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Comparative Studies on the Adsorption of Methylene Blue and Congo Red Dyes in Aqueous Solutions Using Groundnut Hull Modified with Sodium Hydroxide

Augustus Newton Ebelegi[1]; Nimobofa Ayawei[2]; Donbebe Wankasi[3]

[1]Department of Chemistry, Faculty of Science, Federal University Otuoke, Bayelsa, Nigeria.
[2]Department of Chemistry, Bayelsa Medical University, Bayelsa, Nigeria.
[3]Department of Chemical Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Bayelsa, Nigeria.

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Abstract: Adsorption processes utilizing agricultural waste materials have emerged as a sustainable solution for wastewater treatment and environmental remediation. The study investigated the adsorption capacities of groundnut hulls modified with sodium hydroxide for the uptake of methylene blue and Congo red dyes. Through a systematic approach, the study explores the comparative adsorption behaviour of these dyes under varying experimental conditions, including initial dye concentrations. The research employed Langmuir and Freundlich isotherm models to analyse the adsorption data, revealing complex interactions between the dye molecules and the adsorbent surface. The findings underscore the significance of cooperative adsorption processes, shedding light on the mechanisms driving efficient pollutant removal. This study contributes to the understanding of adsorption mechanisms and informs the development of cost-effective and sustainable adsorbents for environmental applications, thereby addressing the pressing challenge of water pollution caused by synthetic dyes. The Langmuir model exhibited a good fit for both dyes, suggesting monolayer coverage and continuous adsorption energy, with correlation coefficient (R^2) values of 0.9716 for Methylene Blue and 0.9418 for Congo Red. It also exhibits high maximum adsorption (Q_{max}) of 13.89 mg/g for methylene Blue and 19.047mg/g for Congo Red. However, the Freundlich model also showed suitability due to the heterogeneous distribution of active sites on the adsorbent, with correlation coefficient (R^2) values of 0.9602 for Methylene Blue and 0.948 for Congo Red. It also exhibits adsorption intensity (1/n) values of 0.6752 for Methylene Blue (which declares that the adsorption process is favourable) and 1.1558 for Congo Red (which suggests a cooperative adsorption process).

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I. INTRODUCTION

Adsorption processes play a crucial role in wastewater treatment and environmental remediation. Agricultural waste materials, such as groundnut hulls, watermelon rinds, rice husks, coconut shells, sugarcane bagasse, etc. have gained attention as promising adsorbents due to their abundance, low cost, and eco-friendly nature. However, the increasing discharge of synthetic dyes into water bodies poses an important environmental challenge (Nizam *et al*., 2021). Most agricultural waste substances have structures that exhibit looseness and porosity with functional groups such as carboxyl and hydroxyl that act as viable adsorption sites which in turn heighten their adsorption capacities (Ebelegi *et al*., 2023).

Agricultural wastes are leftover materials from farming and processing of raw farm products like fruits, vegetables, meat, poultry, dairy products, and crops. They are the remnants from making and processing farm products. There might be valuable things in these leftovers for people, but the expense of gathering, moving, and utilizing them is greater than their worth. (Ebelegi *et al*., 2023).

The disposal of agricultural waste is one of the major environmental issues, which poses adverse effects on ecosystems due to the careless dumping of agricultural waste into the environment. Improper disposal of waste can pollute the air and contribute to an increase in the Earth's temperature. So, we need to make big changes to use agro-waste in a way that can last a long time. This could mean creating ways to make energy that won't run out and making

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new products from living things that have extra value (Bala *et al.*, 2023).

Different types of agricultural waste from different sources abound in the environment, and they are mostly available in different amounts. Agro-wastes are typically made up of cellulose, hemicellulose, and lignin. Lignocelluloses are hard to break because they have a complicated structure. The most prevalent of Agro wastes are residual crops and waste from food processing, and they are generated in large quantities every day during farming and food processing activities. As farmsteads grow into bigger settlements and towns the challenge of proper management of increasing quantities of Agro wastes is getting worse and it is hard to ignore. (Bala *et al.*, 2023).

Adsorption is a highly effective technique for purifying dye-contaminated water due to its affordability, accessibility, simplicity, and efficiency. Compared to other methods, it offers significant advantages, particularly in terms of cost and environmental impact. Consequently, researchers have investigated various adsorbent materials, such as zeolites, clays, fibers, activated carbon, membranes, chitosan, and ion exchange resins, for their ability to adsorb contaminants. These materials have been utilized in diverse applications, including wastewater treatment and the removal of fats and oils. (Ebelegi *et al*., 2016).

Methylene blue and Congo red are synthetic dyes commonly used in various industries, including textiles, printing, and dyeing. These dyes are known for their complex chemical structures and resistance to biodegradation, posing significant challenges for wastewater treatment.

Methylthioninium chloride, commonly called methylene blue, is a salt used as a dye and as a medication ("Adsorption", 2022). Methylene blue dye (MBD) (CI No. 52015) is a heterocyclic aromatic chemical compound (Patel & Vashi, 2015).

The methylene blue dye used was discovered by Caro in 1878.It is a basic cationic dye, heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}N_3SCl$, Molecular Weight=319.85. λmax = 663nm (Dash, 2010).

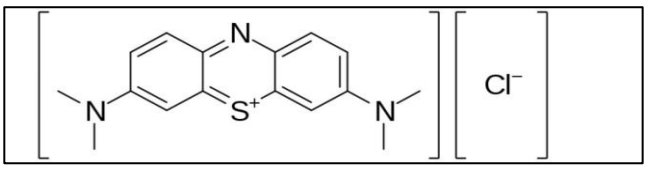


Fig 1 Molecular Structure of Methylene Blue

Congo red is an organic compound, the sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid). Congo red is water-soluble, yielding a red colloidal solution; its solubility is greater in organic solvents. The use of Congo red in the textile industry has long been abandoned, primarily because of its carcinogenic properties, but it is still used for histological staining ("Adsorption", 2022). It is a secondary diazo dye; (formula: $C_{32}H_{22}N_6Na_2O_6S_2$; λmax = 497nm; molecular weight: 696.66 g/mol) (Dash, 2010).

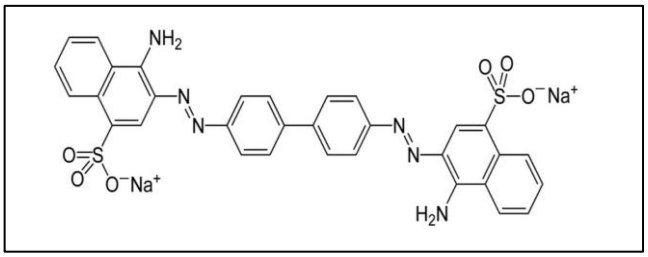


Fig 2 Molecular Structure of Congo Red

Groundnut (*Arachis hypogaea*) is a nutritious leguminous crop, grown mainly for seed and oil worldwide. Groundnut hulls (shells) not to be confounded with groundnut peels are the leftover product obtained after the removal of groundnut seed from its pod. This is the abundant agro-industrial waste product which has a very slow degradation rate under natural conditions. However, Groundnut hulls contain various bioactive and functional components which are beneficial for mankind. Commercially, it is used as a feedstock, food, filler in fertilizer and even in bio-filter carriers. But most of the deserted groundnut hulls are burnt or buried resulting in environmental pollution. Thus, new technologies need to be developed in order to attain zero waste production and direct this otherwise waste product into meaningful use in food, feed, paper and bioenergy industries (Duc *et al*., 2019).


Fig 3 Groundnut Hull Biomass

Despite the potential of agricultural waste as adsorbents, the comparative adsorption behaviour of Methylene blue and Congo red onto groundnut hulls modified with sodium hydroxide has not been widely studied. Therefore, there is need for a systematic study in order to establish definite optimization procedures for the removal of these dyes from aqueous solutions using batch adsorption process. This study focuses on the adsorption of methylene blue and Congo red onto groundnut hulls modified with sodium hydroxide under various experimental conditions. The research will explore the effect of initial dye concentration on the adsorption process.

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By elucidating the adsorption behaviour of Methylene blue and Congo red onto modified groundnut hulls, this work provides insights for the development of cost-effective and sustainable adsorbents for environmental applications.

II. MATERIALS AND METHOD

➢ *Reagents and Materials*

Distilled Water, Dyes (Methylene Blue & Congo Red), Stewart Reciprocating Shaker, Aluminum Foil, Analytical Weighing Balance, Electronic Weighing Balance, Micropipette, Sodium hydroxide-NaOH solution (1M), Sample Containers, Microwave oven, UV/VIS Spectrophotometer. All reagents used for this study were of analytical grade.

➢ *Sample Preparation/Chemical Activation*

The precursor material used for this study was purchased from local traders at the Swali market, Yenagoa, Bayelsa State, Nigeria. The outer shells of the groundnuts were removed by hand in order to separate the nuts inside. The hulls were washed with distilled water several times and sun dried for six (6) days. The groundnut shells were crushed into powder using a regular blender and then sorted by size using a sieve (710 micrometers). The crushed hulls were put into a sealed container for later use.

➢ *Modification of Groundnut Hull Using NaOH Solution*

Approximately ten grams (10 g) of Untreated Groundnut hull was weighed and mixed with 1M NaOH solution in a 250 mL beaker and the mixture was subjected to microwave radiation for 5 minutes and allowed to cool at room temperature, filtered and washed with distilled water to remove excess reagents. The residue obtained was further oven dried at 60˚C for 24 hrs. The dried NaOH treated biomass was crushed and sieved into particle size less than 710 µm and labeled GH-NaOH (Ebelegi *et al*., 2022).

➢ *Preparation of Methylene Blue Adsorbate Solution*

About 0.3 g of Methylene Blue powder was dissolved in 1000 mL of distilled water (300 mg/L), this served as the stock solution for serial dilutions into 60 mg/L, 80 mg/L and 100 mg/L respectively.

➢ *Preparation of Congo Red Adsorbate Solution*

About 0.3 g of Congo Red powder was dissolved in 1000 mL of distilled water (300 mg/L), this served as the stock solution for serial dilutions into 60 mg/L, 80 mg/L and 100 mg/L respectively.

➢ *Adsorption Studies*

Equilibrium adsorption experiments were conducted in batches at room temperature with a Stewart Reciprocating Shaker at 100 rotations per minute. The contact time was evaluated on samples of 0.2 g of Groundnut hull modified with Sodium hydroxide (NaOH) in 10 mL of dye solution, the sample was tested with 60 mg/L, 80 mg/L and 100 m/L of Congo Red solution and Methylene Blue solution respectively for 120 minutes (Augustus *et al*., 2017).

Equilibrium concentrations of the supernatant Methylene Blue solutions were analyzed with the UV/VIS Spectrophotometer at λmax = 664 nm after calibration. Those for Congo Red were analyzed at λmax = 490 nm.

- *Data Management*

The amount of dyes adsorbed on the groundnut hull modified with sodium hydroxide were calculated using the equation: $Q_e = (C_o - C_e) \times \frac{V}{M}$; where C_o and C_e are initial and final concentrations (mg/L), Q_e is the amount adsorbed (mg/g), V and M are solution volume (mL) and mass (g) respectively. The percentage adsorption (% Ads) or removal efficiency (R_E) was calculated using the following expression; $\% Ads = \frac{(C_o - C_e)}{C_o} \times 100\%$.

III. RESULTS AND DISCUSSIONS

➢ *Calibration Plots:*

The calibration plots for the dyes are shown below in figures 4 and 5.

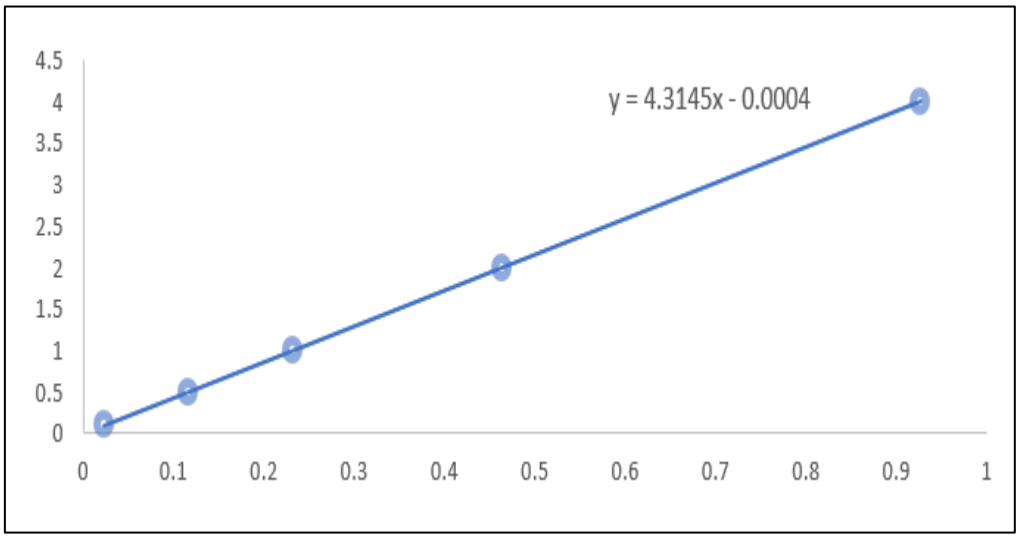


Fig 4 Calibration Plot for Methylene Blue

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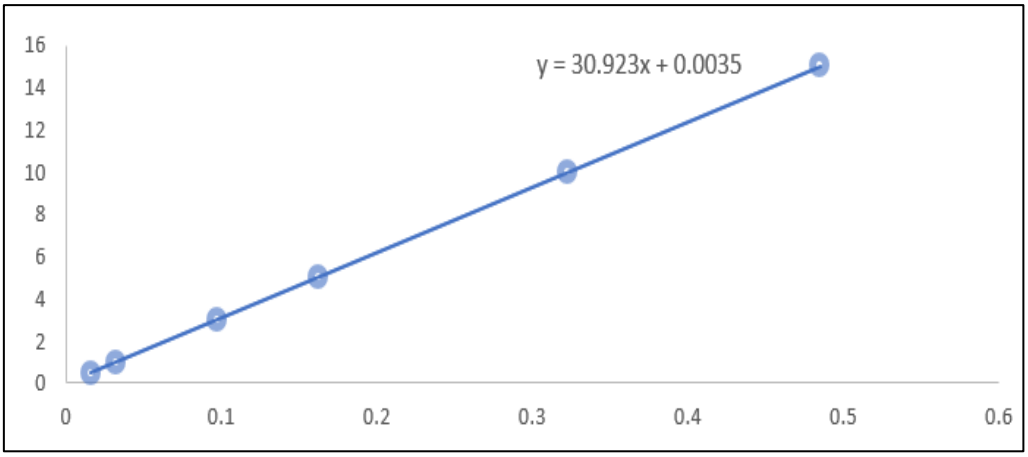


Fig 5 Calibration Plot for Congo Red

➢ *Equilibrium Studies*

- *Effect of Initial Concentration*

In order to study the effect of different concentrations of dye on the adsorption process, three concentrations (60, 80 and 100 mg/L) were used. The concentrations of dye at equilibrium, C_e (mg/L), the amounts of dye adsorbed at equilibrium, Q_e (mg/g), and the amounts adsorbed were calculated and given in Tables 1 and 2, expressed for both adsorbates (Methylene Blue and Congo Red) respectively.

Table 1 Results for Congo Methylene Blue

Co	Ce	% Ads	Qe	1/Qe	1/Ce	lnQe	lnCe
20	0.007	99.967	1.000	1.000	153.374	0.000	-5.033
40	0.013	99.967	1.999	0.500	76.687	0.693	-4.340
60	0.020	99.967	2.999	0.333	51.120	1.098	-3.934
80	0.026	99.967	3.999	0.250	38.385	1.386	-3.648
100	0.041	99.959	4.998	0.200	24.459	1.609	-3.197

Table 2 Results for Congo Red

Co	Ce	% Ads	Qe	1/Qe	1/Ce	lnQe	lnCe
20	0.002	99.991	1.000	1.000	555.556	0.000	-6.320
40	0.004	99.991	2.000	0.500	277.008	0.693	-5.624
60	0.005	99.991	3.000	0.333	184.615	1.099	-5.218
80	0.006	99.992	4.000	0.250	158.174	1.386	-5.064
100	0.008	99.992	5.000	0.200	120.557	1.609	-4.792

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In order to ascertain removal efficiency the effect of varying the concentration of adsorbate on percentage adsorption was studied by increasing the adsorbate dose from 20 mg/L to 100mg/L for groundnut hull modified with sodium hydroxide (GH- NaOH).

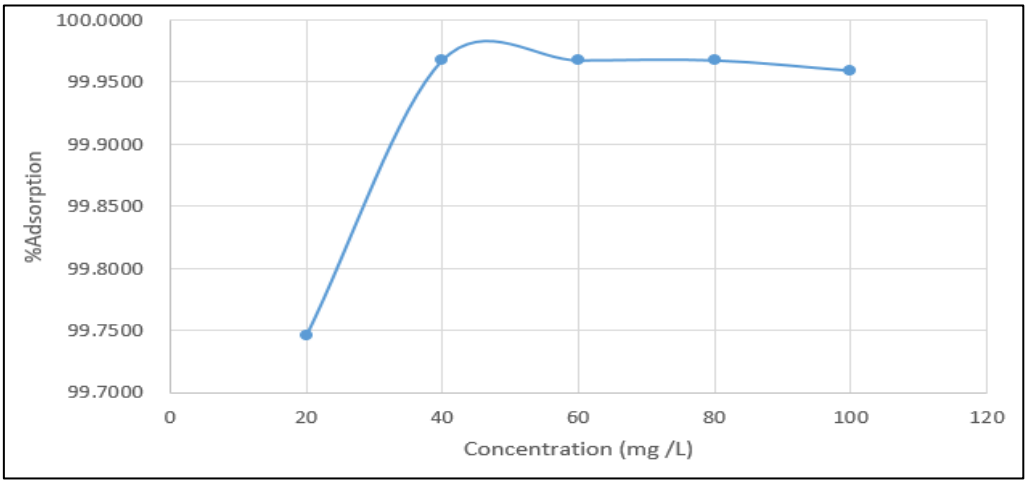


Fig 6 Plot of Removal Efficiency Against Adsorbate Concentration for Methylene Blue Uptake by GH-NaOH

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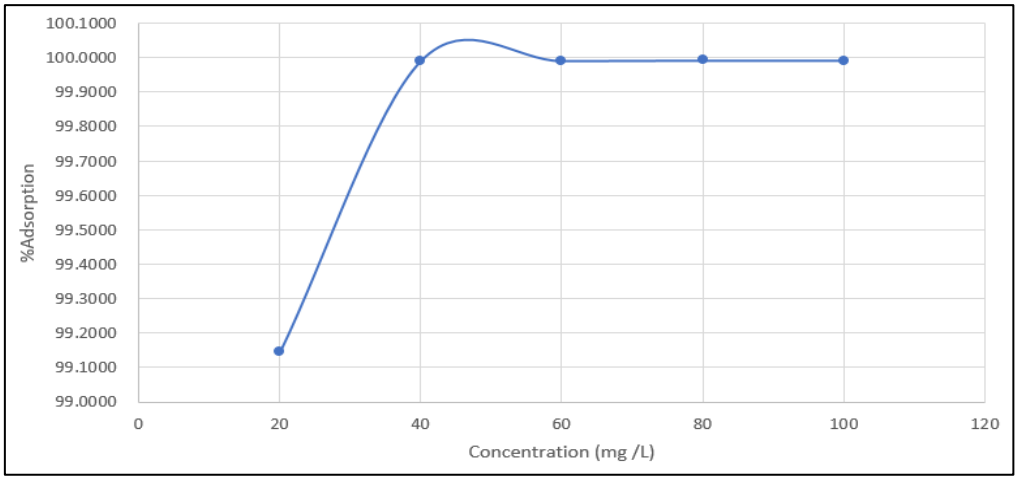


Fig 7 Plot of Removal Efficiency Against Adsorbate Concentration for Congo Red Uptake by GH-NaOH

Tables 3 and 4 show the removal efficiency of GH-NaOH for both dyes (Methylene Blue and Congo Red). The leap in % adsorption at low adsorbate concentrations shows the availability of adsorption sites on the adsorbent at the onset of the adsorption process, while the gradual decrease in the percentage of dye adsorbed with increase in concentration of adsorbate may be ascribed to rapid occupation of all available adsorption sites.

- *Adsorption Isotherms*

The Adsorption Isotherms were studied using initial concentrations of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L of adsorbate with an adsorbent dosage of 0.2 g/L. Two adsorption Isotherm models (Langmuir and Freundlich) were adopted to investigate Methylene Blue and Congo Red behaviour on Groundnut hull modified with sodium hydroxide (GH-NaOH). The parameters of the two adsorption Isotherms are listed in Tables 6 and 7.

Table 5 Equilibrium Isotherm Equations

Isotherm Type	Linear Equation	Plotting	Parameters
Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_{max}K_L}\frac{1}{C_e} + \frac{1}{Q_{max}}$	$\frac{1}{C_e}\ vs\ \frac{1}{Q_e}$	$\frac{1}{Q_{max}} = Intercept$ $Q_{max} = \frac{1}{Intercept}$ $K_L = \frac{1}{Q_{max} \times Slope}$
Freundlich	$lnQ_e = lnK_f + \frac{1}{n}lnC_e$	$lnC_e\ vs\ lnQ_e$	$lnK_f = Intercept$ $K_f = e^{Intercept}$ $\frac{1}{n} = Slope$ $n = \frac{1}{Slope}$

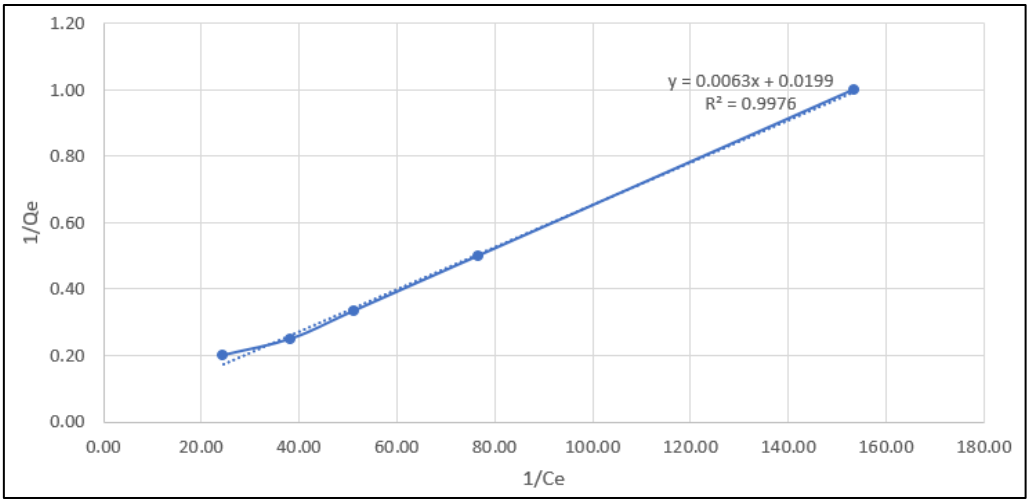


Fig 8 Langmuir Plot for Adsorption of Methylene Blue Onto GH-NaOH

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The Langmuir isotherm for Methylene Blue gives high correlation coefficients (R^2 = 0.9716), and also exhibits high maximum adsorption (Q_{max} = 13.89 mg/g), with a separation factor, (R_L = 0.023) greater than zero (0) and less than one (1), therefore this isotherm type is favourable (Ayawei *et al.*, 2017).

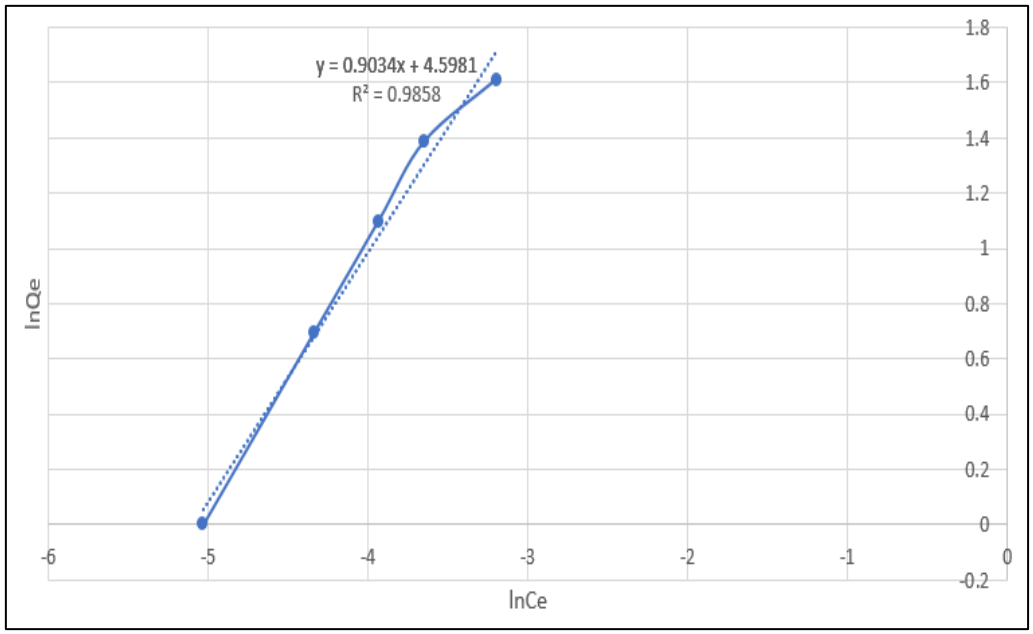


Fig 9 Freundlich Isotherm Plot for Adsorption of Methylene Blue Onto GH-NaOH

Freundlich isotherm also favours the experimental data due to high correlation coefficients (R^2 = 0.9858) and this may be attributed to the heterogeneous distribution of active sites and multilayer adsorption on the groundnut hull modified with sodium hydroxide, it also exhibited adsorption intensity (1/n = 0.6752) being greater than zero (0) but lesser than one (1). Therefore, it can be inferred that the isotherm type is favourable, although the Langmuir isotherm is best fit for describing the reaction mechanism as the R^2 is greater.

- *Congo Red*

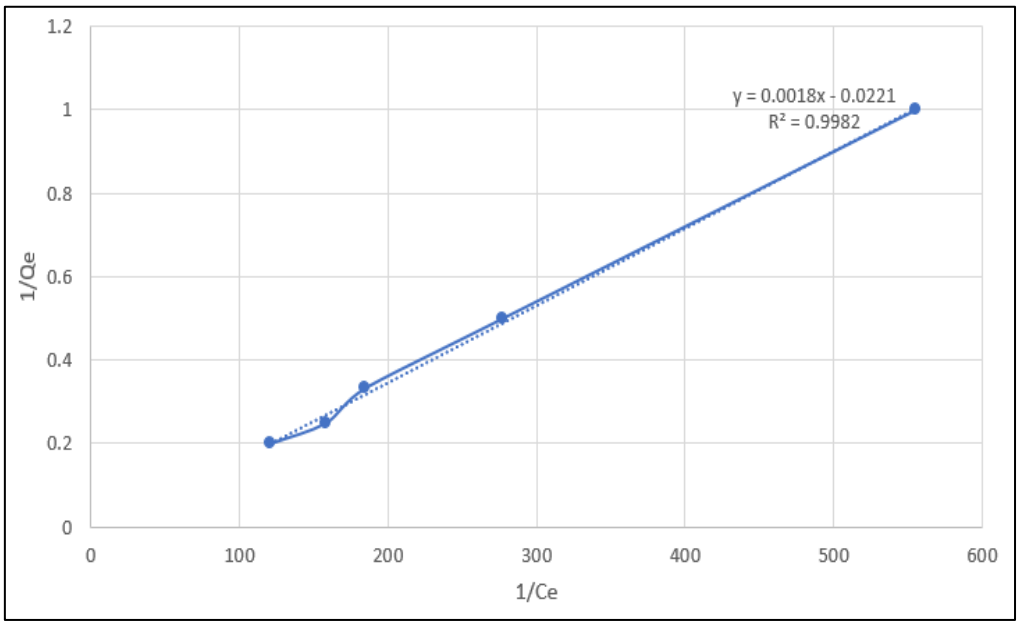


Fig 10 Langmuir Isotherm Plot for Adsorption of Congo Red Onto NaOH

Langmuir isotherm for Congo Red gives high correlation coefficients (R^2 = 0.9982) with a separation factor, (R_L = 0.013) greater than zero (0) and less than one (1), therefore this isotherm type is favourable. However, it exhibits maximum adsorption capacity (Q_{max} = 19.047 mg/g). Thereby making the Langmuir isotherm model fit for describing the adsorption process.

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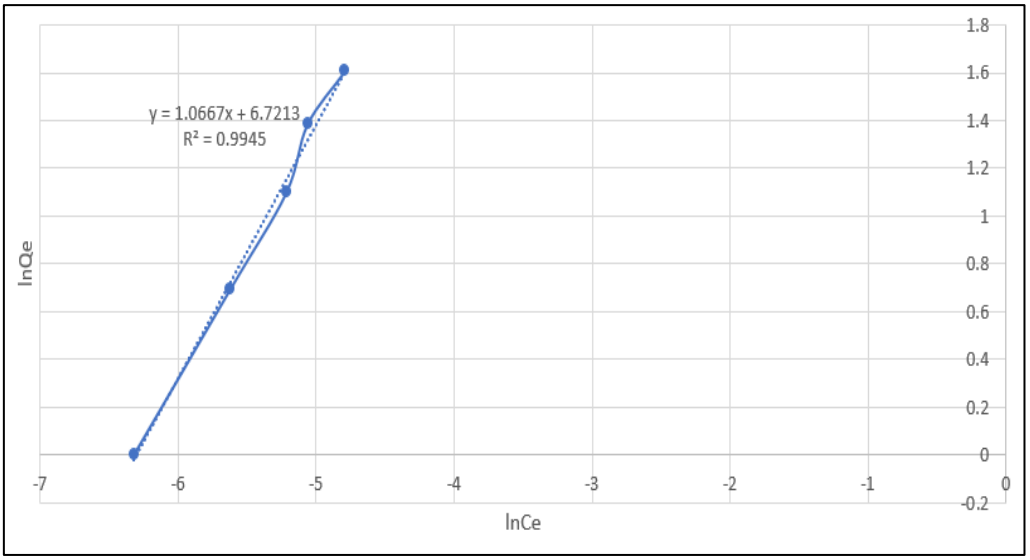


Fig 11 Freundlich Isotherm Plot for Adsorption of Congo Red Onto GH-NaOH

Freundlich isotherm also fit the experimental data due to high correlation coefficients (R^2 = 0.9945) and this may be attributed to the heterogeneous distribution of active sites and multilayer adsorption on the adsorbent (GH-NaOH), however, it exhibited adsorption intensity (1/n = 1.1558) being greater than one (1) which depicts cooperative adsorption. Hence, it can be inferred that there was a cooperative adsorption process, which comprises physisorption and chemisorption, although the Freundlich isotherm is best fit for describing the reaction mechanism as the R^2 is closer to one.

Table 6 Characteristic Parameters of the Adsorption Isotherm Models for Methylene Blue Adsorption by Groundnut hull Modified with Sodium Hydroxide

Isotherm Model	Isotherm Parameter	Results
Langmuir	R_L	0.023
	Q_{max} (mg/g)	13.89
	R^2	0.9716
Freundlich	1/n	0.6752
	n	1.48
	R^2	0.9602

Table 7 Characteristic Parameters of the Adsorption Isotherm Models for Congo Red Adsorption by Groundnut hull Modified with Sodium Hydroxide

Isotherm Model	Isotherm Parameter	Results
Langmuir	R_L	0.013
	Q_{max} (mg/g)	19.047
	R^2	0.9418
Freundlich	1/n	1.1558
	n	0.865
	R^2	0.948

IV. CONCLUSION

The adsorption behaviour of Methylene Blue and Congo Red onto groundnut hull modified with sodium hydroxide (GH-NaOH) was investigated, focusing on the effects of initial concentration and adsorption isotherms. The following observations are made:

- The effect of varying concentrations of dye on adsorption revealed a gradual decrease in the percentage of dye adsorbed with an increase in the concentration of adsorbate for both Methylene Blue and Congo Red. This observation suggests rapid adsorption saturation at higher concentrations, potentially due to limited adsorption sites.
- The Langmuir and Freundlich isotherm models were employed to analyze the adsorption data. For Methylene Blue, both models exhibited favourable fits with high correlation coefficients, indicating a cooperative adsorption process. Likewise for Congo Red, the Langmuir and Freundlich isotherm models both describe the adsorption process well.
- The presence of cooperative adsorption processes suggests complex interactions between the dye molecules and the adsorbent surface. Understanding these interactions is crucial for optimizing adsorption processes

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for environmental remediation and wastewater treatment applications. Further research could explore the mechanisms driving cooperative adsorption and its implications for practical applications.

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