Study the Performance of Low Cost Material (Peanut Hulls) for Dye Adsorption Using Inverse Fluidized Bed

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Abstract
The present study dealt with the removal of methylene blue from wastewater by using peanut hulls (PNH) as adsorbent. Two modes of operation were used in the present work, batch mode and inverse fluidized bed mode. In batch experiment, the effect of peanut hulls doses 2, 4, 8, 12 and 16 g, with constant initial pH =5.6, concentration 20 mg/L and particle size 2-3.35 mm were studied. The results showed that the percent removal of methylene blue increased with the increase of peanut hulls dose. Batch kinetics experiments showed that equilibrium time was about 3 hours, isotherm models (Langmuir and Freundlich) were used to correlate these results. The results showed that the (Freundlich) model gave the best fitting for adsorption capacity. Different size ranges of peanut hulls (PNH) were fluidized by a downward flow of an methylene blue dye dissolved in water in an inverse fluidization mode. In the inverse fluidized bed experiments, the hydrodynamics characteristics, the effect of initial methylene blue concentration Co 5, 10 and 20 mg/L, particle size 1.18-2, 2-3.35 and 3.35-4 mm, mass of adsorbent 25, 60 and 80 g, superficial fluid velocity 0.016, 0.019 and 0.027 m/s and effect of chemical modification were studied. The optimum conditions of adsorption in inverse fluidized bed were initial concentration was 5 mg/L, particle size was 1.18-2 mm size, mass of PNH is 80 g and superficial fluid velocity was 0.019 m/s. Also the adsorption capacity of PNH increased after modification by Nitric acid. UV-Spectrophotometer was used to determine the methylene blue concentration.

Keywords: Wastewater treatment, Adsorption, Peanut hulls, dyes removal, inverse fluidized bed.

Introduction
One of the major environmental pollution is wastewater. Wastewater comes from homes, commercial establishments, industries and public institutions which use water for various purposes. This polluted water comes from the domestic and also from the industries because of the increase of population and industrial expansion especially in the developed countries. Contaminants such as heavy metal, cyanide, toxic organics, nitrogen, phosphorous, phenols, suspended solids, color and turbidity from the industries and untreated sewage sludge from the domestics became a great concern to the environment and public health. Wastewater from food coloring, cosmetics, paper and textile industries is polluted by dyes. When those
colored effluents enter rivers or any other surface water systems, they upset biological activities [1]. Ground-water systems are also affected by these pollutants because of leaching from the soil. Dyes can cause allergic dermatitis, skin irritation, cancer and mutation [2].

Adsorption has been found to be a successful technique for controlling the extent of water pollution due to dyes, metallic species, surfactants and other organic pollutants ([3], [4] and [5]). As a technique in water pollution control, adsorption requires less investment. The design of the necessary equipment is simple and such equipment can be operated easily. In these respects, adsorption is more efficient and convenient than other conventional treatment techniques. Activated carbons are conventionally used for the removal of contaminants from liquids and gases because of their structural, textural and sorption peculiarities ([6]; [7] and [8]). However because of their high cost, activated carbons are now being replaced by other low-cost materials. In addition, activated carbons suffer losses of approximately 15 – 20 % during the regeneration process. Various other non-conventional adsorbents like Fuller's earth and fired clay, silica [9], biogas residual slurry [10], Fe3+/Cr3+ hydroxide sludge [11], China clay [12], peat moss and rice hulls [13], coconut husk [14] and fly ash [15] have been reported as efficient adsorbents in removing color.

Many researches are directed to find low cost adsorbents for clarifying colored effluents. Agricultural residues were found to be effective adsorbents, which can be used once as such and then re-used as a fuel by combustion [16]. The ability of using peanut hulls as dyes adsorbent was investigated in this study using batch mode and inversed fluidized bed mode. Inversed fluidized bed is a pilot plant used in case of the particle density is less than the fluid density [17], and the hydrodynamics characteristics with some variables such as concentration change, mass of PNH, flow rate and chemical modification were studied. In Batch experiments, equilibrium modeling was carried out by Langmuir and Freundlich models and a correlation between the two isotherms and experimental data was investigated.

**Experimental Work Materials**

**Adsorbent**

Peanut hulls were collected from the local market. The collected biomaterial was extensively washed with tap water to remove soil and dust, sprayed with distilled water and then dried in an oven at 80 °C to a constant weight. Dry biomass was crushed and sieved to different particle sizes; some of this biomaterial were modified by steeped in dilute nitric acid solution (1% v/v) overnight before being washed several times with distilled water and dried at 80 °C and then preserved in the desiccators for further uses. Characteristics of Peanut hulls are shown in Table 1.

**Table 1: Physical Characteristics of Peanut hulls**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Light to dark brown</td>
</tr>
<tr>
<td>Oder</td>
<td>Essentially none</td>
</tr>
<tr>
<td>Moisture</td>
<td>6.5%</td>
</tr>
<tr>
<td>Bulk density</td>
<td>68 lb/ft³</td>
</tr>
<tr>
<td>Carrying capacity for Water</td>
<td>51%-52%</td>
</tr>
<tr>
<td>Absorption of water</td>
<td>168%-169%</td>
</tr>
</tbody>
</table>

**Adsorbate**

Methylene blue (CI 52015) was used as adsorbate, which is a heterocyclic aromatic chemical compound with the
molecular formula $C_{16}H_{18}N_{3}SCl$, and wavelength 664 nm.

**Experimental Modes**
Two types of experiments were carried out:
1- Batch experiment
2- Inverse fluidized bed experiments

**1) Batch Experiments**
Batch experiments were used to obtain the equilibrium isotherm curves and then the equilibrium data. All experiments were carried out at 25 °C, rpm =150 and pH =5.6. Five 1 liter flasks were used; each flask contained 600 ml solution with an initial MB concentration of 20 mg/l (which was prepared by dissolving 0.02 gram in 1 liter of water). Peanut hull doses that were 2, 4, 8, 12 and 16 g, respectively were used in the five flasks. Samples were collected from the flasks and tested using UV- Spectrophotometer (Shimadiza – 160) and wavelength 664 nm.

**2) Inverse Fluidized Bed Experiments**
Column experiments were carried out for measuring hydrodynamic characteristics and for measuring the breakthrough curves for the systems. Experiments were carried out at various initial MB concentrations ($C_0$) 5, 10, 20 ppm, flow rate (u) 0.016, 0.019, 0.022 m/s, particle size 1.18-2, 2-3.35, 3.35-4 mm and mass of peanut hulls 25, 40, 60, 80 g. Also a set of experiments were carried out to study the effect of chemical modification on the capacity of adsorption at conditions. The schematic representation of experimental equipment is shown in Figure 1.

![Fig. 1: the experimental unit of inverse fluidized bed](image)

**Results and Discussion**

**A. Batch Experiments**
Adsorption isotherm studies were performed to obtain equilibrium isotherm curves and data required for the design and operation of inverse fluidized bed. The adsorption isotherm curves were obtained by plotting the weight of the solute adsorbed per unit weight of the adsorbent ($q_e$) against the equilibrium of MB on PNH at 25 °C. The obtained data was correlated with linear form of Langmuir and Freundlich models. These models can be described in Eq. 1 and Eq. 2, respectively. [18]:

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

Where:
- $C_e$ is the equilibrium concentration of adsorbate (mg/ L)
- $q_e$ is the amount adsorbed at equilibrium per gram adsorbent (mg/ g)
- $q_{max}$ is the maximum adsorption (mg/g) and b (L/mg) is the Langmuir constant related to the adsorption capacity and energy of adsorption, respectively [19].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \ldots(2)$$
Where:
- \( q_e \) is the amount of adsorbate adsorbed per unit weight (mg/g of adsorbent)
- \( C_e \) is the equilibrium concentration of the adsorbate (mg/L)
- \( K_f \) and \( n \) are the Freundlich constants; \( n \) gives an indication of how favorable the adsorption process is.

The parameters for each model were obtained from linear form of the equation to the experimental data, which can be represented in Figures 2 and 3, respectively. All the parameters with their correlation coefficients are summarized in Table 2.

It was found that the correlation coefficient value was higher for Freundlich than Langmuir. This indicates that the Freundlich isotherm is clearly the best fitting isotherm to the experimental data.

### Table 2: Isotherm parameters for MB Adsorption onto PNH with the correlation Coefficient

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_{\text{max}} )</td>
<td>61.7</td>
</tr>
<tr>
<td></td>
<td>( B )</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient ( (R^2) )</td>
<td>0.969</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( k_f )</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>( 1/n )</td>
<td>0.608</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.644</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient ( (R^2) )</td>
<td>0.988</td>
</tr>
</tbody>
</table>

#### B. Inverse Fluidized Bed Experiments

### 1- Hydrodynamic Characteristics of Inverse Fluidized Bed

Pressure drop, minimum fluidized velocity and bed expansion are the most important hydrodynamic characteristics of inverse fluidized bed. The determination of pressure drop in fluidized bed is a very important parameter for the efficient and economical operation of the column, since it facilitates determining friction factor; i.e. energy loss and conditions of stable flow regimes of inverse fluidized bed for the given operation.

The hydrodynamic characteristics of inverse fluidized beds of adsorbent particles are represented by the fluidized bed pressure drop that can be measured either experimentally by U-tube monometer connected to the QVF or by equating the pressure drop across the bed to the buoyancy force of displaced fluid, allowing for the weight of the bed [20]. We get the following equation:

\[
\Delta P = (\rho - \rho_p) (1-\varepsilon) (L_b) g 
\]  \( \ldots (3) \)

Where:
- \( \varepsilon \) = void fraction of the bed, given by:

\[
\varepsilon = 1 - \left[ \left( m_p / \rho_p \right) / \left( \pi D^2 L_b \right) \right] 
\]  \( \ldots (4) \)

Where:
- \( m_p \) = mass of adsorbent
- \( D \) = inside diameter of column

![Fig. 2: Langmuir isotherm for the adsorption of MB using PNH](image1)

![Fig. 3: Freundlich isotherm for the adsorption of MB using PNH](image2)
2- The Density and the External Porosity of the PNH Particles
The value of the granule density can be calculated from the experimental data by using a force balance. The forces acting on the fluidized granules are the buoyancy force ($F_B$), the gravity force ($F_g$) and the drag force ($F_D$). The buoyancy and gravity forces are:

$$F_B = \rho_p V_p g$$ and $$F_g = \rho V_p g$$ \hspace{1cm} (5)

Where $V_p$ is the total volume of particles fluidized in the column. The drag force applied on the particles during fluidization (assuming negligible wall effects) is given by the experimental pressure drop ($\Delta P_{exp}$) multiplied by the cross sectional area of the fluidization column ($A$)

$$F_D = \Delta P_{exp} A$$ \hspace{1cm} (6)

A force balance on the particle gives:

$$F_B = F_g + F_D = \rho_p V_p g + \Delta P_{exp} A = \rho V_p g$$ \hspace{1cm} (7)

Since $m_p = \rho_p V_p$, Eq. 7 can be written as:

$$V_p = (\Delta P_{exp} A + m_p g)/\rho g$$ \hspace{1cm} (8)

And the granule density of the particles is given by $\rho_p = m_p/V_p$

With $V_p$ obtained from Eq. 8. The void volume can be found by subtracting the volume of the particles ($V_p$) from the total volume of the fluidized bed ($V_b$). Hence, the void fraction of the fluidized bed is:

$$\varepsilon = V_b/V_p$$ \hspace{1cm} (9)

Since $V_b = (V_b - V_p)$, then Eq. 9 can be written as:

$$\varepsilon = 1 - (V_p/V_b)$$ \hspace{1cm} (10)

Eq. 8 is of the particular significance since it can be used to calculate the particle density if the pressures drop measurement is reliable. It can also be used to predict the pressure drop across the fluidized bed if the particles density is known [21].

3- Mathematical Models of Bed Expansion
The Richardson–Zaki (R–Z) correlation [22] is among the most useful methods to describe the relationship between the void fraction and superficial velocity in a conventional liquid fluidized bed. The R–Z equation is:

$$\varepsilon = U/U_i$$ \hspace{1cm} (11)

Where $U$ is the superficial velocity and $U_i$ is the settling velocity of a particle at infinite dilution. The R–Z exponent or index ($z$) is a function of the particle terminal Reynolds number ($Re_t$).

$$z = 4.45 Re_t^{-0.1} \text{ for } 200 < Re_t < 500$$ \hspace{1cm} (12)

Where:

$$Re_t = U_d d_p / \mu$$ \hspace{1cm} (13)

Where: $\rho$ is the density of the fluid, $d_p$ is the diameter of solid particles, $\mu$ is the viscosity of the fluid. The settling velocity at infinite dilution ($U_i$) and the terminal velocity ($U_t$) are related by:

$$\log(U_i) = \log(U_t) - d_p/D$$ \hspace{1cm} (14)

The R–Z exponent ($z$) can also be obtained from the experimental data by plotting the logarithm of the superficial velocity against the logarithm of the void fraction

$$\ln U = z \ln(\varepsilon) + \ln U_i$$ \hspace{1cm} (15)

There are very few correlations for an inverse fluidized bed, though several
models are available for correlating bed expansion with fluid superficial velocity in a conventional liquid–solid fluidized bed (such as the R–Z model above). Fan et al. [23] proposed a model based on a drag force function \( f \) which can be used to describe the bed expansion in an inverse fluidized bed. This correlation is expressed in terms of the void fraction of the inverse fluidized bed \( (\varepsilon) \).

Archimedes number \( \text{Ar} = \frac{d^3}{4} \left( \rho - \rho_p \right) \rho g / \mu^2 \) \( \ldots (16) \)

Reynolds number \( \text{Re}_p = \frac{U \rho d_p}{\mu} \) \( \ldots (17) \)

And the ratio of the particle size to the bed diameter is:

\[ f = 3.21 \varepsilon^{-0.05} \text{Ar}^{-0.07} \exp(3.5d_p/D) \ldots (18) \]

In this model, a drag force function "\( f \)" defined as the ratio of the drag force of fluid on particles in a multiparticle system to that in a single particle system is a function of the Archimedes number and the Reynolds number. This drag force function for the inverse fluidization system taken from Fan et al. [23] is:

\[ f = \frac{\text{Ar}}{13.9 \text{Re}^{1.4}} \text{ for } 2 < \text{Re} < 500 \ldots (19) \]

\[ f = 3 \text{Ar} / \text{Re}^2 \text{ for } \text{Re} > 500 \ldots (20) \]

Where the Archimedes number and the Reynolds number at different flow superficial velocities can be calculated from the experimental data. The void fraction of the inverse fluidized bed \( (\varepsilon) \) at different flow superficial velocities can be calculated from Eq. 15. With simplification of the equation suggested by Wen and Ya [24], a more generalized form can be found to find the minimum fluidized bed:

\[ \text{Re}_{mf} = \sqrt{33.7^2 + 0.04084 \text{Ar} - 33.7} \text{ for } 0.4 < \text{Re} < 500 \ldots (21) \]

Where:

\[ \text{Re}_{mf} = \frac{U_{mf} \rho d_p}{\mu} \ldots (22) \]

Where \( \text{Re}_{mf} \) is Reynolds No. at \( U = U_{mf} \)

Where \( U_{mf} \) is the minimum fluidized bed

Eq. 21 should be applicable to inverse fluidization as well assuming that the drag force of the fluid moving with superficial velocity \( (U_{mf}) \) is equal to the buoyancy force which is less than the weight of the particles as described by Karamanev et al., [25].

The experimental data for hydrodynamics studied can be shown in Figures 4, 5 and 6.

![Fig. 4: Inverse Fluidized Bed Pressure Drop vs. Superficial Fluid Velocity of Small PNH Particles size = 1.18-2 mm, mass = 0.06 kg](image)

![Fig. 5: Inverse Fluidized Bed Pressure Drop vs. Superficial Fluid Velocity of Intermediate PNH Particles size =2-3.35 mm, masses =0.025 and 0.06 kg](image)
The experimental results were used to find the percentage error of minimum fluidized bed, the particles density and the initial void fraction (porosity) of the fluidized bed, (all the results are represented in Table 3 and Table 4).

The results show that the minimum fluidized velocity increased with increasing the particles size; the porosity increased with decreasing the particles size.

Table 3: Comparison of the experimental and theoretical minimum fluidization velocities

<table>
<thead>
<tr>
<th>Particles size (mm)</th>
<th>$U_{mf}$ (Exp.; m/s)</th>
<th>$d_p$(mm)</th>
<th>Ar</th>
<th>Re_{mf}</th>
<th>$U_{mf}$ (eq. 22; m/s)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18 – 2</td>
<td>0.009</td>
<td>1.59</td>
<td></td>
<td>22450.5</td>
<td>11.59</td>
<td>0.007</td>
</tr>
<tr>
<td>2 - 3.35</td>
<td>0.016</td>
<td>2.65</td>
<td></td>
<td>119291</td>
<td>43.7</td>
<td>0.0163</td>
</tr>
<tr>
<td>3.35 – 4</td>
<td>0.024</td>
<td>3.67</td>
<td></td>
<td>334774.9</td>
<td>87.9</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Table 4: Calculation of the particles density and the initial void fraction from experimental data

<table>
<thead>
<tr>
<th>Particles size (mm)</th>
<th>Mass (kg)</th>
<th>Δp (pa)</th>
<th>Particles volume (m$^3$)</th>
<th>$\rho_p$ (estim.; kg/m$^3$)</th>
<th>Initial bed height (m)</th>
<th>Bulk density (kg/m$^3$)</th>
<th>Void fraction ($\varepsilon_o$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18-2</td>
<td>0.06</td>
<td>392.4</td>
<td>1.40E-04</td>
<td>428.5</td>
<td>0.145</td>
<td>214.2</td>
<td>0.52</td>
</tr>
<tr>
<td>2-3.35</td>
<td>0.025</td>
<td>215.18</td>
<td>0.69E-04</td>
<td>362.3</td>
<td>0.07</td>
<td>178.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>318.8</td>
<td>1.05E-04</td>
<td>380.9</td>
<td>0.11</td>
<td>200</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>416.9</td>
<td>1.55E-04</td>
<td>387</td>
<td>0.16</td>
<td>200</td>
<td>0.51</td>
</tr>
<tr>
<td>3.35-4</td>
<td>0.04</td>
<td>441.6</td>
<td>1.31E-04</td>
<td>307</td>
<td>0.135</td>
<td>160</td>
<td>0.48</td>
</tr>
</tbody>
</table>

4- Factors Effect on MB Removal
1. Effect of Initial Concentration
The effect of varying MB initial concentration was investigated; it is clear from the breakthrough curves presented in Figure 7. An increase in the initial concentration made the breakthrough curves much steeple, which would be anticipated with the basis of the increase in driving force for mass transfer with an increase in the concentration of solute in solution. The breakpoint was inversely related to the initial concentration; i.e. the time required to reach saturation decreased with increasing the inlet solute concentration. Also this might be explained by the fact that since the rate of diffusion was controlled by the concentration gradient, it took a longer contact time to reach saturation for the case of low value of initial solute concentration. The same conclusion was obtained by Quek and Al-Duri [26].
2. Effect of Particle Size

The effect of changing particle size was also examined. The experimental results showed that fine particle sizes gave a higher MB removal than coarse particle sizes as illustrated in Figure 8. This was due to larger surface area available for fine particles allowing more dye molecules to be bound per gram of fine particles; similar results of particle size effect were reported by Erdem et al. [27].

![Fig. 8: Experimental breakthrough curves for adsorption of MB onto PNH at different particle size (1.18-2 and 3.35-4) mm, Concentration =10 mg/L, mass of PNH =0.04 kg, velocity =0.016 m/s](image)

3. Effect of Flow Rate

In the design of inverse fluidized bed column, the porosity of the bed is the most significant variable and therefore, the bed depth and the flow rate are the major design parameter [17].

The effect of varying the volumetric flow rate was investigated. The experimental results in Figure 9 show that with increasing the velocity from 0.016 to 0.019 m/s, the percentage dye removal will increase from 0.49 to 0.6% respectively at time (600 s), while increasing the flow rate to 0.027, the percentage dye removal will decrease to 0.35% at time (600 s) also. These results can be expressed as at the $U_m$, the porosity is not high, but with increasing the flow, the porosity will increase and then the surface area will increase also. But for higher flow rate, the residence time will be more effective than the porosity; thus the dye removal will decrease. Similar result was found by Bendict et al. [21].

![Fig. 9: Experimental breakthrough curves for adsorption of MB onto PNH at different superficial fluid velocity](image)

4. Effect of Mass of Adsorbent

The effect of adsorbent quantity on dye removal at constant flow rate, MB concentration and the same size of PNH particles is investigated and illustrated in Fig. 10. The breakthrough curves shows that increasing the mass of PNH will increase the breakthrough time and the residence time. Similar results have been reported for the adsorption of MB on Indian rosewood sawdust [28].

![Fig. 10: Experimental breakthrough curves for adsorption of MB onto PNH at different weights (0.025, 0.06, 0.08) kg, concentration =10 mg/L, velocity=0.016 m/s, size = 2-3.35mm](image)
5. Effect of Chemical Modification on PNH Adsorption

Three experiments were repeated to study the effect of chemical modification on the adsorption capacity of PNH; the results were illustrated in Figures 11 and 12. These two figures show that the chemical modification of PNH increases the adsorption capacity of the particles. That was done by two mechanisms: first by increasing the acidity of adsorption sites (hydroxyl group) and second by increasing the surface area due to erosion by nitric acid. The same conclusion was obtained by Thomas et al. [29].

Conclusions

- The percentage of dye removed increased from (70.5%) to (99.7%) with increasing adsorbent dosage from (2 g) to (16 g) and increased with increasing contact time.
- The results showed that the (Freundlich) model gave the best fitting for adsorption capacity; i.e. higher value of $R^2$ (0.988).
- Inverse fluidized bed set of experiments were studied to find the optimum conditions of adsorption and found that the optimum concentration was (5 mg/L), the optimum particle size was 1.18-2 mm size, the optimum mass of PNH was (0.08 kg) and the optimum superficial fluid velocity was (0.019 m/s).

Fig. 11: Comparison between modified and unmodified PNH particles for MB adsorption, concentration = 10 mg/L, mass of PNH = 0.04 kg, velocity = 0.016 m/s, size = 2-3.35 mm

Fig. 12: Comparison between modified and unmodified PNH particles for MB adsorption, concentration = 10 mg/L, mass of PNH = 0.04 kg, velocity = 0.016 m/s, size = 1.18-2 mm

Nomenclatures

- MB methylene blue
- PNH peanut hulls

References

Study the Performance of Low Cost Material (Peanut Hulls) for Dye Adsorption Using Inverse Fluidized Bed

Precursor Composition”, Carbon, Vol. 20, 95.


