Kinetic and thermodynamic studies of the adsorption of dye on to *saccharum officinarum* waste adsorbents

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Abstract: **This work investigated the potential use of activated carbon produced from saccharum officinarum waste as an adsorbent for the removal of dye stuff from aqueous solution. The activated carbon was impregnated using Orth-phosphoric acid for chemical activation. Some physicochemical parameters of the activated carbon studied include, pH, bulk density, ash and moisture content. Adsorption experiments were conducted at varying contact times, initial dye concentration and temperature. Adsorption equilibrium was achieved in less than 40 minutes of contact time. Adsorption of dyes increased with increasing temperature. Thermodynamic characteristics which include free energy, enthalpy and entropy values were assessed using van't Hoff equation. Negative free energy and positive enthalpy values indicate the feasibility as well as endothermic nature of the adsorption event. Positive entropy suggests increased disorderliness at the solid/solution interface during adsorption process. The kinetic study shows that pseudo-second-order model is best fit for the experimental data obtained.**

Keywords: **Chemisorption, bulk density, saccharum, filtrate, kinetic model**

I. INTRODUCTION

Dyes are colored ionizing aromatic and heterocyclic compounds which show affinity towards the substrate to which they arebeing applied. They are generally applied in solution/aqueous to textiles, hair, wood or food. Compositionally, they are aromatic compounds whose structures possess aryl rings (C_6H_5) that have delocalized electron systems (Abazied, 2016). Usually, they find relevance when used for decoration or aesthetical purposes.Substances known as dyes have found applications in textiles, paper, leather, cosmetics and pulp industries. The coloring agents disposed as waste from these industries constitute serious hazards to the environment. Effluents from industrial and domestic wastes even at low concentrations contribute immensely to the increase of contaminants in water bodies globally (Ali *et al.,* 2016). Usually dyes have complex aromatic molecular structures that make them very stable and difficult to biodegrade. Many of them are toxic to some microorganisms and may cause the inhibition of their catalytic capabilities thus leading to serious problems to the ecological systems (Dijali *et al.,* 2015 and Diouri, *et al.,* 2015).Due to systematic accumulation of these pollutants and their increasing levels in the environment, a concern toward their regulation was aroused. The removal of dyes from wastewater becomes imperative and many processes which include sedimentation, coagulation, filtration, ion exchange, solvent extraction, chemical oxidation/precipitation and others were employed with different success levels tested for dye removal and degradation to combat water pollution (Bandary *et al.,*2016 & Fatima *et al.,* 2017). Since water is a necessary compound for the survival of living organisms, it is pertinent to ensure its purity and cleanliness. However, the processes mentioned above are either costly, energy intensive or generate harmful byproducts (Mohammad & Khanom, 2015 and Halder & Islam, 2015).The methods reported by numerous researchers were energy or cost intensive except adsorption process which stands out as highly selective, very efficient, cost effective, easy to operate and both sorbent and sorbate are recoverable. Therefore, adsorption technique is very effective for the removal of dye materials at low concentration. Khan*et al.,* 2012, reported that; a good adsorbent shall possess large surface area, good pore size distribution, strong polarity for moiety separation and efficient functional groups attachment to the adsorbent surface. However due to high cost of activated carbon, researchers'recourse to use low-cost sustainable biomass materials as adsorbent for the removal of dye materials from wastewater (Asif & Chen, 2017 and Tasar *et al.,* 2014).

Saccharum Officinarum family is among the most widely cultivated crops annually in Northern Nigeria. The specie produced millions of stalks waste that have no established large scale use but rather, dumped as refuse. Toadd value to the trash (sugar-cane stem waste), the crop is assessed for use as adsorbent for waste water treatment. The objective of the research is to examine saccharum officinarum waste as an adsorbent forCongo red dye removal under the following operating conditions such as: contact time, initial concentration and temperature change. Likewise, kinetic and thermodynamic studies of the adsorption were also investigated.

II. MATERIALS AND METHODS

Reagents

All the chemicals used in this work were of Analar grade (98—99.5%) supplied by BDH England (UK).

Instruments

Some of the instruments/apparatus used include; Glass funnels, crucibles, furnace bicep, sieve, weighing balance (PA 214, Ohaus, USA), oven (UNB 300, Memmet; Germany), shaker (Ika.HS-501, Werke), furnace (Muffle, FM 515; P-

Select Pizzato, Italy),FTIR spectrometer (M-530, USA) and UV-visible spectrophotometer (UV-752, PecMedical; USA).

Preparation of adsorbent

Ripe saccharum officinarum (saccharum) stem were collected from vendors in Damaturu town of Yobe state Nigeria. After the sugar juice was chewed, saccharumwastewas washed thoroughly with warm water to remove sand and other water soluble substances, then rinsed with distilled water before drying in an oven at 105°C for five hours. 30g of saccharum waste was added to 300cm^3 of 10% (v/v) phosphoric acid solution and impregnated for 14hours.The samplewas washedafter impregnation until a constant solution of pH 7 was obtained. The saccharum waste sample was dried in an oven for 8hours at 100°C, carbonized in a muffle furnace in the absence of oxygen and at inert conditions at temperature ≥450°C for 1hour. The activated carbon was cooled inside the furnace and sieved through a 1mm size mesh to remove particles with higher sizes. The activated carbon was stored in a moisture free container for further use.

Characterization of Adsorbent

Certain physical and chemical parameters affecting adsorption were determined. These include; bulk density (using graduated cylinder tapping method as described in ASTM 1999), pH, ash and moisturecontents (using muffle furnace and dry crucible dish methods respectively as both described in AOAC (1995). Fourier transform infrared spectroscopy was employed to identify the functional groups present in the structure of the adsorbent.

Experimental procedure

A stock solution of 0.3g/l of Congo red dye (adsorbate) was prepared by dissolving 0.3g of dye in 1L distilled water. Working solutions were obtained by diluting the stock solution with distilled water to prepare series of concentrations such as 0.005g/L, 0.010g/L, 0.015g/L, 0.020g/L, 0.025g/L, 0.030g/L and 0.035g/Las per the requirement. Absorbance of these concentrations were measured using UV-visible spectrophotometer (UV-752, PEC Medical) at (**λ_{max}**) 495nm. The standard calibration plot was obtained from the known concentrations of the dye solution and the measured absorbance.The slope obtained from the calibration plot was used to determine the concentration of Congo red dye in the solution after adsorption had occurred.To establish at which time do the adsorption of dye from the solution is optimum, 0.3g of the adsorbent was mixed with 50 ml of 0.045g/L of the adsorbate. Series of samples were prepared and agitated for 4hours. The samples were examined at specific time intervals (after every 30 minutes) then withdrawn and filtered. The filtrate was taken for absorbance reading. This procedure was carried out at five different temperatures (30°C, 35 °C, 40 °C, 45 °C, and 50 °C). A plot of adsorbed concentration against time for each temperature was determined.

To establish adsorbent mass that would have the highest adsorption of dye from the solution, mass of adsorbent was varied from 0.30—1.80g at an interval of 0.30g. 50ml of 0.05g/L of adsorbate was added to each mass of adsorbent which was agitated thoroughly for the time gotten from contact time for each temperature. The filtrate of each test was measured for absorbance using UV-spectrophotometer which was used to deduce the residual concentration. The concentrations of dyestuff in the filtrate were determined by using standard curve.

The parameters generated from adsorption dosage and contact time were used to investigate the combined effects in the adsorption of sorbate onto saccharum officinarum waste (bio-sorbent). Initial dye concentration was modified ranging from 0.0075 to 0.045g/L (incremental amount of 0.0075g/L). Each concentration obtained was filtered and the adsorbed concentration was calculated from their respective initial/residual dye concentrations. The procedure described was carried out at five different temperatures. The result obtained was used to determine the following adsorption variables;

$\% \text{ Adsorption} = \frac{Ci-Ce}{\text{Ci}} X\ 100$ ………………..(i)

$q_e = (C_i - C_e) / S$ ……………. (ii)

$S = m/v$ ………………………(iii)

Where; C_i and C_e are the initial and equilibrium concentrations of dye solution (g/L)

m is the mass of adsorbent and v is the initial volume of dye solution

q_e is the dye adsorption capacity at equilibrium

Adsorption thermodynamics

The thermodynamics of the dye adsorption process was investigated by measuring different thermodynamic parameters at various temperatures, such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) values from the following equations:

$\Delta G = -RT \ln k_c$ ……………. (iv)

$\Delta G = \Delta H - T\Delta S$……………...(v)

$\ln k_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$………………(vi)

$k_c = = Qe/Ce$………………(vii), source (Zakir *et al.,* 2018 and Na *et al*., 2018).

R is the universal gas constant, k_c is the concentration equilibrium constant and T is the temperature in kelvin scale (k).The values of ΔH and ΔS were obtained from the slope and the intercept of the plot of$\ln k_c$ versus$\frac{1}{T}$(k^{-1}). The activation energy (E_a) was determined from the straight-line plot of ln k_c versus$\frac{1}{T}$ using Arrhenius equation;

$\ln k_c = \ln A - \frac{\text{Ea}}{\text{RT}}$…………………(viii).

The slope of the curve would be ($-\frac{Ea}{R}$).

Adsorption kinetics investigation

For kinetics investigation, pseudo-first-order kinetics was applied on the data obtained. To check the effect of contact time between (30—180min) on adsorption, initial concentration of 0.05g/L of dye substance was prepared and 50ml of this was used for the study. 0.3g of adsorbent was added to the dye solution and was agitated. After certain time interval (every 30 minutes), sample was removed and analyzed for dye concentration using UV-visible spectrophotometer. The concentration of dye adsorbed at different time intervals was determined using the following relation:

$q_t = \frac{(Ci-Ce)}{w} \, x \, V$……….(ix), where q_t is the concentration of dye adsorbed at any time t, Ci and Ce are initial and equilibrium concentrations respectively. w is the weight of adsorbent in (g) and V is the volume of solution taken (ml).

The adsorption kinetics and rate constants were determined using kinetic models for pseudo-first-order and pseudo-second-order models. The pseudo, first and second order adsorption kinetics from the equilibrium adsorption were calculated from the following equations:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \text{ ………………… (x)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \text{……………….…. (xi)}$$

where q_e and q_t are concentrations of dye solutions adsorbed onto saccharum waste at equilibrium and at a time t, respectively. k_1 and k_2 are the rate constants for the pseudo-first and pseudo-second-order kinetics respectively.The first-order constant was determined in linear form by plotting ln (q_e – q_t) versus t. A plot of $\frac{t}{q_t}$versus t was used to obtained pseudo-second-order rate constant.

III. RESULTS AND DISCUSSION

Some physical parameters of saccharum (waste) adsorbent including pH, ash, moisture content and Bulk density as obtained in this study are highlighted in this discussion. Saccharum waste with pH value of 6.74 is near neutral. The value is close to 7.0, is an indication that the saccharum officinarum adsorbent can be used for the treatment of dyestuff. pH range of 6—8 is acceptable for the activated carbon (Okiemmen *et al.,* 2008).

Moisture content is the amount of water lost from substance upon drying to a constant weight is directly affected by both physicochemical characteristics of materials which enable it to absorb the exiting water in the environment. Saccharum waste with 7.40 % showed low moisture content compared to 10% reported by Solener*et al.,* (2008). Low moisture suggests that activated carbon can be stored for a long time. Total ash is a measure of the mineral oxide contents of the activated carbon on a weight basis (non-carbon content of the activated carbon). Ash content value of 0.25% was obtained for saccharum waste. High content of ash is an indication of mineral element presence.High amount of inorganic mineral composition is an indication of good activated carbon.Values reported for coconut shell and wood activated carbons were in the range of 2—3% and 5% respectively.The result from this study falls far below those of coconut shell and wood activated carbons which indicatespresence of low mineral oxide as reported by Kim *et al.,* 2015.

Bulk density is the density of the carbon at maximum packing efficiency. It considers both the solids and the pore space in carbon materials and was found to be 0.0816 (g/cm^3) for this sample. The result shows that the activated carbon is less dense than water. Bulk density is an important variable in the design of adsorption column. It determines the mass of carbon that can be contained in a filter at given solid capacity and the amount of treated liquid that can be Retained by the filter cake (Okiemmen *et al.,*2008). The lower the bulk density values the high liquidvolume it will filter in the available cake space. This property enables easy separation of thecarbon when mix with adsorbate solution upon whichit acts (Kyas, 2013).

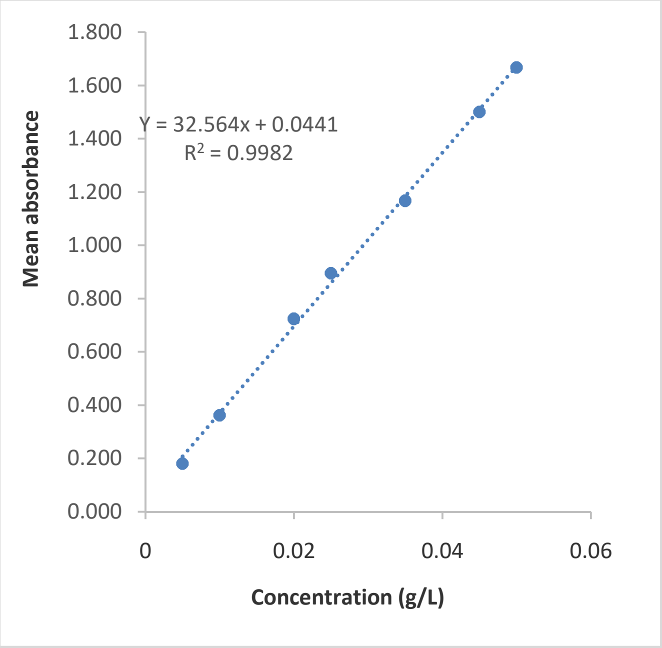

Fig. 1: Calibration curve for standard solutions of Congo red dye

Fig.1 shows the standard curve of absorbance versus concentration for the adsorbate solution. The equation of the graph is y = 32.564x + 0.0441 which was used to obtain the residual concentration for the subsequent experiments. The correlation coefficient "R^2" value is 0.9982 which shows the precision of the curve. A plot of amount of dye adsorbed versus sorbent mass was shown in Fig. 2. The curve showed one sharp peak at 0.4g and then flattened.

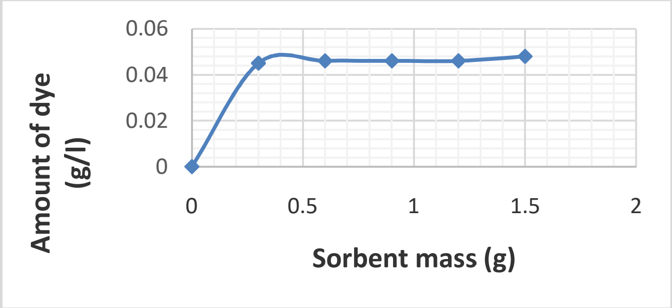

Fig. 2: Variation of dye removal with sorbent mass at 30°C

This was obtained at 30°C and suggests the best mass of sorbent for the removal of a given amount of the sorbate is 0.4g at a given temperature. The result indicates that mass of sorbent has effect on the adsorption of dye material. The curve suggests an optimum dye adsorption at a certain saturated mass value, hence adsorption is dependent on the mass of adsorbent and contact time used (Diouri, *et al.,* 2015).Effect of contact time on the amount of dye adsorbed is presented in Fig.3. The plot shows that at the beginning the amount of dye adsorbed increased with an increase in contact time. The process of adsorption is fast until it reaches equilibrium at 30 minutes, then the curve flattened. This can be attributed to the availability of large adsorption sites of the adsorbent. After the first cliff appeared, a plateau was formed. This indicates that surface pores on the adsorbent were saturated and desorption was initiated.

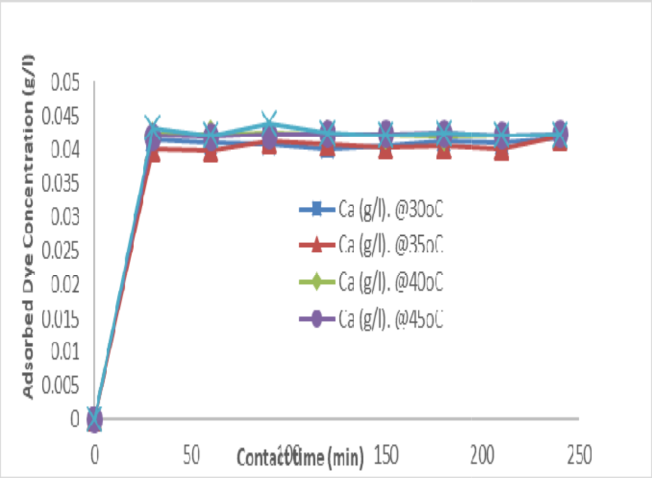

Fig. 3: Effect of contact times on adsorbed dye concentration at different temperatures

The rate slowed down in the final stage as the migration of the solute into the interior of the adsorbent declined (Belay & Hayelom, 2014). From the curves obtained, it can be deduced that temperature has effect on dye adsorption and contact time. Higher amount of dyestuff was adsorbed at higher temperatures with 30°C, 45°C, and 50°C giving the highest values whilst 35°C showed the least amount.Fig.4 shows the plot of ln k_c versus inverse of temperature in kelvin units using the Arrhenius equation for the determination of activation energy (E_a). The results for activation energy value (E_a) and other thermodynamic parameters were evaluated and listed in Table 2. Equation (v) was used to calculate the change in Gibbs free energy and entropy values at varying temperatures.

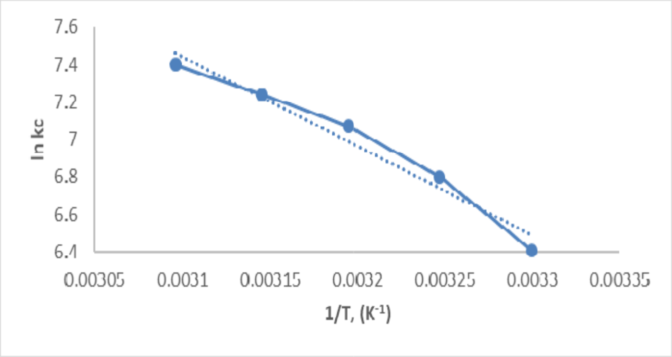

Fig. 4: Plot of ln k_c versus 1/T for dye adsorption on modified saccharum waste

Pseudo-first order and second-order kinetic models were tested on the experimental data obtained in this study to arrive at the first and second order adsorption rate constants (k_1, min^{-1}) and (k_2, $g.mg^{-1}.min^{-1}$) as described under adsorption kinetics and the graphs for the linear plots were shown in Figures 5 and 6 respectively. The results of k_1, k_2 and q_e were evaluated and presented in Table 3.

In this study, kinetic investigation was conducted at different time intervals for the adsorption of dye material. Results suggest that the amount of dye adsorbed increases sharply at the start of the reaction andgradually the magnitude of adsorption decreases with time.

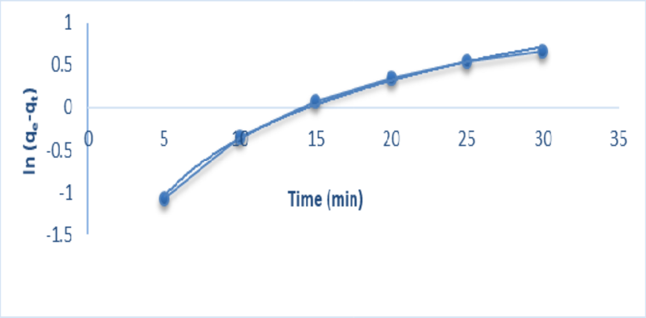

Fig. 5: Pseudo-first order plot for dye adsorption at different times

Results for the thermodynamic parameters showed negative values for Gibbs free energy at all temperatures under study and the value increases with increase in temperature. The negative ΔG^0values suggest that the adsorption process is thermodynamically spontaneous as well as feasible. However, increase in Gibbs free energy with increase in temperature indicates better sorption at elevated temperature. The positive value for enthalpy change indicates that the adsorption of dyestuffis endothermic. The entropy value was found positive which pointed to an increased randomness in the system at the solid/solution interaction during adsorption occurrence.

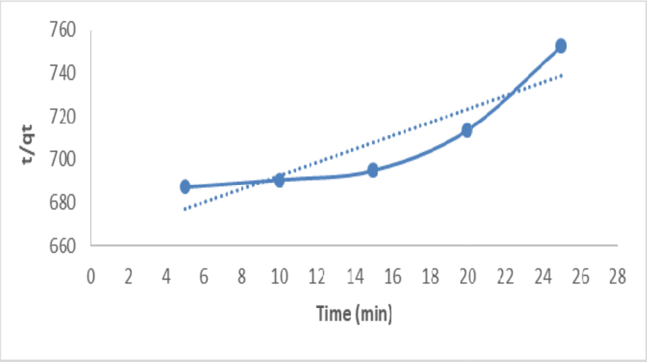

Fig. 6:Pseudo-second order plot for dye adsorption at different times

However, similar results were obtained for ΔH and ΔS by Zakir and Deepa (2018), but with slight difference in values for ΔG^0. The same authors reported Gibbs free energy values in the range of -14.096 to -4.577 which is close to what is obtained in this work. The calculated activation energy value was found to be 37.568kJ.mol^{-1}and is shown in Table 2. The value suggeststhat; high temperatures are favored to drive the endothermic process which indicates chemisorption adsorption.

Table 2: Thermodynamic parameters for the adsorption of dye onto saccharum waste

Parameters	Temperature (K)	Results
ΔG (kJ.mol^{-1})	303	-16.122
	308	-16.901
	313	-18.398
	318	-19.141
	323	-19.872
ΔH (kJ.mol^{-1})		37.568
ΔS (kJ.mol^{-1}.K^{-1})	303	0.184
	313	0.178
	323	0.172
E_a (kJ.mol^{-1})		37.568

To obtain values for pseudo-first-order kinetic model as suggested by Lagergren and Sven (1898), ln (q_e- q_t) was plotted against time interval. The value of adsorption rate constant k_1 was obtained from slope of the line and q_e from intercept. The value of correlation coefficient (R^2>0.9) is high enough to suggest that pseudo-first-order kinetic model fits to describe the adsorption process. Nonetheless, the rate constant value (k_1= 0.988)is less than 1, in a similar manner, the calculated and experimental q_e valuesdo not agree, therefore pseudo-first-order kinetic model does not describe the process.

Table 3: Kinetic parameters for dye adsorption onto saccharum waste

Kinetic Model	Parameters	Results
	q_e	0.0714
Pseudo-first order	K_1	0.9877
	R^2	0.9974
	q_e	0.3249
Pseudo-second order	K_2	3.0777
	R^2	0.9874

The linear form of the pseudo-second-order kinetic model equation as reported by (Ho and McKay, 1999); shown in equation (xi)of this work, was employed to obtain the pseudo-second-order rate constant (k_2) ofadsorption.The calculated k_2 value was 3.078 which shows second-order rate constant is higher than first order. Since k_2 > k_1, it implies thatrate of adsorption for pseudo-second order kinetic is faster than first-order kinetic model; hence the former is favored than the latter. Likewise, the calculated and experimental values for $q_e$were similar and also, when we compare the correlation factor value (R^2= 0.987), for pseudo-second-order kinetic; it suggests that pseudo-second-order model fits the kinetics of adsorption of Congo red dye used for this investigation.

IV. CONCLUSION

This work has indicated that saccharum officinarum stem can be used as adsorbent for the removal of dyestuff from aqueous solution. The adsorption process is dependent on contact time, initial dye concentration and temperature. The study indicated that maximum removal was achieved in less than 90 minutes of contact time.Negative ΔGvalues obtained for all temperatures and positiveΔG indicated that, the adsorption was spontaneous and endothermic. With an increasing positive values of ΔS, randomness of the system also increases at the solid/solution interface. The kinetic study showed that pseudo-second-order kinetic model fits better to describe the adsorption process. Thus both thermodynamic parameters and kinetic investigation revealed that the adsorption of dyestuff onto saccharum waste adsorbent is feasible and favorable.

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