

Chemistry of Pyrolysis and Kinetic Studies of Shea Nut (*Vitellaria paradoxa*) Shells Activated Carbon for Textile Wastewater Treatment

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ABSTRACT: Phosphoric acid (H_3PO_4) and Zinc chloride ($ZnCl_2$) catalyzed shea nut shells, subjected to a one way activation scheme was employed to study the adsorption kinetics and mode of diffusion of industrial dye uptake. Thermodynamics data obtained in this study indicate that the sorption of dye spontaneously increases with time and decreases after equilibration was reached. The adsorption follows the pseudo second order kinetic model which gave the least % SSE (0.449-1.348), best linearity ($R^2=0.998-0.999$) and closer agreement between the experimental and calculated q_e values (q_e exp., 96.985/ q_e cal., 100.00). Mode of transport deviate from the intraparticle diffusion model. According to this study, percent dye removal coupled with the close proximity of generated data to those reviewed in literatures, is an indication that shea nut shells could compare, to a good extent with commercial activated carbon for organic dye removal from dyestuff wastewater.

KEY WORDS: Pyrolysis, *Vitellaria paradoxa*, Shea nuts, Activated carbon, Textile effluent, Wastewater.

INTRODUCTION

Wastewater treatment is a sure way of reducing environmental degradation posed by agricultural, industrial and human activities[1]. One of the major causes of environmental pollution is industrial effluent.

Effluent discharged from dyeing industries is highly colored; of low BOD are high COD. The disposal of this colored water can be toxic to aquatic life [2] The dyes upset the biological activities in water bodies, poses

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health threat since they are mutagenic and carcinogenic and can cause severe damage including kidney dysfunction, reproductive system, liver, brain and CNS malfunctioning [2].

Many conventional methods such as chemical oxidation, coagulation, precipitation as well as biological techniques can be used for removal of dyes and metal ions from aqueous solutions. Among many new technologies is the utilization of plant residues as adsorbents [3]. A wide variety of carbons have been prepared from agricultural wastes. These includes peanut hulls, baggage pith, wood products, corn cob coir pith, fish waste etc [1-4]. Commercially available activated carbon is expensive especially in countries where economy plays a very big role. It is therefore better to find low cost precursors to be used as adsorbent. This present article reports the feasibility of shea nut shells as potentially low cost adsorbent material for the removal of dyestuff with more emphasis on the activation chemistry and kinetics of adsorption.

EXPERIMENTAL SECTION

Materials and Methods

Polluted effluent (Adsorbates) used in this study is Chellco textile industrial dye wastewater. It was collected at the effluent reservoir in the main factory site, Kaduna - Nigeria. The wastewater concentrate was diluted to the required concentration as described elsewhere[5]. A 1000mg/L concentration was first prepared and from which series of working concentrations ($10\text{-}50\text{ mgL}^{-1}$) were obtained. shea nut shells was procured from Rikoto Zuru emirate of Kebbi state, Nigeria. The shell samples were washed and oven dried at 110°C before activation, Using the one way thermochemical activation scheme as earlier described [6]. The thermochemical activation is a process that depends upon the action of inorganic chemical compounds such as ZnCl_2 and H_3PO_4 used in this research to dehydrate the organic molecules during pyrolysis (another name for cracking, carbonization or calcinations). In this study, 3g of the pretreated and grinded shea nut shells was mixed with 3cm^3 , 1molar activation agents. The mixture was allowed to stand for one hour before igniting in a furnace fired at 800°C for a five minutes and 10 minutes dwell time [6].

Chemistry of pyrolysis

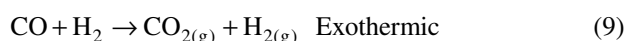
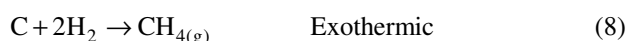
Thermal conversion process involves 3 stages [7].

(a) Combustion: This is a complete thermal oxidation of the shea nut shells. At this stage, there is still adequate oxygen in the system to allow breakage of carbon bonds. During reduction of carbonaceous materials, excited oxygen molecule reacts with carbon until the entire available bond is broken. This process is exothermic [7].



Eqs. 1-4 revealed that the primary emission of combustion are $\text{CO}_{2(\text{g})}$, $\text{H}_2\text{O}_{(\text{g})}$, $\text{NO}_{2(\text{g})}$, $\text{SO}_{2(\text{g})}$ and $\text{CO}_{(\text{g})}$.

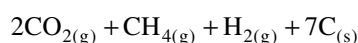
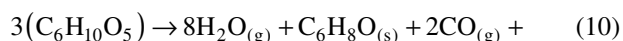
(b) Gasification: If the amount of oxygen in the combustion chamber were reduced to below the amount required for combustion, the process is termed gasification. This thermal system leads to a partial burning by forcing carbon molecules to pair with limited (only one) oxygen molecule and thus, increase the production of carbon monoxide (Co)



This system is also exothermic and self sufficient the net process is endothermic for gasification process [8].

(c) Pyrolyzation (thermal distillation): In this stage, the remaining char from gasification, can be manipulated through a combination of thermal cracking and condensation reaction in the absences of oxygen. This highly endothermic reaction required extensive external energy. distillation of char or pyrolysis yield two usable by-products, (a) combustible gas, mainly saturated hydrocarbon (methane) and (b) activated carbon [8].

Equation representing complete pyrolysis is given as (x).

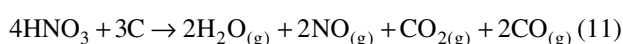


Pyrolysing units are designed to achieve temperature ranging from 315° C to 925 °C. Harvesting of the useful off gases from pyrolysis of municipal solid waste has not been successful because of difficulties obtaining pure final gas, the technical complexity of the system and financial consideration for strict heating control [9].

Cooling

Carbon is allowed to return to ambient (surrounding) temperature. Experimental results revealed that carbon proceed at high T °C with rapid cooling adsorb basic material more rapidly as does, the slower cooled carbon for removal of acidic substances. As cooling proceed slowly, oxygen came in contact with surface of carbon, forming chemically-attractive oxide groups [7].

The use of activating agent is for pore size development. The area occupied by the activating agent remains as developed pores after the washing process to remove the residual chemical. Such chemical is capable of producing the hot spot adsorption area in charcoal as shown below



The water vapor produces the hot spot adsorption area [10].

Batch mode adsorption studies:

The entire experiment was carried out at room temperature, $27 \pm 2^\circ\text{C}$. 10 mL dye solution (1000mg/L) and 0.1g adsorbate ($< 2.0\text{mm}$ aperture size) were taken into a 25 mL Erlenmeyer flask and sealed. The samples were allowed to equilibrate at predetermined time (15, 30, 45... and 90 min.). The absorbance values of the dye solution before and after treatment were measured, using Jenway 610 model spectrophotometer at the pre-determined maximum wavelength (640nm). The experiment was conducted in triplicate [11,12]. The characteristics of the generated adsorbents was presented elsewhere [13].

RESULTS AND DISCUSSION

Fig. 1a shows removal of dye by various sorbents as a function of initial dye concentration. Acid (H_3PO_4) catalyzed sorbents proves to present higher percent dye removal. This is pronounce for the carbon activated at longer time, (SS/A/15/ C_o : 74.172 -84.80%). The 10mg/L concentration dyes were the most adsorbed (59.60 -84.80%) compared to the 50mg/L dye solutions

(33.144-74.172%). This could be linked to the less and a more competition for adsorption sites in the former and later cases respectively. Colour removal from the 40mg/L solution gave values that are closely related to those values by the 50 mg/L. This is an indication of near equilibration for the chosen optimum initial dye concentration of 50 mg/L.

Fig. 1b represents the effects of contact time on dye uptake. Quantitative removal of most of the dye was obtained at a short time (15-60 minutes). This is in agreement with the work by [5]. The equilibrium time was deduced from the least absorbance (high adsorption) values for each series. This term is a very useful parameter for wastewater treatment. It gave the corresponding equilibrium concentration (C_e) and amount of adsorbed per unit dose of adsorbent (q_e). Fig. 1b, with an auto appended table showed a gradual increase of removal percentage with time. Occurrence at 90 min. contact time is an indication of slight desorption for most of the series, dye removal percentage ranges between 94.724-97.99, 93.467-92.714, 75. 182-98. 985 and 96. 482- 97. 489% for SS/A/5, SS/Z/5, SS/A/15 and SS/Z/15 sorbent respectively. The lower and higher ranges are values for 90 minutes interaction (with extent of slight desorption) and 60-75 min. interaction, which are evidence of equilibration. The extent at which dye removed by SS/Z/15/t is greater than that of SS/Z/5/t could be linked to high pore size development which possibly resulted from longer activation time as achieved in the former.

The percent dye removal (% RE) was calculated for each run by following the expression in Eq. (1) below:

$$\text{RE}(\%) = ((C_i - C_e) / C_i) \times 100 \quad (12)$$

While the adsorption capacities of the adsorption for each concentration of dye at equilibrium were calculated using Eq. (2):

$$q_e (\text{mgg}^{-1}) = (C_i - C_e) V / m \quad (13)$$

Where C_i and C_e (mg/L) were the initial and final concentration of dye solution, q_e (mgg^{-1}) is the amount of dye adsorbed per unit mass of adsorbent which is also a measure of adsorption capacity. V is the volume of dye solution (L) while m is the carbon dose (g) [14].

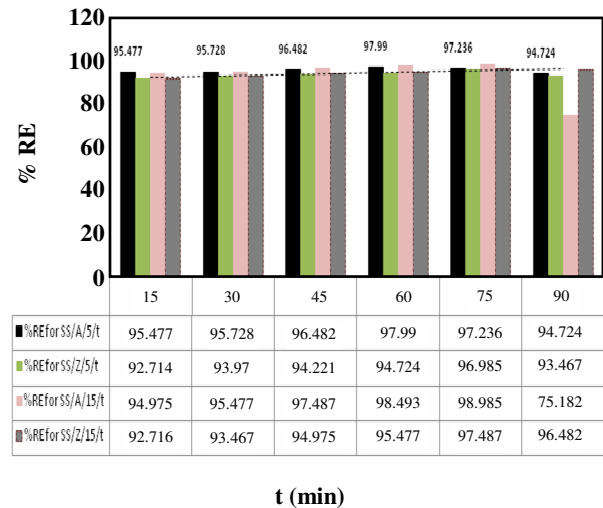
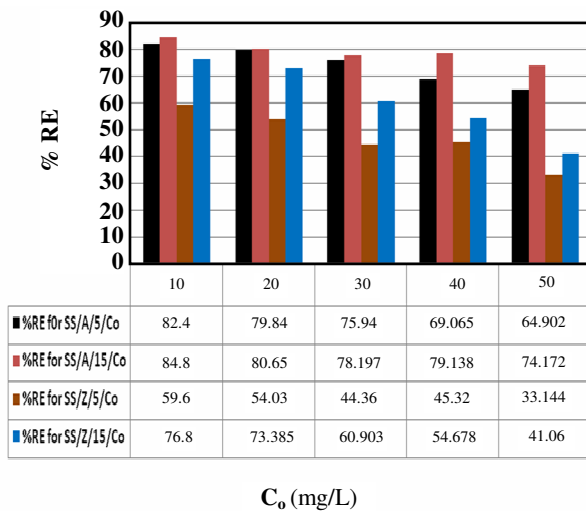


Fig. 1: a) Percentage of dye removal onto acid and salt catalyzed shea nut shell activated carbon, b) Effect of contact time on % dye adsorbed onto acid and salt treated SS sorbent.

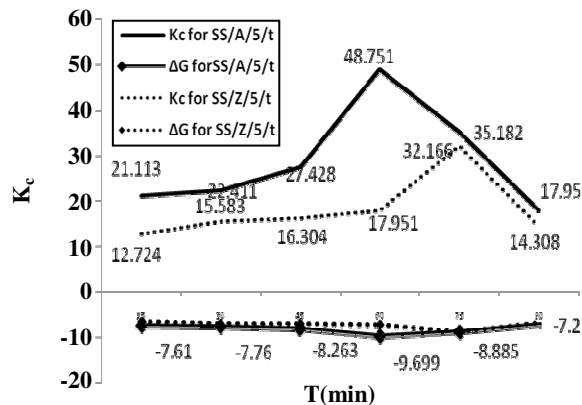


Fig. 2: Thermodynamic equilibrium constant (K_c) and gibbs free energy (ΔG) of dye uptake by SS/A/5 and SS/Z/5 sorbents.

Fig. 2 represents the thermodynamic equilibrium constant (k_c) and Gibbs free energy (ΔG) values for sorption of dye onto SS biosorbent. The change in Gibbs free energy was investigated, using Eqs. (3) and (4) below [15].

$$\Delta G = -RT \ln K_c \quad (3)$$

$$K_c = c_a/c_e \quad (4)$$

Where K_c is the equilibrium constant, C_a and C_e are the solid and equilibrium phase concentrations in mg/g and mg/L respectively. T is the temperature in Kelvin while R is the gas constant.

As the contact time increases, ΔG values becomes more negative, an indication of increase spontaneity

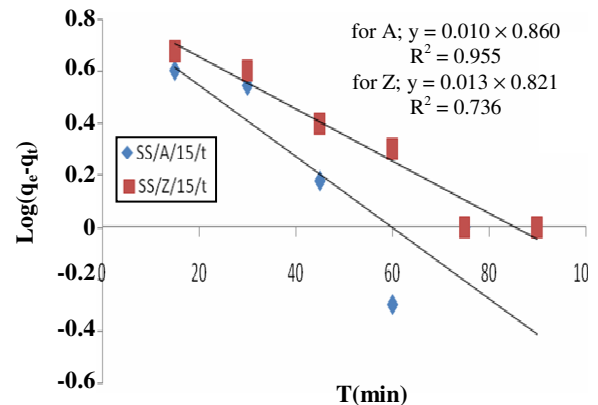


Fig. 3: Pseudo first order kinetics for adsorption of dye onto acid and salt catalyzed SS carbon (5 minutes activation).

with increase in k_c (the ratio of the adsorbed concentration and equilibrium concentration). The characteristic decrease of k_c and ΔG values at 75 min. is an indication that equilibration limit has been exceeded. SS/A/5/t gave a higher k_c value (98.502), and signifies more adsorption onto the solid phase.

Batch kinetic study

Two kinetic and one transport models were used to test the adsorption process of dye uptake. The pseudo first order equation given by Lagergren and Svenska was described [11] as Eq. (5a):

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (5a)$$

Table 1: Pseudo first order experimental data of dye uptake by acid and salt catalyzed SS bio adsorbents.

Sorbents	Equation(y=)	R ²	K ₁ (min ⁻¹)	q _e cal.(mg/g)	q _e exp.(mg/g)	% SSE
SS/A/5/t	-0.009x+0.581	0.974	0.021	3.811	97.990	42.118
SS/Z/5/t	-0.013x+0.821	0.737	0.030	6.622	96.985	40.412
SS/A/15/t	-0.010x+0.860	0.955	0.023	7.244	98.995	41.032
SS/Z/15/t	0.013x+0.821	0.736	0.030	6.628	97.487	40.633

SS/A/5 - shea nut shells, treated with, H₃PO₄ activated for 5 minute dwell time. SS/Z/15 – shea nut shells, treated with ZnCl₂, activated for 15 minute dwell time.

Table 2: Pseudo second order experimental data of dye uptake by acid and salt catalyzed SS bio adsorbents.

Sorbents	Equation(y=)	R ²	K ₂ (gmg ⁻¹ min)	q _e cal.(mg/g)	q _e exp.(mg/g)	% SSE
SS/A/5/t	0.010x+0.003	0.999	0.033	100.00	97.990	42.118
SS/Z/5/t	0.010x+0.002	0.998	0.050	100.00	96.985	40.412
SS/A/15/t	0.010x+0.012	0.999	0.008	100.00	98.995	41.032
SS/Z/15/t	0.010x+0.005	0.999	0.020	100.00	97.487	40.633

SS/A/5 - shea nut shells, treated with, H₃PO₄ activated for 5 minute dwell time. SS/Z/15 – shea nut shells, treated with ZnCl₂, activated for 15 minute dwell time.

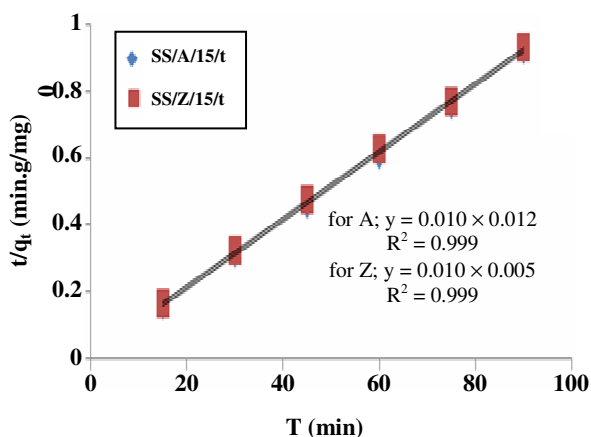


Fig. 4: Pseudo second order kinetics for adsorption of dye onto acid and salt catalyzed SS carbon (15 minutes) activation..

And also presented [16] as Eq. (5b):

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t. \quad (5b)$$

Where q_e and q_t are the amount of dye adsorbed at equilibrium and time, t (min), respectively and K_1 is the rate constants for first order model (min⁻¹). Values of k_1 were obtained from plot type in Fig. 3 for a typical pseudo first order kinetic experimental data on Table 1

Generated data were also tested using the pseudo second order kinetic model [12] expressed as Eq. (6a & b).

$$t/q_t = 1/h + (1/q_e) t \quad (6a)$$

h is the initial adsorption rates given as Eq. (6b):

$$h = k_2 q_e^2 \quad (6b)$$

where k_2 (gmg⁻¹min) is the rate constant of the second order adsorption.

A plot of t/q_t versus t (Fig. 4) gives a linear relationship which the slope (q_e) and intercept, k_2 are determined (Table 1).

The two models were compared for their fitness for industrial dye uptake by four series of shea nut shells activated biosorbent. Accepted kinetic model for a given adsorption is characterized by three common validity test;

(i) A good and high correlation coefficient, R^2 indicating the applicability and reliability of a given model.

(ii) A close agreement between the calculated and experimental q_e values.

(iii) The accepted model must have the least values for the sum of error squares (% SSE), which is determined as equation 7

$$SS E (\%) = \sqrt{\sum (q_{e,exp} - q_{e,cal})^2 / N} \quad (7)$$

Where N is the number of data points [11,12,16].

Findings from this study showed that the data range for pseudo second order kinetics plots falls within the ranges; $R^2 = 0.998-0.999$, % SSE = 0.449- 1348 and $q_{e,cal} = 100\text{mg/g}$ while $q_{e,exp}$ falls within the range

Table 3: Intraparticle diffusion model experimental data of dye uptake by acid and salt catalyzed SS bio adsorbents.

Sorbents	Equation(y=)	R ²	K _{id} (min ^{1/2})	C _i
SS/A/5/t	0.486x+93.41	0.766	0.486	93.410
SS/Z/5/t	0.762x+89.57	0.843	0.762	89.570
SS/A/15/t	0.926x+91.07	0.948	0.926	91.070
SS/Z/15/t	0.952x+88.64	0.931	0.952	88.640

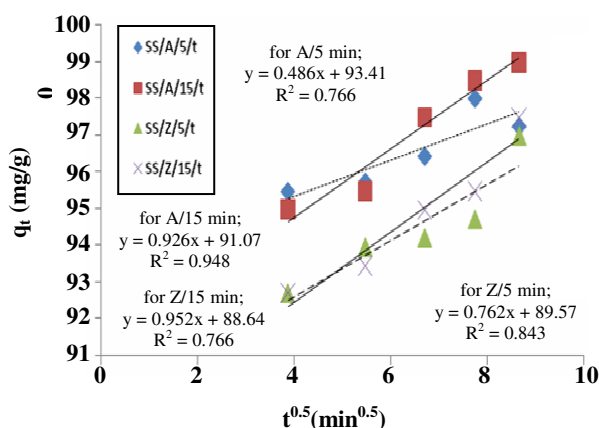


Fig. 5: Intraparticle diffusion plot for adsorption dye onto acid and salt catalyzed SS carbon (5 and 15 minutes activation).

of 96. 985-98. 995mg/g for the series. This values are more favorable in justifying the adsorption of dye onto SS biosorbent as following second order kinetic model than the pseudo first order model, whose corresponding data include 0.736 – 0.974, 40. 412 – 42.118 and 100:3.811 – 7.244 for R², % SSE and q_e cal: exp respectively. The rate of dye sorption by acid treated SS/A/5/t,(0.033) is about 2 times slower than that of SS/Z/5/t,(0.050) while SS/Z/15/t, adsorb 2 times faster,(k₂=0.020) compared to its corresponding acid catalyzed biosorbent(K₂=0.008) units in gm⁻¹min. This could be linked to a higher mesopore created by the ZnCl₂ modified biosorbent.

The transport process was studied, using the intraparticle diffusion model. This model was design to investigate the mechanism of dye adsorption. The intraparticle plot is an empirical found functional relationship, common to adsorption process where sorption varies almost directly with square root of time (t^{1/2}) instead of contact time (t) as presented in Fig. 5.

According to the theory earlier proposed [11,17], the intra particle diffusion equation is given as Eq. (8):

$$q_t = k_{id} t^{1/2} + C_i \quad (8)$$

where k_{id} (mgg⁻¹ min^{1/2}) is the rate constant of stage i, which is obtained from the straight line plot of q_t versus t^{1/2}. C_i is the intercept.

Disregarding the linearity (high R² value) of the intraparticle diffusion plot, the sorption mechanism assumes this model if the following conditions are met:

- (i) High R² values to ascertain applicability
- (ii) Straight line which passes through the origin for the plot area q_t vs. t^{1/2}.
- (iii) Intercept C_i < 0. A validity test which deviates from (ii) and (iii) above shows that the mode of transport is affected by more than one process [12].

Results in this analysis gave a good linearity (R² = 0.766 - 0.948), with an excessively high C_i values (88.64 - 93.41) as displayed on Table 3. The plot straight lines does not pass through the origin (Fig. 5). It does imply that sorption mechanism is not by intraparticle diffusion. This studies is in good agreement with the kinetic test of methylene blue removal by papaya seed [12] and Bamboo based activated carbon [13] which all modeled into the pseudo second order kinetics.

CONCLUSIONS

This present study revealed the feasibility of shea nut shells as an effective biomass for dye uptake bio-adsorbent with relatively high percent dye removal. Generally, adsorbents derived at higher activation time (SS/A/15/t and SS/Z/15/t) proved to be a better attractant for the dyestuff under the stated experimental condition. The absorption kinetic data does not follow the first order but can be predicted by the pseudo second order kinetic model, having fulfilled the validity tests. The R² values of intraparticle diffusion plots and their very high intercept C_i >> 0 proves that adsorption mechanism is governed by more than one process and not by intraparticle diffusion.

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