Removal of particles from wastewater using locally prepared activated carbon: Equilibrium, kinetic, thermodynamic and Optimization study

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ABSTRACT- *Brewery industry produces high volume of effluent and Total Suspended and Dissolves Particles (TSDP) is one of the major constituents of the effluent that have been reported worldwide. The adsorption of Total Suspended and Dissolved Solid Particles (TSDP) onto African Star Apple Activated Carbon (ASAAC) was carried out in this work. The adsorbent capacity was enhanced by treatment using 0.1M NH_4Cl. The batch studies on adsorption of TSDP were conducted by varying adsorbent dose, contact time, solution pH and solution temperature. The maximum removal (80.5%) was achieved at dose of 1.0g and 60minutes. The sorption data obtained was subjected to Freundlich and Langmuir Isotherm studies. The data fits well to both isotherm models. The values of the Freundlich and Langmuir constants as well as dimensionless factor R_L suggest favourable and monolayer adsorption. Kinetic data were fitted to the models of Lagergren, Pseudo Second-Order and Intraparticle Diffusion, which followed more closely to the Pseudo Second-Order Model. The Effect of temperature and thermodynamic parameters obtained showed that the adsorption reaction was endothermic. The results obtained on the factor plots agreed with the results obtained on the one factor plots showing good optimization. The African star apple Carbon Activated in Ammonium chloride (ACAA) was successfully used for the removal of TSDP from the Brewery Effluent and the technique appears industrially applicable and viable.*

Index Terms–Adsorption Isotherms, kinetics, Thermodynamic, Activated Carbon, Multiple Factor Optimization.

I. INTRODUCTION

The problem of protecting the environment from pollution and contamination by various types of effluent discharges is now in the focus of attention all over the world. Brewery industries are one of the major industries that produce high volume of effluent and its effluent can be generally be characterized as high-strength organic waste with moderate high TSDP concentration. Brewery Effluent (BE) is the combination of waste water from various stages of the production; malting, milling, wort boiling, stabilization, maturation, fermentation and clarification (Sen and Demirer, 2003). Brewery Effluent (BE) uses a large amount of water in which malting, milling and clarification uses most of the water. Considering the volume generated and effluent composition, the brewery effluent is rated as one of the most polluting effluent among all industrial sectors (Sen and Demirer, 2003). Organic components in brewery effluent are generally easily biodegradable and mainly consist of sugar, soluble starch, ethanol, volatile fatty acids etc. The effluent solids consist of spent grains, waste yeast, hot trub, and total suspended dissolves particles (Shilpi *et al*., 2008). Since most of these TSDP are non-degradable and toxic (Calace *et al*., 2002), their concentration in industrial effluents must be reduced to acceptable levels before discharging them into the environment. Several methods have been developed for the removal of TSDP from water and wastewater to decrease their impact on the environment. These methods include; coagulation and flocculation (Faria *et al*., 2004), adsorption using various adsorbents (Parida and Mishr, 1996; Rozada et al., 2003), chemical oxidation (Fu and Vitaraghavan, *et al*., 2002), anaerobic decolourization (Muthukumar *et al*., 2005) and reverse osmosis (Maas and Chaudhari, 2005). Adsorption is preferred over these processes because of its efficiency. The most widely used adsorbent for this purpose is activated carbon, but commercially available activated carbons are expensive and they may not be economical for wastewater treatment. Therefore, non-conventional low cost adsorbents have been also utilized for TSDP removal in BE. A low-cost activated carbon from African star apple seed has been prepared using a thermal carbonization technique and subsequently used for TSDP removal as shown in fig 1. In this paper, experiment was carried out to estimate the batch adsorption capacity of the locally prepared activated carbon. Adsorption Isotherm, Kinetic study, Thermodynamic parameters and Factorial effects was studied. The effect of contact time, solution pH, solution temperature and adsorbent doses were investigated. The aim of this research was to explore the feasibility of using African star apple seed - based activated carbon for the removal of TSDP from brewery wastewater.

Fig. 1. African Star Apple Fruit and Seed.

II. MATERIALS AND METHODS

A. Adsorbate Preparation and Characterization.

The effluent sample was collected from Nigerian Brewery, Enugu, Nigeria, using 10 litres jerry can. The jerry can was filled to the brim with the effluent in order to expel entrapped air. The jerry can was corked and remained sealed until the commencement of the analysis (Obiora-Okafo and Onukwuli, 2013). Physicochemical analyses of the effluent sample presented in table 1 were determined following the standard method water and wastewater purification APHA-AWWA/WEF (1998).

Table 1. Characterization of the Brewery Wastewater Sample.

Parameters	Values
PH	6.54
Turbidity (NTU)	426.00
TDS (mg/l)	505.80
TSS (mg/l)	268.3
BOD_5(mg/l)	472.000
COD (mg/l)	851.81
Temperature (^{o}C)	31.5
TS (mg/l)	990
Total hardness (mg/l)	69.0000

B. Preparation of Adsorbent

African Star Apple Seed (ASAS) used as a precursor for the preparation of activated carbon was collected from Enugu, Nigeria. The seed was extensively washed with running tap water for 30minutes to remove dirt and other particulate matter. It was rinsed in distilled water and dried at $110^{o}C$ for 24h to remove the moisture content. The dried samples were easily crushed into small pieces and sieved to the size of 0.5-3mm and stored in an airtight container. 250g of the samples were placed on a metal mesh located at the bottom of a tubular reactor under 150 cm^3/min flow rate of purified nitrogen gas. During this period of semi carbonization, the heating rate was kept constant at $10^{o}C$ /min. The temperature was increased from room temperature to $40^{o}C$ and kept constant for 2h. The char produced was allowed to cool at room temperature under nitrogen flow at the same flow rate and stored in an air-tight container. The sample was soaked with 0.1M NH_4Cl solution such that the liquid to solid Impregnation Ratio (IR) is:

$$IR = \frac{10ml\ of\ NH_4Cl}{One\ gram\ of\ carbon} \qquad (1)$$

The Impregnated sample was placed inside the tubular furnace with nitrogen gas flow rate of 150cm3/min and heating rate of 10oC/min. The temperature was increased from room temperature to 700oC. Once the activated temperature reached 700oC the gas flow was switched to CO2 at the same flow rate and kept constant for 1h. The prepared activated carbon was cooled to room temperature under nitrogen gas flow maintaining the same flow rate mentioned above; and then washed with distilled water until the pH of the washing solution reached 6.5 - 7. The washed sample of the activated carbon were dried and stored in an airtight container for further experimental procedures (Obiora - Okafo and Onukwuli, 2013). The yield of activated carbon was obtained as the ratio of final weight of the activated carbon after washing and drying to the weight of the dried precursor initially used. It was calculated based on the following equation:

$$Yield\ (\%) = \frac{Wf}{Wo}\ x\ 100 \qquad (2)$$

Where W_f and W_o are the weight of final activated carbon product (g) and the weight of dried sawdust (g), respectively.

C. Batch Studies

Batch experiment was carried out at temperature ($30^{o}C$) to determine the equilibrium adsorption isotherms. Each batch studies were done by adding different adsorbent mass (0.2 - 1.0g) of ACAA into 0.02L of the effluent and stirring at 150rpm. After shaking the samples, they were subjected to TSDP analysis according to (APHA - AWWA, 1998). For TSDP analysis, the samples were collected after putting in five different containers which were labeled accordingly. The initial absorbance (A_O) of the effluent was taken using spectrophotometer before the batch adsorption experiment. After the mixing and shaken, the content of each beaker was filtered through what man GF/C filter paper, the final absorbance (A) of the effluent was determined using spectrophotometer at wavelength of 570nm. The amount of each TSDP adsorbed by African Star Apple Activated Carbon in Acid (ACAA) at equilibrium was calculated using Eq. (3):

$$q_e = \frac{(Co - Ce)}{M}\ V \qquad (3)$$

Where C_o and C_e (mg/l) are the liquid-phase concentrations of TSDP at initial and equilibrium time t, respectively. V is the volume of the solution (liters), and M is the mass of dry adsorbent used (gram).

D. Effect of Adsorbent Dosages and Contact time.

The effect of ACAA dosage on the adsorption process was investigated by varying time (5 – 60 min.) for different doses at temperature $30^{o}C$, pH 2 and stirring speed 150rpm.

E. Effect of Solution Temperature

The effect of solution temperature on the adsorption process was examined varying the adsorption temperature at $30^{0}C$, $35^{0}C$, $40^{0}C$ and $45^{0}C$ by adjusting the temperature controller of the water bath shaker with varying dosages while other parameters such as stirring

speed and adsorption time were remained constant. The solution pH was original without any adjustment.

III. RESULTS AND DISCUSSIONS

A. *Effect of Contact Time.*

It has been observed from fig. 2 that the removal of TSDP decreased with time till the equilibrium was attained. A high initial slope of the curve indicated the initial rapid removal of TSDP at beginning of contact time. This may be due to the fact that at the beginning of the sorption process all the reaction sites are vacant and hence the extent of removal is high (Izadyar and Rahima, 2007). After a rapid initial slope, there is a phase that the rate of removal is slow with reaching almost a constant value. At 60min., the time is efficient for carrying out the batch adsorption studies.
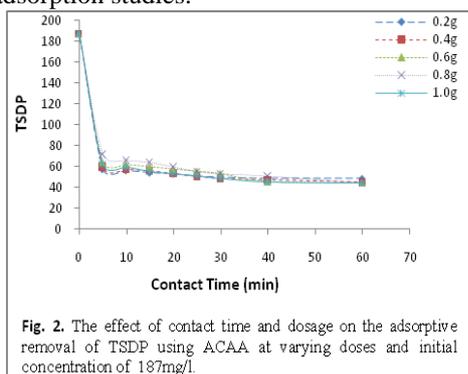
Fig. 2. The effect of contact time and dosage on the adsorptive removal of TSDP using ACAA at varying doses and initial concentration of 187mg/l.

B. *Effect of Contact Time on Removal efficiency*

A plot of percentage removal and contact time was shown in fig 4. The sorption efficient (%) was calculated using;

$$\text{Adsorption Efficiency } (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (4)$$

C_o and C are the initial and final concentration, mg/l.

Fig. 3 shows that the percentage of TSDP removal increases with increasing adsorbent dosage and contact time. When the adsorbent dosage increase, the number of sorption sites at the adsorbent surface will increase, as a result of increase in the percentage of TSDP removal from the solution (salleh *et al*., 2011 and Ofomaja, 2008). The result also showed that rate of adsorbed TSDP onto ACAA was initially rapid and then slowed down gradually until equilibrium was attained. It could be explained that a large number of vacant surface sites were available for adsorption during the initial stage of the sorption process and after a lapse of time; less remaining vacant sites were available (Obiora-Okafo, 2013). All the curves obtained were smooth indicating formation of monolayer on the surface of the adsorbent (Asfouret *et al*., 1985). Fig. 3 also indicated that the optimum dose for the TSDP uptake was 1.0g occurring at 80.5%.
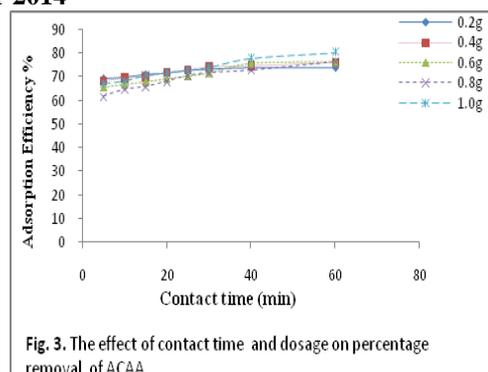

Fig. 3. The effect of contact time and dosage on percentage removal of ACAA.

C. *Effect of Adsorption Amount and Contact Time.*

The effect of the amount adsorbed (q) was calculated and plotted on fig. 4 using

$$q = \frac{(C_o - C)}{w} \quad (4)$$

Where, C_o and C are the concentrations of the adsorbate before and after adsorption respectively, mg/l. W is the weight of the adsorbent in effluent (g/l), q is the adsorption amount (mg/g). Adsorption amount increased with the increased in contact time. Contact time is also an important factor affecting removal and most adsorption occurs in the initial half time and increases very slowly later. This is attributed to the availability of a larger member of adsorption sites in beginning, similar result have been reported by Sharma and Kareer (2006) for adsorption of cobalt on rice husk.
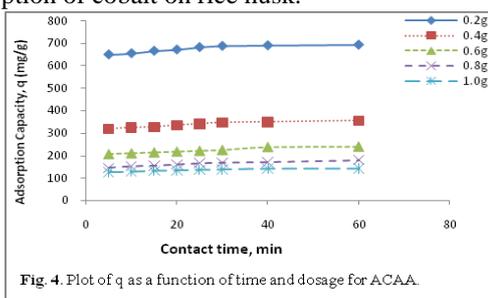

Fig. 4. Plot of q as a function of time and dosage for ACAA.

D. *Equilibrium Adsorption Isotherms.*

The isotherms results were analyzed using the Langmuir, Freundlich and Temkin isotherms. These three isotherms represent surface adsorption. Surface adsorption is the simplest model of adsorption on a surface by which localized adsorption takes places on an energetically uniform surface without any interaction between adsorbed molecules (Suzuki, 1990). **Langmuir model** is based on the assumption that fixed individual sites exist on the surface of the adsorbent: that each of these sites being capable of adsorbing one molecule, resulting in a monolayer one molecule thick over the entire carbon surface. The maximum adsorption occurs when the surface is covered by a monolayer of adsorbate (Langmuir, 1918). The linear form Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \qquad (5)$$

Where C_e (mg/l) is the equilibrium concentration of the adsorbate, q_e (mg/l) is the amount of adsorbate adsorbed per unit mass of adsorbent, Q_o (mg/g and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The plot of C_e/q_e Vs. C_e shows the applicability of Langmuir isotherm (Hu *et al.*, 2006). The value of Q_o and K_L are determined from slope and intercept of Langmuir plot in fig. 5 and are 8.06mg/g and 0.01881/mg. The applicability of these isotherm models gives high values of the correlation coefficients (R^2 values is 0.976) suggest favourable and monolayer adsorption. The essential characteristics of Langmuir isotherm can be described by the dimensionless parameter.

$$R_L = \frac{1}{1+bC_0} \qquad (6)$$

Where, C_o is the initial TSDP conc. mg/l The factor R_L indicates whether adsorption is favourable or not. The values of R_L have found to be between 0 and I which suggests favourable adsorption (Sharma *et al.*, 2006; Meena and Rajagopal, 2003), as shown in table 2.
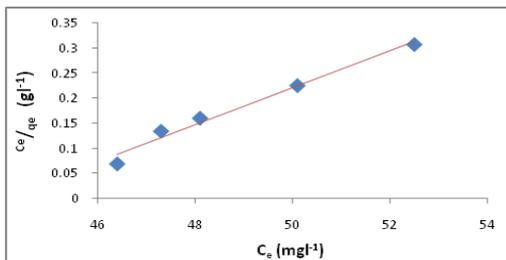

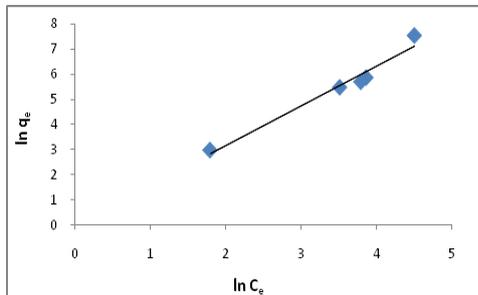Fig 5. The linearized Langmuir adsorption isotherm of TSDP onto ACAA at PH = 7, and T = 30⁰C.

Fig 6. The Linearized Freundlich isotherm of TSDP onto ACAA at PH = 7, and T = 30⁰C.

Freundlich Isotherm

The empirical Freundlich equation based on sorption on heterogeneous surface (Longhinetti *et al.*, 1998) is given below:

$$q_e = k_f C_e^{1/n} \qquad (7)$$

Where k_f and n are the Freundlich constant characteristics of the system. The Linearized form of the Freundlich equation can be given as:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f \qquad (8)$$

Where C_e is the equilibrium concentration (mg/l) and q_e is the amount adsorbed (mg/g). Linear plot of $\ln q_e$ versus $\ln C_e$ shows that the adsorption follows Freundlich isotherm model as well (fig 6). k_f and n were calculated from the intercept and slope of the plot. The constants were found to be 0.036 and 5.07 respectively.

E. Adsorption Kinetics

The kinetics of adsorption controls the process efficiency (Manju *et al.*, 1998). The kinetics of removal of TSDP was studied using three kinetic models, The Lagergren model (Pandey *et al.*, 1985), The Pseudo Second - Order model (Ho *et al.*, 1998) and The Intraparticle Diffusion model (Weber and Morris, 1963).

Lagergren Model or Pseudo First - Order Model.
Lagergren proposed a pseudo-first-order kinetic model, which is expressed as:

$$\frac{dq_e}{dt} = K(q_e - q) \qquad (9)$$

Which q_e is the amount of TSDP adsorbed at equilibrium per unit mass of adsorbent (mg/g), q is the amount of TSDP adsorbed at any given time t, and K is the rate constant for Pseudo – first order adsorption (min⁻¹). By using the boundary condition and simplifying the Eq. (7), it becomes:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{K_1}{2.303} t \qquad (10)$$

The plot of Log $(q_e - q)$ versus t is shown in fig 7. The first order rate constant K_{ad} was obtained from the slope of the straight line. The correlation coefficients and rate constant were calculated and are given in Table 3. The correlation coefficients were in good agreement with the Pseudo first - order kinetics and in the range of (0.92 – 0.98).

Table 2. Langmuir and Freundlich adsorption isotherm constants for adsorption of TSDP on adsorbent.

Adsorbent	Langmuir Constants				Freundlich Constants		
	Q(mg/g)	b(l/mg)	R_L	R^2	K	n	R^2
ACAA	8.06	0.0188	0.221	0.976	0.036	5.07	0.967

Table 3. Kinetics studies for the adsorption of TSDP on the ACAA

Type	Parameters	0.2g	0.4g	0.6g	0.8g	1.0g
Pseudo First-Order	q_e	71.29	43.15	51.17	43.15	33.57
(Lagergren Model)	K_{ad}	0.071	0.064	0.051	0.041	0.074
	R^2	0.969	0.943	0.971	0.984	0.928
Pseudo Second-	K_2	0.0005	0.0013	0.002	0.0019	0.004
Order Model.	q_e	1000	500	250	200	166.67
	R^2	0.999	0.998	0.998	0.998	0.999
Intraparticle Diffusion	K'_d	1.678	1.353	1.31	1.216	0.665
Model	R^2	0.802	0.886	0.931	0.925	0.868
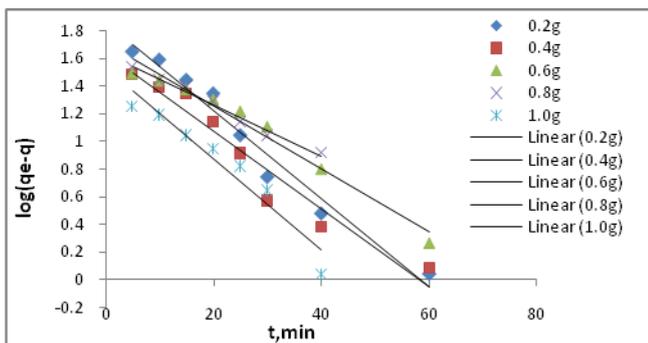
Fig. 7. Kinetics of TSDP removal according to the Lagergren model at different doses of ACAA
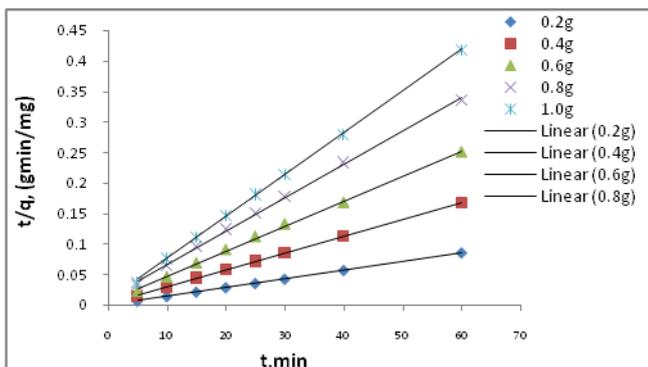
Fig. 8. Kinetics of TSDP removal according to the Pseudo-second order model at different doses of ACAA
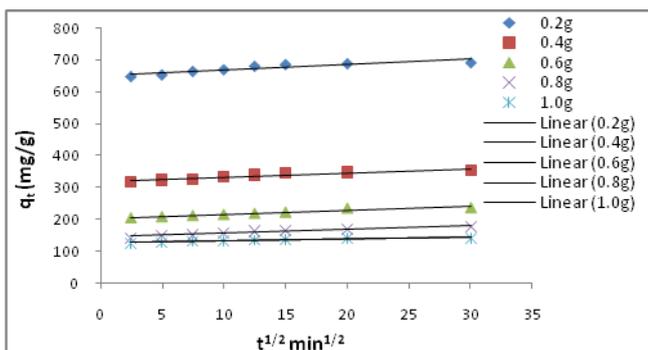

Fig. 9. Kinetics of TSDP removal according to the intraparticle diffusion model at different masses of ACAA

Pseudo-Second order

A Pseudo second-order reaction model can also be applicable to kinetics of sorption. The pseudo-second-order equation by Ho and Mc kay (1998) predicts the behaviour over the whole range of adsorption and is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

Where K_2 (g/mg min) is the pseudo-second-order rate constant. The linear plot of t/q_t versus t gave $1/q_e$ as the slope and $1/K_2 q_e^2$ as the intercept (fig. 8). From the plot and correlation coefficient obtained on table 3, it can be concluded that the process of TSDP adsorption fits better to Pseudo second - order kinetics since the R^2 showed a very good linear relationship between the two variables ($R^2 > 0.998$).

Intraparticle Diffusion Model

The Intra-particle diffusion varies with square root of time (Weber and Morris, 1963) as shown below:

$$q_t = K_{id} t^{0.5} \qquad (11)$$

Where q_t is the amount adsorbed at time t (mg/g), t the time (min) and k_d is the Intra-particle diffusion coefficient or rate constant (mg/gmin$^{-1/2}$). The k_{id} values were determined from the slope of linear plot between q_t vs. $t^{0.5}$ shown in fig. 9 at different masses of adsorbent (0.2 – 1.0g). The Intra-particle diffusion had also shown some role in the adsorption of TSDP onto adsorbent. The linear plot for a wide range of contact time between adsorbent and adsorbates does not pass through the origin, such deviation from the origin or near saturation is attributed to the difference in rate of mass transfer in the initial and final stages of adsorption.

F. Effect of Temperature and Thermodynamic Parameters

Adsorption studies were carried out at four different temperatures (30, 35, 40 and 45°C). The thermodynamic parameters were determined as:

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303\,R} + \frac{-\Delta H^0}{2.303\,RT} \qquad (12)$$

Where q_e is the maximum TDSP adsorbed per unit mass of AACA, mg/g; C_e is the equilibrium concentration, mg/l; R is the universal gas constant, (8.314 J mol/K); T is the absolute solution temperature, K; ΔS^o is the change in standard entropy, (KJ/mol K) and ΔH^o is the change in standard enthalpy, (KJ/mol). Experimental data considered for calculation of thermodynamic parameters (ΔG^o, ΔS^o and ΔH^o) are in the linear range of equilibrium adsorption isotherm (Kaushik *et al.*, 2006).

The values of ΔH^o and ΔS^o can be calculated, respectively from the slope and intercept of the plot of log $\left(\frac{q_e}{C_e}\right)$ versus 1/T as shown in fig. 10. Gibbs free energy (ΔG^o) can then be calculated using the relation below:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (13)$$

Where ΔG^o is the change in standard free energy, (KJ/mol). With an increase in Temperature, adsorption capacity increased, thereby indicating the adsorption as an endothermic process (Kaushik *et al.*, 2006). Also, increase in temperature brings about increase in the number of active sites available for adsorption resulting to an enhancement of percentage adsorption of TSDP onto adsorbents. The values of thermodynamic parameters, for the ACAA are given in Table 4. Positive value of ΔS^o suggests an increasing randomness at the adsorbent/solution interface which occurs in the internal structure of the adsorption. The positive value of ΔH^o indicates that the adsorption process is an endothermic process. Change in enthalpy was obtained at a value of 24.53KJ/mol indicating slightly predominantly chemisorption process. The activation energy (Ea) was found to be indicating chemisorption process due to the slightly higher value. The negative value of ΔG^o indicates that adsorption processes are spontaneous at all the solution temperature. Similar result was reported in the literature for adsorption of basic dye using acid treated Kenaf fibre char (Dalia *et al.*, 2012) and the adsorption of malachite green dye onto carbon derived from palm flower waste (Nethaji *et al.*, 2010).

Table 4. Thermodynamics parameters for the adsorption of TSDP on the adsorbents.

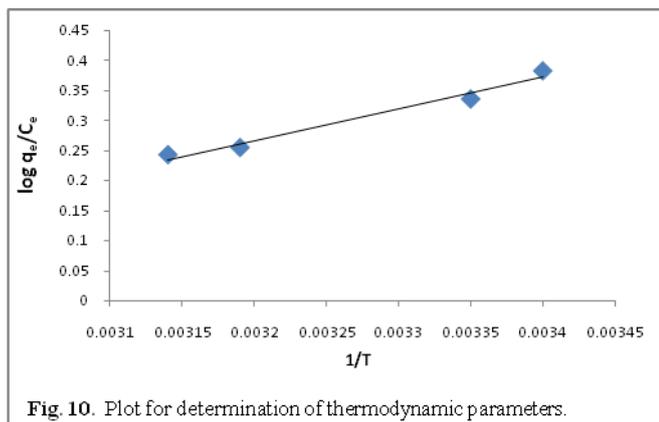| Adsorbent	R^2	ΔH^o	ΔS^o	$--\Delta G^o$		
		kJ/mol	kJ/molk	KJ/mol		
				303K	308K	313K
ACAA	0.999	24.53	0.651	172.72	175.98	179.3

Fig. 10. Plot for determination of thermodynamic parameters.

G. Adsorption Factorial Design on ACAA.

The factorial design experiment was used to study the adsorption of BE using ACAA. The optimization was done to know the best out of a number of possible options and the most desirable or favourable. The factorial design was achieved using the Design Expert 8.0 statistical software. The factorial was done based on the three level designs. The factors that can affect the process include:

X_1 = Adsorbent Doses (g)
X_2 = Contact time (min).
X_3 = Stirring speed (rev/min)

The half normal plot shown on fig (11) shows the percentage probability and normal effects indicating there is no error estimated. By showing all the effects indicates that they are all included in the model. The one factor plots for ACAA at varying Adsorbent doses, Contact time and Stirring Speed shown in fig 12, indicates that the optimum adsorbent dose range was 0.6 – 1.0g. The optimum stirring time obtained was between 32.5-60min and the optimum stirring speed obtained was 15rev/min. The 3D-Surface plots for ACAA at varying Adsorbent doses, Contact time and Stirring Speed were shown in fig 13. From the plots, it was deduced that the optimum condition for plot on Fig. 13a was at stirring time 32.5min and adsorbent mass of 0.2g. Fig. 13b gave an optimum result at stirring speed 15rev/min and 1.0g adsorbent mass. Also Fig. 13c gave an optimum result at stirring speed 15rev/min and 60min stirring time. The average optimum result obtained showed that the best stirring time was between 32.5 – 60min. and 0.6 – 1.0g doses. The results obtained on the 3D-Surface plots agreed with the results obtained on the one factor effect plots shown on fig. 12.

IV. CONCLUSION

The present study showed that natural adsorbents prepared from African star apple seed can be effectively used as adsorbent for the removal of TSDP from BE. Batch adsorption studies showed that removal is dependent upon process parameters like; Contact time,

effluent concentration, adsorbent doses, stirring speed and solution temperature. The maximum adsorption took place in the stirring time range of 32.5 - 60min stirring speed of 15rev/min and adsorbent mass of 0.6 - 1g. The sorption data obtained at optimized conditions have been subjected to Freundlich and Langmuir Isotherm studies. The data fits well to both the Freundlich and Langmuir isotherm indicating favourable and monolayer adsorption. The kinetics study showed that the Pseudo second-order reaction model fitted better. The adsorption process was endothermic and spontaneous in nature. Therefore, high temperature favours the adsorption process. The factorial effect data generated and plotted agreed well with the One Factor at a Time (OFAT) results. All the information indicated that the ACAA exhibited potential applications in the fields of effluent treatment for the removal of micro organic particles (TSDP).

V. ACKNOWLEDGEMENT

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Fig. 11. Half Normal Plot
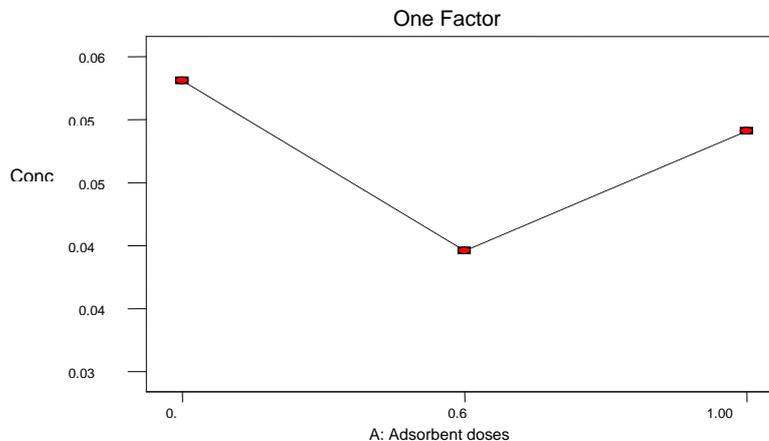
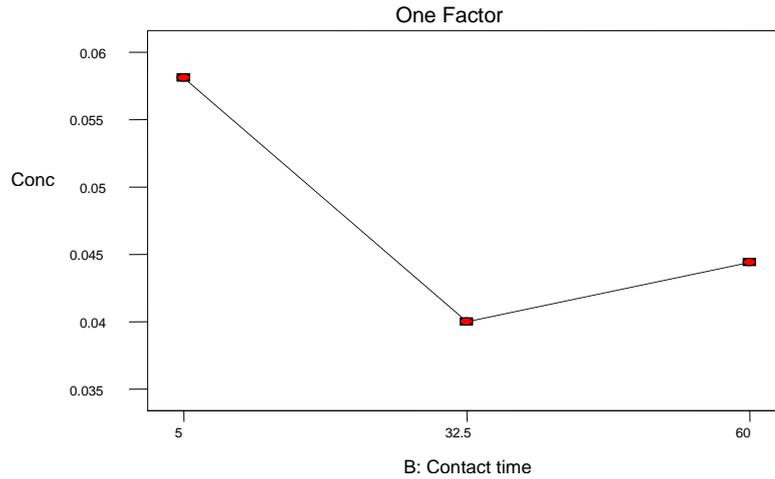Design-Expert® Software
Factor Coding: Actual
Conc.

● Design Points

X1 = B: Contact time

Actual Factors
A: Adsorbent doses = 0.2
C: Stirring speed = 10

Design-Expert®
Factor Coding:
Conc

● Design

X1 = C: Stirring speed

Actual
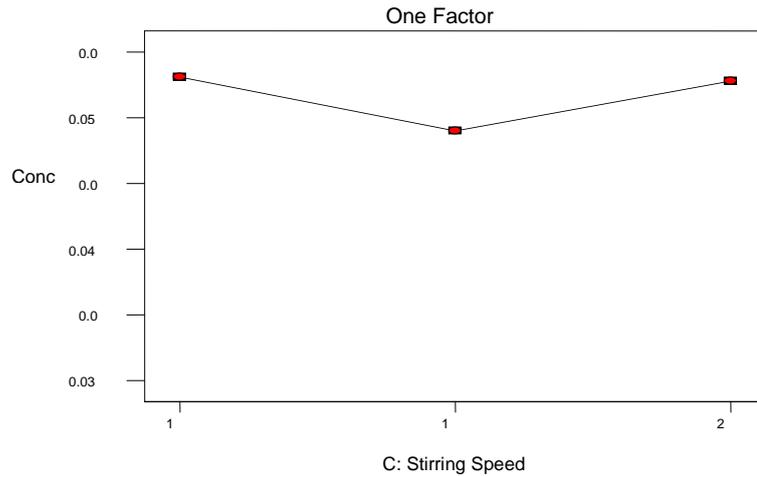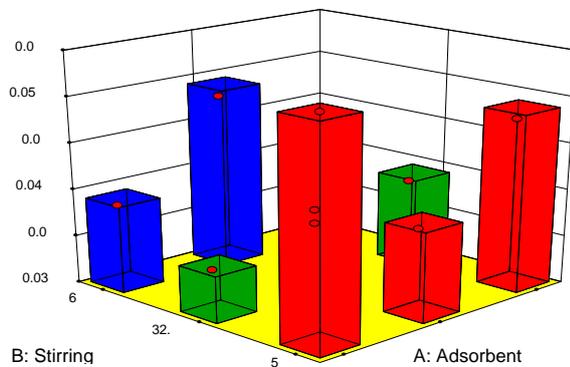A: Adsorbent doses =
B: Contact time =

Fig. 12. One Factor Plots for AACA at Varying Adsorbent Doses, Contact Time and Stirring Speed.
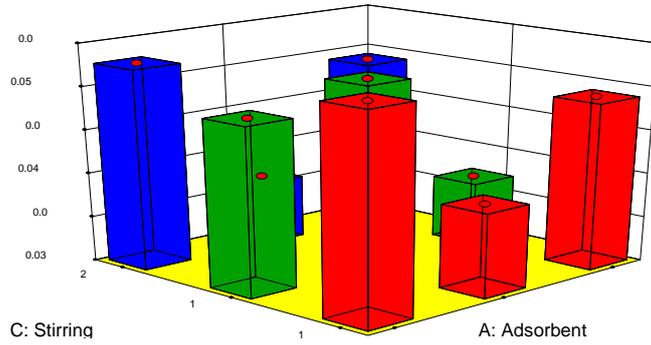

Design-Expert®
Factor Coding:
Conc

X1 = A: Adsorbent
X2 = B: Contact
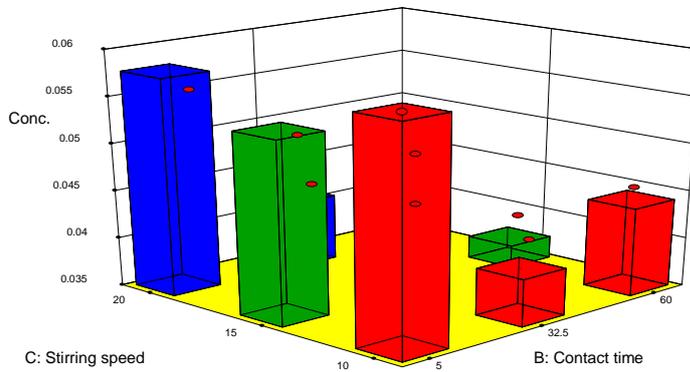
Actual
C: Stirring speed =

Fig. 13. The 3-Dimensional Surface Plots for AACA at Varying Adsorbent Doses, Contact Time and Stirring Speed.