Adsorptive removal of cationic dye from aqueous solution using chemically modified African Border Tree (*Newbouldia laevis)* bark

*[1]AJAELU, C JOHN ; [1]NWOSU,VIVIAN; [1] IBIRONKE, LARA;[1]ADELEYE, ADEBAYO

[1]Department of Chemistry and Industrial Chemistry, Bowen University, Iwo, Nigeria
[*]Corresponding Author Address: ajaelujohn46@gmail.com

ABSTRACT: This study investigated the biosorption efficiency of sodium hydroxide modified African Border tree (SMABT) bark powder on Safranin O, a cationic dye. The SMABT was characterized by Fourier Transform Infrared Spectroscopy (FTIR). As the initial dye concentration increased, the amount of Safranin O removed increased. The kinetic studies were described by pseudo first order and pseudo second order. The pseudo second order fitted very well into the kinetic experimental data. Freundlich, Langmuir, Temkin and Dubinin–Radushkevich (D–R) models were employed to describe the adsorption of Safranin O to SMABT and also to evaluate the isotherm constants. Langmuir model was the best of the four to excellently fit into the experimental data. The maximum uptake capacity of SMABT for Safranin O dye was 90.9 mg/g.

Rapid industrialization has increase the presence of dyes in the environment. These dyes are produced or used by industries such as food, pharmaceutical, cosmetic, dyestuffs, textile, paper and plastics. The dye effluents from these industries result in coloured wastewater. It was found that colour was the first contaminant to be recognized in wastewater (Banat et al., 1996). Many of the dyes are toxic and carcinogenic and these pose a serious hazard to aquatic living organisms (Vijayaraghavan and Yun 2008). Dyes also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem (Walsh *et al*., 1980). In addition, dyes have a tendency to sequester metal and may cause microtoxicity to fish and other organisms (Walsh et al., 1980).

Diverse but expensive methods which have been used to remove dyes include flocculation, oxidation, irradiation, electrolysis, precipitation, ozonation, ion exchange, membrane filtration, electrochemical destruction and activated carbon. Among the various methods of dye removal, the use of agricultural materials, also known as biosorption, has been proven to be superior since it is more cost effective, efficient, readily available, generates no sludge or by products. Some of the adsorbents that have been used to remove dyes include *Cassia siamea* (Ajaelu *et al*., 2011), *Mangifera indica* (Ajaelu *et al*. 2015), watermelon (Ahmad *et al*., 2015), *Senna alata* (Ajaelu et al. 2017), *Moringa oleifera* (Bello *et al*.

2017), Walnut shell (Ojo *et al*. 2017), Corn cob (Ojedokun and Bello 2017). Safranin-O, also known as basic red 2, is a basic dye. Basically, Safranins are the azonium compounds of symmetrical3,7-Diamino-2,8-dimethyl-5-phenylphenazin-5-ium   chloride**.** Safranin-O is widely used in textile industry and it creates hazard due to its disposal into water bodies (Daru, 2005). African border tree is also known as *Newbouldia laevis* with lush, tropical looking leaves and pink flower. It belongs to the shrub category and the family Bignoniaceae. In this study chemically modified *African Border Tree* (SMABT) was used to remove Safranin O, a cationic basic dye, from simulated waste water.

MATERIALS AND METHODS

The African Border Tree bark was obtained from Iwo town in Osun State. The Safranin O, sodium chloride, sodium hydroxide and hydrochloric acid used were of analytical grade. Distilled water was used throughout this study. Fig 1 shows the chemical structure of Safranin O.

The African Border Tree bark was washed to remove sand and air dried after which it was oven-dried at 105°C overnight. It was then ground and screened through a 1mm sieve to obtain the geometric size. 25 g of the African Border Tree was mixed with 0.5 M NaOH in the ratio of 1:20 under agitation in a Stuart Orbital Electrical Shaker for 1h. The modified sample was then washed with distilled water and dried at 105°C. The modified sample was called

[*]Corresponding Author Address: ajaelujohn46@gmail.com

sodium hydroxide modified African Border Tree (SMABT) and stored in an air tight plastic bag.

Instrumental analysis of SMABT: The functional groups on the surfaces of SMABT was analyzed by Fourier Transform Infrared Spectrophotometer, Agilent Technologies Cary 630 FTIR spectrometer. A sample press, which is part of the ATR interface, was used to ensure that the ground SMABT was in good contact with the sensor surface. Scanning range in the region of 4,000–650 cm^{-1} at 4 cm^{-1} resolution.

Batch Adsorption studies: Adsorption studies were carried out by determining the solution pH, initial Safranin O concentration, mass of adsorbent and contact time. The solution pH was adjusted by adding either 0.1 M NaOH or 0.1 M HCl solutions before adsorption experiment. Batched adsorption studies were carried out in a 250 mL standard flask using 20 mL Safranin O solution, with required dosage of adsorbent at 25 °C. The flasks were placed on an electric shaker running at 300 rpm until adsorption equilibrium was obtained. The concentration of Safranin O was determined using a Jenway_6305 ultraviolet spectrophotometer. All the experiments were performed in duplicate and the mean value was taken for later calculation.

Adsorption capacity of the SMABT was calculated using the following expression:

$$q_e = \frac{(C_o - C_e)V}{w} \qquad (1)$$

$$\% \text{ sorption capacity} = \frac{(C_o - C_e)}{C_o} x100 \qquad (2)$$

Where q_e (mg/g) represents the amount of adsorbed Safranin O per amount of adsorbent, C_e (mg/L) is the equilibrium concentration of Safranin O in solution while C_o (mg/L) is the initial concentration of Safranin O in solution; V is the volume of the solution, L; m is the mass (g) of the SMABT.

Determination of pH point of zero charge: 10 ml of already prepared 0.5M NaCl was poured into eleven 250 ml beakers each and the pH was conditioned to different pH ranging from 2 to 12 by adding drops of NaOH (to increase) or HCl (to decrease). 0.1 g of the SMABT was then poured into each of the pH conditioned NaCl solutions. The beakers were covered and kept for 24 hrs after which their pHs were taken and recorded.

RESULTS AND DISCUSSION

Characterization of SMABT: FTIR spectrum (Fig.2) of SMABT after adsorbing Safranin O dye indicated that there are existences of some functional groups

responsible for adsorption. A strong and broad band appeared at 3338 cm^{-1} and is attributed to the OH-stretching vibration. The absorption band at 2898 cm^{-1} was attributed to C-H stretching vibration of alkane. The absorption value at 1593 cm^{-1} was assigned to antisymmetric stretching of COO- group**.** The vibrational absorption band at 1420 and 1459 cm^{-1} were both assigned to the OH bending. This indicates that adsorption occurred through the interaction of the cationic dye (Safranin O) with the OH and COO- functional groups on the surface of SMABT.

pH point of zero charge: The pH point of zero charge (pH_{PZC}) of SMABT was obtained and the result is presented in Figure 2. The SMABT pH_{PZC} obtained was 8.0. Anion adsorption is favoured at pH values lower than the pH_{PZC} while cation adsorption is favoured by pH values higher than the pH_{PZC} (Farahani *et al*. 2011).
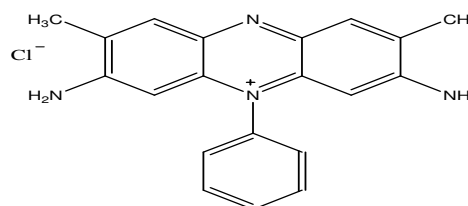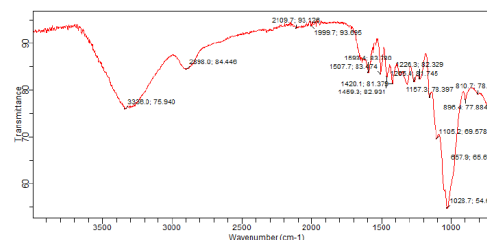

Fig. 1 Chemical Structure of Safranin O

Fig. 2 FTIR of sodium hydroxide modified *African Border Tree* (SMABT)

Effect of pH: The concentration of ions is considered as one of the vital parameters that influences the adsorption of dyes in aqueous solution. The percentage adsorption capacity of SMABT for Safranin O decreased gradually with increase in the pH from 2 to 12 as shown in Fig. 3. Similar result was obtained by Bello *et al*., (2017). The difference in the adsorption capacity as the pH increases may be due to the formation of different ionic species and surface charges. Fig. 4 shows the effect of pH point of zero charge on SMABT. The pHpzc obtained for SMABT was 8. When the pH_{PZC} is higher than the pH value, the Safranin O dye is of monomeric molecular and cationic forms (Deshpande *et al*., 2002). Thus the dye can easily access the adsorbent pore structure. When the pH_{PZC} is lower than the pH value, there is

the existence of zwitterion form of Safranin O dyes in the solution mixture. This form leads to the dimerization of the Safranin O dye molecules. These Safranin O (dimerized) molecules are unable to access the pores of the adsorbent because of their size, thus resulting in the decrease in the adsorption capacity as the pH increases. Ghanadzadeh *et al*. (2002) obtained similar result on the aggregation of rhodamin B dye on microporous solid host.

*Effect of mass of biomass***:** The mass of biomass plays a vital role in the adsorption of dyes. Fig. 5 shows the graph of q_e against mass of biomass. At higher SMABT to Safranin O concentration ratio, the sorption of the dye is higher. When the SMABT to Safranin O concentration ratio is lower, there is slow

superficial sorption onto the adsorbent surface which is as a result of higher concentration of solute (Safranin O) remaining in solution. In addition, a specific amount of SMABT adsorbent can only adsorb a specific amount of Safranin O. The decrease in the amount of Safranin O adsorbed at the SMABT surface with increase in adsorbent dose is due to the concentration gradient or split in the flux between Safranin O dye concentration in the solution and the Safranin O concentration on the surface of SMABT. Therefore, the amount of Safranin O dye adsorbed onto unit mass of adsorbent (SMABT) decreased with increasing adsorbent weight, thus causing a reduction in amount of dye adsorbed (q_e) as the mass of adsorbent increases. Zafar *et al.,* (2006) obtained similar results.
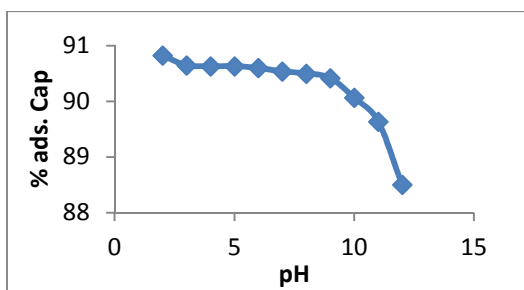

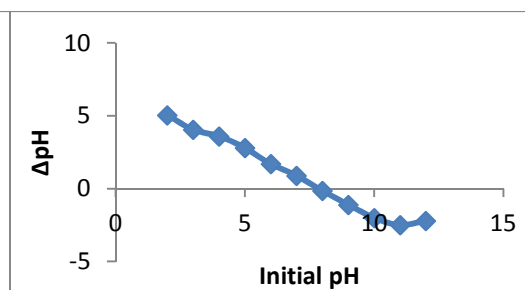**Fig. 3** The effect of pH on the adsorption of Safranin O on SMABT

Fig. 4 The effect of pH point of zero charge on the adsorption of Safranin O on SMABT

Effect of initial dye concentration: Initial concentration of dyes affects its adsorption unto an adsorbent. At the early stage, the surface of the SMABT is devoid of Safranin O. Then the amount of Safranin O begins to increase on the surface of the SMABT. Desorption of Safranin O also occurs until equilibrium is attained when the rate of adsorption equals the rate of desorption of Safranin O. In Fig. 6 it can be seen that the adsorption of Safranin O unto SMABT increases with increase in the initial concentration of the dye. At 20 mg/L the adsorption capacity was 3.93 mg/L while at 120 mg/L it was 22.1 mg/L.

Adsorption kinetic studies: Kinetics studies of adsorption is very vital for it makes available valuable information on dye adsorption mechanism

of reaction. To determine the kinetics of the adsorption of Safranin O on SMABT, two kinetic models, Langergren first-order and pseudo- second order, were employed. The Langergren pseudo-first order equation is given below:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

Where q_e (mg/g) and q (mg/g) are the biosorption capacities of the biosorbent at equilibrium and at any time t, respectively; k_1 is the langergren rate constant of the pseudo- first order biosorption. The plots of log (q_e-q) versus t (min) for different Safranin O concentrations give straight lines (Figure not shown). From the plots, k_1 and q_e are determined from the slope and intercept respectively as shown in Table 1.

Table 1: The parameters for pseudo-first and pseudo-second order kinetic models for the adsorption of Safranin O on SMABT

Parameters	20 mg/L	40 mg/L	60mg/L	80 mg/L	100mg/L	120mg/L
		Pseudo-first order				
$q_{e(exp)}$	23.5	36.6	58.7	78.4	96.9	116
$q_{e(calc)}$	13.2	11.4	7.44	14.5	21.6	9.95
$k_1 \times 10^{-3}$ (min^{-1})	0	2.0	0	2.0	4.0	0.01
SSE	6.88	19.3	36.3	45.2	53.3	75.0
		Pseudo-second order				
$q_{e(calc)}$	23.5	38.6	58.7	76.9	100	111
$k_2 \times 10^{-4}$ (gmg^{-1}min)	2.07	0.82	4.0	0.13	0.03	0.05
R^2	1	1	0.999	1	1	1
SSE	0.20	0.13	0.06	1.04	2.18	3.54

AJAELU C. JOHN, NWOSU VIVIAN, IBIRONKE L, ADELEYE M. A.

The linearized form of the pseudo-second order kinetic

Model is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \qquad (4)$$

The plot of t/qt against t(s) as reflected in Fig. 7 shows that pseudo second order model is a better model for describing the adsorption kinetics of Safranin O on SMABT because it has high R^2 values ($R^2 \geq 0.999$) and its q_{calc} are very close to that of the q_{exp} as compared to that of pseudo first order model.

Adsorption Isotherm: Four isotherms, namely Freundlich, Langmuir, Temkin and Dubinin–Radushkevich isotherms were employed to illustrate the observed experimental adsorption equilibrium data. The isotherms are stated below:

The Freundlich isotherm: The Freundlich equation is an empirical equation applied to describe heterogeneous systems. It is represented as

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \qquad (5)$$

Where k_F (Lg^{-1}) is associated with the adsorption capacity. Freundlich isotherm is shown in Figure 8 while the results are reported in Table 2. The R^2 value of Freundlich isotherm is lower than that of Langmuir but higher than that of Temkin and D-R. The value n gives an indication of the favourability of the adsorption process. When the value of n is less than 1 the adsorption is said to be unfavourable, but if it is greater than 1 it is favorable (Xiong et al. 2010). The value of n obtained in this study is greater than 1 which indicates that the adsorption process is favorable.

The Langmuir isotherm model: The Langmuir isotherm model for monolayer adsorption has gained wide application to dye sorption process. It is applicable to homogeneous systems where there is no interaction between the adsorbate molecules (Foletto

et al. 2011). The linear form of the equation is

$$\frac{C_e}{q_e} = \frac{1}{A_o b} + \frac{C_e}{A_o} \qquad (6)$$

Where A_o is the Langmuir maximum adsorption capacity (mg/g) and b is the Langmuir constant related to the binding site affinity and the adsorption energy in Lmol^{-1}, q_e, is the adsorption capacity at equilibrium (mg/g) and C_e is the equilibrium concentration of Safranin O (mg/L) in solution. From Table 2, the maximum adsorption capacity for the adsorption of Safranin O unto SMABT is 90.9 mg/L. Langmuir isotherm is shown in Fig. 9. The correlation factor of Langmuir isotherm showed that it gives a very good fit and it is the best among the four isotherms for describing the adsorption of Safranin O on SMABT. A dimensionless equilibrium parameter, E_L, is one of the vital characteristics of Langmuir equation. It is expressed as

$$E_L = \frac{1}{(1 + aC_o)} \qquad (7)$$

Where a is the Langmuir equilibrium constant in Lmol^{-1} and C_o is the initial dye concentration in mg/L. E_L value of 0.003 which is between 0 and 1 shows that the adsorption of Safranin O unto SMABT is favourable.

Temkin isotherm

Temkin isotherm is characterized by the uniform distribution of binding energy [Yang et al. 2011]. The linear form of the equation is given

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \qquad (8)$$

$$B = \frac{RT}{b} \qquad (9)$$

Therefore, $q_e = B \ln A + B \ln C_e \qquad (10)$

The graph of q_e against $\ln C_e$ in Fig. 10 shows a very good fit. The values of A, Temkin isotherm equilibrium binding constant (Lg^{-1}), and B, Temkin equilibrium constant which corresponds to the variation of adsorption energy (kJmol^{-1}), are shown in Table 2.
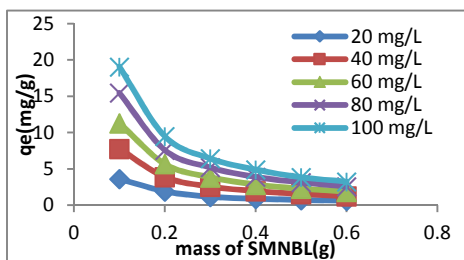

Fig. 5 Effect of mass of modified African Border Tree (SMABT) on the adsorption of Safranin O
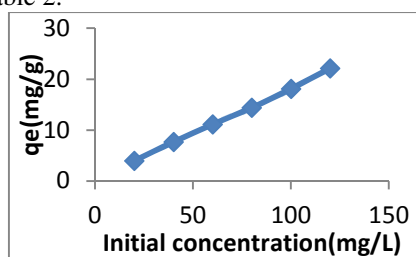

Fig.6 Effect of initial concentration on the adsorption of Safranin O on SMABT

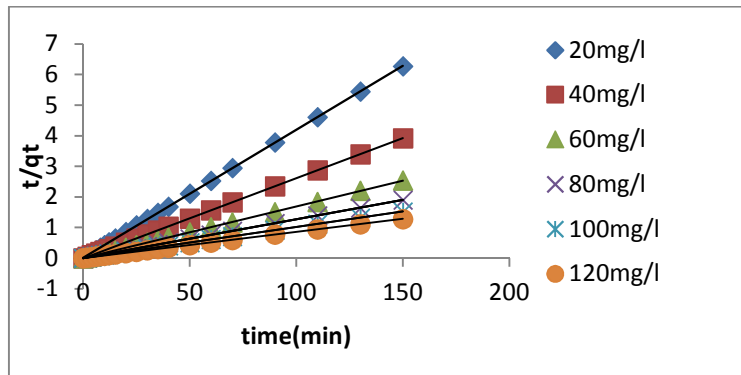*AJAELU C. JOHN, NWOSU VIVIAN, IBIRONKE L, ADELEYE M. A.*

Fig.7 Pseudo second order kinetics for the adsorption of Safranin O on SMABT

Dubinin–Radushkevich (D–R) isotherm: The Dubinin–Radushkevich (D–R) isotherm is more inclusive than the Langmuir isotherm for it does not assume a homogenous surface or constant sorption potential (Carzon et al. 2012). It is used for the estimation of the characteristic porosity of the biomass as well as the mean free energy of adsorption. The equation is given by

$$\ln q_e = \ln q_x - \beta \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \qquad (11)$$

where q_e is the amount of Safranin O adsorbed at equilibrium, β is a constant related to the adsorption

energy, q_x is the maximum adsorption capacity, ε is the Polanyi potential, that is equal to

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \qquad (12)$$

The linear form of Eq. (10) is,
$$\ln q_e = \ln q_x - \beta \varepsilon^2 \qquad (13)$$

Table 2 gives the R^2 value for the plot of q_e against ε^2. The q_x and β values in Table 2 were calculated from the slope and intercept of the plots (Fig. 11).
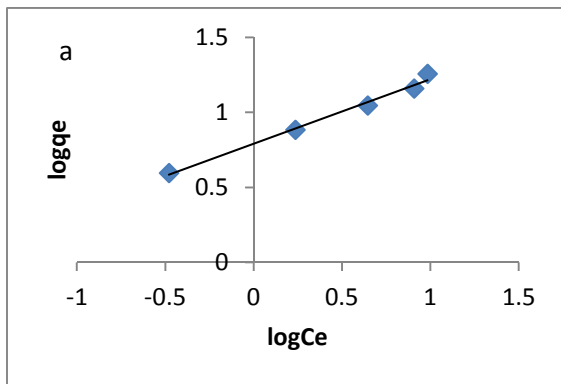

Fig. 8: Freundlich isotherm for the adsorption of Safranin O on modified African Border Tree
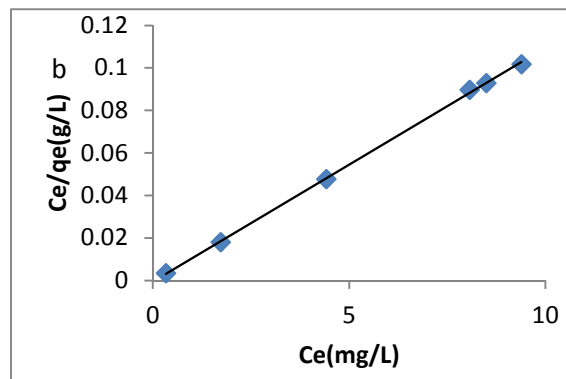

Fig. 9: Langmuir isotherms for the adsorption of   Safranin O on modified African Border Tree

Table 2: Freundlich, Langmuir, Temkin and Dubinin–Radushkevich Isotherms for the adsorption of Safranin O on modified African Border Tree

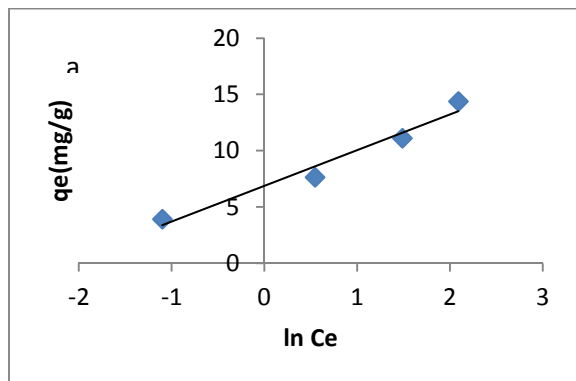| Freundlich	Langmuir	Temkin	D-R
$K_F = 6.17$	$A_o = 90.9$ mg/g	$A = 8.84$ mg/g	$q_x = 2.86$ mg/g
$n = 2.32$	$b = 18.3$ L/mg	$B = 793.6$	$\beta = 3.0 \times 10^{-4}$
$R^2 = 0.988$	$R^2 = 0.999$	$R^2 = 0.96$	$E = 26.7$ kJ/mol
	$E_L = 0.003$		$R^2 = 0.788$

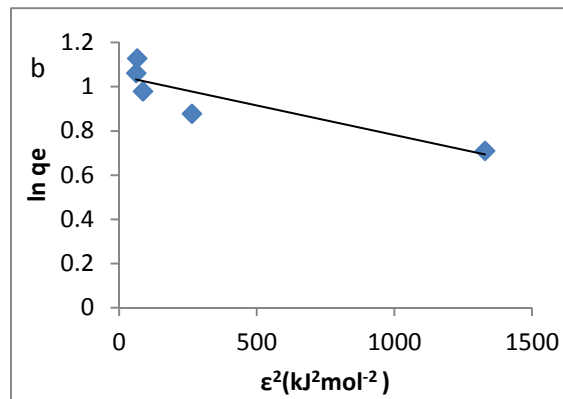**Fig. 10** Temkin isotherm for the adsorption of Safranin O

on SMABT

Fig. 11: Dubinin–Radushkevich (D–R) isotherm for the adsorption of Safranin O on SMABT

Table 3: Adsorption capacities of some adsorbents unto Safranin O dyes

Adsorbent(s)	Adsorption Capacity(mg/g)	Reference
Alkali-treated Rice Husk	9.77	Chowdhury.et,al 2011
Pretreated Rice Husk	45.58	Chowdhury.et.al 2011
Alkali–treated Mango Seed	31	Maekbala.,et.al 2012
Walnut shell	40	Zaghbani.,et.al 2008
Guava leave	47.62	Ojedokun and Bello 2017
NaOH-treated rice Husk	37.97	Chowdhury.et.al 2012
Pineapple peels	21.7	Mohammad.,et.al 2014
Senna alata	23.8	Ajaelu et al. 2017
Sodium hydroxide modified		
African Border Tree	90.9 mg/g	This study

The mean free energy of biosorption, E, was obtained from the equation

$$E = 1/\sqrt{2\beta} \qquad (14)$$

The magnitude of *E* value gives information about the biosorption mechanism as chemical ion-exchange or physical sorption. As reported by Atkins (2006), physisorption, is due to weak van der Waal forces between the adsorbent and the adsorbate. The magnitude of the energy of physisorption is in the region of less than 20 kJ/mol. Atkins further stated that covalent bond exist between the adsorbate and the adsorbent in chemisorption in which the substrate (adsorbent) is limited to monolayer coverage. The value of E, the mean free energy of biosorption, obtained in this study as reflected in Table 3 was higher than 20 kJ/mol, and Langmuir isotherm (monolayer coverage) best fitted the surface coverage in this study. Similar result was obtained by Adebowale et al. (2014). The correlation factors of the four equilibrium models decreased as follows: Langmuir (0.999) > Freundlich (0.988) > Temkin(0.96) > D-R (0.76). Thus the D-R is not suitable for the description of the adsorption of Safranin O on SMABT. A comparison of the adsorption capacities of some adsorbents on Safranin O is presented in Table 3. The Table showed that SMABT was effective in the removal of Safranin O as compared to some other adsorbents.

*Conclusion***:** The current study revealed that the chemically modified African Border Tree can be used as an adsorbent for the removal of Safranin O from waste water. The optimum operational pH was evaluated as 7. The amount of dye removed increased with increase in the initial concentration of the dye. Kinetic studies showed that pseudo second order was the best for describing the removal of Safranin O using SMABT. Langmuir isotherm also had the highest correlation factor, thus it was the best for describing the equilibrum process.

REFERENCES

Ahmad M. A, Ahmad, N and Bello O. S (2015). Removal of Remazol Brilliant Blue Reactive Dye from Aqueous Solutions Using Watermelon Rinds as Adsorbent. J. Disp. Sci. Technol. 36:845–858, 2015.

Ajaelu, C.J, Ibironke, L, Adedeji, V, Oladunni O (2011). Equilibrium and Kinetic Studies of the Biosorption of Heavy Metal (Cadmium) on *Cassia siamea* Bark. *Am-Eur. J. Sci. Res*. 6(3): 123-130.

Ajaelu C. J, Atolaiye B, Ibironke L, Alao O. A. (2015). Kinetics, equilibrium and thermodynamics of heavy metal ion sequestration onto mango seed biomass (*Mangifera indica*). *J. Chem. Pharmaceutical Res*. 7 (605-617)

Ajaelu C.J, Dawodu M.O, Faboro E.O, Ayanda O.S(2017). Copper Biosorption by Untreated and Citric Acid Modified *Senna alata* Leaf Biomass in a Batch System: Kinetics, Equilibrium and Thermodynamics Studies. Physical Chemistry, 7(2): 31-41.

Atkins P, Paula J. (2006). The extent of adsorption. Atkin's Physical Chemistry. 8th Ed. Pp 916-918.

Bello O.S, Lasisi B.M, Adigun O. J, Ephraim V. (2017). Scavenging Rhodamin B dye using *Moringer oleifera* seed pod. Chem. Specn. and Bioavail. 29(1): 120-134.

Cazón, JP; Bernardelli, C; Viera, M; Donati, E; Guibal E (2012). Zinc and cadmium biosorption by untreated and calcium-treated *Macrocystis pyrifera* in a batch system. *Bioresource Technology* 116: 195–203.

Chowdury. S, Mishra. R, Kushwara. P, and Das P. (2011). Adsorption of dyes on activated carbons: influence of surface chemical groups. Biorem. J., 15, 77-89.

Chowdury. S, Mishra. R, Kushwara. P; Saha. P (2012). Colour removal from industrial effluents a comparative review of available technologies. *Asia-Pa4c. J-Chem En*g. 7: 236-29

Daru.U. (2005). Chromate removal from water using red mud and crossflow microfiltration, *Desalination*, 181,135-143.

Deshpande A.V, Kumar U. (2002). Effect of method of preparation on photophysical properties of Rh B impregnated sol-gel host. *J. Non-cryst*. Solids. 306(2): 149-159.

Foletto, E.L.; Collazzo, G.C.; Mazutti, M.A.; Jahn, S.L. (2011) Adsorption of textile dye on zinc stannate oxide: Equilibrium, kinetic and thermodynamics studies. *Sep. Sci. Technol*., 46: 2510.

Ghanadzadeh A, Zanjanch M.A, Tribandpay R. (2002). The role of host environment on the aggregation properties of some ionic dye materials. *J. Mol. Struct*. 616: 167-174.

Malekbala, M.R., Soltani, S.M., Yazdi, S.K. and Hosseini, S. (2012). Equilibrium and Kinetic Studies of Safranin Adsorption on Alkali-Treated Seed Integuments. International Journal of Chemical Engineering and Applications, 3, 160- 166.

Mohammed, M. A., Ibrahim, A., and Shitu, A (2014). Batch Removal of Hazardous Safranin-O in Wastewater Using Pineapple Peels as an Agricultural Waste Based Adsorbent. International Journal of Environmental Monitoring and Analysis. 2(3) : 28-133

Ojedokun, A.I, Bello O.S. (2016). Liquid phase adsorption of Congo red dye on functionalized corn cobs. Journal of Dipersion Sc. And Techn. 38(9): 1285-1294.

Ojo, T.A, Ojedokun A.I, Bello O.S. (2017). Functionalization of powdered walnut shell with orthophosphoric acid for Congo red dye removal. Particulate Science and Technology. 1-7.

Ojedokun A.T., Bello O. S. (2017a). Liquid phase adsorption of Congo red dye on functionalized corn cob. *J. Dispersion Sci. Technol*. 38(9): 1285-1294.

Ojedokun A.T., Bello O. S. (2017b). Kinetic modeling of liquid phase adsorption of Congo red dye using Guava seed based activated carbon. *Appl. Wat. Sci*.7: 1963-1977.

Vijayaraghavan, K. and Yun, Y.S. 2008. Bacterial biosorbents and biosorption. *Biotechnol. Adv*. 26, 266-291.

Walsh, G.E., Bahnar, L.H. and Horning, W.B., 1980. Toxicity of textile mill effluents to freshwater and estuarine algae, crustaceans and fishes. *Environ. Pollut*. A21, 169-179.

Xiong, L; Yang, Y, Mai, J, Sun, W, Zhang C, Wei, D, Chen, Q, Ni, J. (2010). Adsorption behavior of methylene blue onto titanate nanotubes, Chem. Eng. J. 156: 313–320.

Yang Y, Jin D, Wang G, Liu D, Jia X, Zhao Y. (2011) Biosorption of Acid Blue 25 byunmodified and CPC-modified biomass of Penicillium YW01: Kinetic study, equilibrium isotherm and FTIR analysis. *Colloids and Surfaces B: Biointerfaces* 88: 521– 526.

Zafar M. N., Nadeem R., Hanif M. A. (2006). Biosorption of nickel from protonated rice bran. J. Harz. Mat. 143(1-2): 478-485

Zaghbani. N, Hafiane. A; Dhahbi. M (2008). Removal of Safranin T from wastewater using micellar enhanced ultrafiltration. *Desalination,* 348–356.