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ORIGINAL RESEARCH

Adsorption Isotherms studies of the removal of Indigo Blue dye from aqueous solution using chemically modified coconut shell

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Abstract:

Introduction: The conversion and utilization of agricultural wastes in environmentally friendly processes have transformed these materials into useful rather than waste materials.

Aim: This study investigates the adsorption of indigo blue dye from aqueous solution onto coconut shell, a low cost agricultural waste material in a batch process.

Materials and Methods: Pulverized coconut shell was chemically modified and characterized using the Fourier Transform Infra Red spectroscopy and Scanning Electron Microscopy. Adsorption process using the chemically modified coconut shell was studied as a function of pH, initial dye concentration, adsorbent dose, and contact time. The adsorption equilibrium data were analyzed with Langmuir, Freundlich and Temkin isotherm models.

Results: The results revealed that percentage of the indigo dye adsorbed from aqueous solution varied linearly with the adsorbent dose, concentration and time with maximum percentage dye adsorption of 88.4% at 70 mg dosage, 95.8% at 0.05 mg/L concentration and 90% at 1 hr contact time but varies non-linearly with pH with maximum percentage dye adsorption of 92.9% attained at pH of 5. The adsorption equilibrium data were analyzed with Langmuir, Freundlich and Temkin isotherm models with the Langmuir isotherm having the best fit to the adsorption process with R^2 value of 0.998. The experimental data were best described by the pseudo-second order kinetics model. FTIR analyses reveal that the adsorption process was through a chemical interaction of the dye with some functional groups at the surface of the adsorbent

Conclusion: The chemically modified coconut shell is an effective adsorbent for the removal of indigo dye from aqueous solution is by chemisorption process with the adsorbent surface energetically homogeneous ($n < 1$).

Keywords: Adsorption, Indigo blue dye, Coconut Shell, Kinetics, Aqueous solution.

All co-authors agreed to have their names listed as authors

1. INTRODUCTION

Indigo blue dye is a vat dye that has found extensive use in the industries. Apart from its use as a textile-colouring agent, indigo and its derivatives are also used as an additive in pharmaceutical tablets and capsules and for medical diagnosis [1 – 4]. Textile industries consume substantial volumes of dyes for wet processing of textiles, the chemicals in these dyes range from inorganic compounds and elements to polymers and organic products. Such extensive use of dyes poses problems such as reducing water transparency, affecting photosynthetic process, and solubility of gases in the body of the water [5]. Effluents from these textile industries require pretreatment for colour prior to disposal into receiving water bodies. This is because this dye-bearing waste water imparts toxicity to aquatic life and damage the aesthetic nature of receiving water bodies' environment [6].

Several methods have been reported for quantitative determination of Indigo blue, including chromatographic, voltametric and spectrophotometric ones. New treatment technologies have been developed in order to meet the legal requirements regarding effluent disposal of this dye as well as to reduce the operating costs of such processes. The Indigo dye is insoluble in water and must be reduced i.e. the oxygen must be removed in the presence of alkali by a reducing agent such as thiourea dioxide (thiox), sodium hydrosulphite, zinc or bacteria before its application. Upon reduction, indigo becomes colourless and water soluble. In reduced state, indigo has a high affinity for cellulosic fibers and enters the open spaces of the fiber. The dyed fibers are then exposed to air, which oxidizes the dye molecule back to its insoluble form. Thus, Indigo dye works by oxidation – reduction reaction (redox reaction).The insoluble dye particles are trapped inside the fiber, colouring them permanently blue. Unlike most dyes, indigo forms a mechanical, not chemical bond with the fabrics [7].

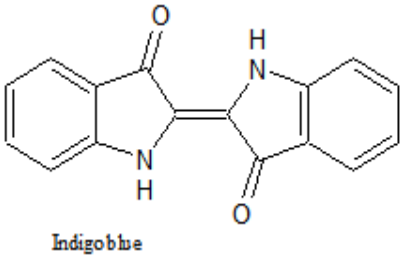

Figure 1: Indigo blue

Coconut shell (*Cocos Nucifera L.*) has been used as a low cost alternative adsorbent for the removal of pollutants (dyes and other natural and inorganic substances) from natural waters. Also, the retention capacity of several metallic ions in aqueous solutions has been previously reported [8] using coconut fiber as the adsorbent. This is a sustainable alternative because of waste reuse.

Adsorption has been reported to be an effective process for colour removal from dye wastewater [9 – 11]. The term 'adsorption' was proposed by du Bois-Reymond but introduced to the literature by Kayser [12] and has found diverse applications from being widely used for the removal of solutes from solutions to the removal of gases from atmospheric air. The extent of adsorption depends on the nature of adsorbent especially its porosity and surface areas. The size and distribution of the macro and micro pores of the adsorbent are key features for effective adsorption, as they determine the ions or molecules that can be adsorbed [13].

Adsorption process can utilizes agricultural materials as well as a wide variety of micro-organisms in dead, pretreated and immobilized form as the adsorbing agents. These materials are cheap to get, environmentally friendly and carry wide range of binding sites for the adsorbate molecules [14].

This present study investigates the use of chemically activated coconut shell as an effective adsorbent for the removal of Indigo blue dye from solution. Adsorption equilibrium data were analysed with Langmuir isotherm [15], Freundlich isotherm [16] and Temkin isotherm [17] models. Adsorption kinetics models and the intraparticle diffusion were used to describe the adsorption processes.

2. MATERIAL AND METHODS

2.1. Apparatus and Reagents

Measuring cylinder, standard conical flasks, Volumetric flasks, Pipette, Burette, filter paper, funnel, paper tape, pH meter, Weighing balance, water bath shaker, UV-Visible spectrophotometer (Beckman coulter), Schimadzu IRAffinity-1S spectrophotometer, Phenonprox Scanning Electron Microscope JEOL-JSM-35CF model.

All chemical reagents used were of analytical grade from BDH chemicals. De-ionized water was used throughout the experiment.

2.2. Modification and Characterization of the Adsorbent (Coconut Shell)

The adsorbent, coconut (Cocos nucifera L.) shell was obtained from a local coconut processing mill in Ikeja, Lagos state, Nigeria. The Indigo blue dye was purchased from a local market in Abeokuta, Ogun state, Nigeria. Indigo blue has molecular formula $C_{16}H_{10}N_2O_2$ (Mol. wt. 262.27 g/mol). It was used without further purification, but just reduction, so as to make it water soluble for the sake of the experiment. Reagents for reduction of the dye include sodium thiosulphate ($Na_2S_2O_4$) and dilute 3M NaOH solutions.

The Coconut shell was modified in a three-step procedure to obtain optimum adsorption of the indigo dye. The reagents for coconut shell's surface treatment were aqueous solutions of 5 %, 10 %, 15 %, and 20 % composition of sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2) of the same composition, and 0.25 %, 0.5 %, 0.75 %, and 1 % potassium permanganate ($KMnO_4$). The coconut shell was firstly treated with the NaOH solution, then with the $KMnO_4$ solution and finally with the H_2O_2 solution, dried at 90 ^oC and cooled to room temperature [18]. The

modified shell was then air- dried, pulverized and sieved to 500 μm size. The pulverized adsorbent was characterized before and after the adsorption process using the Scanning Electron Microscopy (SEM) and Fourier Transform Infra Red (FTIR) spectroscopy.

2.3. Preparation of adsorbate (Dye Stock)

The dye stock solution was prepared by firstly weighing 0.02 g of Indigo blue dye into a beaker containing 50 ml of water, after which 0.12 g of $Na_2S_2O_4$ and 1.2 ml of 3 M NaOH were added.
The solution was then heated at a temperature of 50 ^oC till the colour changed from green to blue; this was done to ensure reduction of dye into its leuco–soluble form as indigo dye is insoluble in water, unless it is reduced to the leuco–soluble form [19] (Figure 2).

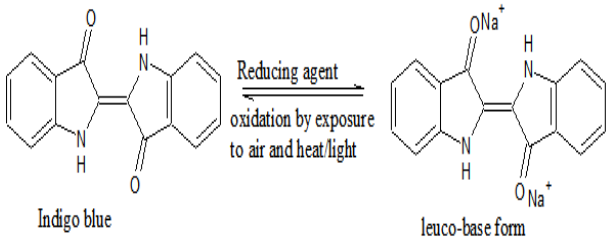

Figure 2: Reduction of insoluble Indigo blue to soluble leuco-base form of Indigo blue.

The resulting solution made was transferred to a 100 ml volumetric flask and made up to mark to prepare 0.2 g/l stock solution of the dye. 0.4, 0.8, 1.2, 1.6 and 2.0 mg/L concentrations were then prepared from the stock solution by serial dilution and used to obtain a calibration curve (Figure 3).

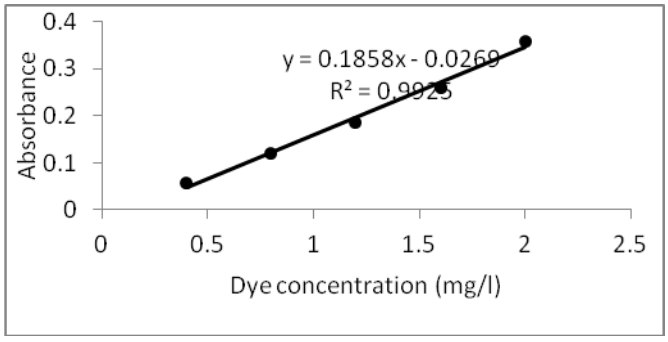

Figure 3: Calibration curve of indigo dye at concentration range from 0.4 to 2.0 mg/L

2.4. Adsorption Batch process

For each experiment, 25 ml of 0.2 mg/L dye solution (concentration was varied in the case of effect of initial concentration) was agitated with 0.5 g of Pulverized Coconut shell (except for effect of adsorbent dose, where the mass of shell was varied) at a constant speed of 200 rpm for 3 hours in a shaker after which they were centrifuged at 4,000 rpm for 20 minutes to separate the supernatant. The experiments were carried out in triplicate after which 5 ml of each supernatant is taken and analyzed for the residual dye content by UV – Visible Spectrophotometer (Beckman coulter) using a λ_{max} of 640 nm.

The effect of initial concentrations of the dye on the adsorption process was determined in the range 0.05 – 0.3 mg/L dye concentration. The effect of the initial pH on the adsorption capacity was investigated in the pH range of 2 – 8. The effect of time on adsorption process was studied at the time range of 3 – 7 hours contact time. The effect of adsorbent dose on the adsorption process was studied using 0.1, 0.3, 0.5, 0.7, 0.9, 0.11, 0.13 and 0.15 g of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Adsorbent

3.1.1. Scanning Electron Microscope Analysis

The Scanning Electron Microscope image of the Coconut shell was taken to have better understanding of the surface morphology of the adsorbent before and after the adsorption experiment. The SEM micrographs at 30 μm and 200 μm magnifications for the modified coconut shell before the adsorption experiments; Figure 4(a – b), show a rough surface with irregular pore sizes for the modified coconut shell, this may be attributed to the crystallization of NaOH solution (used for modification) and the drying at temperature 70 ^oC for 3 hours. The increased surface roughness of coconut shell implies an increasing amount of the exposed cellulose and the strength of natural coconut shell.The SEM micrographs at 30 μm and 200 μm magnifications for the modified coconut shell after the adsorption experiments; Figure 4(c – d), show a rather more smoothen surface, indicating that shell pores have been filled with dye molecules and are no longer visible.

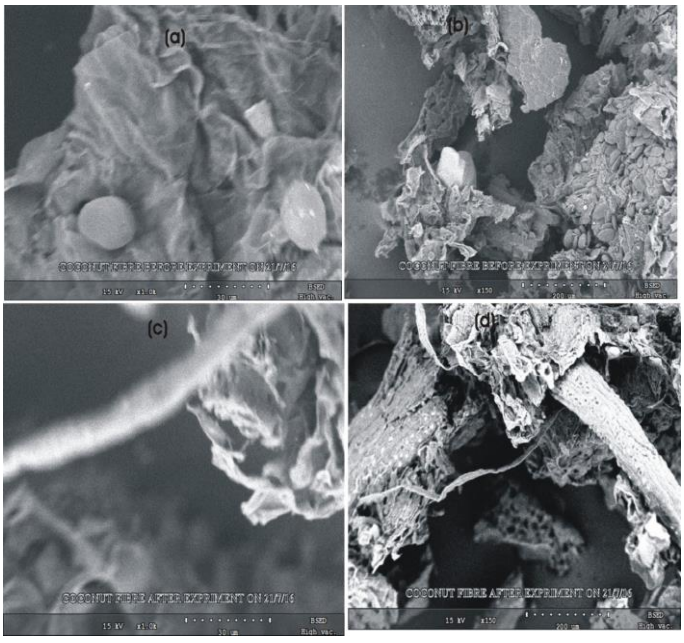

Figure 4: Scanning Electron Micrograph of the crude Coconut shell at (a) 30μm and (b) 200 μm magnifications, (c) 30μm and (d) 200 μm magnifications after adsorption process

3.1.2. FTIR Spectral Analysis

FTIR spectroscopy provides structural and compositional information on the functional groups present in the samples. The functional groups present in the proximate composite of the coconut shell were analyzed by Fourier transform infrared (FTIR) spectroscopy. Figure 5 (a – b) shows IR spectra of raw coconut shell and dye loaded coconut shell respectively. The spectra showed a number of absorption peaks, indicating the complex nature of the coconut shell. Comparison of the spectra before and after the adsorption process shows that a total number of 15 peaks out of the 21 changed. Some peaks like 2299.15 cm^{-1} representing C≡N group, 1112.93 cm^{-1} showing a broad band of C – O and 420.48 cm^{-1} an alkyl halide stretch that were present initially in the shell disappeared completely after adsorption process. There were also shifts in peaks like 1653.00 cm^{-1} to 1654.92 cm^{-1} indicating a broader amide stretch, 1388.75cm^{-1} to 1384.89 indicating an alteration in the already weak N – O group that made it weaker and no longer broad. The shift in the peak at 1157.29 cm^{-1} to 1165.00 cm^{-1} showing a stronger and broader band of C – O which indicates that there is presence of a new substance which is possibly a dye molecule, 1033.85 cm^{-1} to 1070.49 cm^{-1} indicating a longer stretch, 894.97 cm^{-1} to 891.11cm^{-1} indicating a slight change in the alkene =C – H bending,765.74 cm^{-1} to 754.17 cm^{-1} indicating a slight C – Cl stretch, 580.57 cm^{-1} to 576.72 cm^{-1} and 516.92 cm^{-1} to 518.85 also showing a slight change in the C – Br stretch. New wavelength of peaks 1994.40cm^{-1} shows a C=C asymmetric stretch, 1799.59 cm^{-1} indicates a C – O acyl halide and 630.72 cm^{-1} showing the addition of another C – Cl, all these changes indicates the involvement of the functional groups in the adsorption process and that the adsorption type is mostly Chemisorption.

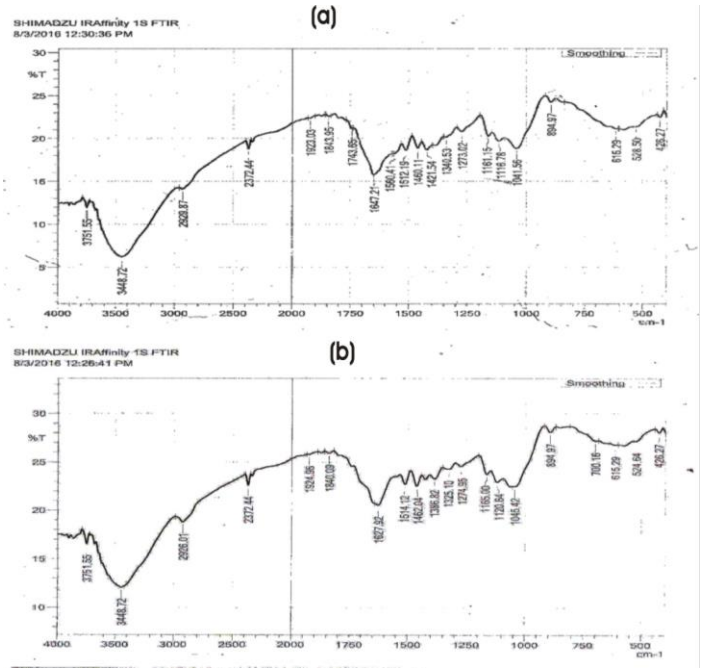

Figure 5: FTIR result of the modified coconut shell (a) before and (b) after adsorption of Indigo blue dye respectively

3.2. Adsorption Laboratory Batch Experiment

3.2.1. Effect of pH

The effect of the variation of pH on the adsorption process is shown in Figure 6(a). The initial pH value for the reduced form of the dye before any further adjustment was 11 which is pH for a strong base. Maximum adsorption of 92.9% occurred at a weak acid pH of 5. This may likely be due to less OH^- ions competing with the OH^- ion of the dye for adsorption sites at that pH and also because of the functional group in the coconut shell that consist of more acidic group than basic functional group, thereby increasing adsorption due to increase in electrostatic force between the H^+ ion on the coconut shell and OH^- ion of the dye molecules.

3.2.2. Effect of adsorbent dose

The percentage of dye removal increased with an increase in adsorbent dosage from 10mg to 70 mg, Figure 6(b) which had 88.4% removal. The increase in adsorption with adsorbent dosage can be attributed to an increase in the adsorption surface area and availability of more adsorption sites. However, on further increase of adsorbent dose, a decrease in percentage adsorption occurred and this may be as a result of overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available to the dye and an increase in the diffusion path length.

3.2.3. Effect of Initial dye Concentration

It was found that the percentage of adsorption decreased with an increase in the initial concentration, Figure 6(c). The increase in the initial dye concentration caused an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration [20]. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of the initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of the initial concentration.

3.2.4. Effect of Contact time

Maximum adsorption of indigo dye was achieved after 1 hour. The preliminary experiments showed that the adsorption of indigo dye is fast at the initial stages and becomes slower near the equilibrium. The rate of indigo adsorption onto the fiber is very rapid during the initial 2 hours and decreases thereafter, as can be seen from Figure 6(d). The time profile of indigo uptake is a single, smooth, and continuous curve leading to saturation, suggesting possible monolayer coverage of indigo dye on the surface of the coconut fibre adsorbent.

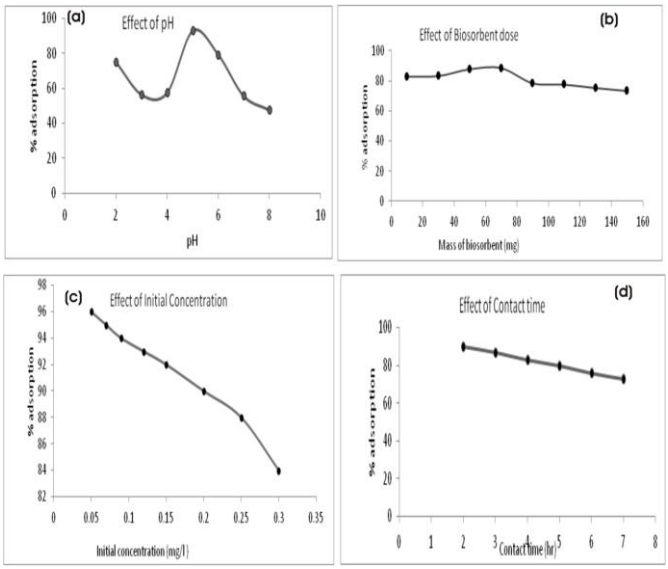

Figure 6: Effects of (a) pH (b) adsorbent dose (c) Initial dye concentration (d) time; on the adsorption of indigo dye by coconut shell from aqueous solution

3.3. Adsorption Isotherms

The Langmuir isotherm model proposed by Langmuir [15] is based on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. It explains monolayer adsorption which lies on the fact that the adsorbent has a finite capacity for the adsorbate i.e., at equilibrium; a saturation point is attained where no further adsorption can occur.
The equation below shows the Langmuir isotherm expressions:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad \ldots\ldots\ldots\ldots (1)$$

The above equation can be linearized to:

$$\frac{C_e}{q_{max}} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad \ldots\ldots\ldots\ldots (2)$$

Where C_e, is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg). The values of K_L and q_{max} can be determined from the slope and intercept of the linear plot of C_e/q_e against C_e, Figure 7(a). The values of R^2, K_L and q_{max} from the Langmuir isotherm are listed in Table 1. The negative value of the K_L for indigo dye indicates that adsorption of indigo dye on modified coconut shell was difficult and it may be due to an increase in ionic radius, which led to an increase in charge density, thus reduction in adsorption capacity.
The Freundlich isotherm model [16] is another most widely applied isotherm in explaining adsorption. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules. It assumes that adsorption energy exponentially decreases on the completion of the sorptional centres in the adsorbent [21].

The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \quad \ldots\ldots\ldots\ldots (3)$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_F is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$) and n, a dimensionless constant, which can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent respectively.
A linear form of the Freundlich equation is generally expressed as:

$$Log\, q_e = Log K_F + \frac{1}{n} Log C_e \quad \ldots\ldots\ldots\ldots (4)$$

The values of K_F and n are calculated from the intercepts and slopes of the plot of $Log\, q_e$ versus $Log\, C_e$. Figure 7(b) shows the Freundlich plots and the isotherm parameters derived from Freundlich plots are listed in Table 1. It is evident from the table that the value of n is negative, thus showing homogenous adsorption site, which doesn't correlate with the Freundlich assumption.
The Temkin isotherm model [17] takes into account adsorbent – adsorbate interactions. This model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent – adsorbate interactions, and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Temkin isotherm is given as:

$$q_e = B_1 K_T + B_1 In C_e \quad \ldots\ldots\ldots\ldots (5)$$

Where B_1 is the Temkin constant related to the heat of adsorption and is given as:

$$B_1 = \frac{R_T}{b} \quad \ldots\ldots\ldots\ldots (6)$$

where B_1 is related to the heat of adsorption. K_T is the equilibrium binding constant (L/mg). The values of K_T and B_1 obtained from the intercepts and slopes of the plots of q_e versus $ln\, C_e$, Figure 7(c) are summarized in Table 1.

All the three isotherm models showed a good correlation coefficient with the experimental data (R^2 > 0.90) (Table 1), which suggests that the adsorption data obtained in the present study could be said to fit the three isotherm models. However, Langmuir isotherm had the highest correlation coefficient of (R^2:0.99) and thus could be considered as the best fit models for the adsorption process, although, the other two models can also be used to account for the adsorption process.

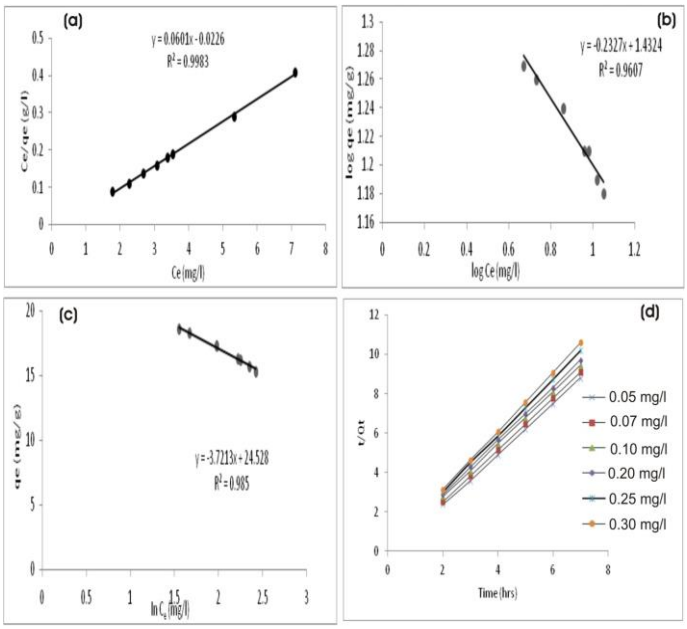

Figure 7: Isotherm plots for the adsorption of indigo dye onto coconut shell at 25 ºC

(a) Langmuir, (b) Fredluich (c) Temkin and (d) Pseudo-second order Kinetic plot of adsorption on indigo onto Coconut shell

Table 1: Isotherm parameters for the adsorption of Indigo blue dye onto coconut shell.

Isotherm Models	Parameters	Values
Langmuir	q_{max}	13.68
	K_L	-0.71
	R^2	0.9964
	R_L	0.033
Freundlich	*N*	-4.3
	K_F	27.06
	R^2	0.9607
Temkin	B_1	3.72
	K_T	0.152
	R^2	0.985

3.4. Adsorption Equilibrium kinetics

The pseudo second order model first proposed by Blanchard et al., [22] is based on the adsorption capacity and can predicts the behaviour for the adsorption process for all dye concentrations. It can also be used to predict chemisorption processes. The pseudo second order kinetics model for the adsorption process can be represented with the expression [23]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \text{..... (7)}$$

Where K_2 is the rate constant of pseudo-second order adsorption ($gmg^{-1}min^{-1}$).

Figure 7(d) shows pseudo-second order plots for the adsorption process at six different concentrations of the dye, K_2 and $q_e$values were determined from the intercepts and slopes of the linear plots respectively and are shown in Table 2. The correlation coefficient (R^2) value for the dye concentration range studied was unity indicating a perfect fit of the process to the second-order kinetic model and its applicability in explaining adsorption data.

Table 2: Pseudo second order Kinetic parameters for adsorption of indigo dye by coconut shell

CO NC. (mg/L)	$q_{e,exp}$ (mg/L)	$q_{e,exp}$ (mg/g)	K_2 $(g/mgmin)$	$q_{e,calc}$ (mg/L)	$q_{e,calc}$ (mg/g)	R^2
0.05	0.079	10.12	1.20	0.078	11.30	1.00
0.07	0.076	10.00	2.00	0.077	11.00	1.00
0.1	0.074	9.70	5.88	0.076	10.00	0.99
0.2	0.073	9.60	8.54	0.073	9.00	0.99
0.25	0.0695	8.00	20.00	0.070	9.20	0.99
0.30	0.0657	6.80	25.00	0.068	8.75	0.99

4. CONCLUSION

Results obtained from this work revealed that chemically modified coconut shell is an effective low cost adsorbent for the removal of indigo blue dye from aqueous solutions. Equilibrium parameters calculated from Langmuir, Freundlich and Temkin isotherms are useful for the explanation of the mechanisms of the adsorption process as indicated by the good linear correlation coefficient values. The adsorption process was concluded to be chemisorption with the adsorbent surface energetically homogenous. The adsorption kinetic data were best described by the pseudo-second order kinetic model.

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COMPETING INTERESTS

Authors declare that no competing interests exist.

Authors' Contributions

Olaniyi k. Yusuff designed the study, wrote the protocol, and corrected the final draft of the manuscript. Omowunmi D. Agboola managed the

analyses of the study and wrote the first draft of the manuscript. Modinah A.O. Abdul Raheem managed the literature searches and corrected the final draft of the manuscript. All authors read and approved the final manuscript**.**

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