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Batch Adsorption of Safranin Dye from an Aqueous Solution of *Balanites aegyptiaca* Seed Coats

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Authors' contributions

This work was carried out in collaboration among all authors. Authors BM, Aisha U. Maigari and UAA designed, supervised and reviewed all the drafts of the manuscript. Authors MMS and Amina U. Maigari carried out the research and wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

This study was aimed at using *Balanite aegyptiaca* seed coats activated carbon (BAAC) as a potential adsorbent to remove safranin dye from aqueous solution. BAAC was prepared from *Balanite aegyptiaca* seed coats using a one-step procedure with 67.27% yield, 3.23% ash content, 695 m^2/g surface area and 203 mg/g iodine number. The FTIR spectroscopy revealed O-H, N-H, C-H, C=C, C-O-H stretching vibrations. The influences of agitation time, initial dye concentration and adsorbent dose were studied in batch experiments at room temperature. The adsorptions were rapid at the first 15 minutes of agitation, with the uptake of 2.746 mg/kg. The adsorption equilibrium was achieved at 90 minutes of agitation. Kinetic studies showed good correlation coefficient for both pseudo-first order and pseudo-second-order kinetics model but fitted well into pseudo-second order kinetic model. The adsorption data fitted well into Langmuir isotherm with correlation coefficient (R^2) very close to unity and Langmuir maximum adsorption constant, $q_m > 1.00$. Thus, the fitting into Langmuir indicates monolayer coverage on the adsorbents. The results showed that BAAC has the potential to be applied as alternative low-cost adsorbents in the remediation of dye contamination in wastewater.

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1. INTRODUCTION

In recent time an agricultural bye-product are not only bye product but they are a resourceful material especially in the production of activated carbon (AC). In developing countries, they are using agricultural bye-product in the production of activated carbon, especially in water treatment. Activated carbon is also called activated charcoal, is a form of carbon processed to have small, low volume pores that increase the surface area available for adsorption or chemical reaction. Activated carbon is a solid, porous and black carbonaceous material that has an essentially graphitic structure [1]. The removal of all non-carbon impurities and the oxidation of the carbon surface distinguished it from elemental carbon. Besides that, AC contains physical characteristics such as large internal surface area and pore volume. The large surface area results in a high capacity for adsorbing chemicals from gases or liquids.

Balanites aegyptiaca (Desert date) is one of the species that is widely distributed in dry land areas of Africa and South Asia [2]. It is very popular in traditional medicine for the treatment of various ailments such as fever, asthma, syphilis, epilepsy, jaundice, constipation, diarrhoea, stomach aches among others [2].

Adsorption is a process that occurs when gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent) forming a molecule or atomic film (adsorb ate). It is different from absorption in which absorption occurs when a substance diffuses into a solid to form a solution. The term sorption encompasses both processes while desorption is the reverse process.

The focus of this research work explored the feasibility of *Balanite aegyptiaca* seed coats activated carbon (BAAC) as a potential adsorbent to remove safranin dye from aqueous solution and optimize the adsorption conditions that will ensure high dyes uptake.

2. MATERIALS AND METHODS

2.1 Sample Preparation

The *B. aegyptiaca* seed coat sample used in this study was collected from Gombe main market Gombe, Gombe State, Nigeria. The choice of this material is based on its low cost, considering its abundance in the remote area. The sample was washed with distilled water to remove all impurities, it was then dried and crushed using a crusher. The crushed particle was sieved to obtain a particle size that range from 1 - 4 mm. the seed coats were dried at 50ºC for 48 h in an oven. The dried seed coats were subjected to alkali pretreatment under such condition; alkali concentration (3%) at a temperature 100ºC and pretreatment time 90 min.

2.2 Production of Activated Carbon

The activated carbon was produced by a slight modification of literature as reported by Abdus-Salam and Buhari [3] were by single-step production method which involves carbonization and activation by thermal decomposition of the raw materials that were already impregnated with the activating agent was adopted. A 70 g of the raw *B. aegyptiaca* seeds (BA) was soaked in 100 ml of 50% (v/v) H_3PO_4 acid at room temperature for 48 h, the phosphoric acid was decanted and the impregnated sample was washed thoroughly with deionized water until the pH reading was almost neutral. The impregnated raw material was carbonized in a muffle furnace at 400ºC for 120 min. After cooling, the carbonized material was weighed to determine percentage yield then pulverized to reduce the size and sieved using a 100 µm sized sieve. Thereafter, samples with diameter ≤ 100 µm were used for other determinations and experiments.

2.3 Determination of the Adsorption Capacity

Batch adsorption experiments were performed at room temperature according to a literature work [3] (25ºC) in a set of Erlenmeyer flasks (250 ml) where solutions of dye (50 ml) with different initial concentrations (2, 5, 10, 15, 20 and 30 mg/l) were contacted with 1 g of the adsorbent. The pH of the solutions was adjusted to the required value by adding either 0.1 M HCl or 0.1 M NaOH solution. The solutions were agitated in an incubator shaker for a period of 4 h. The concentration of Safranin dye in the supernatant solution before and after adsorption was determined using a Jenway 6405 UV/VIS spectrophotometer at maximum wavelength of 665 nm. A calibration curve of absorbance versa concentration was constructed using

spectrophotometric data. The percentage removal of dye was calculated using the following relationship

$$q_e = (C_i - C_f)/M \times V \quad (1)$$

Where q_e is the quantity of dye adsorbed (mg/l), C_i and C_f are the initial and final concentration of the dyes (mg/L), V is the volume of the standard solution used (ml) and M is the mass of the adsorbent (g) used.

2.4 Effect of Agitation Time

A 50 ml of each of the dye solution were measured into a 100 ml flask and contacted with 1 g of the adsorbent at room temperature. The flasks were labeled for time difference of 5, 10, 15, 30, 60 and 90 min and flasks were tightly covered and agitated for the appropriate time using incubator shaker. At the end of the timing scheduled each of the flasks were brought out and suspensions were filtered using Whatmann No. 1 filter paper. The un-adsorbed dye was determined with Jenway 6405 UV/Vis spectrophotometer. The quantity sorbed was calculated from Equation 1.

2.5 Effect of Adsorbent Dosage on Adsorption

The effect of adsorbent dosage on the adsorption of dye ions by the BAAC was performed according to a literature work [4]. A variable mass, 0.25, 0.5, 1, 1.5, and 2 g of the adsorbent were weighed into five different conical flasks. A 50 ml of the 30 mg/l of each dye solutions were measured into the two (2) sets of the five conical flasks (i.e., the experiment was performed on duplicate samples). The flask was labelled for dosage differences. The flasks were tightly covered and agitated for the appropriate time 90 minutes using incubator shaker. At the end of the timing scheduled each of the flasks were brought out and suspensions were filtered using Whitman No. 1 filter paper. The un-adsorbed dye was determined with Jenway 6405 UV/Vis spectrophotometer. The quantity sorbed was calculated from Equation 1.

2.5.1 Adsorption isotherms

Three isotherm equations were used to find out the relationship between the equilibrium concentration of the adsorbate in the liquid phase and in the solid phase. More importantly, to determine which of the isotherms best describes the adsorption process. Experimental data were substituted into the equations and appropriate graphs, constants and other variables were generated for each of the following equations:

a) Langmuir:

$$C_e/Q_e = 1/bq_m + 1/qm(C_e) \quad (2)$$

Where b (L/mg) and q_m (mg/g) are Langmuir coefficient representing the equilibrium constant for the adsorbate-adsorbent equilibrium and the monolayer capacity, C_e is the equilibrium concentration of the solute in the bulk solution (mg/l) and q_e is the amount of solute sorbed per unit weight of adsorbent at equilibrium (mg/g).

The plot of C_e/q_e versus C_e was plotted, the slope and the intercept are $1/q_m$ and $1/bq_m$ respectively.

b) Freundlich:- $K_f C_e^{1/n}$ (3)

The linearized form of Freundlich equation is:

$$\text{Loq } q_e = \log k_f + 1/n\log C_e \quad (4)$$

Where C_e and q_e are the equilibrium concentration of the dyes in liquid phase and in solid phase respectively, K_f and n are Freundlich coefficients relating to overall adsorption capacity (mg/g) and surface heterogeneity (dimensionless) respectively. The plot of log q_e versus C_e, the intercept of the graph is log K_f while the gradient is 1/n.

c) Temkin: $q_e = B\ln A + B\ln C_e$ (5)

Where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). The liberalized Langmuir, Freundlich and Temkin forms were used for graphical plots and the corresponding constants were obtained.

2.6 Kinetics Study

i) Pseudo-first order
ii) Pseudo-second order

3. RESULTS AND DISCUSSION

The study was carried out to determine the adsorption of Safranin dye from aqueous solution by *Balanite aegyptiaca* (Desert Date) seed coat.

The study involves characterization, kinetics and isotherm studies. Below are the results and findings of the study.

The physicochemical parameters of BAAC were determined and recorded in Table 1. The percentage yield was determined to be 50% which was slightly smaller than the yield reported by Abdus-Salam and Buhari [3] (62.27%), [5] (51%), and relatively higher than that of Faust and Aly [6] (46.08%). The pH of the BAAC was determined to be 6.1±0.20 which can be compared with 6.7±0.12 and 6.3.6.8 as obtained by Ekpete and Horsfall [7]. A carbon of pH 6-8 is acceptable for most application such as for sugar decolourization, water treatment etc. pH is affected not only by the reaction of carbon dioxide but also by organic and inorganic solutes present in water. Any alteration in water pH is accomplished by the change in other physicochemical parameters [8]. The moisture content in this research was found to be 15.6% which is relatively higher than that of 15.47% of [3] and 13.2% of Raffiea, et al. [9]. The low amount of moisture indicates that the particle density is relatively small and that the biomaterial should be an excellent raw material for adsorbents to be used in a column or fixed-bed reactors [7]. The Ash content of BAAC was found to be 10% and was a similar value reported by Hesas, et al. [10]. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated carbon for use as adsorbent [7]. The iodine number was determined to be 203.2±0.50 which can be compared with that of 224.90±0.50 of Ekpete and Horsfall [7]. Iodine number is a fundamental parameter used to characterize activated carbon performance. It is a measure of the microspore content of the activated carbon and is obtained by the adsorption of iodine from solution by the activated carbon sample. The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the microspores that adsorption largely takes place [7]. The Surface area was found to be 695 cm^3 which can be compared with that of Abdus-Salam and Buhari [3]. And the value reported is lower than that of 862 m^2/g [9] and 1141 m^2/g [11].

The result for Fourier-transform *infrared spectroscopy* (FTIR) spectra obtained (Table 2) was interpreted based on similar researches such as [12,13]. The FTIR spectra showed a peak at 3483.56 cm^{-1} which ascertain the presence of N-H group (including primary, sec. tertiary amines). The peak at 4424.85 cm^{-1} indicates the presence of O-H stretching. Also, the peak observed at 2932.86 cm^{-1} was attributed with the presence of stretching vibration C-H group such as methyl, methylene and methoxy group for most carbonaceous materials. The peak observed at 1647.26 cm^{-1} shows a prominent peak of C=C stretching vibration of alkene. The peak observed at 470.65 cm^{-1} indicates the presence of C-O-H twist bending vibration as shown in Table 1.

Table 1. Physico-chemical characterization of BAAC

Properties	Composition
Percentage yield (%)	50
pH	6.1
Moisture content (%)	16.3
Ash content (%)	10
Iodine number (mg/g)	203.2
Surface area (m^2/g)	695

Table 2. FTIR Spectrum of BAAC and their assignment

Peaks (cm^{-1})	Assignments
470.65	C-O-H twists
1647.26	C=C stretching vibration
2932.86	C-H assymetric stretching vibration
3483.56	N-H stretching vibration
4424.85	O-H stretching vibration

3.1 The Effect of Concentration

The effect of concentration shows that the influence of equilibrium concentration of the safranin dye followed similar trend Fig. 1. There was a general initial increase in adsorption of safranin dye with an increase in the equilibrium concentrations onto BAAC up to a concentration of 20 mg/L as the maximum quantity adsorbed when adsorption curves formed plateau after which the adsorption dropped. At lower initial concentrations. The initial increase also enhances the interactions between the BAAC surface and the dye molecules. These combine factors enhance the uptake of dye molecule from aqueous phase onto the BAAC. A similar result has been reported by Abdus-Salam and Buhari [3].

3.2 The Effect of Contact Time

The effect of contact time of safranin on BAAC is shown in Fig. 2. A biphasic kinetic was observed:

an initial fast phase (5–15 min) where adsorption was rapid and contributed essentially to the equilibrium uptake of the safranin dye (2674.35 mg/g and 2746.11 mg/g respectively); and a second slow phase (15–90 min) whose contribution to equilibrium was relatively smaller with total amount of safranin dye adsorbed as 2746.11 mg/g and 2799.54 mg/g, respectively. The first phase is an instantaneous phase which is caused by external adsorption on to BAAC. This was followed by a slow phase which was diffusion controlled phase. The process of agitation of the adsorbate-adsorbent phase tends exposing active surfaces which otherwise, may be inaccessible. A similar observation was earlier reported. The optimum time for adsorption of these dyes onto BAAC is 90 min similar result has been reported by Abdus-Salam and Buhari [3].

3.3 The Effect of Adsorbent Dose

The effect of adsorbent dose on the percentage removal of safranin dye was shown in Fig. 3. The equilibrium concentration of the dye decreased with the increase in the dose of the adsorbent. This may be due to the increase in the availability of surface active sites resulting from the increased dose of the adsorbent as shown in Fig. 4. While adsorbent dose increases from 0.25 to 2, the equilibrium concentration of the dye decreases from 5880-744.92 at equilibrium time.

3.4 Adsorption Isotherm

The adsorption isotherm gives information on how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process attains an equilibrium state. The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is known as adsorption isotherm. Langmuir, Freundlich and temkin adsorption isotherm models are employed in this study to describe the experimental adsorption isotherm. The applicability of the isotherm equations was compared by judging the coefficients of determination R^2. The data obtained from this research was fitted well into Langmuir isotherm for safranin dye as shown in Fig. 4 with regression coefficient, R^2, of 0.9872 which is in agreement with the findings of Gulen and Zorbay and Gulen and iskeceli [14,15]. The Freundlich and Temkin models yielded poor R^2 values for safranin dye (not reported). Langmuir adsorption is based on the fact that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface [8].

3.5 Adsorption Kinetics

Adsorption kinetics describes the solute uptake rate which in turns controls the residence time of the adsorbate at the aqueous-adsorbate interface including the diffusion process [16-19]. The data obtained from the influence of time on the adsorption of safranin dye onto BAAC were subjected to the pseudo-first-order Fig. 5 and pseudo-second order Fig. 6 kinetics equations for a test of fitness of data. The linearity of the plots with R^2 values that are very close to unity is an indication that the adsorption process followed both pseudo-first-order and pseudo-second-order kinetic models.

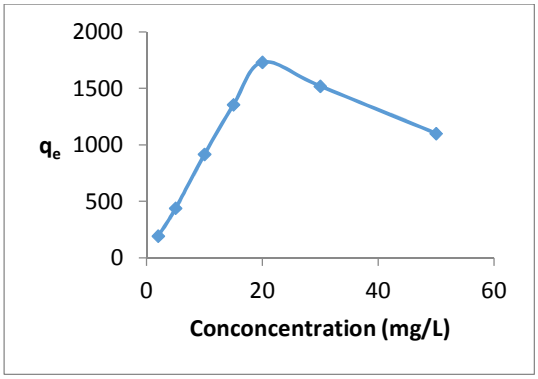

Fig. 1. Effect of concentration

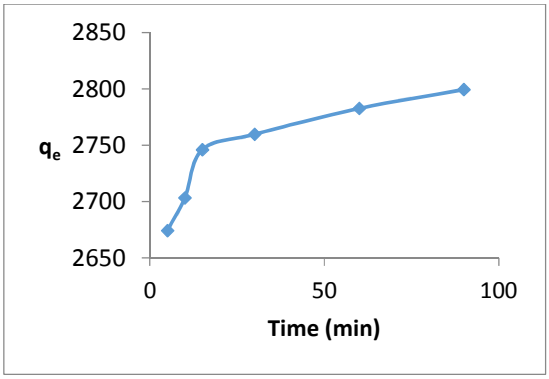

Fig. 2. Effect of contact time

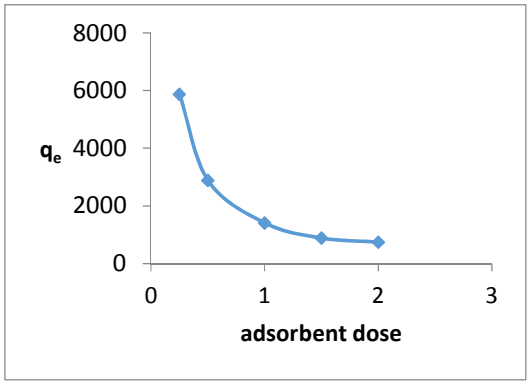

Fig. 3. Effect of effect of dosage

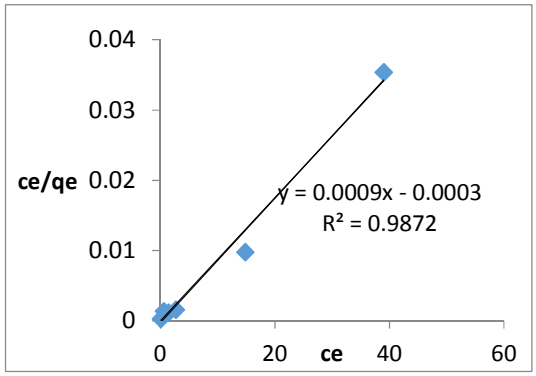

Fig. 4. Langmuir isotherm

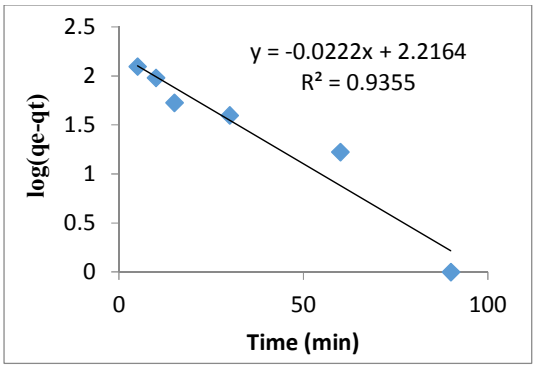

Fig. 5. Pseudo-first order kinetics

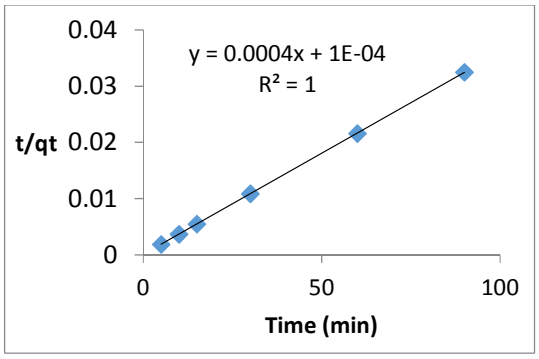

Fig. 6. Pseudo-second order kinetics

4. CONCLUSION

The preparation of activated carbon was achieved through one step process of carbonization with 67.27% yield. The safranin dye uptake increased with increasing concentration and agitation time. The kinetics studies indicate a good correlation coefficient for both pseudo-first and pseudo-second order kinetics model respectively. The isotherm study ascertains a good correlation coefficient which Langmuir isotherm fitted well. Therefor BA can be used for adsorption of dye if properly manage and harnessed. The fitting into Langmuir indicates monolayer coverage on the adsorbents. The results showed that BAAC has the potential to be applied as alternative low-cost adsorbents in the remediation of dye contamination in the waste water.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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