers of

Material and Process Engineering Team (MPET)/RU-NOCHEE of the Department of Chemistry, University of Dschang, Cameroon.

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