Effect of Chemical Modifications on the Adsorptive Ability of Palm Kernel Fiber for Indigo Blue Dye

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Abstract
This research work investigated the potentials of unmodified Palm Kernel Fibers (UPKF) and its modified forms for the adsorption of Indigo blue dye from aqueous solutions using batch adsorption procedures. Characterization of the fibers was done with the scanning electron microscopy (SEM) and FTIR. Adsorption result showed that maximum uptake of 38.3, 31.0, 33.5 and 14.5 mg/g were respectively obtained for Bleached (BPKF), Acetylated (APKF), Mercerized (MPKF) and Unmodified Palm Kernel Fibers (UPKF) adsorbents at an optimum time of 3 h. The sorption kinetic obeyed pseudo second order with the bleached adsorbent (BPKF) having the best fit, and at a certain time limit; intra-particle diffusion controlled the process. Data collected from effect of initial concentration experiments were better fit to the Freundlich isotherm. The result from the thermodynamics of the process showed an endothermic process. Increasing adsorbent dosages led to corresponding increase in the quantity of the indigo dye adsorbed by the different adsorbents. This work revealed the potentials of modified palm kernel fibers over the unmodified fiber for effective removal of Indigo blue dye from wastewater.

Keywords: Adsorption, Indigo dye, kinetics, thermodynamics, modified adsorbents

Introduction
Dyes belong mainly to a class of organic compounds containing varying functional groups on complex aromatic rings. Their usage is widely found in food, plastic, cosmetics, leather and printing, pharmaceutical, paper and pulp industries [1]. Wastewater, with little or no treatment, from most of these industries are discharged directly into surface water bodies and thereby causing pollution, which result endangershman and aquatic life because dye degradation products are commonly carcinogenic, mutagenic, and allergenic [2]. It thus, becomes an issue of paramount importance to treat dye containing wastewater and effluents from industrial processes where dyes are used before they are discharged. Conventionally, treatments such as chemical precipitation, flocculation, electro-floatation, microbial biodegradation, ion-exchange, ozonation and membrane filtration, adsorption and advanced treatment techniques [3-4], have been used to treat and remove dyes from wastewaters but not without limitations or disadvantages in terms of energy requirement such as reagent needed and power supply; sludges that require further treatment before it is suitable for discharge [2, 5]. Adsorption, seems to be the most promising among these methods since its design is simple to adapt and modify, has been efficiently applied to many wastewaters systems without the generation of toxic sludge [6], there’s easy recovery of adsorbate, possibility of tuning adsorbent properties, high regeneration capacity and involves low cost in comparison with other used techniques [7]. Thus, the search for adsorbents that are relatively cheap, indigenous, efficient and largely available had been the concern of researchers and environmentalists. The use of agricultural waste as adsorbents satisfied some of the required features of materials to be considered for use as an adsorbent as these natural waste substances are embodiments of different active functional groups (hydroxyl, acetamido, amino, carbonyl) with binding sites unto which substrate ions could successfully be attached to during adsorption [8]. Different lignocellulosic materials which have shown varying degree of effectiveness towards dye adsorption from wastewater; are palm tree trunk [1], wood sawdust [9], empty palm fruit bunch [10] & sugarcane bagasse [11]. One of the advantages of adsorption over other methods is the possibility of adsorbent modification or tuning the adsorbent properties to improve their performance and adsorption capacity. It was reported that the modification of adsorbent with cationic surfactants resulted in increased adsorption capacity [12]. The palm fibers (date palm) grown for its sweet edible fruits belong to the flowering specie in Arecaaceae family [7]; two oils derived from this fruits are: oil palm and palm kernel oil. The palm kernel fiber used in this work is regarded as one of the agricultural wastes from palm kernel oil production.
This study aimed at examining the effects of different chemical modifications on the adsorption efficiency of palm kernel fiber for indigo blue dye removal from water. Herein, three modifications, acetylation, mercerization and bleaching, and the overall effects of these on the dye adsorption and removal were investigated.

### Materials and Methods

#### Materials

Palm kernel fiber (PKF) materials, used herein were collected from Ikota, a village near Akure, Ondo State Nigeria. Chemicals used were acetic anhydride (acidified), 96% ethanol, alkaline hydrogen peroxide, Sodium hydroxide, Indigo blue dye, Sodium dithionite, Na$_2$S$_2$O$_4$ and Sodium chloride. All the chemicals were sourced from Sigma-Aldrich and used without any treatment.

#### Methods

Palm kernel fibers were subjected to chemical modification with acidified acetic anhydride, sodium hydroxide and alkaline hydrogen peroxide as outlined by Afolabi et al. [10]. The surface structure and different functional groups on both the untreated fibers and treated fibers were subsequently examined with SEM and FTIR respectively and their abilities to adsorb Indigo dye from solution was investigated [13].

### Dissolution of Indigo dye

A stock solution (1000 ppm) of indigo dye was prepared by firstly, making a paste with 1000 mg of the dye in 20 ml 96% ethanol; the paste was made into a thin slurry by stirring and adding a solution containing 100 mg of Na$_2$S$_2$O$_4$, 10 mg NaCl, and 10 mg NaOH with temperature increased to somewhat between 50 and 60°C. After this step, the dye dissolution was transferred to 1000 mL volumetric flask and made to the mark with distilled water. Other desired concentrations were made by successive dilutions from the stock solution [14].

### Determination of maximum wavelength of adsorption of Indigo dye

Using Camspec UV-Visible spectrophotometer the adsorption spectrum of indigo dye from the prepared indigo dye solution was run to determine the maximum wavelength (410 nm) to be used for this work. The calibration curve was linear over tested concentration ranges and thus, the concentration of indigo blue dye in the supernatant solutions before and after the adsorption experiments were calculated.

### Adsorption experiments

Adsorption studies were performed by the batch process using series of designated 250 mL conical flasks, the flasks containing the dye liquorand the fiber (adsorbent) were shaken at 100 rpm rotation speed while the contact time, temperature, initial concentration of dye liquor and adsorbent dosage were varied depending on the experiments to be carried out. The experiments were done by adding a volume of 100 mL of 100 mg/L dye concentration to designated flasks containing 1.0 g of the adsorbents, the flasks were placed on Gallen Kamp orbital shaker and operated between 0.5 h to 4.0 h after which its content was filtered with Whatman filter paper No 42 and the concentration of the filtrate determined to estimate the quantity of dye unadsorbed by the adsorbent. From this value, quantification of dye removed can be calculated from Equation 1.

$$ Q_e = \frac{(C_o - C_e)V}{m} $$

C$_o$ and C$_e$ are the initial and final indigo dye concentration (mg/L); V is the volume of the adsorbate used (L) and m represent the mass of the adsorbent (g).

### Results and Discussion

#### Characterization of the adsorbents

**Scanning electron microscopy analysis**

The surface morphologies of both untreated and treated fibers, as analysed using Scanning Electron Microscope (SEM) in Fig. 1 revealed that the unmodified fibers have rough surfaces which were due to the presence of residual silica nodules, hemicellulose, lignin and other impurities, which was in line with the findings of Mwaikambo and Ansell [15]. This layer is either cleansed thoroughly or completely removed by the chemical treatment with acetic acid/acetic anhydride, alkaline hydrogen peroxide and sodium hydroxide. And thus, on removal of this outer layer, a smoother and more ordered structure is revealed as seen with the modified adsorbents.

![Figure 1: SEM Micrographs of unmodified and modified adsorbents](image-url)
Fourier transform infra-red spectroscopy analysis

The FTIR spectra of the unmodified and the modified palm kernel fibers in Fig. 2 were obtained with resolution range of 400 to 4000 cm\(^{-1}\). The strong OH stretching due to hydrogen bonding of alcohols and phenols in lignin, hemicellulose and cellulose which occurred at 3403 cm\(^{-1}\) in UPKF was shifted to 3407 cm\(^{-1}\) in APKF and MPKF and 3408 cm\(^{-1}\) in BPKF. Weak C-H stretch of methyl, methylene and methoxy groups was observed at 2900 cm\(^{-1}\) in UPKF and at 3000 cm\(^{-1}\) in all modified adsorbents. The band associated with strong CN stretch observed at 2400 cm\(^{-1}\) in UPKF was shifted to 2200 and 2450 cm\(^{-1}\) in APKF; 2300 and 2450 cm\(^{-1}\) in BPKF and 2100 and 2500 cm\(^{-1}\) in MPKF. The peaks at 1490 to 1500 in UPKF were attributed to C-C stretch in aromatics; these were shifted to 1496 cm\(^{-1}\) in APKF and 1550 cm\(^{-1}\) in BPKF and MPKF. The non-aromatic C-H bends were observed at 1100 to 1420 cm\(^{-1}\) in UPKF, 1365 to 1580 cm\(^{-1}\) in APKF; 1200 to 1500 cm\(^{-1}\) in BPKF and 1035 to 1450 cm\(^{-1}\) in MPKF while the C-H aromatic bends occurred at 750 cm\(^{-1}\) in UPKF and observed between 800 to 500 cm\(^{-1}\) in APKF; 920 to 550 cm\(^{-1}\) in BPKF and 900 to 500 cm\(^{-1}\) in MPKF. The FTIR spectra showed there were some changes in the functional groups of the modified adsorbent [13].

Effect of contact time and kinetic modelling

Contact time is an essential sorption parameter that gives useful information on the optimum adsorption time. A gradual increase in the quantity of indigo dye adsorbed (\(Q_e\)) by either UPKF, APKF, BPKF and MPKF was observed, it reached a plateau state at three hours and steadily decline afterwards; thus maximum quantity of dye removal at 3 hours for UPKF, APKF, BPKF and MPKF were 2.2, 4.1, 4.65, and 4.1 mg/g, respectively.

The result in Fig. 3 showed that the rate of removal was higher in the beginning due to the presence of larger adsorbent surface area which indicated that there were more numerous binding sites to which the indigo dye can be attached. Similar observation was reported in [16]. After maximum adsorption was reached, the rate of dye uptake was reduced; this showed that the potency of all these adsorbents reduced after the maximum contact time was reached. Thus, in all subsequent experiments, the contact time of 3 h (180 min) was used.
Adsorption kinetic modelling

Adsorption kinetics describe the rate of dye uptake on the different adsorbents and this rate in turn controls the equilibrium time. The kinetics of adsorbate/adsorbent system is necessary for choosing optimum operating conditions for a full scale batch process; it is essential to the treatment of the aqueous solution, as it offers indispensable information on the potential rate-controlling steps and mechanism of the sorption process [17].

To investigate the kinetics of adsorption of Indigo blue on the kernel fibers, the rate constants were determined in terms of the pseudo-first-order equation, pseudo-second-order equation and intra-particle diffusion equation.

The pseudo-first-order equation describes the kinetics of adsorption process as represented in Equation 2 [16].

$$\log (q_e,1 - q_t) = \log q_{e,1} - \frac{k_1}{2.303} t$$

Where $q_e$ and $q_t$ are the amount of dye adsorbed (mg/g) at equilibrium and at any time $t$ (min) respectively and $k_1$ is the rate constant ($\frac{1}{\text{min}}$). Values of $k_1$ were calculated from the plot of $\log (q_e - q_t)$ versus $t$ for the different adsorbents. The plot of $\log (q_e - q_t)$ versus $t$ (not presented) indicates that such first-order rate expression is not valid to the present systems as all its kinetic expressions, except for UPKF, has correlation coefficient lower than 0.55 [18]. The calculated $k_1$ and $q_{e,1}$ are represented in Table 1.

Table 1: Parameters from the kinetic models

<table>
<thead>
<tr>
<th>Adsorbents/Model Parameters</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ ($\frac{1}{\text{min}}$)</td>
<td>$q_{e,1}$ (mg/g$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>UPKF</td>
<td>0.2067</td>
<td>1.3867</td>
<td>0.6277</td>
</tr>
<tr>
<td>APKF</td>
<td>0.1225</td>
<td>1.086</td>
<td>0.2667</td>
</tr>
<tr>
<td>BPKF</td>
<td>0.2285</td>
<td>1.2752</td>
<td>0.5153</td>
</tr>
<tr>
<td>MPKF</td>
<td>0.1355</td>
<td>1.1392</td>
<td>0.4038</td>
</tr>
</tbody>
</table>

The data of solid-phase dye uptake against time at an initial dye concentration of 100 ppm were further processed for testing the role of diffusion (as the rate controlling step) in the adsorption process. Adsorption process includes the transport of adsorbate from bulk solution to the interior surface of the pores. The rate parameters for intra-particle diffusion ($k_p$) for different adsorbents/dye systems are determined using Equation 4.

$$q_t = k_p t^{1/2} + C$$

Where $k_p$ is a measure of diffusion coefficient (mg/min$^{0.5}$/g); $C$ is the intra-particle diffusion rate constant (mg/g)

Due to mass transfer effects, the shape of $q_t$ versus $t^{1/2}$ plot is curved at a small time limit. All the plots have the same general features, initial linear portion followed by a plateau and then a curve. The initial linear portion may be due to the intra-particle diffusion and the curved portion may be attributed to the bulk diffusion. This phenomenon has been reported for the adsorption of various dyes from aqueous solution using cellulose-based wastes [21]. The values of $k_p$ obtained from the slope of the straight lines are presented in Table 1.
The effect of adsorbent dosage

The effect of adsorbent dosage on the uptake of indigo dye by the kernel fibers was studied with five different adsorbent doses (0.5, 0.1, 1.5, 2.0 and 2.5 g) and the result revealed that the quantity of the indigo dye adsorbed increased with increase in adsorbent dosage.

A very high uptake (intense adsorption) with maximum uptake of 7.9, 8.0 and 9.1 mg/g was noticed with the acetylated, mercerized and bleached kernel fibers respectively while the unmodified kernel fibers have 1.9 mg/g maximum adsorption when 2.5 g of each adsorbent was used. The increase in adsorption with increase in the adsorbent dosage can be attributed to the greater surface area and thus availability of more adsorption sites. Similar results were respectively reported by [4, 21] for the biosorption of cationic dye in aqueous solution onto a lignocellulosic biomass, for the removal of Congo red using activated teak leaf powder.

Effect of initial concentration

This experiment was performed to establish the possible dependence of quantity adsorbed on initial dye concentration (10 – 1000 ppm). The quantity of dye adsorbed (mg/g) increased with increasing initial dye concentration for each of the adsorption systems. This indicated an exponential distribution without a tendency to saturation of the surface. According to the Giles classification, this isotherm is of type \( H_2 \), which implies large slope at low concentrations indicating strong preferential sorption of the solutes [22]. Comparing the modified adsorbents, BPKF has the highest adsorbed amount of dye i.e. quantity adsorbed of 38.3 mg/g, followed by the MPKF with 33.5 mg/g while APKF have 31 mg/g of indigo dye adsorbed with the maximum removal observed at 1000 ppm. The initial dye concentration provided the necessary driving force to overcome the resistances to the mass transfer of Indigo dye between the aqueous phase and the solid phase. The increase in initial dye concentration also enhanced the interaction between the Indigo dye molecules and the adsorbents used.

Adsorption isotherm modelling

The Langmuir and Freundlich Isotherms were used to model the data obtained from the concentration study and from the result, the data fitted to the Freundlich isotherm. The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface containing sites with equal energy and that are equally available for adsorption [23]. However, the Langmuir isotherm was not reported in this work since the experimental data did not fit into the model.

The Freundlich isotherm represented in its linear form in Equation 5 is used to describe sorption onto heterogeneous surface and its constants; adsorption capacity of the adsorbent \( k_f (mg/g(L/mg)) \) and the constant related to the efficiency of the adsorption \((1/n)\) are obtained from the plots of \( log Q_e \) and \( log C_e \).

\[
log Q_e = log k_f + \frac{1}{n} log C_e \quad \text{(Linear form)} \quad 5
\]

\( Q_e \) and \( C_e \) represent the quantity of adsorbate (Indigo blue dye) adsorbed per unit gram of the adsorbent at equilibrium and the final concentration of the adsorbate in the solution at the end of the adsorption experiment, respectively. \( n \) is a constant related to the efficiency of the adsorption process and the favourability of the process is depicted by values of \( 0 < \frac{1}{n} < 1 \) [19].

Values for parameters obtained for the Freundlich isotherm (plot in Fig. 4) presented in Table 2 showed that the Freundlich isotherm fitted well for describing the experimental data for all the systems and from the correlation co-efficient \( (R^2) \), it is apparent that the modified forms of the adsorbent have better correlation than the unmodified fiber.

**Effect of temperature**

Temperature is well known to play an important role in adsorption processes [21]. The sorption of Indigo dye onto unmodified and modified kernel fibers were investigated over temperature range between 30 – 70\(^\circ\)C and it was discovered that an increase in temperature led to a subsequent increase in the quantity of Indigo dye adsorbed onto the kernel fibers. The result showed that as temperature was increased from 30 to 70\(^\circ\)C, the uptake of Indigo dye increased, it was seen that the modified forms of the adsorbents gave higher, \( q_e \), with the bleached fiber taking the first place, followed by the acetylated fiber while the mercerized fiber had the least uptake value. A slight increase in the uptake, \( q_e \), was observed with increasing temperature suggesting an endothermic process. It may be due to the increase in surface activity as temperature increases and because at elevated temperature, the mobility of the Indigo dye increases.

![Figure 4: Freundlich isotherm](image)

**Table 2: Freundlich adsorption isotherm parameter**

<table>
<thead>
<tr>
<th>Adsorbents/Parameters</th>
<th>( k_f )</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPKF</td>
<td>0.024</td>
<td>0.9434</td>
<td>0.9926</td>
</tr>
<tr>
<td>APKF</td>
<td>0.06</td>
<td>0.9568</td>
<td>0.9994</td>
</tr>
<tr>
<td>BPKF</td>
<td>0.07</td>
<td>0.9712</td>
<td>0.9962</td>
</tr>
<tr>
<td>MPKF</td>
<td>0.057</td>
<td>0.9724</td>
<td>0.9972</td>
</tr>
</tbody>
</table>

Subsequently, the constant \( k_f \) related to adsorption capacity, represents the quantity of dye adsorbed by the adsorbent for each equilibrium concentration [23]. From Table 2, the magnitude of \( k_f \) showed that the adsorptive capacity of all the adsorbents were close expect for the unmodified fiber and followed the order of BPKF>APKF>MPKF>UPKF.
Similar result was also recorded when teak leaf powder and different agricultural adsorbents were used for the removal of cationic and anionic dyes [24-25]. By applying the Van’t Hoff equation (Equation 6) the change in enthalpy (ΔH°) for all adsorbents was positive, with BPKF having the lowest. The change in entropy (ΔS°) was found to be 86.75, 5.54, 8.62 and 4.70 J/K/mol for UPKF, APKF, BPKF and MPKF, respectively.

\[ \ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad 6 \]

Where \( K_b \) is the distribution co-efficient of the absorbate (Lg/mol), which represents the ratio between \( C_{eq} \) and \( Q_e \). \( \Delta H^o \) is the enthalpy change of the reaction (kJ/mol), \( \Delta S^o \) is the entropy of the system (J/mol), \( R \) is the Molargas constant (8.313 J/K/mol), and \( T \) is the temperature in Kelvin.

The \( \Delta H^o \) and \( \Delta S^o \) of the adsorption systems were obtained from the slope and intercept of the plot of \( ln K_b \) against \( \frac{1}{T} \). The positive enthalpy (\( \Delta H^o \)) of all the adsorbents further confirmed that the adsorption is an endothermic process [26]. The positive values of entropy (\( \Delta S^o \)) of all the adsorbents showed increased randomness at the solid-solution interface during the adsorption [27] and also signify an increase in the degree of freedom of the adsorbed species, thus favouring adsorption of Indigo dye. The thermodynamic parameters showed that the highest enthalpy (\( \Delta H^o \)) was observed with the UPKF, while the (\( \Delta H^o \)) for the modified adsorbents was highest in the acetylated palm kernel fiber (APKF), whereas, the bleached palm kernel fiber (BPKF) had the least value. The entropy change of the systems showed that UPKF had the highest value, followed by BPKF while APKF and MPKF came third and fourth places respectively. It is also possible to calculate the Gibb’s free energy (\( \Delta G \)) of the system (Equation 7) at various temperature since the value of \( \Delta H \) and \( \Delta S \) have been determined.

\[ \Delta G = \Delta H - T \Delta S \quad 7 \]

The numerical value of \( \Delta G \) decrease slightly with increase in temperature, implying that the reaction may be slightly spontaneous and favourable at higher temperature. It also showed an increasing tendency in the feasibility and spontaneity of Indigo dye adsorption [26].

**Conclusion**

This work revealed the effectiveness of unmodified Palm Kernel Fibers and its modified forms for the removal of Indigo blue dye from aqueous solution. Characterization of the adsorbents by FTIR showed there are active functional groups which could be responsible for binding on the adsorbents and that there were changes or shifts in some chemical functional groups of the modified palm kernel fibers. The various modifications carried out on the Palm Kernel Fibers were Acetylation, Bleaching and Mercerization. A maximum uptake of 4.65, 4.2, 4.1 and 2.2 mg/g were respectively obtained for Bleached (BPKF), Acetylated (APKF), Mercerized (MPKF) and Unmodified Palm Kernel Fibers (UPKF) adsorbents at an optimum time of 3 hours though the quantity of dye uptake differed. It was observed that the sorption kinetic did not follow the pseudo first order but obeyed pseudo second order with the bleached adsorbent (BPKF) having the best fit while acetylated and mercerized fibers possessing same correlation were next and the unmodified showed the least. Intra-particle diffusion controlled the adsorption process at a certain time limit. Increase in initial dye concentration resulted in varying degree of increased dye uptake by all adsorbents and the Freundlich isotherm model provided a good fit for the experimental data. The thermodynamics of the process showed that the adsorption of indigo dye unto all the adsorbents is an endothermic process with positive change in enthalpy (\( \Delta H^o \)). It was discovered that the modified palm kernel fibers had higher adsorption capacity than the unmodified with the bleached fiber having the highest uptake for indigo blue dye.

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