

# Kinetic Studies on Oil Sorption Using Acetylated Sugarcane Bagasse and Groundnut Husk

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**Abstract**– Crude oil spill has a great negative influence on the ecosystem by putting the marine lives at high risk. The treatment of an oil spill remains a challenge to the environmental scientists. Natural organic sorbents are emerging as proper choices for oil spill cleanup due to their availability, eco-friendliness and low cost. In this study, groundnut husk and sugarcane bagasse were treated with acetic anhydride to increase their hydrophobic properties and improve their sorption effectiveness in aqueous environments. The results shows that acetylated sugarcane bagasse are more suitable sorbent than acetylated groundnut husk for oil sorption. The pseudo-first order and pseudo-second order were analyzed and pseudo-second- order provided the best fit with R<sup>2</sup> values of, AGH (0.964), RGH (0.989) and ASB (0.992), RSB (0.996) respectively. The Intraparticle diffusion and Liquid film diffusion mechanism were also analyzed. The intraparticle diffusion mechanism produced a better R<sup>2</sup> than the liquid film diffusion model for the acetylated sorbents which is an indication that penetration into the pores of the materials was more predominant than surface sorption. The results presented in this study indicated that acetylated sugarcane bagasse and groundnut husk are suitable sorbents with the potential for further development for oil spill treatment.

**Keywords**– Oil Spillage, Acetylation, Kinetics, Sugarcane Bagasse and Groundnut Husk

## I. INTRODUCTION

Oil spill is a release of a liquid hydrocarbon into the environment due to human activity and it is a form of pollution. Oil spill has adverse impact on the ecosystem and human health. Oil pollution of the shore, in addition to the reduction of amenity also affects marine shore life and vegetation (Wardley 1983).

As long as oil is explored, transported, stored and used, there is risk of spillage with the potential to cause significant environmental impact. Spilled oil has an undesirable taste and odour and causes severe environmental damage on water fowl material life and affects tourism and economy. Oil spills constitute the most challenging and worrisome problem facing both the oil industries and governments.

In the past two decades, the reuse of agricultural byproducts as oil sorbents has received growing attention due to their low cost and biodegradability (Adebajo et al 2003) . Most agricultural byproducts derived from plants such as rice straw,

sisal and saw dust, kenaf have been investigated for oil spill cleanup applications (Choi and Cloud 1992).

The acetylation reaction is one of the most common techniques used for hydrophobic treatment of lignocellulosic materials (e.g., wood) by substitution reaction of a hydroxyl group (hydrophilic) with an acetyl group (hydrophobic). This reaction is usually carried out by heating lignocellulosic material in the presence of acetic anhydride with or without catalyst (Nwadiogbu et al, 2015). In this study Acetylated groundnut husk and sugarcane bagasse were selected as a natural organic sorbents.

## II. MATERIALS AND METHODS

### A) Materials preparation

Groundnut husk and Sugarcane bagasse were collected from local Market in Enugu metropolis, Nigeria. They were thoroughly washed with clean water to remove dust and fungus. They were dried in sunlight for about 12 hours and then left to dry at 65°C in an oven. They were ground using manual grinding machine, size reduced and sieved through 25 British standard sieves (BSS Sieves). The other reagents and chemicals were obtained from the British Drug House (BDH) and included acetic anhydride, iodine, acetone, ethanol and n-hexane, which were used without further purification.

### B) Soxhlet extraction

To reduce the influence of the fiber extract on acetylation, 10g of the sieved materials were extracted with a mixture of acetone and n-hexane (4:1, v/v) for 5hrs. The extracted samples were dried in a laboratory oven for 16hrs. The extracted content was calculated as percentage of the oven-dried test samples.

### C) Acetylation of the Adsorbents

The acetylation of the groundnut husk and sugarcane bagasse under mild conditions in the presence of iodine using acetic anhydride was carried out using the method reported by Nwabueze et al (2005) which involved acetylation in a solvent free system. The amount of substrate and reactant were combined in a ratio of 1:20(gram dried groundnut husk

and sugarcane bagasse/mL acetic anhydride). The reaction temperature, time and amount of catalyst were 100°C, 1hr and 1%, respectively. The mixture of raw groundnut husk and sugarcane bagasse, acetic anhydride and catalyst were placed in a round-bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermostatic heating device. Then, the flask was removed from the bath, and the hot reagent was decanted. The groundnut husk and sugarcane bagasse were thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and the acetic acid by-products. The new products were dried in an oven at 60°C for 16h prior to analysis.

#### D) Oil Sorption

The sorption of oil from water was carried out using the methods reported by Banerjee et al (2006). A portion of (0.20,0.40, 0.60,0.80 and 1.0)grams of raw groundnut husk and acetylated groundnut husk; raw sugarcane bagasse and acetylated sugarcane bagasse was placed in a 250-mL beaker containing 8g of crude oil dispersed in a 100mL of water at 26°C. The samples were left in the mixture for approximately 2min with little agitation. The sorbents were removed from the beakers using sieve nets. The nets were allowed to drain. The oil-loaded sorbents were dried at 60°C for 30 minutes and re-weighed. The oil sorption capacity was calculated by taking into account the weight of the sorbents and oil and the weight of the sieve net using the formula below:

$$\text{Oil sorption capacity (g/g)} = (S_{st} - S_o) / S_o \quad (1)$$

where  $S_o$  is the initial mass of the dry sorbent,  $S_{st}$  is the mass of the sorbent with oil at the end of the sorption test and the  $(S_{st} - S_o)$  quantity is the net of oil sorbed (all of the masses were measured in grams).

$$q_e = (C_o - C_e)V/m \quad (2)$$

where  $C_o$  is the initial oil concentration in mg/L,  $C_e$  is the equilibrium oil concentration in mg/L,  $V$  is the volume of the solution in liters, and  $m$  is the mass of the adsorbent in g.

### III. RESULTS AND DISCUSSIONS

#### A) Kinetic studies

The sorption kinetic models were applied to the experimental data to analyse the rate and the mechanism of crude oil sorption of the adsorbents. The kinetic models applied to this study are the Lagergren pseudo-first-order, pseudo-second-order, intraparticle diffusion and liquid film diffusion models.

The pseudo-first-order kinetic model, which is also known as the Lagergren equation, is expressed as (Dawodu and Akpomie 2014).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where  $q_t$  and  $q_e$  are the amounts of crude oil sorbed at time  $t$  (sec) and equilibrium respectively in mg/g.  $k_1$  is the pseudo-first-order rate constant ( $s^{-1}$ ). The slope and the intercept of the plots of  $\ln(q_e - q_t)$  as a function of  $t$  were used to determine

the rate constant and  $q_e$ . The pseudo-second-order kinetic model can be expressed as (Ho and Mackay 1998):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where  $k_2$  is the rate constant of pseudo-second-order expression ( $g/mgs^{-1}$ ).

The  $q_e$  and  $k_2$  values were calculated from the slope and intercept of the linear plot of  $t/q_t$  as function of time( $t$ ). The initial sorption rate ( $h$ ( $mg/g s^{-1}$ )) was calculated from the following equation:

$$h = k_2 q_e^2 \quad (5)$$

and the values are listed in Table I and Table II.

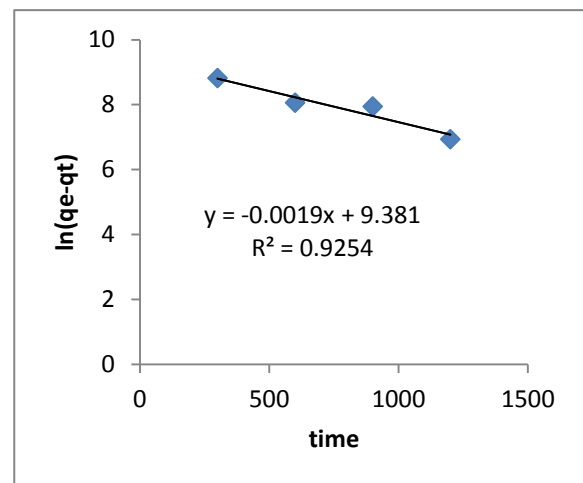


Fig. 1: Pseudo first order kinetic for ASB

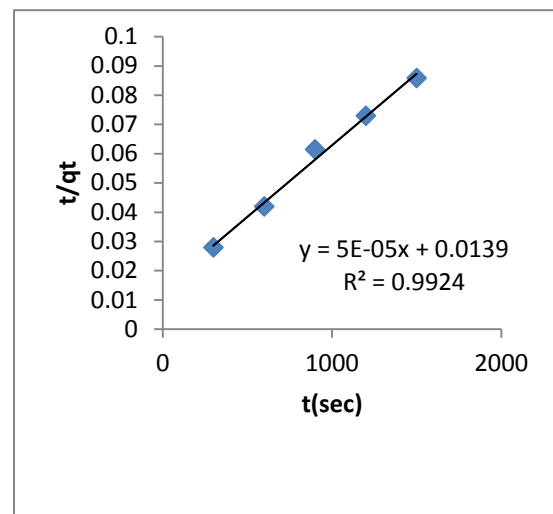


Fig. 2: Pseudo second order kinetic for ASB

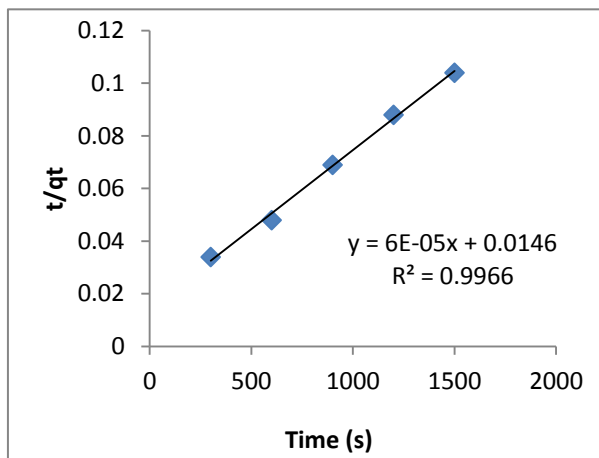


Fig. 3: Pseudo first order kinetics for RSB

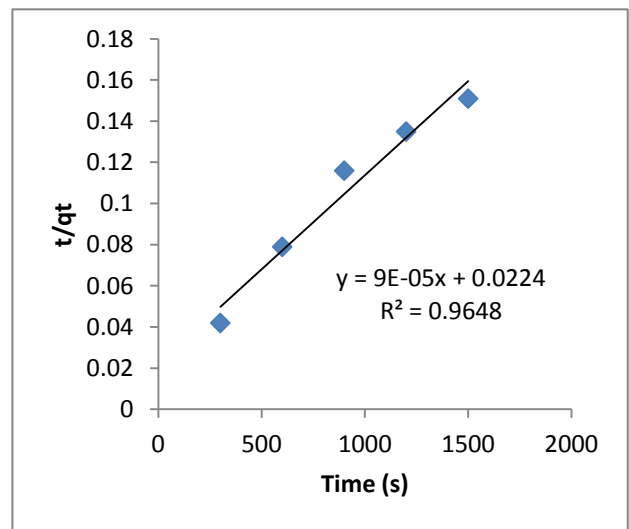


Fig. 6: Pseudo second order kinetics for AGH

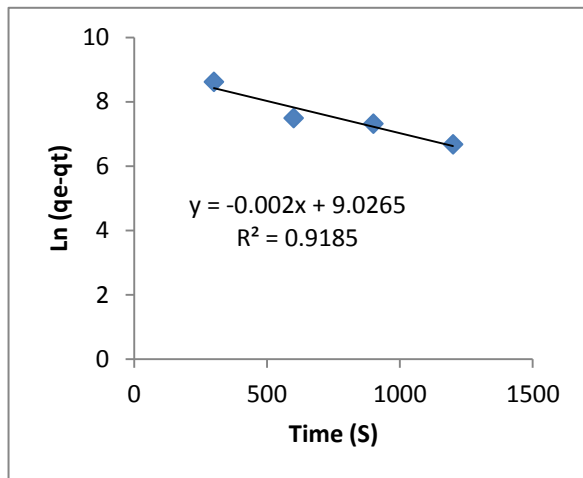


Fig. 4: Pseudo second order kinetics for RSB

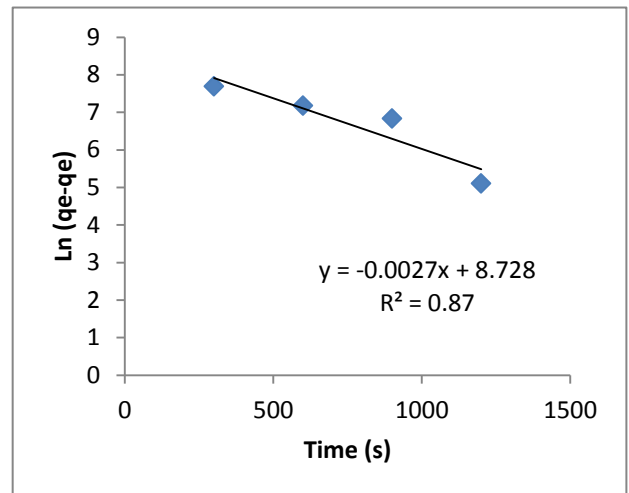


Fig. 7: Pseudo first order kinetics for RGH

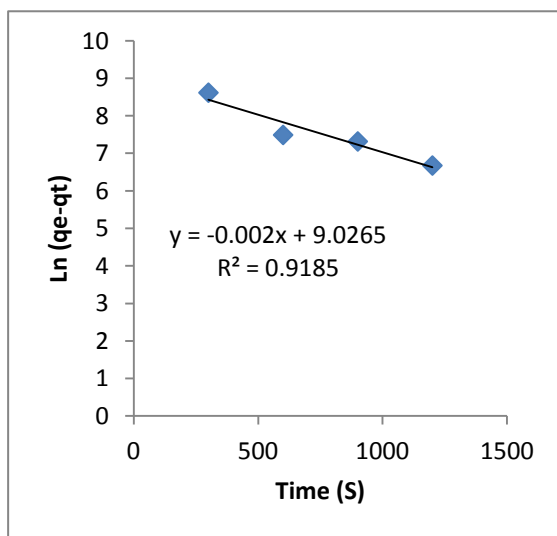


Fig. 5: Pseudo first order kinetics for AGH

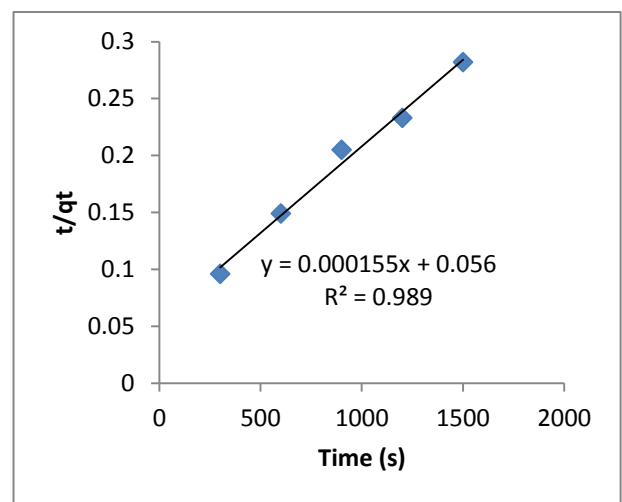


Fig. 8: Pseudo second order kinetics for RGH

Table I and Table II show a comparison of the kinetic parameters for crude oil sorption on AGH, RGH and ASB, RSB. The coefficient regression ( $R^2$ ) for AGH (0.806), RGH (0.87) and ASB (0.925), RSB(0.918) respectively for the Pseudo-first-order kinetic expression. The pseudo-second-order kinetic expression resulted in a higher  $R^2$  value, for AGH (0.964), RGH (0.989) and ASB (0.992), RSB (0.996) respectively. This result indicates that the pseudo-second-order kinetic model produced a better fit to the data. Therefore, the pseudo-second-order kinetic expression is the best kinetic model to explain the sorption of crude oil on AGH, RGH and ASB, RSB, which is in agreement with previous results (Ho et al, 2002).

Table I: Summary of the kinetic model parameters for the sorption of oil on groundnut husk

Kinetic models	AGH	RGH
$q_e$ exp(mg/g)	9940	5325
<b>Pseudo-first-order (Lagergren).</b>		
$q_e$ calc (mg/g)	4337	6173
$k_1$ (s <sup>-1</sup> )	-0.001	-0.002
$R^2$	0.806	0.87
<b>Pseudo-second-order</b>		
$q_e$ calc (mg/g)	11111	6451
$k_2$ (s <sup>-1</sup> )	3.68x10 <sup>-7</sup>	4.29x10 <sup>-7</sup>
$R^2$	0.964	0.989
<b>Intraparticle diffusion</b>		
$K_d$ (meq g <sup>-1</sup> s <sup>-1/2</sup> )	127.1	104.8
$R^2$	0.858	0.981
C	4558	1362
<b>Liquid film diffusion</b>		
$K_{fd}$ (meq g <sup>-1</sup> s <sup>-1/2</sup> )	-0.001	-0.002
$R^2$	0.806	0.869

The Intraparticle diffusion model can be expressed as (Nwadiogbu et al, 2015).

$$q_t = k_d \cdot t^{1/2} + I \quad (6)$$

Where  $k_d$  is the intraparticle diffusion rate constant (mg/g s<sup>1/2</sup>) and  $I$  is the intercept. The intercept of the plot is shown in Table I and indicated the presence of a boundary layer effect. When the intercept is larger, surface sorption contributes more to the rate-determining step is greater. The  $k_d$  constant was obtained from the slope of the plot of  $q_t$  as a function of  $t^{1/2}$ . Intraparticle diffusion is the rate-determining step when the plot is linear and passes through the origin (Dawodu and Akpomie, 2014). Based on the results in Table I and Table II, a high regression coefficient ( $R^2$ ) and a non-zero intercept ( $I$ ) was obtained.

The deviation from the origin is due to the difference in mass transfer between the initial and final stages of the sorption process (Das and Mondal, 2011). The good

regression indicating that an intraparticle diffusion mechanism was not the only rate-limiting step.

Table II: Summary of the kinetic model parameters for the sorption of oil on sugarcane bagasse

Kinetic models	ASB	RSB
$q_e$ exp(mg/g)	17490	14415
<b>Pseudo-first-order (Lagergren).</b>		
$q_e$ calc (mg/g)	11860	8316
$k_1$ (s <sup>-1</sup> )	-0.001	-0.002
$R^2$	0.925	0.918
<b>Pseudo-second-order</b>		
$q_e$ calc (mg/g)		
$k_2$ (s <sup>-1</sup> )	20000	16667
$R^2$	1.92x10 <sup>-7</sup>	2.57x10 <sup>-7</sup>
	0.992	0.996
<b>Intraparticle diffusion</b>		
$K_d$ (meq g <sup>-1</sup> s <sup>-1/2</sup> )		
$R^2$	299.5	236.2
C	0.951	0.869
	6035	5626
<b>Liquid film diffusion</b>		
$K_{fd}$ (meq g <sup>-1</sup> s <sup>-1/2</sup> )		
$R^2$	-0.001	-0.002
	0.926	0.918

When the transport of the adsorbate from the liquid phase to the solid phase plays a significant role in the sorption, liquid film diffusion can occur. The equation representing liquid film diffusion kinetics can be expressed as (Taffarel and Rubio 2009):

$$\ln(1-F) = -k_{fd} \cdot t \quad (7)$$

where  $F$  is the fractional attainment of equilibrium ( $F = q_t/q_e$ ) and  $k_{fd}$  is the rate constant (meq g<sup>-1</sup> s<sup>1/2</sup>). A plot of  $\ln(1-F)$  as a function of  $t$  with a zero intercept would suggest that the kinetics of the sorption process are controlled by diffusion through the liquid film surface surrounding the solid sorbent. The linearity of the plot (Table I and Table II) indicated the high applicability of this model. In addition, the intraparticle diffusion mechanism produced a better  $R^2$  than the liquid film diffusion model for the acetylated sorbents which is an indication that penetration into the pores of the materials was more predominate than surface sorption.

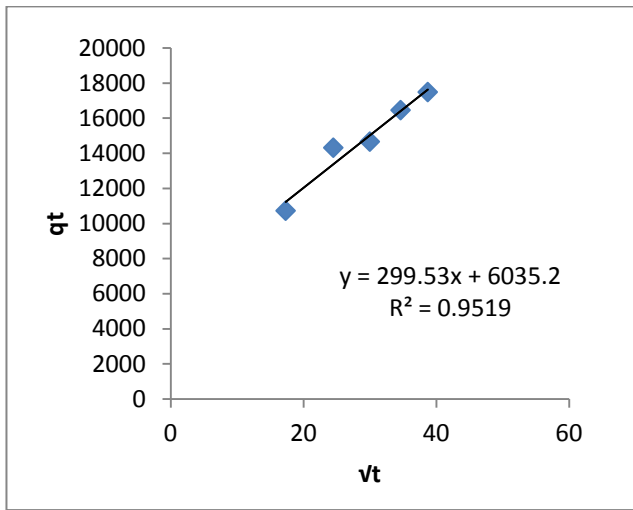


Fig. 9: Graph of Intraparticle diffusion for ASB

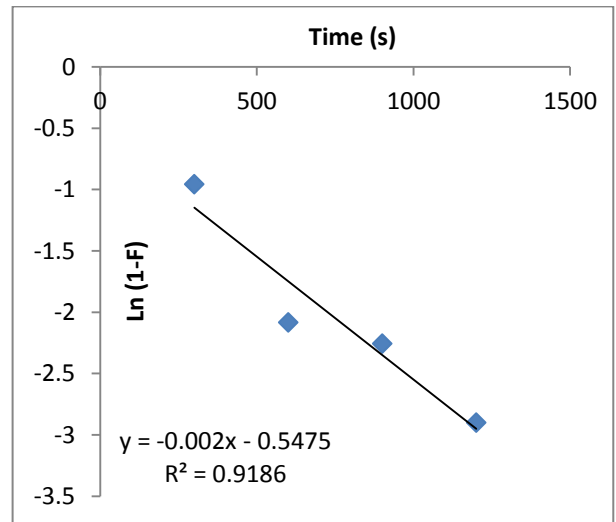


Fig. 11: Graph of Film diffusion for RSB

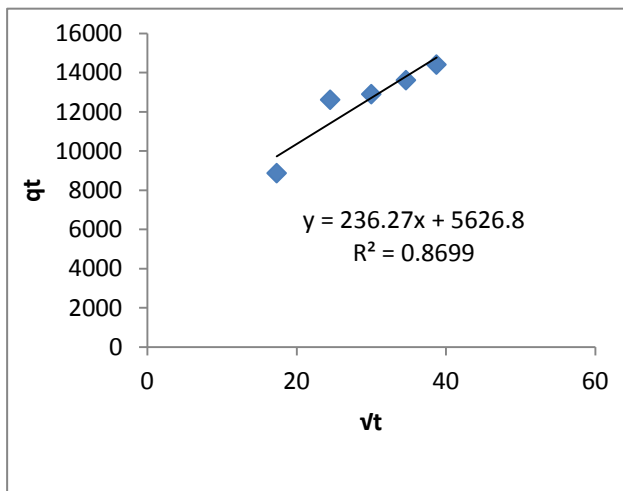


Fig. 10: Graph of Film diffusion for ASB

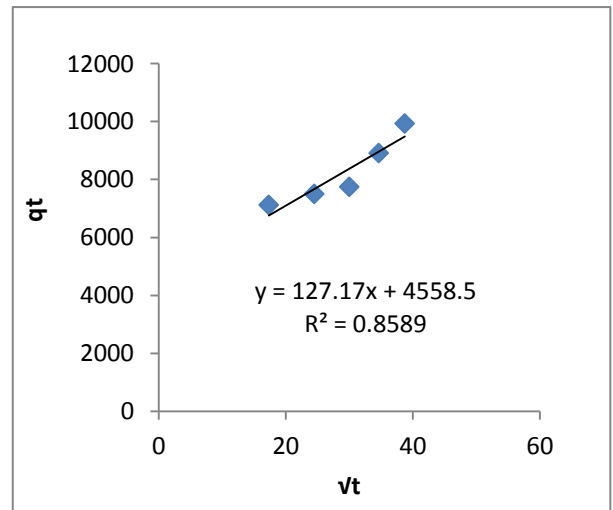


Fig. 12: Graph of Intraparticle diffusion for AGH

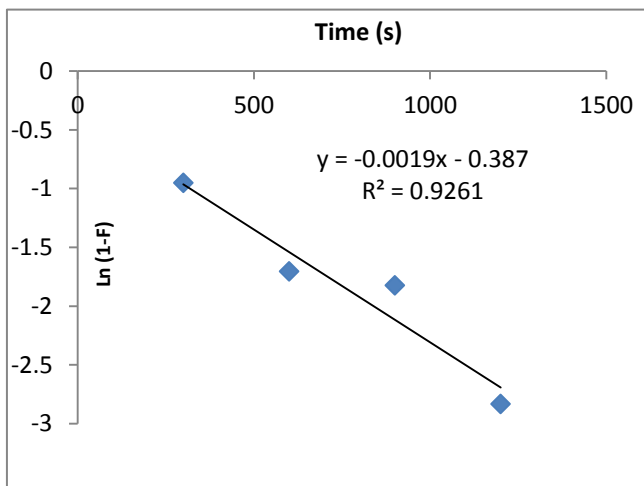


Fig. 11: Graph of Intraparticle diffusion for RSB

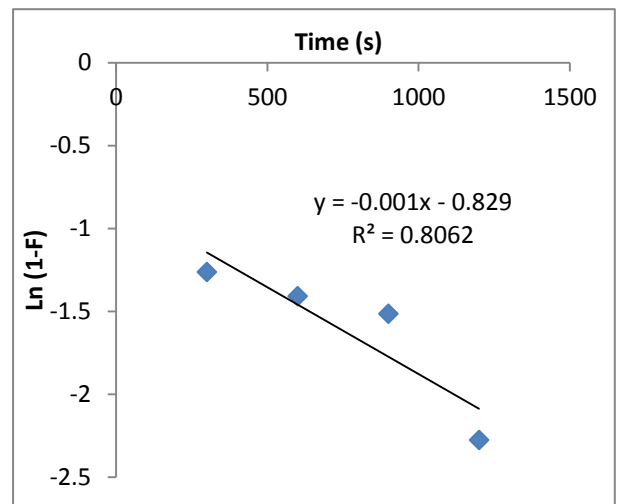


Fig. 13: Graph of Film diffusion for AGH

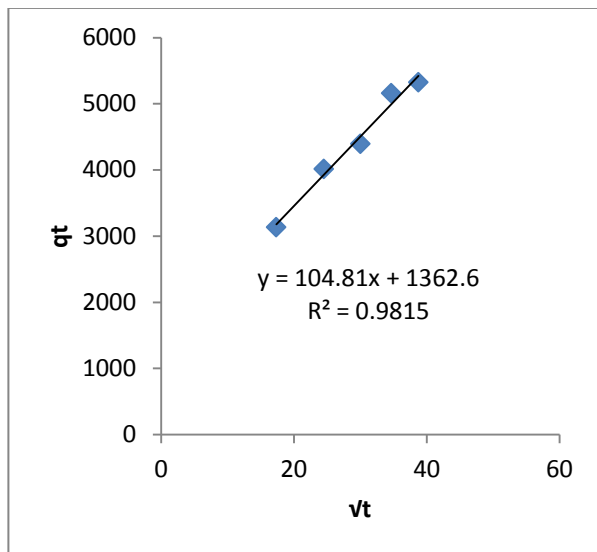


Fig. 14: Graph of Intraparticle diffusion for RGH

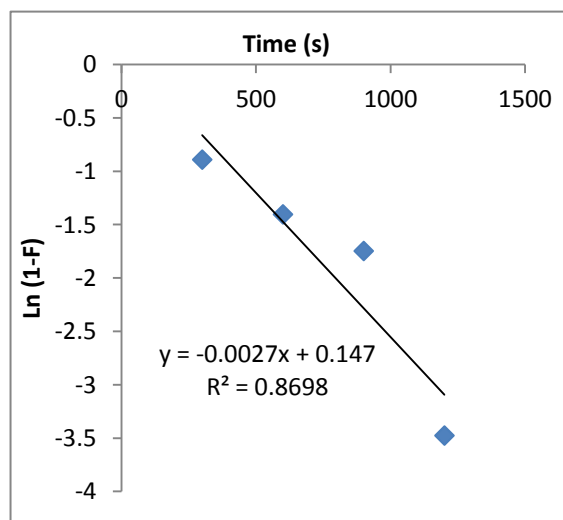


Fig. 15: Graph of Film diffusion for RGH

#### IV. CONCLUSION

The ability of groundnut husk and sugarcane bagasse (an agro waste) materials as a natural adsorbent to remove oil spill has been investigated. The sorption behavior of adsorbents was substantially enhanced after modification with acetic anhydride. The results indicated that the experimental data fitted the pseudo-second-order kinetic model. Acetylated sugarcane bagasse and groundnut husk are very promising alternative sorbents for crude oil because the material is cheap and biodegradable.

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