

Potential of Rice husk ash for removal of phenol in aqueous solution.

¹Kangpe N. S., ¹Alemika D.Y., ¹Egga E. S., and ²Marti D. M.

¹Department of Chemistry,
University of Jos, P.M.B. 2084, Jos.
²College of Education Azare, Bauchi State.

Abstract

The pollution of water with phenol from chemical industries is a highly important environmental problem because of the propagation of the pollution and its unfavorable consequences to life. The potential of rice husk ash for the removal of phenol from aqueous solution was investigated in a batch process. Isothermal studies were carried out under different experimental conditions of contact time, adsorbent dose and initial phenol concentration. The suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were also investigated for each phenol-adsorbent system. The result showed high efficiency of rice husk ash for phenol removal and also the data for the phenol-adsorbent systems fit the Freundlich model best within the concentration range studied. It can be inferred that rice husk ash can be used as a low cost adsorbent for phenol removal from aqueous solution.

Keywords: Adsorption, rice husk ash and phenol

1.0 Introduction

There is a growing concern about wide spread contamination of surface and ground water by various organic compounds due to the rapid development of chemicals and petrochemical industries over the decades [1]. Many industrial wastes contain phenolic compounds which are difficult or impossible to remove by conventional biological treatment processes [2]. The US Environmental protection Agency (USEPA) reported that phenol is the 11th of 126 chemicals designated as priority pollutants [3]. Phenol is very soluble in water and notice as bad taste and odour in water supplies. It forms chlorophenol in the presence of chlorine in drinking water which has a medicinal taste that is pronounced and objectionable [2,4]. Phenolic compounds are harmful to organisms at low concentrations and most of them are classified as hazardous pollutants because of their potential harm to human health. Phenolic compounds are common contaminants in waste water and are generated from petrochemicals, petroleum, coal conversion, paper, textile and pharmaceutical industries. Among various water pollutants, phenol and its derivatives are the most toxic because of their carcinogenic nature [5].

Rice husk also called hull, is the coating of the seed or grain of the rice plant. It is made up of hard materials, including silica and lignin, which protects the seeds during the growing season and is indigestible to humans and about 20% by weight of the whole grain [6]. It is considered a waste in the rice mill and often burned in the open to produce rice husks ash (RHA) or dumped on the waste land. The whole rice grain is dehusked by milling or winnowing to separate the grains from the husks (hulls). Rice husk is difficult to ignite and does not burn easily, it is highly resistant to moisture penetration and fungal decomposition (good insulation material), has high silica content (poor fodder), bulky and dusty, requiring large volumes for storage and transport. When burned, the rice husk ash is about 17-26%, containing more than 95% silica by weight with high porosity and large surface area [7 - 9]. Rice husks are used in juice extraction, brewing, silicon carbide production, pillow stuffing and as ingredients in animal feeds. It is also used as fuel source for grain drying and parboiling and for electricity generation in the modern rice milling industry. It is an excellent insulator and has applications in industrial processes such as steel foundries and manufacture of insulation materials for houses and refractory bricks. It is an active pozzolan and has applications in the cement and concrete industry for the manufacture of low cost building blocks and

Corresponding author: *Kangpe N. S.*, E-mail: kangpen@unijos.edu.ng, Tel.: +2348033672039

production of high quality cement. The rice husk ash has high adsorption capacity and is used to adsorb oil on hard surfaces and potentially to filter arsenic from water. It is used to synthesize siliceous raw materials such as clay materials due to its high porosity [4, 10].

Current methods for removing phenols from waste water include adsorption on activated carbon (as in carbon fillers), chemical oxidation, deep well injection, incineration, solvent extraction and irradiation [11, 12]. Among these methods, adsorption has gained considerable attention owing to its high efficiency for treating aromatic compounds in aqueous solution/streams due to the characteristics of the adsorbent such as high surface area, high adsorption capacity, microporous structure and special reactivity. Activated charcoal or carbon removes many of the impurities contained in the water and waste water but the process is expensive due to high cost of adsorbent and the variable performance of carbon regeneration. South African coal fly ash has been used to remove both inorganic heavy metals [13] and organic phenolic compounds. It is also used to treat acid mine drainage, phosphates from waste water and sources of metal oxides. Literature reported of its potential to remove and retain a substantial amount of phenols from solution [14]. Other agricultural waste materials that have been used to remove phenolic compounds and its derivatives from waste water include water hyacinth ash, rubber seed coat.

In the present research, rice husk ash, which is available and economically cheap, is investigated as adsorbent of aqueous phenol contaminants and to present a cheap and effective alternative to activated carbon and also provide an improved agricultural waste management by converting waste materials to useful materials in scientific processes.

2.0 Materials and Methods.

Sample collection and preparation:

The rice husk was collected from a rice milling company in Lafia Local Government of Nassarawa state of Nigeria. It was sieved to obtain residue with particle size 180 μ m and above. It was thoroughly washed with distilled water to remove adhering soil and clay, air-dried and kept in a desiccator for further work. The rice husk ash was then obtained by burning the treated rice husk at 400 $^{\circ}$ C and 600 $^{\circ}$ C, respectively, in a muffle furnace for three hours.

Preparation of phenol solutions: Phenol solutions (1% v/v) was prepared by dissolving 10g of phenol crystals in distilled water and made up to 1000ml. Phenol solution containing 2.5, 5.0, 7.5, 10.0 and 12.5mg/ml phenol were prepared by series of dilutions of the initial solution and calibration curve plotted using the corresponding absorbance values.

Determination of Ash content: 30g of the prepared sample was placed in crucibles and inserted into a muffle furnace and heated to 400 $^{\circ}$ C for three hours in triplicate, another sample was heated to 600 $^{\circ}$ C for the same time in triplicate. The crucibles were then removed, cooled and weighed. The weight of the ash was expressed as a percentage of that of the initial sample using the relationship

$$\text{Percentage Ash} = (\text{weight of ash} / \text{weight of sample}) \times 100\% \quad (1)$$

Adsorption Experiments: Adsorption was carried out at room temperature. 0.1g of each of the adsorbent was added to a 20ml portion of 1% phenol solution and shaken at 90rpm using an orbit shaker for 60 minutes. The mixture was then filtered and the concentration of the filtrate determined using the spectrophotometer. Five control bottles, three containing only phenol solution with no adsorbent were used to check and if necessary correct for phenol volatilization and adsorption onto walls of the container and filter paper during the experimental procedure, and two containing distilled water with two an adsorbent to check for presence of contaminants in the adsorbent and water.

Effect of contact time: The contact time was varied from 20-100 minutes with 20 minutes intervals to investigate the phenol uptake efficiency.

Effect of adsorbent dose: Various Doses: - 0.05, 0.15, 0.25, 0.35 and 0.45g of adsorbent per 20ml phenol solution were used. Other parameters kept as described above and the phenol uptake efficiency investigated.

Effect of initial phenol concentration: The effect of the initial phenol concentration on the phenol uptake efficiency was investigated with initial phenol concentrations of 2.5, 5.0, 7.5, 10.0 and 12.5g/L. The 2.5, 5.0, 7.5 and 10.0g/L solutions were prepared by diluting 5, 10 and 15ml of the 1% phenol solution, respectively, up to 20ml and the 12.5g/L solution was prepared by fetching 20ml of a phenol solution prepared by dissolving 1.25g of phenol crystals in 100ml of distilled water. All other factors were as described in the procedure above.

Determination of final phenol concentration, phenol adsorption and phenol removal efficiency: The absorbance of each phenol solution after adsorption was determined using a spectrophotometer. The concentration values corresponding to the obtained absorbance on the calibration curve plotted is then calculated using the straight line equation and recorded as the final concentration. The difference between the initial and final phenol concentration are recorded as the concentration adsorbed.

The amount of phenol adsorbed per gram of phenol (mg/g) in each process is given by

$$Q = (C_o - C_f) \times V \div M \quad (2)$$

Where

Q= amount of phenol adsorbed (mg/g)

C_o= initial phenol concentration (mg/ml)

C_f = residual phenol concentration after adsorption (mg/ml)

V = Volume of phenol used (ml)

M = mass of phenol present in portion of original solution (g)

Phenol removal efficiency is given by

$$E = P \times 100\% \tag{3}$$

Where E = Phenol removal efficiency and amount of phenol removed or adsorbed (g/g) is

$$P = Q - 1000 \tag{4}$$

3.0 Results and Discussion

The results are shown on tables and graphs

Table 1: Results of values for calibration curve

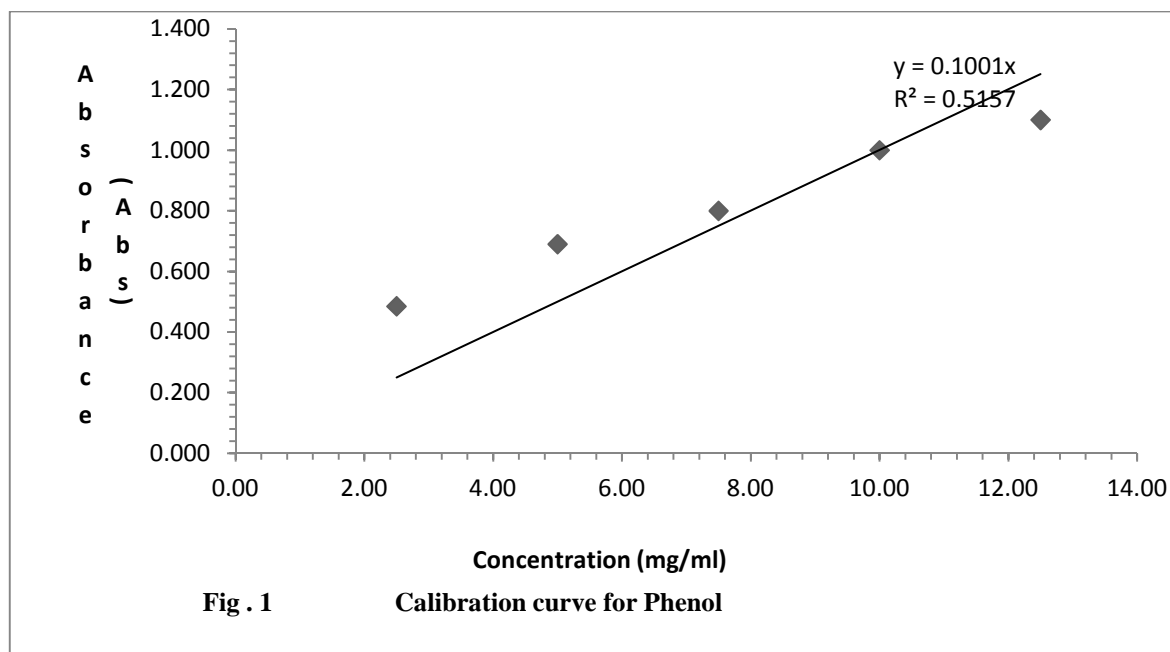
Concentration(mg/ml)	2.50	5.00	7.50	10.00	12.50
Absorbance	0.485	0.690	0.800	1.000	1.100

Table 2: Results of Ash content Determination

	RHA-400		RHA -600	
Sample weight before ashing (g)	30.00	30.00	30.00	30.00
Sample weight after ashing(g)	5.962	6.142	10.581	11.355
% ash content	19.87	20.47	35.27	37.85
Average ash content	20.17±0.300		36.56 ± 1.29	

Table 3: Results of Constants for Freundlich and Langmuir Isotherm models

Adsorbent	Langmuir Constants			Freundlich Constants		
	Q_{max}	α	R^2	K	1/n	R^2
RHA-400	0.0420	-0.3651	0.4619	7.7419	36.940	0.6662
RHA-600	0.0620	-0.3830	0.4672	2710	-1.4436	0.7521



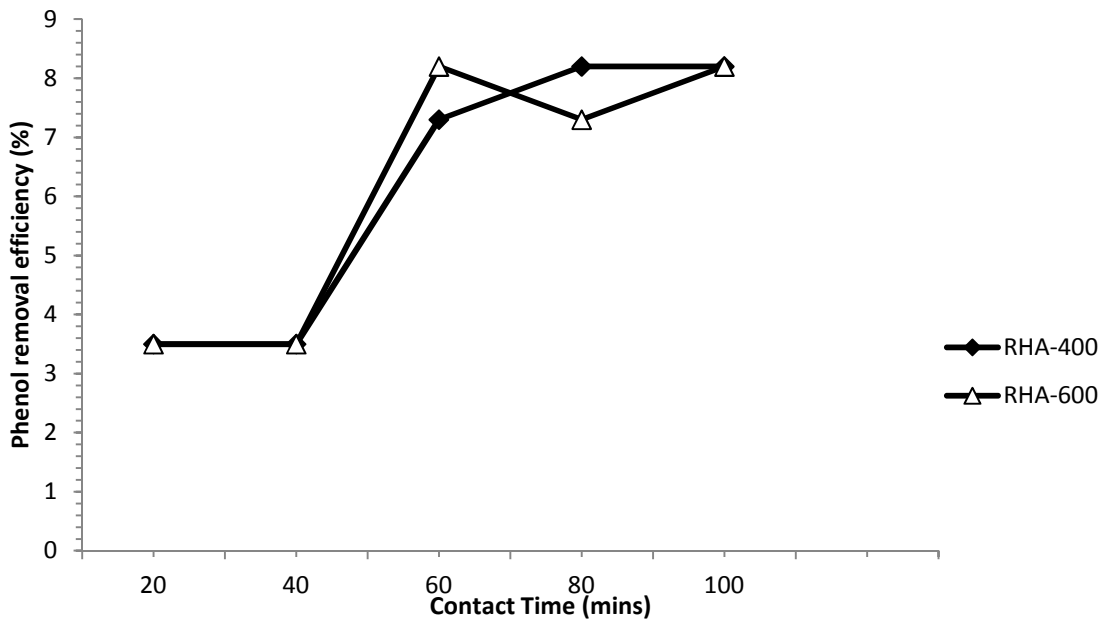


Fig. 2 Effect of Contact/Agitation Time on phenol adsorption

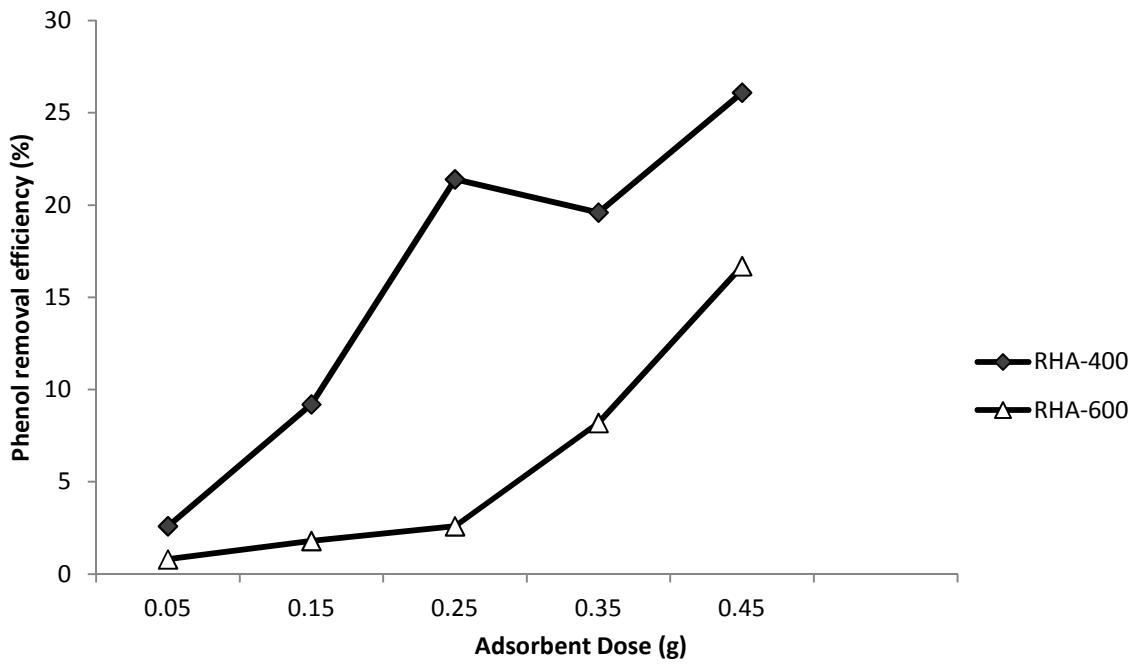
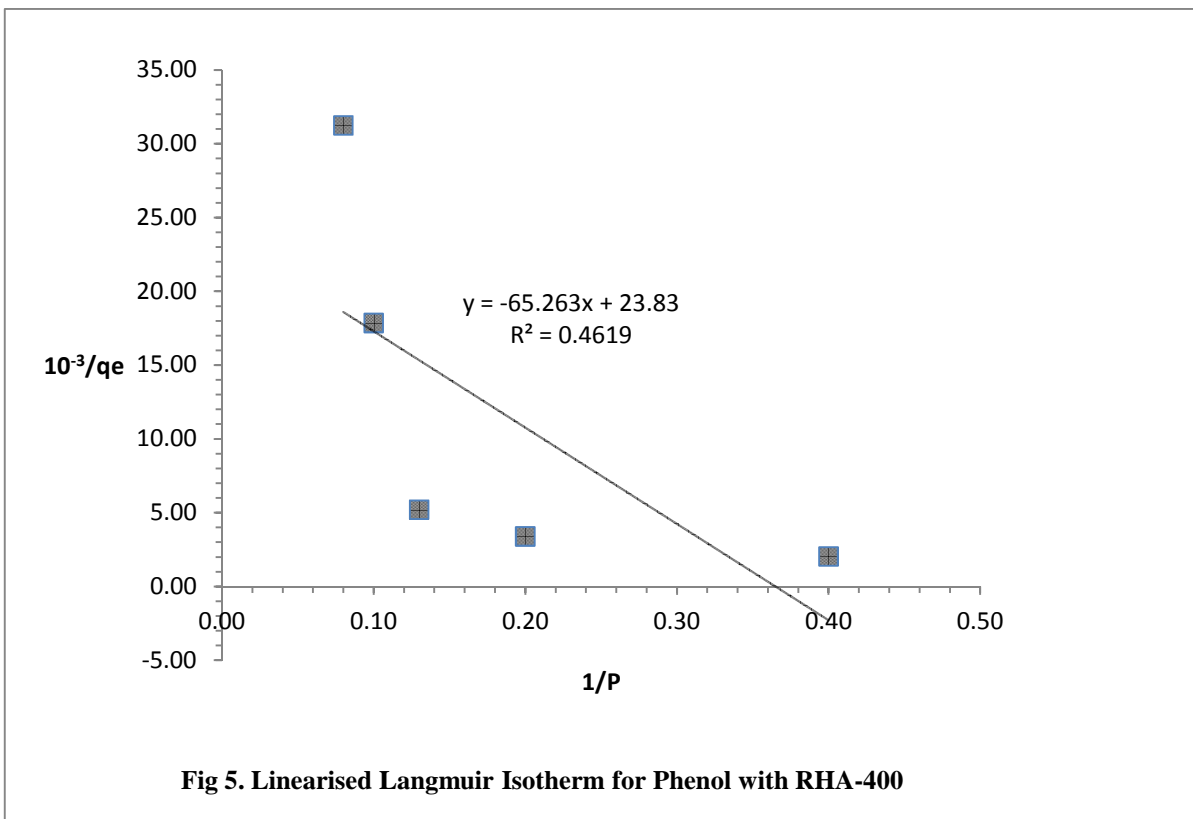
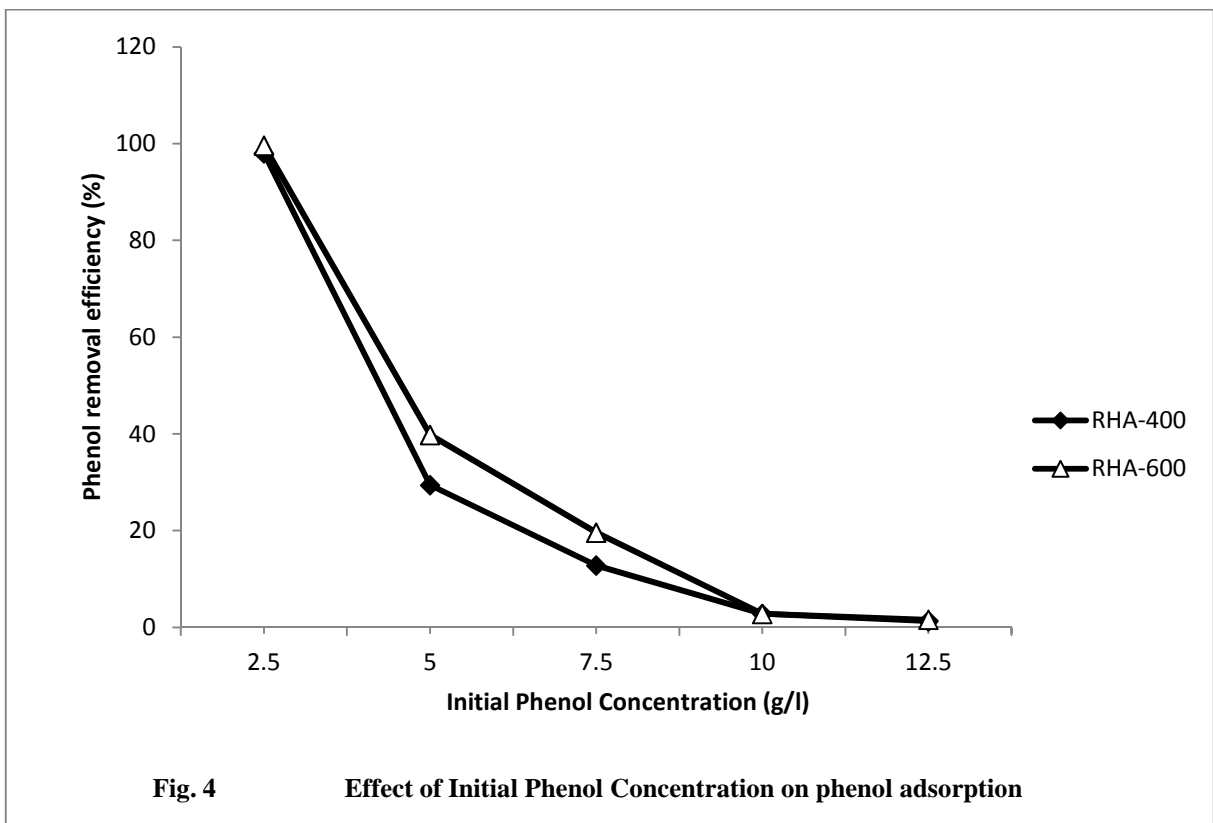
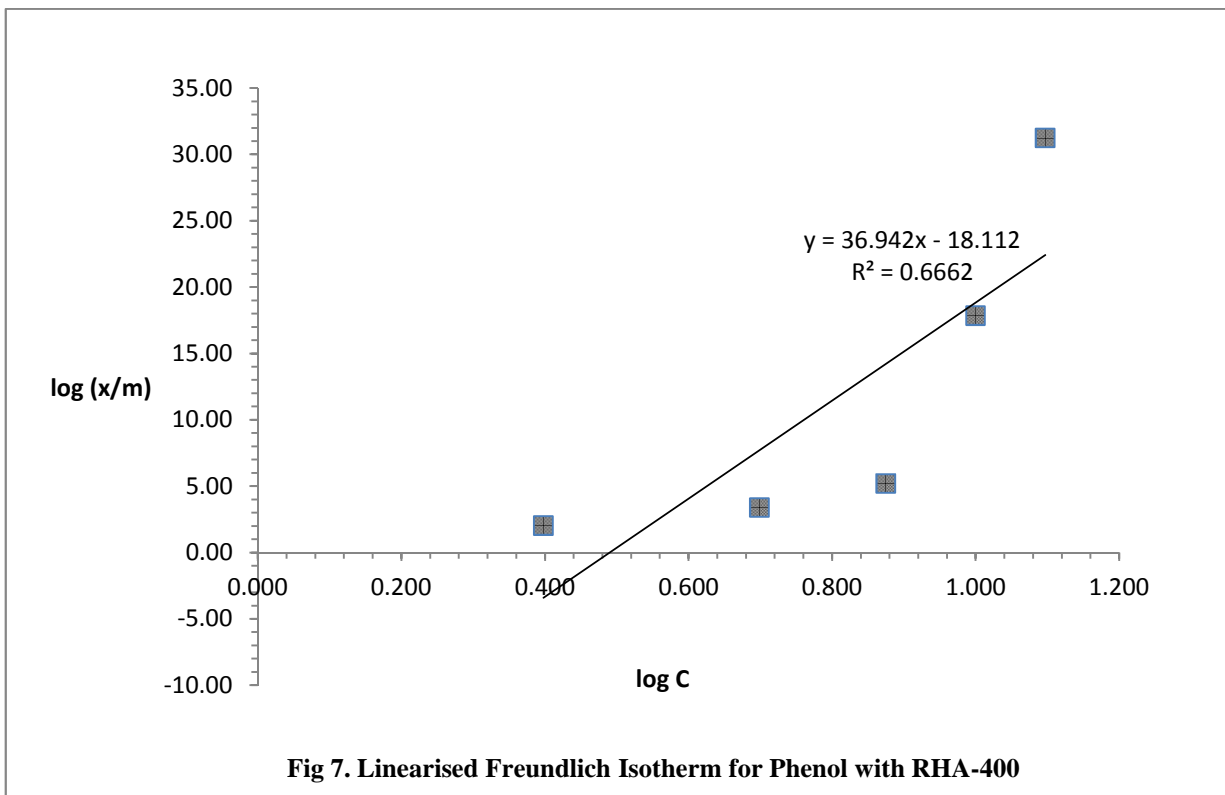
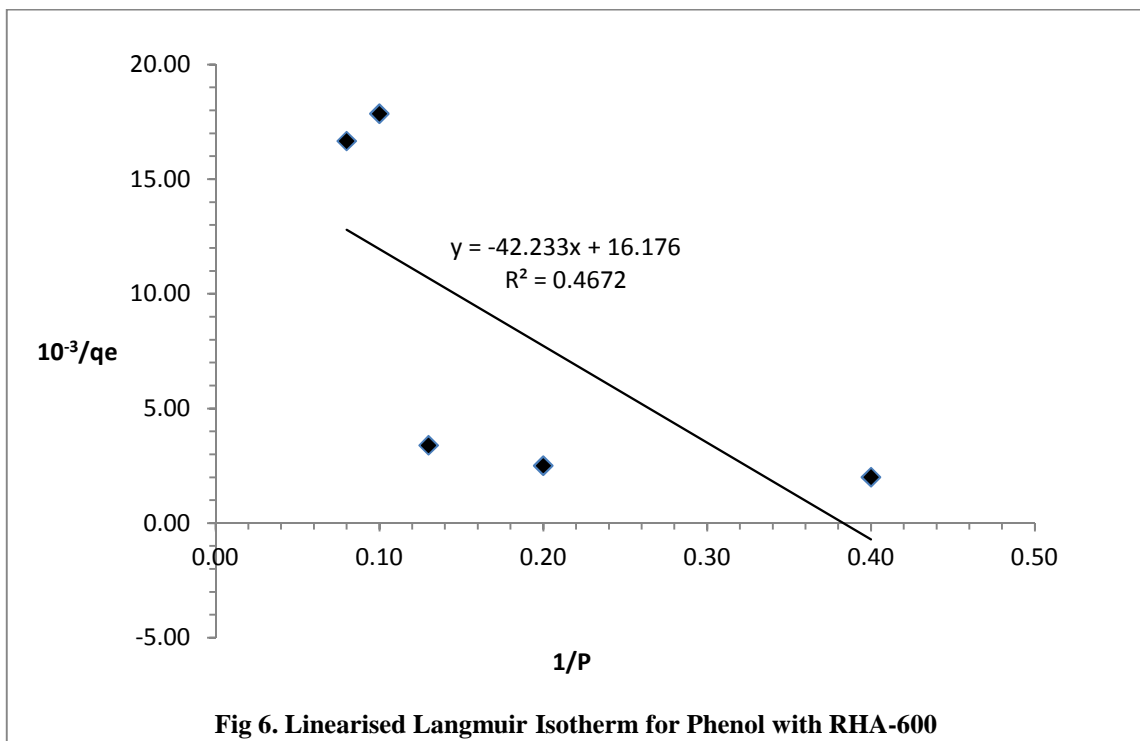


Fig. 3 Effect of Adsorbent Dose on phenol adsorption





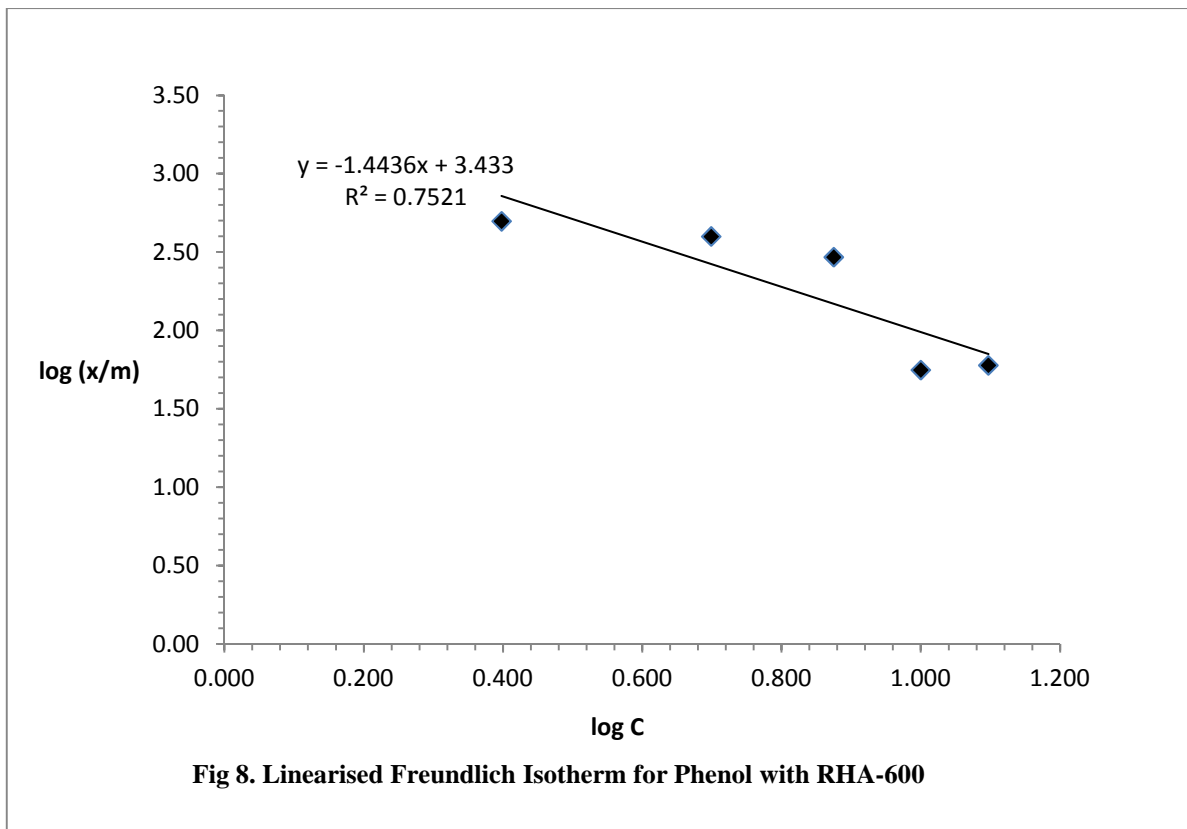


Fig 8. Linearised Freundlich Isotherm for Phenol with RHA-600

Table 1 is the result for the calibration curve. The ash contents for rice husk ashes at 400°C and 600°C are shown in Table 2. RHA-600 has higher ash content, which indicates a larger surface area, which in turn favours its surface reactions such as adsorption. This also agrees with [5] that showed that the specific surface area of rice husk ash increased with higher ashing temperature.

Figure 1 is the graph of calibration curve which is used as a standard. Rapid adsorption was observed within the first 80 minutes for the RHA-400 beyond which no appreciable adsorption occurred. For the RHA-600, rapid adsorption occurred within the first 60 minutes beyond which adsorption rate gradually reduced only to increase again as shown in Figure 2. This is possibly because further shaking after equilibrium time only leads to desorption of already adsorbed molecules. The results indicate that the sorption process can be very fast as reported by [15, 16] because the largest amount of phenol attached to the sorbent within the first 60-80 minutes.

The adsorption rate increased with increased in adsorbent dose for the two adsorbents as shown in Figure 3 due to an increase in the number of available sites for phenol adsorption. RHA-400 proved to be the better adsorbent with variation of adsorbent dose. This also agrees with [15]. The initial phenol concentration also affects the adsorption efficiency as shown in Figure 4. Increased initial phenol concentration decreased adsorption efficiency [15 - 17]. This may be due to the competition of more phenol molecules for the same available site for adsorption present in the 0.1g adsorbent used.

Table 3 shows the values obtained for the Langmuir and Freundlich constants. The Langmuir constants Q_{max} and α are related to the maximum adsorption evaluated from the intercept and slope of the linear plot of the experimental data of $1/Q_e$ versus $1/P$ shown in Figures 5 and 6 for the two adsorbents. At high surface coverage, data would deviate from a straight line. The magnitude of Q_{max} indicates that the amount per unit weight of sorbent to form a complete monolayer on the surface appears to be quite higher for phenol-RHA-600 system than for the phenol-RHA-400 system. The Freundlich isotherm as shown in Figures 7 and 8 for the RHA-400 and RHA-600 respectively shows higher K value for the RHA-600, which indicates a higher uptake of phenol from aqueous solution and is more favoured than uptake by RHA-400. Also for the $1/n$, the uptake of phenol is more favoured for the RHA-600 than for the RHA-400 since values of $1/n$ indicate a better adsorption mechanism and relatively stronger bonds between the adsorbate and adsorbent [18]. The R^2 values, which are a measure of goodness-of-fit, show that both the Langmuir and Freundlich isotherm models can describe the adsorption data, though the Freundlich model describes it better.

4.0 Conclusion

The results obtained show that the adsorption process was fast and equilibrium occurred within 60-80 minutes. The results also show that an increase in adsorbent dose increases adsorption efficiency, while increase in initial phenol concentration decreases adsorption efficiency. The adsorption data fit the Freundlich isotherm best within the concentration range studied and RHA-600 showed better phenol removal than RHA-400 due to its higher ash content and surface. It can be concluded that rice husk when ashed at 600°C has a good potential for phenol adsorption in aqueous solution with a high adsorbent dose at concentration less than 2.5g/L and contact time of about 60 minutes. Therefore, rice husk ash is a low cost, natural and abundant source for the removal of phenol from aqueous solution.

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