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

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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.

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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 Safranin O, a cationic basic dye, from simulated waste water.
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:

\[ q_e = \frac{(C_o - C_e)V}{w} \]  
(1)

\[ \% \text{ sorption capacity} = \frac{(C_o - C_e)}{C_o} \times 100 \]  
(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, \( L \); \( w \) 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\text{PZC}) of SMABT was obtained and the result is presented in Figure 2. The SMABT pH\text{PZC} obtained was 8.0. Anion adsorption is favoured at pH values lower than the pH\text{PZC} while cation adsorption is favoured by pH values higher than the pH\text{PZC} (Farahani et al. 2011).

![Fig. 1 Chemical Structure of Safranin O](image1)

![Fig. 2 FTIR of sodium hydroxide modified African Border Tree (SMABT)](image2)

**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 pH\text{PZC} obtained for SMABT was 8. When the pH\text{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\text{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](image1)

**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:

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

(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.

| Parameters | 20 mg/L | 40 mg/L | 60 mg/L | 80 mg/L | 100 mg/L | 120 mg/L |
|------------|---------|---------|---------|---------|----------|----------|
| $q_{e(exp)}$ | 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     |
| SIE        | 6.88    | 19.3    | 36.3    | 45.2    | 53.3     | 75.0     |
| $q_{e(calc)}$ | 23.5    | 38.6    | 58.7    | 76.9    | 100      | 111      |
| $k_2 \times 10^4$ (gmg$^{-1}$min$^{-1}$) | 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     |

*Table 1: The parameters for pseudo-first and pseudo-second order kinetic models for the adsorption of Safranin O on SMABT*
The linearized form of the pseudo-second order kinetic model is expressed as

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \]  

(4)

The plot of \( \frac{t}{q_t} \) against \( t \) as reflected in Fig. 7 shows that the 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.

Adsortion 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

\[ \log q_e = \log k_F + \frac{1}{n} \log C_e \]  

(5)

Where \( k_F (\text{L}^g \text{mg}^{-1}) \) 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

\[ \frac{C_e}{q_e} = \frac{1}{A_o b} + \frac{C_e}{A_o} \]  

(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 \( \text{Lmol}^{-1} \), \( q_e \) 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

\[ E_L = \frac{1}{1 + aC_o} \]  

(7)

Where \( a \) is the Langmuir equilibrium constant in \( \text{Lmol}^{-1} \) 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

\[ q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \]  

(8)

\[ B = \frac{RT}{b} \]  

(9)

Therefore,

\[ q_e = B \ln A + B \ln C_e \]  

(10)

The graph of \( q_e \) against \( \ln C_e \) in Fig. 10 shows a very good fit. The values of \( A \), Temkin 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.
Adsorptive removal of cationic dye from aqueous solution

**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

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

(11)

where \(q_e\) is the amount of Safranin O adsorbed at equilibrium, \(\beta\) is a constant related to the adsorption energy, \(q_x\) is the maximum adsorption capacity, \(\varepsilon\) is the Polanyi potential, that is equal to

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]  

(12)

The linear form of Eq. (10) is,

\[
\ln q_e = \ln q_x - \beta \varepsilon^2
\]  

(13)

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

**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 |
|------------|----------|--------|-----|
| \(K_F = 6.17\) | \(A_r = 90.9 \text{ mg/g}\) | \(A = 8.84 \text{ mg/g}\) | \(q_L = 2.86 \text{ mg/g}\) |
| \(n = 2.32\) | \(b = 18.3 \text{ L/mg}\) | \(B = 793.6\) | \(\beta = 3.0 \times 10^4\) |
| \(R^2 = 0.988\) | \(R^2 = 0.999\) | \(R^2 = 0.96\) | \(E_L = 26.7 \text{ kJ/mol}\) |
| | | | \(R^2 = 0.788\) |
Adsorptive removal of cationic dye from aqueous solution

Fig. 10: Temkin isotherm for the adsorption of Safranin O on SMABT

![Graph](image)

**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. 2011 |
| Pineapple peels                  | 21.7                      | Mohammad et al. 2014 |
| *Senna alata*                    | 23.8                      | Ajaelu et al. 2017  |
| Sodium hydroxide modified        |                           | This study          |
| African Border Tree              | 90.9 mg/g                 |                    |

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

$$E = rac{1}{\sqrt{2\beta}}$$

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 equilibrium process.

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Adsorptive removal of cationic dye from aqueous solution

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