

EQUILIBRIUM KINETICS AND THERMODYNAMIC STUDIES OF THE ADSORPTION OF TARTRAZINE AND SUNSET YELLOW

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Abstract

Batch adsorption experiment was carried out on freema (combination of Tartrazine and Sunset Yellow) an adsorbent prepared from moringa pod. The adsorption capacity of the adsorbent was determined. Effect of such factors as initial concentration of the adsorbate solution, contact time with the adsorbent, pH of the dye solution, and temperature of the dye solution on the adsorption capacity of the adsorbent was determined. The result showed that the optimum adsorption was attained at pH of 3, adsorption equilibrium was attained within 60 min. The adsorption capacity increases with increase in initial concentration of the dye solution. The result of the kinetics study showed that the adsorption process was better described by the pseudo-second order rate equation. The adsorption process fitted well with both Freundlich ($R^2 = 0.983$) and Langmuir ($R^2 = 0.933$) models. Thermodynamic result showed ΔH and ΔS were all negative. Gibbs free energy change (ΔG) increases with increase in temperature of the dye solution.

Keywords: Adsorption, Kinetics, Thermodynamics, Sunset yellow, Tartrazine.

1. Introduction

There has been increasing scientific concern about the hazardous effects of coloured dyes, which are widely used in many industries such as textile, leather, paper, plastics, and food technology to colour the final products (Mohamed, 2004). The presence of small amounts of dye in water is highly visible and undesirable. Dyeing effluent discharged into stream or river may make them unacceptable for public consumption (Gao *et al.*, 2007). Moreover, discharging untreated industrial effluents containing dyes decreases penetration of sunlight into the water (Qiu *et al.*, 2010) and affect the photosynthetic activity significantly (Qiu *et al.*, 2009).

Various techniques have been employed for the removal of dyes from wastewaters. 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 process (Mahmoud *et al.*, 2007).

Adsorption has been studied as an alternative to treat effluents contaminated with dyes, to a low initial investment, simplicity of project and higher efficiency than the conventional processes. The adsorption process takes away the material completely irrespective of the toxicity and it does not introduce another. This process is becoming a promising technology because of those factor and especially regeneration capacity (Crini and Badot, 2008; Robinson *et al.*, 2001; Qiu *et al.*,

2015). Adsorption on activated carbon, a typical adsorbent has been extensively investigated through the past years in colour removal of various organic pollutants (Gad and El-Sayed, 2009).

The adsorbent prepared from *Moringa oleifera* pod by chemical treatment has been used successfully for cadmium adsorption (Wale and Wale, 2010). It has also been used for effective adsorption of acetic acid (organic solutes) and potassium permanganate (inorganic solute) (Taj *et al.*, 2011). Tartrazine and Sunset Yellow in freema are potential environmental nuisance which requires necessary remediation off the environment. The objective of this study was to determine the feasibility of remediating aqueous medium of freema (a combination of Tartrazine and Sunset Yellow) by application of chemically treated *Moringa oleifera* pod as adsorbent; thus, reducing or removing them from aqueous environment. To carry out the investigation therefore, the equilibrium, kinetic and thermodynamic of adsorption of combined preparation of Tartrazine and Sunset Yellow (freema) were studied.

2. Materials and Methods

2.1 Materials

The adsorbent employed was already prepared from *Moringa oleifera* pod by chemical treatment. The activated carbon was produced using the methods of carbonization and chemical activation. The raw material, *Moringa oleifera* pod were impregnated with phosphoric acid (85 % by weight) using the weight ratio of raw material and phosphoric acid at 1:1. The mixture was carbonized in a muffle furnace at 500 °C for 1hr. The product was washed with hot distilled water until it attained neutral pH and dried in an oven at 105 °C for 4 hrs. The dry biomass was crushed and sieved into particle size 0.045 mm - 0.150 mm.

The adsorbate was a combined preparation of Tartrazine and Sunset Yellow (freema). Tartrazine (I), trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonato phenylazo)-*H*-pyrazole-3-carboxylate is an azodye with molecular formula $C_{16}H_9N_4Na_3O_9S_2$ (Figure 1) and molecular weight 534.4, while Sunset yellow is a petroleum derived orange azodye. It is a food dye known as Disodium 6-hydroxy-5-[(4sulfophenyl)azo]-2-naphthalenesulfonate (Figure 2).

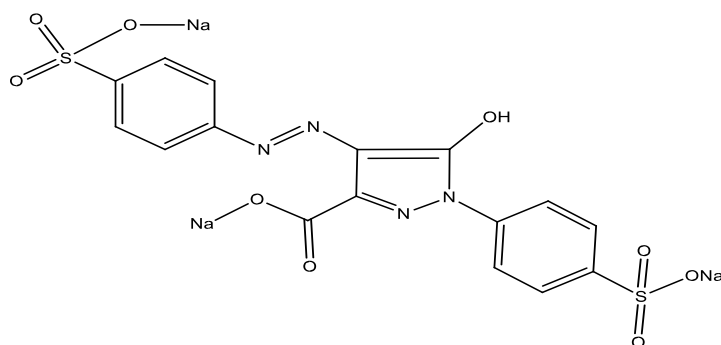


Figure 1: Structure of Tartrazine

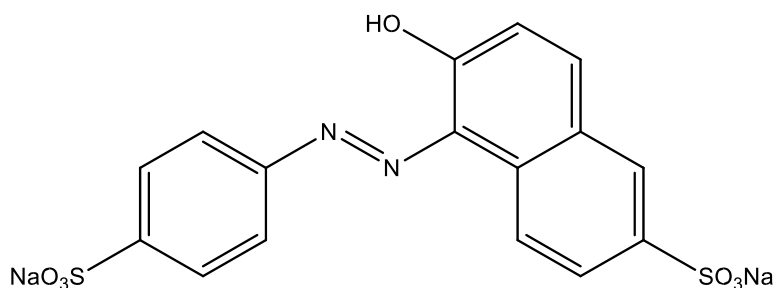


Figure 2: Structure of Sunset Yellow

2.2 Adsorption Experiment

The adsorption capacity was determined by carrying out a series of batch adsorption experiment studied the effect of various parameters. The experiments were conducted to investigate the effect of pH (be 3, 5, 7, 9 and 11), contact time (from 30 – 150 mins) initial adsorbate concentration ((20, 40, 60, 80 and 100) mg/L.) and adsorbent dosage (0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g). All the adsorption experiments were carried out at room temperature ($30 \pm 2^\circ\text{C}$). The initial pH was adjusted with 0.1M HCl or 0.1M NaOH. Time course experiments were investigated by shaking the sorption mixture of (adsorbent and adsorbate) at various predetermined interval and conditions. The mixtures left were filtered and the filtrate analysed for the adsorbate concentration, blank solutions without adsorbent were also shaken and the concentrations determined. This was used as initial concentration. The detail work was discussed under each parameter. (Taj *et al*, 2011)

The concentrations of adsorbate in the solution before and after adsorption were determined using a double beam UV-Vis spectrophotometer (Shimadzu DU 730) at its maximum wavelength of 375 nm Each batch of the experiment was duplicated under identical conditions of temperature, concentration of adsorbate, mass of adsorbent, medium, pH and adsorption period. The mean values of results were noted. The adsorption capacity of solute per unit mass of adsorbent (q_e , mg/g) was calculated using adsorption system mass balance equation given as follows:

$$q_e = \frac{v(c_i - c_f)}{w} \quad (1)$$

where: v = volume of solution (L), w = amount of dry adsorbent/ substrate (g), c_i = initial concentration (mg/l) and c_f = final concentration (mg/l).

The percentage of dye uptake (% uptake) was also calculated using Equation (2).

$$\% \text{ uptake} = \frac{c_i - c_f}{c_i} \times 100 \quad (2)$$

2.2.1 Effect of adsorbent dose

A 50 ml of 50 mg/L of the dye solution was placed in 5 separate containers and 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g of adsorbent was weighed into each solution of adsorbate. The pH was set at 3

and was put in a shaker for 1h. The solutions were filtered and the absorbance of the filtrate was taken then the adsorption capacity was thus determined.

2.2.2 Effect of contact time

50 ml of 50 mg/L of the dye solution was prepared in 5 separate places and 0.2 g of adsorbent was weighed in each of the solutions and were put in a mechanical shaker. The solutions were taken out after the other at time interval of 30mins ranging from 30 – 150 mins. The absorbance of the filtrate was taken in each case to determine the respective adsorption capacity.

2.1.4 Effect of pH

50 ml of 50 mg/L of the dye solution was prepared in 5 separate places and 0.2 g of adsorbent was weighed in each of the solutions, the pH of the solutions were varied with 0.5M Sodium hydroxide (NaOH) and 0.5M Hydrochloric acid (HCl) to be 3, 5, 7, 9 and 11. HCl was used to reduce the pH while NaOH was used to increase the pH. The solutions were put in a shaker for 1hr and were filtered afterwards, the absorbance of the filtrate was taken, and the adsorption capacity was calculated from it. Taj *et al*, 2011

2.1.5 Effect of concentration

Solutions of different concentrations ranging from 20 – 100 mg/L were prepared in a sample bottle. The concentrations are (20, 40, 60, 80 and 100) mg/L. adsorbent of 0.2g added to 50ml of each solution was shaken for 2hrs. The absorbance of the respective filtrate was taken, and then the adsorption capacity was determined.

2.1.6. Effect of temperature

50 ml of 50 mg/L of solution was prepared in 5 bottles, 0.2 g of adsorbent was added to each of the solutions, and are separately put in a mechanical shaker at different temperatures of (30, 40, 50, 60 and 70) °C for contact time of 1hr. The adsorption capacity at each temperature was thus calculated.

3. Results and Discussion

3.1 Effect of concentration of adsorbate on the adsorption.

Figure 3 shows the effect of initial concentration of adsorbate in the solution on the adsorption. The plot of amount adsorbed (q_e) against the initial concentration of adsorbate in the solution was displayed. The result shows that the amount adsorbed increased with increase in initial concentration within 20 – 100 mg/L, which is similar to the result reported by Wale and Wale, (2010) in the adsorption of cadmium from aqueous solutions using the same adsorbent. This increase was tending toward marginal at higher concentration of adsorbate. The sites of adsorption might have been filled up, the amount adsorbed thus getting to maximal, irrespective the amount of solute in the mixture.

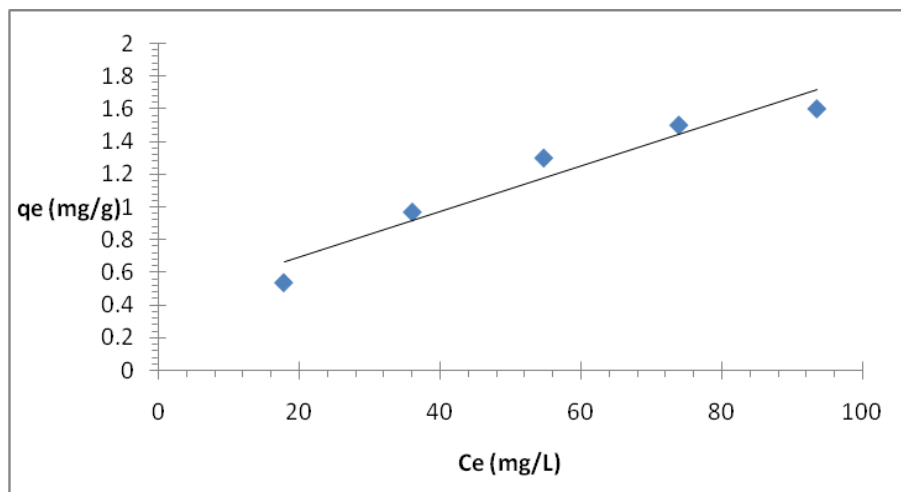


Figure 3: Effect of concentration of adsorbate on the adsorption process

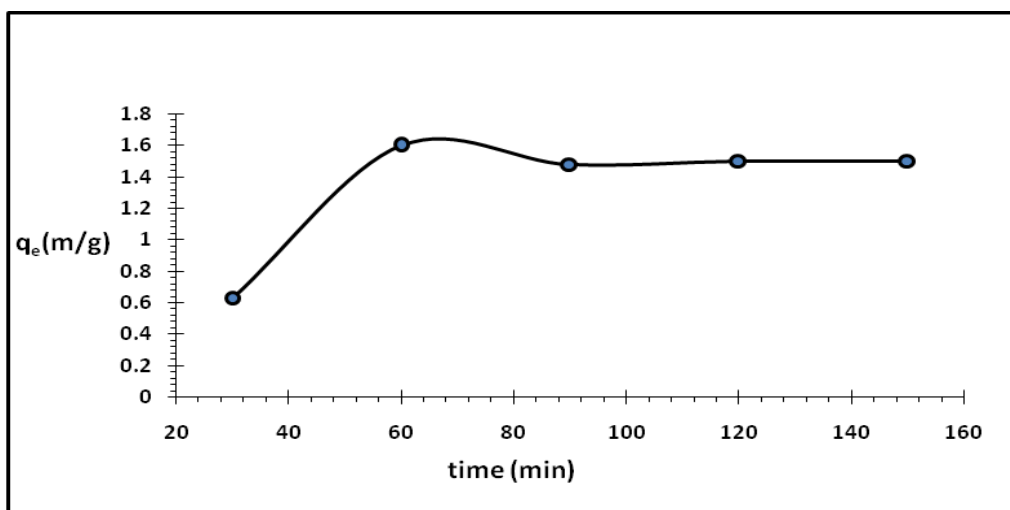


Figure 4: Effect of contact time with the adsorbent on freema adsorption

3.3 Effect of pH

The adsorption of the freema (the combined dye) was pH dependence as displayed in Figure 5. The Figure indicates that with increase in pH (between 3 -11), the amount of adsorbate adsorbed decreased. This was in line with the result obtained by Qiu *et al.* (2015). As observed in the Figure, there was sharp reduction from pH 3 to pH 7 as against pH 7 to pH. 11

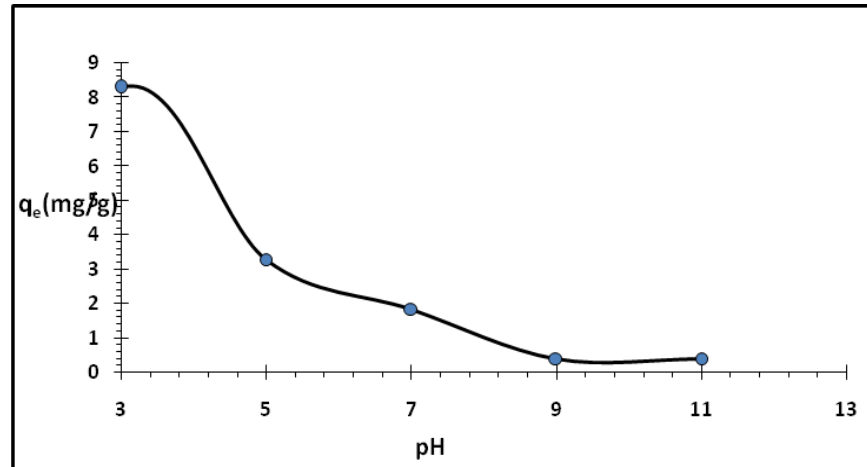


Figure 5: Effect of pH on freema adsorption

3.4 Effect of adsorbent dose

Figure 6 shows the graph of amount adsorbed against mass of adsorbent. The graph indicates that the amount of adsorption increases with increase in mass of adsorbent (between 0.2 – 1.0 g). The graph shows that the increase in amount adsorbed is little at higher dose of adsorbent.

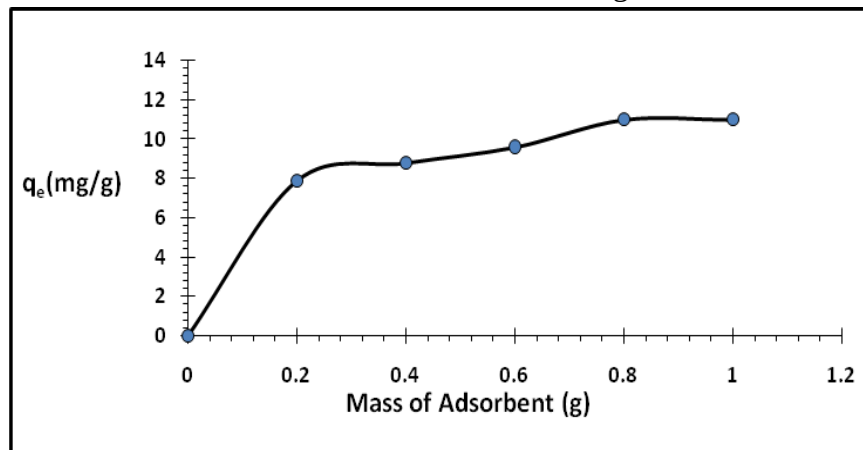


Figure 6: Effect of adsorbent dose on adsorption

3.5 Effect of temperature

The effect of temperature was carried at temperatures of 40 °C, 50 °C, 60 °C, 70 °C and 80 °C at pH 3 and at concentration of 50mg/L. The graph in figure 7 shows that the amount adsorbed decreases with increase in temperature within 40 - 80 °C.

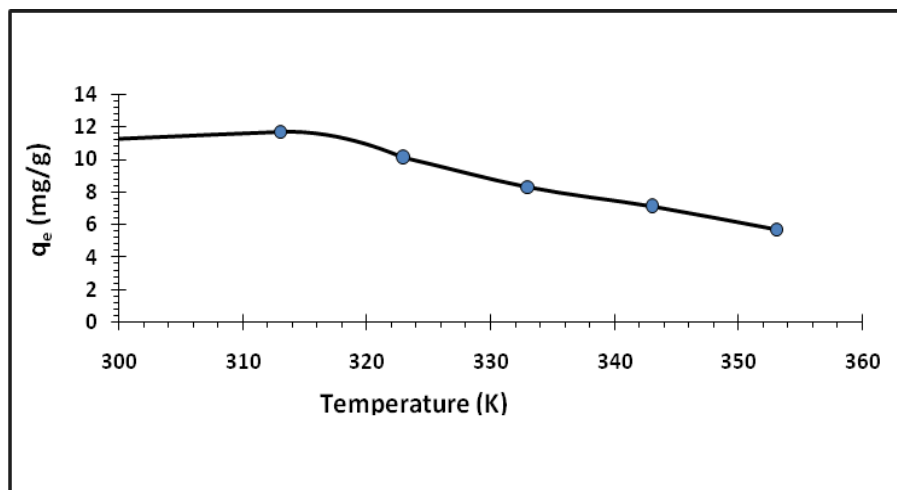


Figure 7: Effect of temperature on adsorption of freema

3.6 Adsorption Isotherms

Adsorption is a surface phenomenon in which some materials (adsorbate) is concentrated from a bulk vapor or liquid phase on to the surface of a porous solid (adsorbent). Usually the amount adsorbed is only a fraction of a monolayer. Thus to adsorb a substantial amount of material, the adsorbent must have a large specific surface area (Hirasaki, 1993). The two major adsorption isotherm models are Freundlich and Langmuir models.

The adsorption isotherm is an equation relating the amount of solute adsorbed onto the solid and equilibrium concentration of solute in solution at constant temperature. Several isotherm equations are available. In this study, the adsorption data correlated with the Freundlich (Freundlich, 1906) and Langmuir (Ozacar and Sengil, 2003) models. Often the amount adsorbed is measured as a function of the partial pressure or concentration at a given temperature and the result expressed as an adsorption isotherm.

i. The Freundlich Isotherm:

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 for the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich equation 3 in its linearized form is expressed as follows: (Freundlich, 1906)

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), K_f the Freundlich constant, $\left(\frac{1}{n}\right)$ is the heterogeneity factor, which is related to the capacity and intensity of the adsorption respectively, and C_e is the equilibrium concentration (mg/L). The value of K_f and $\left(\frac{1}{n}\right)$ can be obtained from the slope and intercept of the plots of $\ln q_e$ against $\ln C_e$.

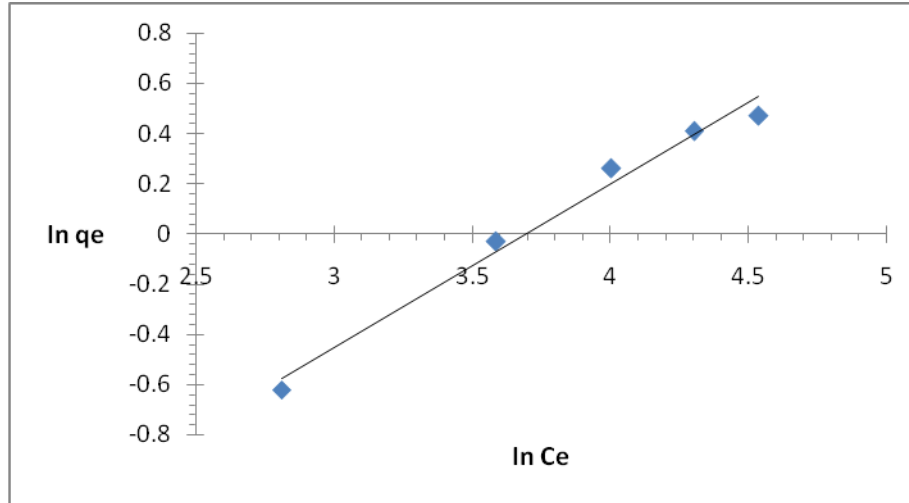


Figure 8: Freundlich Isotherm model for freema adsorption

ii. The Langmuir Isotherm:

Langmuir isotherm is considered a best model that accounts on 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 follows: (Langmuir, 1918) equation (4).

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (4)$$

Where C_e and q_e has usual meaning and q_m and b are the Langmuir constant related to the capacity and energy of adsorption respectively.

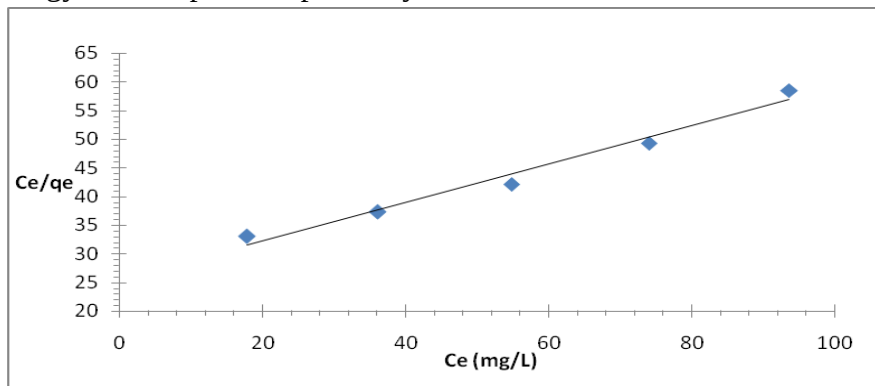


Figure 8: Langmuir Isotherm for freema adsorption

The experimental data on the effect of initial concentration on the adsorption of dyes was fitted into the Freundlich and Langmuir adsorption isotherm model represented in Figures 8 and 9 respectively. The R^2 values for Freundlich and Langmuir are 0.983 and 0.9777 respectively. This

indicates that the adsorption process is more fitted into the Freundlich isotherm than the Langmuir isotherm.

Table 1: The values of parameters and correlation coefficient for each isotherm model

Freundlich		Langmuir	
R^2	0.983	R^2	0.933
K_f	11.019	q_m	2.999
N	1.541	b	0.013

3.7 Adsorption Kinetics

Kinetics is key factor for adsorption investigation because it can predict the rate at which a pollutant is removed from aqueous solutions and provides valuable data for understanding the mechanism of adsorption process. Adsorption of organic dyes on metal oxide surface is influenced by three mass transfer processes which are external diffusion of dye molecules from liquid phase to the solid surface, intraparticle diffusion of dye molecules in the interior pores and actual adsorption (El Gamal *et al.*, 2015).

Several models are available to investigate the adsorption mechanism such as pseudo-first-order, pseudosecond-order, intramolecular diffusion and Elovich models. The pseudo-first-order adsorption rate (Lagergren, 1989) and pseudo-second-order adsorption rate developed by Ho and McKay (Ho & McKay, 1999) have the following linear forms.

Pseudo-first-order equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots \dots \dots 5$$

Pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots 6$$

Where k_1 and k_2 are rate constants of adsorption, q_t is adsorption capacity at time t , q_e is the adsorption capacity at equilibrium condition.

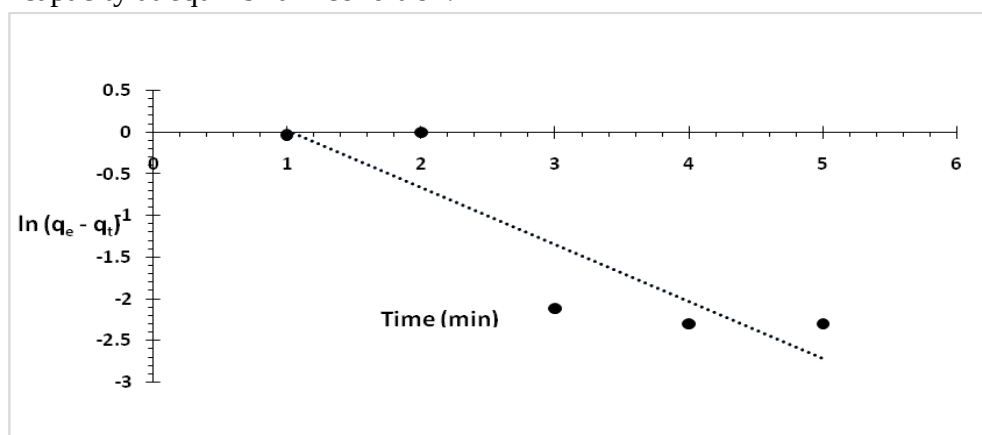


Figure 8: Pseudo-first Order Kinetics for freema adsorption

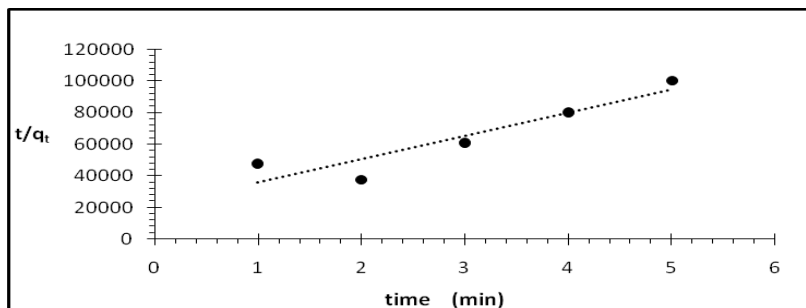


Figure 9: Pseudo-second order kinetics for freema adsorption

The R^2 value for Pseudo-first Order is 0.7846 (Fig. 9) while the R^2 value for Pseudo-Second Order is 0.8586 (Fig. 9). The comparison of the R^2 values shows that the adsorption process follows the Pseudo-second order kinetics suggesting that chemisorption and internal and external mass transfer mechanisms were important factors in the adsorption process.

Table 2: Kinetic parameters of the pseudo-first order and pseudo-second order

Pseudo-first order		Pseudo-second order	
R^2	0.7846	R^2	0.8586
Q_e	2.018	Q_e	0.00007
K_1	-0.684	K_2	10,000

3.8 Adsorption Thermodynamics

The variation of the adsorption capacity with temperature usually is used to give an account on the favourability of the adsorption process. Thermodynamic parameters were calculated by the Van't Hoff's equation which is expressed in equation 7

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

Where ΔH is the change in enthalpy, ΔS is the change in entropy, T is absolute temperature while K_e and R are constants.

Also, the Gibbs free energy change ΔG was calculated using the equation (8).

$$\Delta G = -RT \ln K_e \quad (8)$$

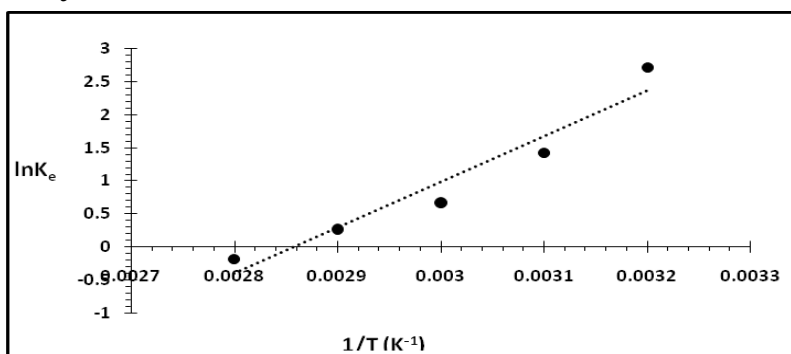


Figure 10: $\ln K_e$ vs $1/T$ of the thermodynamics of freema adsorption process

From Figure 10, the values of the other thermodynamic parameters like ΔG , ΔH and ΔS are calculated from the slope and the intercept.

The ΔH value is -57.449KJ/mol while the value for ΔS is -0.164KJ/mol/K. The negative value of ΔH indicates that the adsorption is exothermic in nature. In comparison with Mafra et al (2013) in the Adsorption of Remazol Brilliant Blue on an Orange peel Adsorbent. The values of ΔH obtained are positive which indicates that the adsorption process is endothermic. This is as a result of the increase in the amount adsorbed with increase in temperature leading to decrease in Gibbs Free Energy Change.

Table 3: Change in Gibbs free energy (ΔG) at various temperature.

Temperature ($^{\circ}$ K)	ΔG (KJ/mol)
313	-3070
323	-4428
333	-2287
343	-1145
353	495

The Change in Gibbs free energy (ΔG) of the adsorption process at different temperatures is initially negative from temperatures from 313K to 343K but becomes positive at temperature of 353K. The negative values of (ΔG) shows that the adsorption is spontaneous. It is observed that the (ΔG) values increases with increase in temperature, which indicates that increase in temperature does not favour the adsorption process.

Table 4: Thermodynamic Data of Adsorption Process

ΔH (KJ/mol)	-57.449
ΔS (KJ/mol)	-0.164
R^2	0.9367

4. Conclusion

The batch study of adsorption capacity of combination of Tartrazine and Sunset Yellow) on adsorbent made from pods of moringa has been carried out. The experimental data obtained shows that the adsorption capacity of moringa pod depends on parameters like temperature, time, pH and Initial concentration. The time required to reach equilibrium is 60 mins, and the adsorption capacity was at maximum pH 3. The adsorption fitted on both Freundlich and Langmuir isotherms with R^2 values 0.983 and 0.9777 respectively but best fitted with Freundlich with R^2 value 0.983. The thermodynamics of the adsorption indicates that the process is exothermic due to the negative values of ΔH , ΔS value is also found to be negative. The negative

value of ΔG indicates that the adsorption is spontaneous but the increase in values of ΔG with increase in temperature shows that the increase in temperature does not favour the adsorption process.

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