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Sorption studies of crude oil on acetylated rice husks

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ABSTRACT

Acetylated rice husks (ARH) have been studied as sorbents for crude oil spill cleanup operations in the aqueous environment. Sorption kinetics and isotherm studies were carried out under various experimental conditions. The experimental data were particularly tested with the pseudo-second-order kinetic model, the Langmuir isotherm model and the Freundlich isotherm model. The crude oil absorptive behavior of the acetylated rice husks has been discussed and the experimental methods adopted for the determination and estimation of the sorption coefficients have also been described. The correlation values for the isotherms models studied showed that the data better fitted the Langmuir model than the Freundlich model. Adsorption was therefore monolayer and the optimum theoretical monolayer sorption capacity was 10.31g/g rice husks. These values indicated that the acetylated rice husks are suitable sorbents with potential for further development for oil spill treatment.

Keywords: Oil spillage, acetylated rice husks, sorption capacity, kinetics, isotherms.

INTRODUCTION

Agricultural by-products and their modified products serve as absorbents for crude oil (and its products) cleanup operations in the aqueous environment [1]. Crude oil pollution is an impairment of the environment with crude oil and its refined products as the major pollutants. Treatment of petroleum contaminated sites is a subject of almost unlimited scope. If proper remediation measures are not taken, the organic pollutants released from spills can lead to surface and ground water contamination, which can be potentially toxic to biota and humans [2]. The mechanism for oil sorption by lignocellulose fibers is controlled by fiber adsorption on

the fiber surface and capillary action through its lumen [3]. Fibers float and have high sorption capacity [4]. Thus they may be structured into continuous belts, sheets, booms or pads which would simplify sorbent deployment, retrieval and disposal of oil laden sorbent. Fibers are reusable and easier to control in either open or confined spaces and facilitate collection [3], [4]. The sorptive capacity in a vast range of solids depends on the surface area and pores [4]. Lignocelluloses have more surface area than nonporous materials. Therefore they are a good candidate for sorption materials. At the initial stage, oil is sorbed by some interaction and van der Waals forces between the oil and the natural sorbent in the fiber surface [4]. This sorption is due to the fact that there is physical trapping of oil on the fiber surface through its irregular surface morphology. Sorption of oil within the fiber occurs by diffusion through internal capillary movement into sorbent lumens [5].

Equilibrium sorption is considered an important property for biodegradable materials relative to their storage conditions. Several mathematical models can be used to fit the experimental data [6]. The sorption kinetics which describes the solute sorption rate is an important characteristic in evaluating the efficiency of sorption. The adsorption isotherm yields the equilibrium temperature curve, essential adsorption information and guidelines for selecting methods of adsorption and partition [7]. Equilibrium relationship between the sorbents and the sorbates are described by sorption isotherms which gives the capacity of a sorbent for a sorbate [8]. Sorption models of oils and other organic substances on several sorbents have been previously studied [9, 10, 11, 12, 1, 13, 14]. The most studied models are the Freundlich and Langmuir models. The sorption process is generally studied by plotting the equilibrium concentration of a compound in the sorbent as a function of its equilibrium concentration in gas phase or in solution at given temperature.

This study therefore reports the sorption model and crude oil absorptive behavior of acetylated rice husks. Kinetics of the sorption procedure was also studied and the pseudo-second-order rate model equation was used to describe the method of sorption. Two isotherm models were used to fit the experimental data: The Langmuir and the Freundlich model. The Langmuir model was chosen for the estimation of maximum sorption capacity to biomass surface saturation. The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the ARH.

MATERIALS AND METHODS

2.1 Materials and Reagents

Raw Rice husks (RRH) samples were obtained from a local rice mill in Kura Local Government Area, Kano state, Nigeria. Acetic anhydride, acetone, ethanol and NBS were AnaLaR grade reagents from Riedel de Haën and BDH, no further purification were carried out. The crude oil samples were collected from Nigerian National Petroleum Corporation – Kaduna Refinery.

2.2 Sample preparation

The RRH was thoroughly washed with water to remove unwanted substances. The washed husks were oven dried at 60°C to constant weight. To have reliable and reproducible data, sorption test requires accurate preparation of the sorbent sample including sieving, homogenization, and sterilization procedure. The latter was used to avoid microbial degradation of the chemical under investigation during the experiment. The particle size distribution was controlled using the

BS410/1986 laboratory test sieves of 1.4mm aperture size screens. The physical and proximate characteristics of RRH are listed in table 1. Soxhlet extraction of RRH was carried out using a 250mls mixture of hexane/acetone (4:1) as solvents and extracted for 4hrs due to the presence of fatty acids, free alcohols and other extractives present. The extracted samples were dried in a laboratory oven for 16hours. The purpose of the fiber refining was to maintain the integrity of the fibers.

2.3 Acetylation of Rice Husks

The acetylation of the rice husk in a solvent free system was carried out using the method reported by sun *et al.*, [15]. The experiment was tried at several temperature and reaction time, using several concentrations of NBS. The Acetylated rice husk (ARH) produced were thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid by-product. The weight percent gain due to acetylation (on oven dried basis) was calculated thus:

$$WPG(\%) = \left[\frac{\text{weightgain}}{\text{originalWeight}} \right] \times 100$$

The samples used were ARH9 acetylated at optimum conditions and ARH14 with the optimum sorption capacities. The acetylation conditions used for these samples are presented in table 2.

2.4 Equilibrium sorption studies

The sorption of oil from water was carried out using the methods of Choi and Cloud [3], with some modifications.

For sorption isotherms studies, 1g each of the RRH and ARH was placed in a beaker containing a mixture of crude oil displaced in 100ml of water in 200ml beakers at 26°C. The concentrations of crude oil in the beakers varied from 0.45 to 20g/100ml of water. The samples were left in the mixture for 10mins with little agitation. The sorbents were then removed from the beakers using sieving nets. The nets were allowed to drain and then the oil sorption capacity (OSC) of the sorbents determined.

The OSC of the sorbents were obtained with the formula;

$$OSC = \frac{\text{new weighed gain}}{\text{Original weight}} \times 100$$

The sorption of a chemical on a solid from a water based solution may be seen as the result of a reversible reaction (sorption-desorption) which reaches a final equilibrium conditions between the concentration of the chemical in the two phases [16]. The equilibrium sorption of crude oil on RRH and ARH was modeled using adsorption type isotherms. Since the adsorption isotherms are important to describe how adsorbates will interact with adsorbents and are critical for design purposes, the correlation of equilibrium data using an equation is essential for practical sorption operations [17]. The two isotherm equations adopted in this study to describe the sorption equilibrium are the Langmuir and Freundlich models.

In Sorption Kinetics studies, the sorbent mass used for the kinetic studies was 0.5g for ARH and 1g for RRH at 26°C. The sorption procedure was carried out at different times ranging from 1-60mins. The concentration of oil used throughout the batch experiment was constant at 10g/100ml of water. The sorbents were removed with the aid of sieving nets and the OSC of the sorbents determined.

The rate of sorption of a molecule unto a surface is an essential parameter when designing batch sorption systems, consequently it is essential to establish the time dependence of such systems under various process conditions. The experimental data were further evaluated based on the pseudo-second-order kinetic rate model proposed by Ho *et al.* [18].

RESULTS AND DISCUSSION

The properties of RRH and ARH have been determined and listed for comparison in table 1.

Table 1: The physical and proximate analysis of raw and acetylated rice husks.

Characterizing Properties	RRH	ARH
Moisture content (%)	14.2	-
Ash content (%)	19	19
Volatile content (%)	64.7	66.1
Fixed Carbon (%)	16.3	18.9
Bulk density (uncompacted) (Kg/L)	168	191
Bulk density (compacted) (Kg/L)	224	252
Relative density	74.6	81
Porosity (%)	71	49.1
Swellability (%)	582	374
ASE (%)	--	35.69

The acetylation conditions for the samples tested and their OSC have also been reported in table 2.

Table 2: shows the acetylation conditions undergone by the samples

Sample	Acetylation conditions				
	Time(hr)	T(°C)	%NBS	WPG	OSC
RRH	-	23	-	-	1.90
ARH9	1	100	1	10.8	6.62
ARH14	3.5	100	1	19.6	9.44

3.1 Equilibrium sorption studies of rice husks and acetylated rice husks.

Effect of contact time

Crude oil uptake was studied in batch experiments as explained earlier. The results as shown in figure 4 explains the effect of sorption time (2-60mins) on oil uptake and as expected, sorption capacity slightly increases with the contact time from the first 2mins. This effect may be due to adsorption on first surface which then start to penetrate the inner microscopic voids [19]. The

results also showed the fast and stable nature of the process as only a slight difference was observed between the initial and final contact time. This result is consistent with the findings of Hussein *et al.* [20].

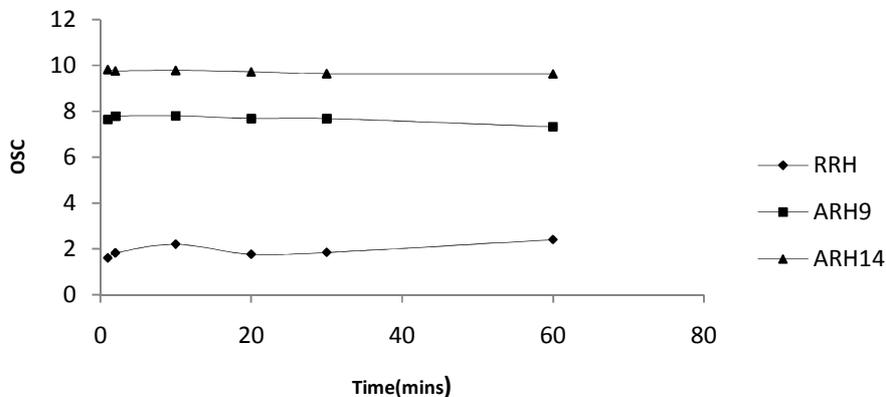


Figure 1: Effect of sorption time on oil sorption capacity

To explain the sorption kinetics of crude oil on RRH and ARH, the experimental data obtained were further tested with the pseudo-second-order rate expression of Ho *et al.* [18], and the results are shown in figure 5. The pseudo-second-order kinetic model equation is usually expressed as

$$t/q_t = 1/h + t/q_e \quad (5)$$

Where $h = k_2 q_e^2$ can be described as the theoretical rate constant as t approaches zero. q_t is the amount of crude oil on the biomass surface (mg/g) at any time t . q_e is the amount of crude oil sorbed at equilibrium (mg/g). k_2 is the pseudo-second-order rate constant (g/mg min). If the pseudo-second-order kinetics is applicable, the plot of t/q_t vs. t will give a linear plot, which allows computation of q_e , k_2 and h without having to know any parameter beforehand.

The pseudo-second-order rate expression of Ho *et al.* [18], [21] has been applied widely to the sorption of metal ions, dyes, herbicides, oils and organic substances from aqueous systems [22]. The model is based on the sorption capacity of solids but contrary to previous models, it describes chemisorption over the whole adsorption time [23]. The advantage of this model is that there is no need to know the equilibrium capacity from the experiments as it can be calculated from the model [24].

According to Ho *et al.* [18], if the plot is linear, then the sorption process may be described as chemisorption. A linear relationship was observed for the ARH samples. The value of the sorption capacity of the biomass q_e , the pseudo-second-order rate constant k_2 , the initial sorption rate constant h , and the coefficient of determination R^2 were evaluated from the plot and presented in table 3. The data showed that modification of biomass by NBS catalyzed acetylation enhances the equilibrium sorption capacity of the biomass towards the crude oil. The rate constant decreased from 0.164 to -0.276g/mg.min from RRH to ARH9 towards the crude oil and decreased further to -1.179g/mg.min in ARH14. The sorption mechanism is a fast and stable process which means that sorption also took place inside the pore matrices of the modified

materials created by the cross linking effect of the two carbonyl group present in each of these modified materials [1]. The sorbed molecules are held to the surface of the fiber by covalent forces of the same general type as those occurring between bound atoms in molecules [9]. Furthermore the coefficients of determination R^2 , for acetylated samples were found to be 0.999 and 1 indicating that the sorption process was that of chemisorption and that the acetylated materials are suitable sorbents for oil sorption.

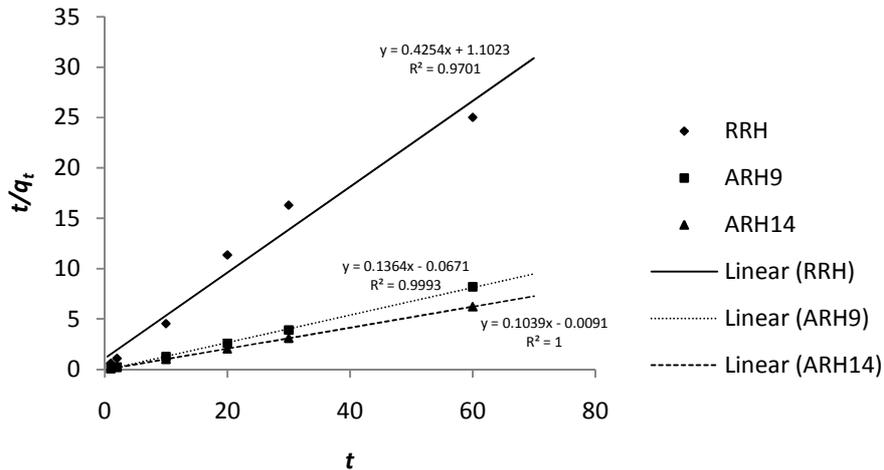


Figure 2: The Pseudo-second-order rate equation model

Sorption isotherm studies

The sorption isotherms of crude oil on the samples were studied at a constant temperature of 23°C. The increase in the OSC of the ARH and RRH indicated that the oil removal was dependent on the initial oil concentration. The reproducibility increased as the optimum pick-up was approached until they became constant. As oil increased in concentration, the sorption capacity of rice husks also increased until it reached a plateau. Figure 1 illustrates the sorption isotherms of the raw and acetylated rice husks. The effect of acetylation is also observed in the chart.

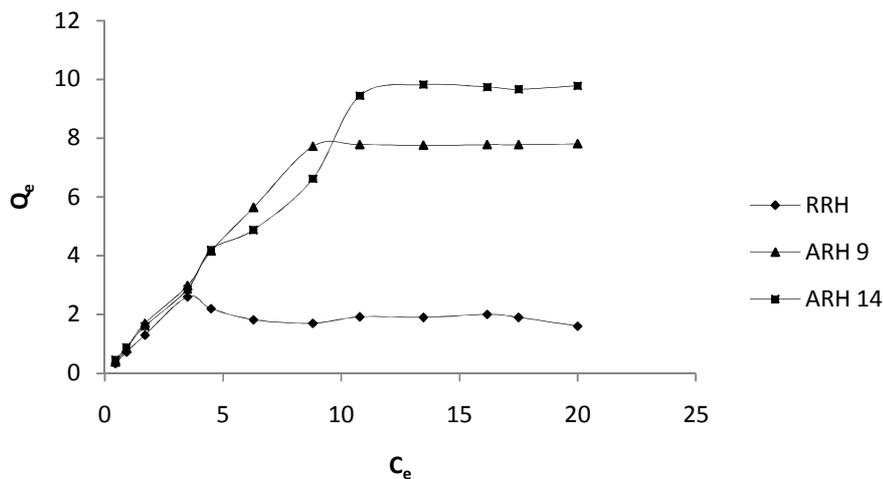


Figure 3: The sorption isotherm of raw and acetylated rice husk

The results showed that the acetylation of RRH in the presence of NBS enhanced the equilibrium OSC (Q_e) of the sorbents towards crude oil. To facilitate the estimation of the sorption capacities, the experimental data were fitted into the Langmuir and the Freundlich isotherm models. The Langmuir and Freundlich isotherms are the most commonly used solid to liquid phase isotherms. These isotherms relate the amount of oil sorbed at equilibrium per unit weight of sorbent, Q_e (mg/g) to the sorbate concentration at equilibrium, C_e (mg/L). According to the Langmuir's model, adsorption occurs uniformly on the active sites of the sorbent, and once an adsorbate occupies a site, no further sorption can take place at that site. The Langmuir model [25] is defined by the equation

$$Q_e = (abC_e)/(1 + bC_e) \tag{1}$$

The linearized form is expressed as

$$C_e/Q_e = 1/ab + 1/a(C_e) \tag{2}$$

Where, b is a Langmuir coefficient related to the affinity between the sorbent and sorbate and a is the maximum OSC to form a complete monolayer on the surface bound at high C_e (g/100ml). In the Langmuir's model, the mass of the solute sorbed per unit mass of sorbent (Q_e), increases linearly by increasing the solute concentration at low surface coverages, approaching to an asymptotic value a when adsorption sites approaches saturation [16]. The Freundlich model [26] equation describes non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The isotherm model can be defined as

$$Q_e = KC_e^{1/n} \tag{3}$$

Where, k and n are Freundlich constants. k is the relative indication of adsorption capacity (L/mg) and n indicates the intensity of adsorption. The linearized Freundlich model equation applied is expressed as

$$\text{Log } Q_e = \text{log } K + (1/n)\text{log } C_e \tag{4}$$

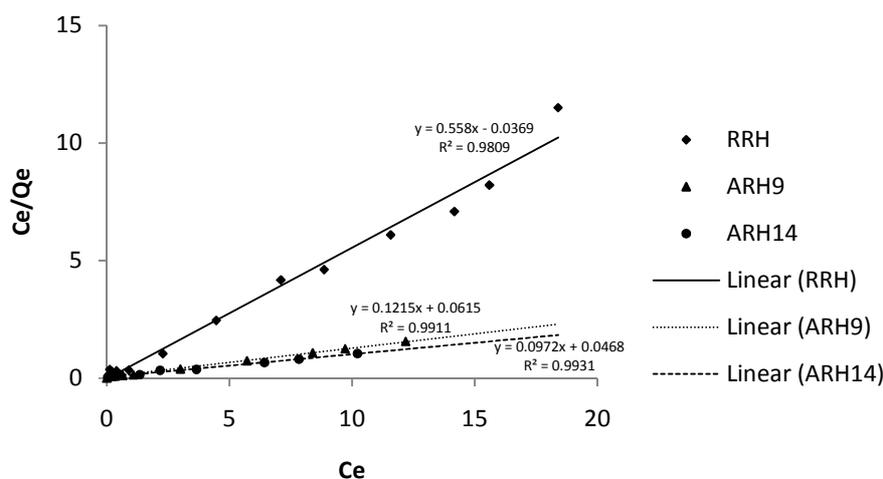


Figure 4: Langmuir isotherm model

The plot of C_e/Q_e against C_e for sorption of crude oil by acetylated rice husks is illustrated in the Figure 2.

The isotherm constants and their correlation coefficients, R^2 , are listed in table 3. Figure 5 shows the Freundlich model for the acetylated rice husks sample.

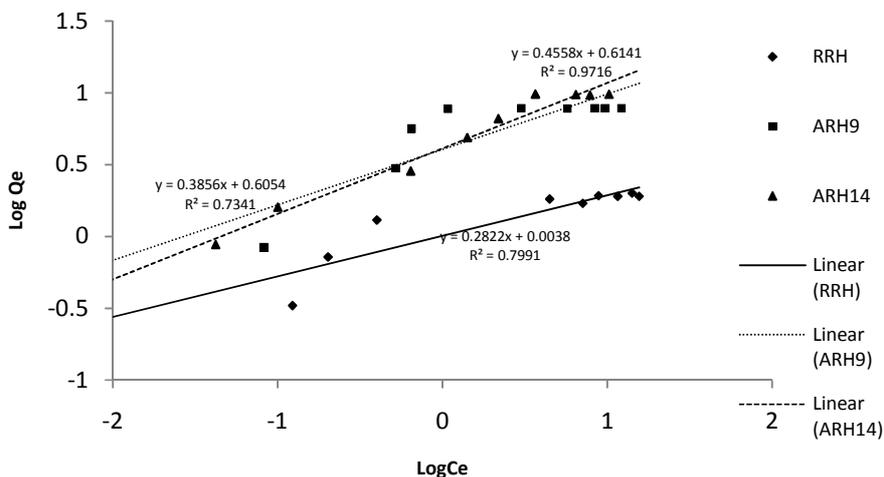


Figure 5: Freundlich isotherm model

$\log Q_e$ against $\log C_e$ is plotted and the constants may be evaluated from the slope n and the intercept $\log K$. Plot of $\log Q_e$ against $\log C_e$ is given in figure 5. The isotherm constants and their correlation coefficients, R^2 , are listed in table 3. The magnitude of the exponent, n gives an indication of the favorability of the adsorption. It is generally stated that values of n in the range 2-10, 1-2, less than 1 represents good, moderately difficult and poor sorption characteristics respectively. The values of n for this isotherm are between 2 and 10, indicating that the sorption process is good. This is because the long chains of the oil were able to penetrate into the pores of the ARH. Similar results were produced when a range of modified cellulose materials as sorbents were used for crude oil sorption by Okoro *et al.* [1].

Table 3: Table of the values of the Langmuir, Freundlich and pseudo-second-order rate models

	Langmuir model			Freundlich model			Pseudo-second-order model		
	a	b	R^2	k	n	R^2	k_2	q_e	R^2
RRH	1.7921	-15.5	0.980	1.0069	3.5461	0.799	0.1639	2.3529	0.970
ARH9	8.2645	1.9836	0.991	4.0272	2.5974	0.734	-0.2761	7.3529	0.999
ARH14	10.3093	2.1087	0.993	4.1115	2.1978	0.971	-1.1788	9.7087	1.000

Based on the coefficient of determination values R^2 , it can be concluded that the experimental data better fitted the Langmuir model than the Freundlich model as the R^2 values of the Langmuir model tend to be much closer to 1 than those obtained from the Freundlich isotherm. Therefore, the adsorption can be described as monolayer and the Langmuir theoretical monolayer sorption capacity a for ARH9 and ARH14 are 8.26 and 10.31g/gRH respectively. The

values of the coefficient of determination indicated that the ARH biomass is an excellent biomaterial for the removal of oil from aqueous environments.

CONCLUSION

Sorbents with higher weight percent gain due to acetylation have shown higher values for sorption capacities. The equilibrium concentration is dependent on the chemical modification of the biomass which indicates that the removal of oil may be enhanced more rapidly onto chemically modified biomass. The Freundlich and the Langmuir models have been used to explain the sorption behavior of crude oil on raw and acetylated rice husks. The results of the coefficient of determination showed that the experimental data fitted the Langmuir model better than the Freundlich model. The sorption procedure is monolayer and favorable. The results showed that the acetylation of rice husks enhanced the equilibrium sorption capacity of the biomass towards the spilled oil. Hence these modified cellulose materials could be used for cleansing aquatic environments, mangroves and wetlands of spilled oil films arising from oil exploration and exploitation of crude and refined petroleum products. Kinetic studies have also shown that the sorption process is chemisorption. The rapid uptake and high absorption capacity make the acetylated rice husks a very promising alternative sorbent for crude oil spill. The determined parameters could be useful for the design of remediation techniques.

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