J. Chem Soc. Nigeria, Vol. 44, No. 5, pp 937 -947 [2019]

STUDIES ON THE ADSORPTION OF TARTRAZINE AND SUNSET YELLOW DYES FROM AQUEOUS SOLUTION USING ACTIVATED GBAFILO (*Chrysobalanus icaco)* SHELL

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Received 17 July 2019; accepted 20 August 2019, published online 29 August 2019

Abstract

The potential of activated *Chrysobalanus icaco* shell for the removal of anionic dyes: tartrazine and sunset yellow from aqueous solution by batch adsorption experiment was investigated in this study. The adsorption capacity of the adsorbent was determined through consideration of the effects of pH, adsorbent dose, temperature, contact time and initial dye concentration. The results showed that the optimum adsorption for removal of tartrazine dye occurred at pH 1.0 while that of sunset yellow dye was at pH 2 and that adsorption equilibrium was attained within 120 min. The adsorption capacity of the adsorbent was found to increase with increase in initial concentration of the dyes and with values for tartrazine ranging from 5.97 mg/g to 23.40 mg/g and that of sunset yellow from 4.05 mg/g to 19.65 mg/g. The equilibrium adsorption of the dyes was analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models and the correlation coefficients (R^2values) obtained showed that the Freundlich isotherm ($R^2 = 0.896$) provided the best description for tartrazine dye adsorption while that of Sunset Yellow dye was best described by Dubinin-Radushkevich isotherm with R^2value obtained as 0.984. The kinetic data of the tartrazine and sunset yellow dyes adsorption were best interpreted by Pseudo second-order kinetic

Keywords: Adsorption Isotherm, adsorption kinetics, *Chrysobalanus icaco,* sunset yellow dye, tartrazine dye

Introduction

There has been an increasing scientific concern about the hazardous effect of coloured dyes which are widely used in many industries such as textile, leather, paper, plastics and food technology to colour the final products [1]. Dye is a type of organic compound that can provide bright and lasting colour to other substances [2]. Various techniques have been employed for the removal of dyes from wastewater. These methods include: adsorption, Nano-filtration, electro-kinetic, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, ozonisation, supported liquid membrane, liquid-liquid extraction and biological processes. Among the various methods of dye removal, adsorption has been reported to be the most effective method that provides promising results [3]. Many scientific workers have investigated the feasibility of cheap and abundant substances for the removal of dye pollutants from aqueous solution [4-7].

This work investigates the use of activated Gbafilo shell as a biosorbent for the removal of sunset yellow and tartrazine dyes from aqueous solution under different experimental conditions. The study includes an evaluation of the effects of various operational parameters such as initial dye concentration, adsorbent dose, temperature, contact time, and pH on the dye adsorption process. The equilibrium adsorption behaviour of the adsorbent was studied using different adsorption isotherm models.

Gbafilo (*Chrysobalanus icaco*) is a medicinal herb that serves a number of purposes such as therapeutic agent for treatment of undesirable clinical conditions. It is recommended in the treatment of diabetes [8]. It is commercially grown in tropical rainforest of some western Central African countries such as Nigeria, Ghana, Congo and Senegal. The seeds are economically and medically important, been traditionally utilized for preparation of special soup, control of blood pressure, malaria, fever and treatment of stomach disorder.

Tartrazine for example is an azo dye, usually present in many drugs, food products and cosmetics. The contact of the dye is reported to result in various health problems like hypersensitivity [9], allergy and asthma [10], Skin eczema [11] and Immuno suppressive effects [12]. It is also known to have mutagenic and carcinogenic effects [13],

Sunset Yellow dye is a colorant used in drug dosage forms such as tablets and capsules. It is a water-soluble azo dye that imparts a reddish-yellow colour to different food items. A study has reported that FD & C Yellow No.6 dye affects brain health and induce hyperactivity in children but no carcinogenic (cancer-causing) potential has been reported [14].

Materials and Methods

Adsorbent Preparation

Gbafilo (*Chrysobalanus icaco*) shell was procured from Orie Ugba market in Umuahia Abia State, Nigeria. The shells were washed for several times with normal tap water, followed by distilled water to remove adhered dust particles. They were sundried for a day and were kept in an oven for 24 h at 110^{o}C. The production of activated carbon from the shells was done using the methods of carbonization and chemical activation. In this process, 50 ml from 85% phosphoric acid was taken and mixed with 50 g of adsorbent (ratio 1:1) and placed in a muffle furnace for 1 h at 550^{o}C. The product was washed with hot distilled water until it attained a neutral pH (pH 7.0). It was then dried in an oven at 105^{o}C for 4 h. The dried biomass were crushed and sieved to obtain the required particle size and were kept for the adsorption experiments without any further modification.

Adsorbate Preparation

The entire reagents used in the study were of analytical grade and were used without further purification. Tartrazine dye and Sunset yellow dye solutions were prepared by dissolving 1.0 g of each dye in 50 ml of distilled water in a beaker. Then 50 ml of each solution was placed in a 1litre volumetric flask and made up to the meniscus mark with distilled water to obtain a stock solution of 1000 mg/L concentration of the dyes solution. Several working solutions which include: 30, 50, 80, 100, 150 mg/L were then prepared from the stock solutions by serial dilution.

Batch Adsorption Study

Batch adsorption experiment was applied to determine the effects of pH, initial dye concentrations, adsorbent dose, contact time and temperature. In the determination of the Influence of pH, tartrazine and sunset yellow dyes solution of initial concentration of 150 mg/L each was used and the solution pH adjusted to different pH values of 1.0, 2.0, 4.0, 6.0, 8.0 and 10 by the dropwise addition of 0.1 M of NaOH or 0.1 M of HCl solution as the case may be. In the batch adsorption study, 0.1 g of the adsorbent was placed in different 250 ml Erlenmeyer flasks and 20 ml of the dyes solution were added and left for a contact time of 120 min at a temperature of 30^{o}C using thermostatic water bath shaker (SHZ-82). At the end of the given contact time of adsorption, the solutions were filtered into another empty beakers using Whatman No.1 filter paper. The filtrate was then taken to the UV-Vis Spectrophotometer (model: 752) to determine the concentration of dye solution remaining.

The effect of initial dyes concentration on the adsorption process was investigated by preparing different concentrations of the dyes solution from the 1000 mg/L stock concentration of the dyes. The pH of tartrazine dye solution was maintained at 1.0 and pH of sunset yellow dye solution was maintained at 2.0. Exactly 0.1 g of the adsorbent was placed in different 250 ml flasks and 20 ml of the dyes solution were added and left for a contact time of 120 min at a temperature of 30^{o}C using thermostatic water bath shaker (SHZ-82). At the end of the given contact time of adsorption, the solutions were filtered into another empty beakers using Whatman No.1 filter paper. The filtrate was then taken to the UV-Vis Spectrophotometer (model: 752) where the absorbance reading was taken to determine the concentration of dye solution remaining.

The effects of adsorbent dose, temperature and contact time were investigated by carrying the adsorption process at different masses of the adsorbent (0.1, 0.2, 0.3, 0.4 and 0.5 g), different experimental temperatures of 27°C, 40°C, 50°C, 60°C and 70°C and different contact times of 30, 40, 60, 90, 120, 150 and 180 min. The pH of the solutions were kept at 1.0 and 2.0 respectively for tartrazine dye and sunset yellow dye while the initial concentration of both dyes was maintained at 150 mg/L. The batch adsorption studies were carried out on 0.1 g of the adsorbent as earlier described and the residual concentration of the dyes in solution determined using the UV-Vis Spectrophotometer.

Data Analysis

The percentage of the dyes solution removed and the adsorption capacity of the adsorbent (Gbafilo shell) were calculated from equations (1) and (2) as given:

$$\% R = \frac{C_0 - C_e}{C_0} \times \frac{100}{1} \qquad (1)$$

$$q_e(mg/g) = C_0 - C_e \times \frac{v}{g} \qquad (2)$$

Where q_e (mg/g) is the amount adsorbed at equilibrium, C_o (mg/L) is the initial dyes concentrations in solution, C_e (mg/L) is the dyes concentrations remaining in the solution at equilibrium, v (L) represents the volume of dye solution and m (g) is the dry mass of the adsorbent.

Results and Discussion

Adsorbent Characterization

The infrared spectra of the adsorbent were obtained using a Fourier transform infrared spectrometer (model; Cary 630 by Agilent Technologies USA). Figure 1 displays the FT-IR spectra of Gbafilo shell in its natural form. The spectra exhibited several peaks indicating that Gbafilo shell is composed of various functional groups which possibly helped in binding of the dye molecules.

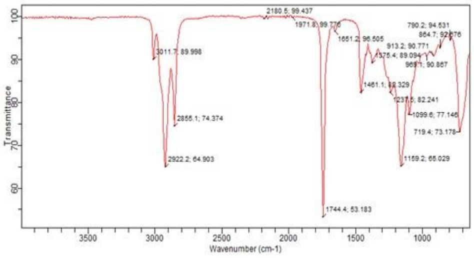

Figure 1: FT-IR spectra of Gbafilo shell.

Table 1: FT-IR spectra of Gbafilo shell in its natural form.

Compounds	Functional groups	Band position (cm^{-1})
Alcohol	O-H	3011.7
Alkene, alkyl	C-H	2922.2
Alkene, alkyl	C-H	2855.1
Alkynes	C≡C	2180.5
Carbonyls	C=O	1744.4
Alkene	C=C	1651.2
Amines	C-N	1159.2
Alcohol	C-O	1099.6
Alkyl halides	C-Cl	790.2
Alkyl halides	C-Cl	719.4

Effect of solution pH

The pH of a solution plays an important role in controlling the surface charge of an adsorbent, the degree of ionization of the adsorbate in the solution as well as dissociation of various functional groups on the active sites of the adsorbent [15]. In most cases, pH is termed as the 'master variable'. The adsorption experiment of the anionic dyes (tartrazine and Sunset Yellow) was performed in a pH range of 1–10 at 30^0C for 120 min. The effect of pH on the adsorption of dyes under consideration unto the adsorbent is shown in Figure 2. From the plots, it was observed that maximum amount of Tartrazine dye adsorbed occurred at pH 1 with a value of 29.68 mg/g corresponding to 98.93% removal while that of sunset yellow dye occurred at pH 2 with a value 19.20 mg/g corresponding to 64% removal. The least amounts adsorbed were observed at the pHs of 4 and 6 for tartrazine and Sunset Yellow dyes respectively and with percentage removals of 70.07% and 58.67% for tartrazine and Sunset Yellow dyes respectively. It can be interpreted here that with the increase in pH, the positively charged sites of the adsorbent get decreased and the surface of the adsorbent progressively becomes negatively charged. This leads to decrease in adsorption of the anionic dyes from the system due to electrostatic repulsion between the dyes and the negatively charged surface and a similar result had been recorded [16]. Also at high pH values, the OH^- ions compete effectively with anionic dyes causing a decrease in sorption of the dyes from aqueous solutions. At a low pH (pH < 4), a significantly high electrostatic force of attraction exists between the positively charged surface of the Gbafilo shell and anionic dye, hence enhancing the dye removal. Therefore, at lower pH values, the adsorbent surface becomes protonated, thereby enhancing increased adsorption of the dyes onto the adsorbent due to electrostatic attraction between positively charge surface and the negatively charge dye molecules. It can be concluded here that the removal of tartrazine and sunset yellow dyes is drastically affected by increasing pH values. The present finding is supported by earlier research on the removal of tartrazine onto Chitin and Chitosan [17].

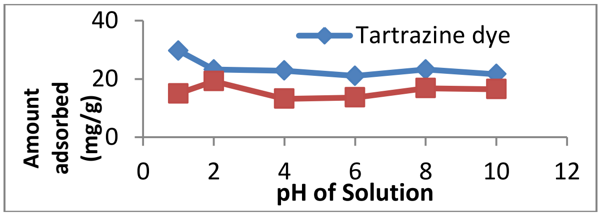

Figure 2: Amount of dyes adsorbed by the adsorbent as a function of initial pH of solution

Effect of Adsorbent dose

One of the most critical parameters for rapid and efficient dye removal is size and amount of adsorbent in the reaction mixture which must be optimized. The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. The effect of adsorbent dose on the amount of dyes adsorbed is shown in Figure 3. The adsorption capacity decreased with increase in adsorbent dosage from 0.1 g to 0.5 g for both tartrazine and Sunset yellow dye and with values decreasing from 23.40 mg/g to 5.88 mg/g and 17.10 mg/g to 3.60 mg/g respectively. The effect of adsorbent dose on the percentage dye removal is also shown in Figure 4. An increase from 76.00% to 80.00% with increase in adsorbent dose from 0.1 g to 0.5 g was noted for Sunset Yellow while an increase from 78.00% to 98.07% was recorded for tartrazine dye from 0.1 g to 0.5 g. Maximum percentage removal was observed at adsorbent dose of 0.3 g (99.33% and 99.44%) for Sunset Yellow and tartrazine dye respectively. The increase in percentage adsorption with increase in adsorbent dosage can be attributed to greater surface area and the availability of more adsorption surface sites on the adsorbent. It was observed that initially, the percentage removal increased rapidly with the increase in adsorbent dose till 0.3 g which is the critical dose, after which the percentage removal began to decrease for Sunset yellow dye and the percentage removal almost reached a constant value for tartrazine dye. This may be due to the saturation of adsorption sites of adsorbent particles by the dyes.

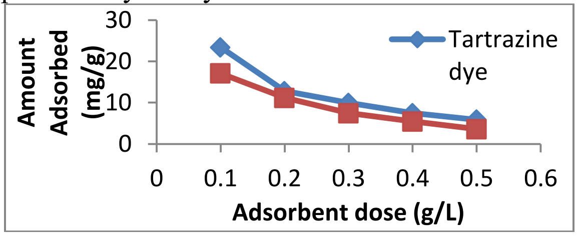

Figure 3: Amount of dyes adsorbed as a function of adsorbent dose

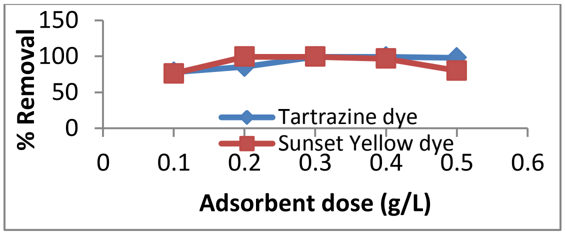

Figure 4: Percentage adsorption of the dyes as a function of adsorbent dose

Effect of temperature

The effect of temperature on the adsorption of the dyes was carried out at temperatures of 27 ^{o}C, 40°C, 50 °C, 60 °C, 70 °C and at pH 1 for tartrazine, pH 2 for sunset yellow and at constant initial concentration of 150 mg/L. The plots in Figure 5 show that the adsorption capacity decreases with increase in temperature from 27 - 70 °C for the two dyes. This may be attributed to the weakening of the bonds that bind the anionic dyes to the active sites on the adsorbent. Similar results had been reported [18, 19], showing that with increase in temperature, a decrease in adsorption capacity is observed. Furthermore, an initial increase in amount adsorbed was observed for tartrazine dye with an initial increase in temperature from 27 to 40 ^{0}C. This correlates the fact that with an increase in temperature of a solution, the surface pores on the adsorbent are enlarged leading to increased rate of adsorption. It was also observed that with further increase in temperature, rate of adsorption decreased, which could still be attributed to the fact that increase in temperature will weaken the bonds between the dye ions and the active sites on the adsorbent surface.

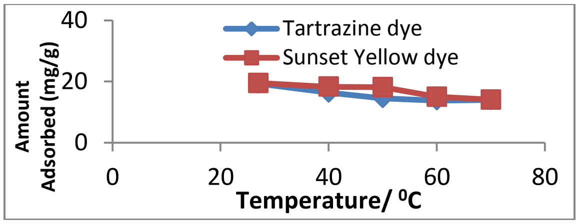

Figure 5: Amount of dyes adsorbed as a function temperature

Effect of initial dye concentration

An increase in adsorption capacity for both anionic dyes on the adsorbent with an increase in initial dye ion concentration was observed as shown in Figure 6. With an increase in dye concentration from 30 mg/L to 150 mg/L, an increase in the amount of tartrazine from 5.97 to 23.40 mg/g and sunset yellow from 4.05 to 19.65 mg/g was recorded. This increase may be attributed to an increasing concentration gradient acting as an increasing driving force to overcome all mass transfer resistances of the dye molecules between the aqueous and solid phase, leading to an increased equilibrium sorption until saturation is achieved. A similar trend was observed for the biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge [20]. The effect of initial dye concentration on the percentage adsorption of tartrazine and sunset yellow onto the adsorbent is also shown in Figure 7. A decrease in percentage adsorption of both dyes on the adsorbent with increase in initial dye concentration was observed. In fact, with increase in initial dye concentration from 30 to 150 mg/L, the percentage adsorption of tartrazine decreased from 99.47 to 78.00%. Similarly, the percentage adsorption of sunset yellow also showed a decrease from 90.00 to 87.33%. This decrease in percentage adsorption with increasing initial dye concentration is due to the fact that at lower concentrations, more of the anionic dyes under consideration would be removed by the abundant active sites on the adsorbent but at higher concentrations, more dye ions would be left un-adsorbed due to saturation of the active sites of the adsorbent. The result observed is similar to the earlier results reported [21].

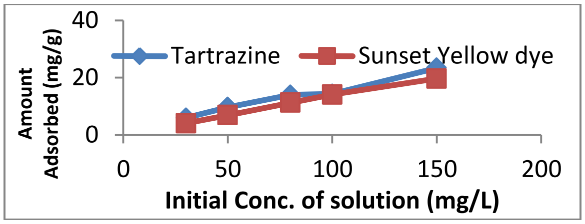

Figure 6: Amount of dyes adsorbed as a function of initial dye concentration

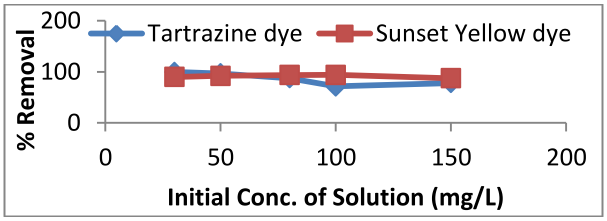

Figure 7: Percentage dyes removal as a function of initial dye concentration

Equilibrium Adsorption Isotherms

Adsorption isotherms indicate the distribution of the adsorbates between the bulk liquid phase and the solid phase when the adsorption process attains equilibrium. The analysis of the isotherm data through fitting into different isotherm models is an important step in finding a suitable model that can be used for design purposes. The adsorption capacity of the adsorbent was investigated using the Langmuir, Freundlich,Temkin and Dubinin - Radushkevich adsorption isotherms.

Langmuir Isotherm Model

Langmuir isotherm is considered as the best model that accounts for formation of monolayer of dye molecules on solid surface. A well-known linear form of the Langmuir equation assuming monolayer adsorption on a homogeneous adsorbent surface is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad (3)$$

Where q_e is the adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively reflects the affinity of the adsorbate for the adsorbent, q_{max} is the maximum adsorption capacity corresponding to monolayer coverage (mg/g). The constants, q_{max} and K_L were determined from the slope and intercept of the linear plots of C_e/q_e against C_e (Figures 8 and 9). The constants were calculated and presented in Table 2. The relatively high R^2 values of 0.527 and 0.874 for sunset yellow and tartrazine dyes respectively indicate a fairly good fit to the Langmuir model.

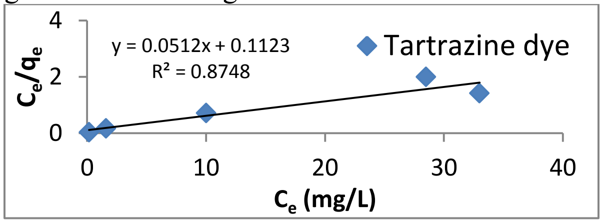

Figure 8: Langmuir isotherm plot for adsorption of tartrazine dye onto Gbafilo shell.

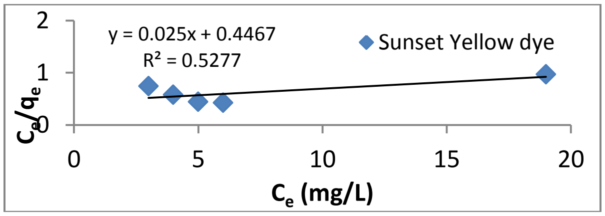

Figure 9: Langmuir isotherm plot for the adsorption of sunset yellow dye onto Gbafilo shell

Table 2: Langmuir isotherm constants for the adsorption of the dyes onto the adsorbent.

Adsorbates	K_L(L/mg)	q_{max} (mg/g)	R^2
Tartrazine dye	0.455	19.61	0.874
Sunset yellow dye	0.056	40.00	0.527

Freundlich Isotherm Model

The Freundlich isotherm considers multilayer adsorption with heterogeneous energetic distribution of active sites accompanied by interaction between adsorbed molecules. The Freundlich equilibrium isotherm equation is an empirical relation involved in the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich equation in its linearized form is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} log\ C_e \qquad (4)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_F the Freundlich constant, (1/n) is the heterogeneity factor and both constants K_F and n are related to the intensity and capacity of the adsorption process respectively. Linear plots of $\log q_e$ against $log\ C_e$ confirm the Freundlich isotherm (figures 10 and 11) from which the constants K_F and (1/n) were obtained from the intercept and slope of the plots and presented in Table 3. The correlation coefficients (R^2 values) were high for the Freundlich Isotherm model indicating a good fitting for the model. This also reveals the heterogeneous surface for the adsorbent and a possibility of multilayer adsorption of the anionic dye. It is also worthy to note that if the values of n lie between 1 and 10, a favourable adsorption process is indicated [22]. The n values of 4.673 and 1.309 obtained for the adsorption of tartrazine and sunset yellow dye molecules respectively in this study indicate a favourable adsorption by the adsorbent.

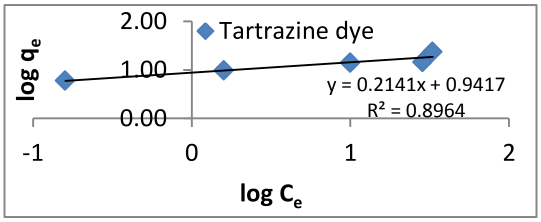

Figure 10: Freundlich isotherm plot for adsorption of tartrazine dye onto Gbafilo shell

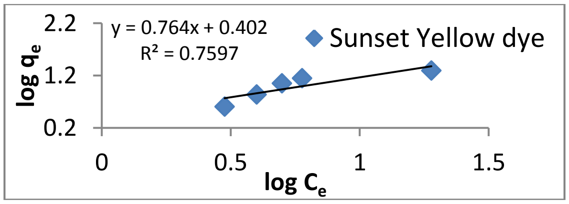

Figure 11: Freundlich isotherm plot for adsorption of sunset yellow dye onto Gbafilo shell

Table 3: Freundlich isotherm constants for the adsorption of the dyes on the adsorbent.

Adsorbates	K_F	1/n	n	R^2
Tartrazine dye	8.729	0.214	4.673	0.896
Sunset yellow dye	2.523	0.764	1.309	0.759

Temkin Isotherm Model

The linear form of the Temkin model is expressed as:

$$q_e = BlnA + BlnC_e \qquad (5)$$

where C_e (mg/L) is the equilibrium concentration of dye solution, q_e (mg/g) is the amount of dye solution adsorbed at equilibrium, $B = RT/b_T$, where T(K) is the absolute temperature, R is the ideal gas constant (8.314J/mol K) and b_T (J/mol) is the Temkin constant. The constant B is related to the heat of adsorption and A (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The constants A and B for the adsorption process were determined from the intercept and slope of the linear plots of q_e versus ln C_e as shown in Figures 12 and 13. The Temkin isotherm parameters and R^2 values obtained from the plots are presented in Table 4. It can be concluded that the Temkin Isotherm also gave a good fit to the experimental data and in particular for adsorption of sunset yellow onto the adsorbent.

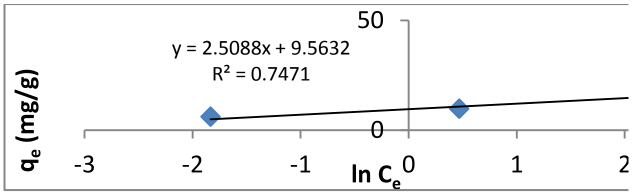

Figure 12: Temkim isotherm plot for adsorption of tartrazine dye onto Gbafilo shell.

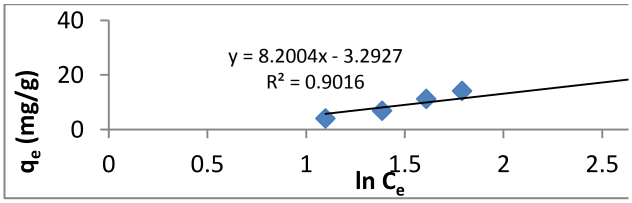

Figure 13: Temkim isotherm plot for adsorption of sunset yellow dye onto Gbafilo shell

Table 4: Temkin isotherm constants for the adsorption of the dyes on the adsorbent.

Adsorbates	A (L/g)	B (mg/g)	R^2
Tartrazine dye	45.286	2.508	0.747
Sunset yellow dye	0.699	8.200	0.901

Dubinin - Radushkevich Isotherm Model

The D–R isotherm model is applied to estimate the apparent free energy and characteristics of adsorption. The isotherm is similar to the Langmuir type but it is more general because it is used to determine the occurrence of adsorption on both homogenous and heterogeneous surfaces. The linear form of D–R isotherm can be expressed as:

$$\ln q_e = \ln q_m + \beta\varepsilon^2 \qquad (6)$$

where q_e (mg/g) is the adsorption capacity, q_m (mg/g) is the theoretical saturation capacity, β (mol^2/J^2) is a constant related to the mean free energy of adsorption per mole of the adsorbate and ε is the Polanyi potential expressed as:

$$\varepsilon = RT \ln (1+1/C_e) \qquad (7)$$

where C_e (mg/L) is the equilibrium concentration of dyes in solution, T(K) is the absolute temperature and R is the gas constant (8.314J/mol K). The D - R isotherm model is applied by a linear plot of ln q_e versus ε^2 from which the constants β and q_m were obtained from the slope and intercept of the plots respectively. The D-R isotherm plots for the adsorption of tartrazine and sunset yellow dye onto Gbafilo shell are shown in Figures 14 and 15. The isotherm parameters obtained are presented in Table 5. The high correlation coefficient (R^2 = 0.984) obtained for adsorption onto sunset yellow showed that the model provides the best description for adsorption of sunset yellow dye onto the adsorbent compared to the other models.

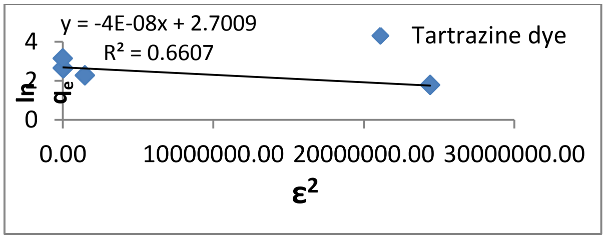

Figure 14: Dubinin - Radushkevich isotherm plot for adsorption of tartrazine dye onto Gbafilo shell

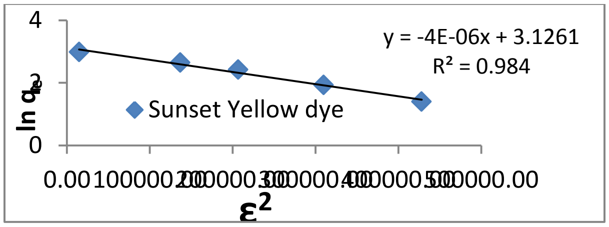

Figure 15: Dubinin-Radushkevich isotherm plot for adsorption of sunset yellow dye onto Gbafilo shell

Table 5: Dubinin-Radushkevich isotherm constants for the adsorption of the dyes on the adsorbent.

Adsorbates	**q_m (mg/g)**	**B (mol^2/J^2)**	R^2
Tartrazine dye	14.88	-4×10^{-8}	0.660
Sunset yellow dye	22.78	-4×10^{-6}	0.984

Effect of contact time

The effect of the contact time on the adsorption of tartrazine and sunset yellow dye unto the adsorbent is shown in Figure 16. It is observed that the rate of removal of the dye molecules from solution was initially rapid and then diminished gradually until an equilibrium time beyond which there was no significant increase in the removal rate. The fast adsorption rate at the initial stages may be due to the presence of abundant active sites on the adsorbent at the initial time which become used up with time as a result of saturation of the sites on attainment of equilibrium [23]. It was observed that the same equilibrium time was observed for the two dyes. As shown in the Figures, the equilibrium amounts adsorbed were 19.65 mg/g and 23.80 mg/g for sunset yellow molecules and tartrazine respectively at equilibration time of 120 min. A contact time of 2 hours was utilized in the current study to ensure equilibrium sorption of both dye molecules on the adsorbent.

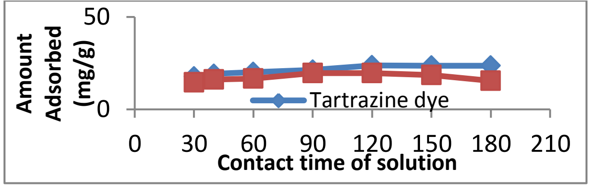

Figure 16: Effect of contact time on the amount of dyes adsorbed by the adsorbent

Kinetic Analysis

Kinetics is a key factor for adsorption investigation because it can predict the rate at which a pollutant is removed from aqueous solution and provides valuable data for understanding the mechanism of adsorption process. Several models are available to investigate the adsorption mechanism but the present study is restricted to application of pseudo first-order and pseudo second-order kinetic models.

Pseudo first-order model

The pseudo first-order kinetic plots for the adsorption of tartrazine and sunset yellow molecules on the adsorbent is shown in Figures 17 and 18. The constants k_1 and $q_{e(cal)}$ were obtained from the slope and intercepts of the plots and are shown in Table 6. From the R^2 values obtained for sunset yellow dye as shown in Table 6, it is observed that the pseudo-first order model did not provide a good fit to the experimental data, due to the low R^2 value, actually 0.174. The R^2 value for sorption of tartrazine dye was as high as 0.952 but still lower than that of the pseudo-second order model. The values of the $q_{e(exp)}$ also showed great deviation from the $q_{e(cal)}$ for the pseudo first-order model for both dye molecules onto Gbafilo shell. The low R^2 values and the large difference between the calculated and experimental equilibrium amount adsorbed (q_e values) simply showed that the adsorption of the two dye molecules onto the adsorbent did not follow the pseudo first-order kinetic mechanism.

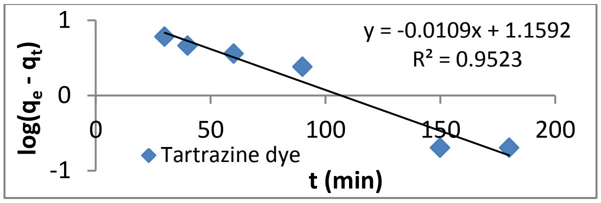

Figure 17: Pseudo first-order plot for adsorption of tartrazine dye onto Gbafilo shell

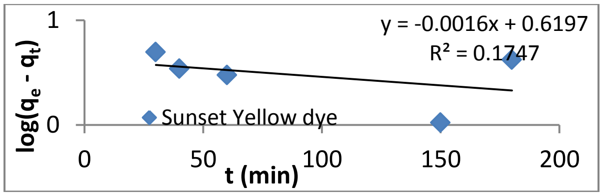

Figure 18: Pseudo first-order plot for adsorption of sunset yellow dye onto Gbafilo shell

Table 6: pseudo first-order kinetic constants for the adsorption of the dyes onto the adsorbent.

Adsorbates	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2
Tartrazine dye	23.80	14.421	0.023	0.952
Sunset yellow dye	19.65	4.159	0.002	0.014

Pseudo second-order model

The applicability of the pseudo second-order model was tested by a linear plot of t/q_t versus t for the adsorption of tartrazine and Sunset yellow molecules unto Gbafilo shell as shown in Figures 19 and 20. The constants $q_{e(cal)}$ and k_2 were calculated from the slope and intercept of the plots respectively as shown in Table 7. It is observed from the values of the linear regression coefficient (R^2 values) which are 0.997 and 0.955 for both dyes, that pseudo second-order model presented the best fit to the adsorption data of tartrazine and Sunset yellow dye adsorption unto the adsorbent. Also, the values of $q_{e(cal)}$ were closer to the values of $q_{e(exp)}$ compared to those of the pseudo first-order model. This good fit presented by the pseudo second-order model suggests that chemisorption mechanism may be the rate-limiting step for the sorption of these dye molecules and that the internal and external mass transfer mechanisms were important factors in the adsorption process [24].

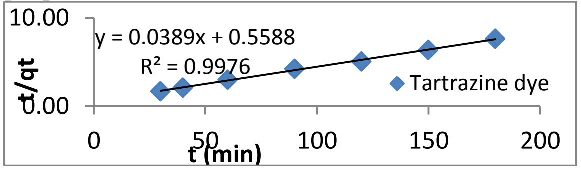

Figure 19: Pseudo second-order plot for adsorption of tartrazine dye on Gbafilo shell

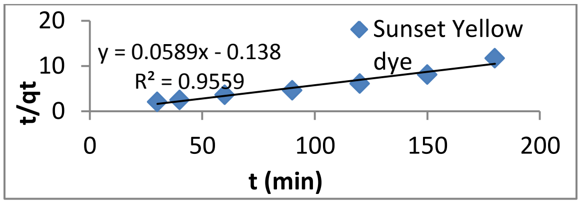

Figure 20: Pseudo second-order plot for adsorption of sunset yellow dye on Gbafilo shell

Table 7: pseudo second-order kinetic constants for the adsorption of the dyes onto the adsorbent.

Parameters	Adsorbates	
	Tartrazine dye	**Sunset yellow dye**
$q_{e(exp)}$ (mg/g)	23.80	19.65
$q_{e(cal)}$ (mg/g)	26.316	17.241
k_2 (g/mg min)	0.0026	-0.024
h (mg/g min)	1.801	-7.134
R^2	0.997	0.955

Conclusion

This study demonstrates that Gbafilo (*Chrysobalanus icaco*) shell is a viable, cost effective adsorbent material for the adsorption removal of tartrazine and sunset yellow dyes from aqueous solution. The adsorption of these anionic dyes were found to be highly dependent on pH, contact time, initial dye concentration, adsorbent dose and temperature. The maximum adsorption for tartrazine was at pH 1 and pH 2 for sunset yellow. The adsorption kinetic data best fitted into the pseudo second-order for both dyes and the equilibrium isotherm best fitted into the Freundlich isotherm for tartrazine and Dubinin-Radushkevich isotherm for sunset yellow. It is therefore concluded that Gbafilo shell could be efficiently utilized in the adsorption of these dyes at the studied pH.

References

1. M. Mohamed (2004). Acid dye removal: comparison of surfactant–modified mesoporous FSM 16 with activated carbon derived from rice husk. *Journal of Colloid Interface Science*. 272: 28-34.
2. R. Han and M. Tang (2008). Kinetics and Isotherms of Neutral Red Adsorption on Peanut husk. *Journal of Environmental Sciences*, 20(9):1035-1041.
3. A. S. Mahmoud, A. E. Ghaly, and M. S. Brooks (2007). Removal of dye from textile wastewater using plant oils under different pH and temperature conditions. *American Journal of Environmental Science*, 3: 205-218.
4. K. S. Low and C. K. Lee (1995). The removal of cationic dyes using coconut husk as an adsorbent. *Ibid*. 13(2): 221.
5. M. Arami, N. Y. Limaea, N. M. Mahmoodi, N. Salman and N. Tabrizi. (2005). Removal of dyes from coloured textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. *J. Colloid Interface Sci*. 288: 371.
6. N. Nasuha, B. H. Hameed and A. T. M. Din (2010). Rejected tea as a potential low-cost adsorbent for the removal of Methylene Blue. *J. Hazard. Mater*. 175: 126.
7. A. Ahmad, M. Rafatullah, M. H.Ibrahim and R. Hashim (2009). Scavenging behavior of meranti sawdust in removal of Methylene Blue from aqueous solution. *J. Hazard. Mater.* 170: 357.
8. B. L. Hart (2005). The Evolution of herbal medicine: Behavioural perspectives. *Anim. Behav. Soc*., 70: 975-989.
9. S. D. Lockey, Sr. (1977). Hypersensitivity to Tartrazine (FD & C yellow No.5) and other dyes and additives present in foods and pharmaceutical products. *Ann. Allergy* 38: 206
10. R.Pohl, R. Balon, R. Berchou. and V. K.Yeragani (1987). Allergy to tartrazine in anti-depressants. *Am. J. Psychiatry* 144: 237
11. J. Devlin. and T. J. David (1992). Tartrazine in atopic eczema. Arch. Dis. Child 67, 709
12. I. Koutsoqeorqopoulou, C. Maravelias, G. Methenitou. and A. Koutselinis (1998). Immunological aspects of the common food colorants, Amaranth and Tartrazine. Veterin. Human. *Toxicol.* 40: 1
13. K. T. Chung (1983). The significance of azo-reduction in mutagenesis and carcinogenesis of azo dyes Muta. Res/Rev. Gen. *Toxicol*. 114: 269.
14. J. Huff (1982). Environmental Health Perspectives. FD&C Yellow, *Br. J. Cancer*, 6(45): 209-210
15. F. K. Onwu and Ogah, S. P. I. (2010). Studies on the effect of pH on the sorption of cadmium(ll), nickel(ll) and chromium(Vl) from aqueous solution by African White Star Apple (*C. albidium*) shell. *African Journal of Biotechnology*, 9(42):7086-7093.
16. A. S. Ozcan, B. Erdem and A. Ozcan (2004). Adsorption of Acid blue 193 from Aqueous solutions onto BTMA-Bentonite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 280(1):44-54
17. G. L. Dotto, M. L. G. Vieira and L. A.A Pinto (2012). Kinetics and mechanism of tartrazine adsorption onto chitin and chitosan. *Ind. Eng. Chem. Res*. 51: 6599
18. N**.** Mosallanejad and A, Arami, (2012). Kinetics and Isotherm of Sunset Yellow Dye Adsorption on Cadmium Sulfide Nanoparticle Loaded on Activated Carbon. *Journal of Chemical Health Risks*, 2(1): 31-40
19. K. O. Amadi, F. K. Ekuma, C. M. Ngwu and G. Ekwenye (2018). Isotherms and

Thermodynamic Studies on Biosorption of Co(ll), Cu(ll) and Ni(ll) ions from aqueous solution using carbonized biosorbent derived from Pilinut (*Canarium ovatum*) seed. *Journal of Scientific and Engineering Research,* 5(6):265-275

20. J. Gao, Q. Zhang, K. Su, R. Chen, and Y. Peng (2010). Biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge. *Mater.*, 174 (1-3): 215 – 225
21. F. H. Wale and J. M. Wale (2010). Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent Moringa Oleifera pod. *Journal of Physical Chemistry*, 57: 385–471
22. B. Das and N. K. Mondal (2011). Calcareous soil as a new adsorbent to remove lead from aqueous solution: Equilibrium, Kinetic and Thermodynamic studies. *Universal Journal of Environmental Research and Technology*. 1(4): 515-530.
23. V. K. Gupta, C. K Jain, A.Imran, M. Sharma and V. K. Saini (2003). Removal of cadmium and nickel from wastewater using bagasse fly ash - a sugar industry waste. *Water Research*, 37: 4038-4044.
24. F. O. Okeola, E. O. Odebunmi, O. M. Ameen, M. A. Amoloye, A. A. Lawal and A. G. Abdulmummeen (2017). Equilibrium, kinetic and thermodynamic studies of the adsorption of tartrazine and sunset yellow. *Arid Zone Journal of Eng. Tech and Environ*. 13(2):268-280.