Batch and Fixed Bed Comparative Study on the Dye Bio-
Sorption Properties of *Cedrus Libani* (Elizabeth Leaf) on
Methylene Blue, Bismarck Brown Y and Indigo Dye

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**Abstract:**
The adsorption properties of *Cedrus libani* (Elizabeth leaf) on methylene blue dye, Bismarck brown Y dye and indigo dye was studied using both the batch process and fixed bed methods. This was done in order to compare the effectiveness of each of the methods over each other in the adsorption process. The biomass was characterized using the scanning electron microscope (SEM) as well as the Fourier Transform Infrared Spectroscope (FTIR) before and after adsorption in order to determine the functional groups responsible for the adsorption. The amount of dye adsorbed per unit mass of the biomass ($q_e$) was calculated and found to be dependent on contact time, pH, biomass dose, biomass particle size, dye concentration, dissolved sodium and calcium salts and temperature. Optimal pH of 2 was determined for the adsorption of Bismarck brown Y dye and indigo dye while pH of 4 was determined for methylene blue dye. The $q_e$ value for the fixed bed adsorption was determined to be 12.98mg/g compared to the 11.28mg/g for the batch process using methylene blue dye. This indicates a better adsorption in the fixed bed technique over the batch process. However, the $q_e$ values fluctuated using the Bismarck brown Y and indigo dyes. Generally, the results show a better adsorption in the fixed bed technique over the batch process. Indigo dye was found to be the least adsorbed, while methylene blue dye was the most adsorbed. The adsorption pattern was fitted for Langmuir adsorption isotherm model.

**Keywords:** Bio-sorption, *Cedrus libani*, adsorbent, batch process, fixed bed technique

1. **Introduction**
In recent times, the use of bio-sorption techniques for the removal of dye contaminants from solutions has been found to be superior to other techniques based on simplicity of design and operation (Tong et al., 2010). Activated charcoal is widely employed as an adsorbent, nevertheless, the use of activated charcoal could be regenerated after use, though the regeneration process is very expensive and may lead to a loss of carbon. The regenerated product may have a slightly lower adsorption capacity in comparison with the virgin activated carbon. This has resulted in the attempts by various workers to prepare low cost alternative adsorbents which may replace activated carbon in pollution control through adsorption and to overcome their economic disadvantages (Gupta et al., 2003).

Adsorption, such as of dye molecules (adsorbate) on biomass as adsorbent material, is a mass transfer process which involves the accumulation of adsorbate at the interface of two phases such as liquid-solid interface. Fixed bed adsorption process is ubiquitous throughout the chemical process and other industries (Vannapusa et al., 2005). The cyclic batch operating mode using fixed bed is widely used which is virtually in all practical cases an unsteady state rate-controlled process. This means that conditions at any particular point within the fixed bed vary with time. Adsorption only occurs in a particular region of the bed known as the mass transfer zone (MTZ) which moves the bed.

2. **Experimentals**

2.1. **Material Preparation**
The methylene blue dye, Bismarck brown Y dye, indigo dye used in these investigations were obtained from qualikem laboratory, Owerri, Nigeria. Other materials obtained from here include analytical grade sodium hydroxide pellets, concentrated hydrochloric acid, sodium chloride, calcium chloride, distilled water etc. The *Cedrus libani* (Elizabeth leaf) used was obtained from Ikorodu, Lagos, Nigeria and identified at the department of crop science, Federal university.
of technology, Owerri, Nigeria. The biomass was washed severally with distilled water to remove any dirt form it. The washed biomass was air dried for ten days until constant weight was obtained. The biomass was grinded with a new sonic blender to avoid any form of contamination. It was screened using 600-850-micron size sieves and were stored in an air tight containers ready for adsorption measurement.

2.2 Characterization of the Bio-Sorbent

The surface structure and morphology of the Cedrus libani (Elizabeth leaf) was characterized at 1000X magnification, 500X magnification and 250X magnification respectively for their surface morphologies using a scanning electron microscope (SEM) (FEI-Inspect) (Oxford instruments-x-max) which was equipped with an energy dispersive x-ray (EDAX) spectrophotometer employed for the elemental analysis. The biomass was further characterized for their fundamental functional groups before and after adsorption experiments using a Fourier Transform Infrared (FTIR) spectrophotometer (Perkin Elmer, England) in the wavelength range of 350-400nm using KBr powder and fluka library for data interpretation.

2.3 Effect of Contact Time on Adsorption (Batch Process)

Experiments were carried out by mixing 40mg of the biomass in a dye solution of 90mg/L of methylene blue dye, Bismarck brown Y dye and indigo dye. Agitations were made at the range of 30-180 minutes in a shaker at 250rpm. After each time, the sample was taken out and centrifuged, the left out supernatant solution was analyzed for dye absorbance at 600nm for methylene blue, 320nm for Bismarck brown Y and 360 nm for indigo dye in a U.V spectrophotometer. These tests were carried out in triplicates and the mean values reported.

2.3.1 Effect of Biomass Dose on Adsorption (Batch Process)

Experiments were carried out by mixing biomass of different doses (10-100mg) with different dye solutions of concentration90mg/L, agitations were made for three hours in a shaker at 250rpm. The left outs supernatant solution was analyzed for dye absorbance in a U.V spectrophotometer at different wavelengths for methylene blue dye, Bismarck brown Y dye and indigo dye.

2.3.2 Effect of Ph on Adsorption (Batch Process)

Experiments were carried out by mixing40mg of biomass in a 90mg/L of different dye solutions at different pH ranges of (2-11). After three hours of agitations in a shaker at 250rpm, the samples were centrifuged. The supernatant solutions were analyzed in a u.v spectrophotometer for the individual dyes.

2.3.3 Effect of Dye Concentration on Adsorption (Batch Process)

Equilibrium experiments were performed by mixing 40mg of the biomass with different dye concentrations (30-180mg/L) of the different dyes. Agitations were made for three hours in a shaker at 250rpm, after which the samples were centrifuged. The supernatant solutions were collected and analyzed in a U.V spectrophotometer for the dyes.

2.3.4 Effect of Dissolved Salts on Adsorption (Batch Process)

Experiments were carried out by mixing 40mg of biomass in 90 mg/L dye solutions containing NaCl and CaCl₂ solutions. Two different electrolyte concentration, 0.10 M and 0.20M were employed for each electrolyte’s concentrations, 0.10 M and 0.20M were employed for each electrolyte. After three hours of agitation in a shaker at 250rpm, supernatant solution analyzed for dye absorbance in a U.V spectrophotometer.

2.3.5 Fixed Bed Technique

![Figure 1: Fixed Bed Apparatus](https://i.imgur.com/3jK5g.png)
In order to compare the effectiveness of the fixed bed technique with the batch process, experiments were carried out with the optimal parameters already established with the batch process. These include a pH of 4 for methylene blue dye, pH of 2 for Bismarck brown Y and indigo dyes, 0.10M dissolved NaCl and CaCl$_2$, 90mg/L dye solution, 40 mg biomass dose. The fixed bed equipment was set up by packing wire gauze, glass wool in that order in a graduated condenser. Then, the dye solution pressurized from down to top with a peristaltic pump (CHEM-TECH. model X030-XB-AAAA365, China) to where the sample is collected for UV analysis in a U.V spectrophotometer (CAMSPEC M 106 Model, England) by monitoring the adsorbance changes at wavelength of maximum absorbance already determined for methylene blue dye, Bismarck brown Y dye and indigo dye.

2.3.6. Study Based On Biomass Dose

Experiments were carried out with the optimum biomass dose established using the batch process which is 40mg for all the dyes. A flow rate 10m$^3$/s bed height of 1cm and 90mg/L dye solutions were employed. The samples collected were analyzed with a U.V spectrophotometer for dye absorbance was converted to concentration by the use of Beer-Lambert law which expresses the relationship between absorbance and concentration.

2.3.7. Study Based on pH

The optimal pH of 4 for methylene blue dye and pH of 2 for Bismarck brown Y and indigo dye, flow rate of 10m$^3$/s, bed height of 1cm and 90mg/L different dye solutions were employed in this study. The samples collected were subjected to U.V analyses for dye absorbance.

2.3.8. Study Based on Dissolved NaCl and CaCl$_2$ Solutions

The optimal value of 0.10M obtained for both NaCl and CaCl$_2$ solutions from the batch process was used in these determinations. The flow rate of 10m$^3$/s, 1cm bed height, 40mg biomass dose and 90mg/L dye solutions were employed in these determinations. The collected samples were subjected to U.V analysis for dye absorbance.

Note: The amount of dye absorbed per gram biomass ($q_e$) was calculated using the expression below

$$q_e = \frac{V \times (C_o - C_e)}{M}$$

where $V$= Volume of the sample in dm$^3$

$C_o$= Initial dye concentration in mg/L

$C_e$= Equilibrium dye concentration in mg/L

$M$= Mass of the biomass in g.

3. Results and Discussion

![Figure 2: SEM Morphology of Cedrus Libani (X500)](image2)

![Figure 3: SEM Morphology of Cedrus Libani (X1000)](image3)
The SEM micrographs of *Cedrus libani* showed the presence of unevenly dispersed granules or cavities on the surface of the biomass. These cavities provide sites where molecules of the dyes could be trapped. The SEM micrographs of (X500) and (X1000) magnifications are shown in figures 1(a) and 1(b) respectively.

![Figure 4: FTIR Spectrum of Cedrus libani before Adsorption](image)

The FTIR spectrum of *Cedrus libani* before adsorption shown in figure 2.0(a) reveal the presence of five major functional groups. The functional groups include OH, or NH at 3420nm, C-H at 2925.71nm, C≡N, C≡C at 2363.57nm, C=O, C=C at 1645nm. As could be seen, the *Cedrus libani*spectra (scanned between 350-400nm) revealed broad peaks around 3420nm which lie well between 3200-3600nm. This corresponds to the presence of OH functional group on the surface of the biomass (Meroufel *et al*, 2013, Eman *et al*, 2013). Other prominent peaks were observed around 1645nm and 1430nm and are due to carbonyl (C=O) stretching from aldehydes or ketones as also reported by (Dotto *et al*, 2013). The peaks observed around 1031nm was attributed to the C=O stretch due to primary alcohols. The combination of these functional groups arising form –OH and C=O suggest the occurrence of carboxylic functional group was responsible for the adsorption.

![Figure 5: FTIR Spectrum of Cedrus libani before Adsorption](image)
Figure 6: FTIR Spectrum of Cedruslibani with Methylene Blue Dye after Adsorption

Figure 7: FTIR Spectrum of Cedruslibani before Adsorption

Figure 8: FTIR Spectrum of Cedruslibani with Bismarck Brown Y Dye after Adsorption
After the adsorption process as shown in figures 2.0(b), 3.0(b) and 4.0(b) respectively, there were depressions of the original peaks indicating the functional groups that were responsible for the adsorption. The displacements occurred at 2931.00nm and 2365.71nm indicating that the following functional groups C-H, C≡N and C≡C were responsible for the adsorption process. Furthermore, the functional groups did not disappear totally after the adsorption process, this indicates that the interaction of dye molecules with Cedrus libani was indeed a physical process.
It was also observed that the percentage removal efficiency of the adsorbent increased significantly when the adsorbent dose increased form 10-40mg. The value of $q_e$ decreased marginally when the adsorbent dose increased form 50-100mg. The primary reason for the above is that the adsorption sites remain unsaturated and the number of sites available for adsorption increased by increasing the adsorbent dose up to the adsorbent dose of 40mg. At higher adsorbent dose, there is a very fast superficial adsorption to the adsorbent surface than when the adsorbent dose is lower. Thus, with increasing adsorbent dose, the amount of dye adsorbed per unit mass of the adsorbent is reduced, thus causing a decrease in $q_e$ value. A similar effect was previously reported (Vadivehan et al., 2005, Wang et al., 2004).

Also, the result of the findings indicated that the effect of changing the concentration of NaCl and CaCl$_2$ from 0.10M to 0.20M on the adsorption of the dye molecules on to the biomass decreased the value of $q_e$ and the percentage removal efficiency. This could be attributed to the competitive effect between the dye ions and the cations from the salt for sites available for sorption process. Another reason could be that as the ionic strength of the dyes and the active sites decreased, so, adsorbent decreased. As Ca$^{2+}$ has more contribution to the ionic strength and more positively charged than Na$^+$, the effect of Ca$^{2+}$ on adsorption is more serious than Na$^+$ in the same mole concentration. Similar findings have been reported by other researchers (Vadivehan et al., 2005).

The rate of adsorption was also found to be dependent on pH. As could be seen from figure 3.6. A pH of 4 favored a maximum adsorption of methylene blue while a pH of 2 favored the maximum adsorption of Bismarck brown Y dye and Indigo on to Cedrus libani. Several reasons may be attributed to the dye adsorption behavior of the sorbent relative to the large number of active sites, and also the chemistry of the solute in solution. At lower pH values, the surface of the adsorbent would be surrounded by hydrogen ions which compete with the dye ions binding sites of the sorbent. At high pH values, the surface of the biomass particle may be negatively charged which engages the positively charged dye cations through electrostatic forces of attraction. Similar findings were reported by other researchers (Wang et al., 2003).
It was observed that the percentage removal efficiency of the dyes increased significantly when the adsorbent dose increased from 10mg to 40mg. The value of $q_e$ decreased marginally when the adsorbent dose increased from 50mg to 100mg. The primary reason for the above is that the adsorption sites remain unsaturated and the number of sites available for adsorption increased by increasing the adsorbent dose up to the adsorbent dose of 40mg. At higher adsorbent concentration, there is a very fast superficial adsorption onto the adsorbent surface than when the adsorbent dose is lower. Thus, with the increasing adsorbent dose, the amount of dye adsorbed per unit mass of the adsorbent is reduced, thus causing a decrease in $q_e$ value. A similar effect was previously reported. (Vadivehan et al., 2005; Wang et al. 2004, Waranusatigul et al., 2003).

![Figure 14: Effect of Dye Concentration](image)

It was observed that the equilibrium uptake increased with the increase of initial dye concentration before equilibrium was reached at the range of experimental concentration. This is as a result of the increase in the driving force of the concentration gradient. In the same conditions, if the solution was bigger, the active sites of the biomass were surrounded by much more dye ions. So, the value of $q_e$ increased with increase in the dye concentration. Other studies have revealed the same pattern of results about initial dye concentration on adsorption capacity of biomass. (Kumar et al., 2005; Vadivehan et al., 2005; Waranusatigul et al., 2003; Yimer et al., 2014).

| Adsorbent before (batch)       | $q_e$ (mg/g) | Adsorbent after (fixed bed) | $q_e$ (mg/g) |
|-------------------------------|-------------|----------------------------|-------------|
| Methylene blue (pH4)           | 0.980       | 11.28                      | 0.306       |
| Bismarck brown Y (pH2)         | 0.602       | 12.60                      | 0.518       |
| Indigo dye (pH1)               | 0.722       | 2.28                       | 0.601       |

Table 1.0: Absorbance and $Q_e$ Value for Adsorption for Batch and Fixed Bed Technique

Having obtained the optimal parameter of adsorption form the batch process, these optimal values were used in the fixed bed technique in order to evaluate the effectiveness of both techniques. Table 3.1 shows a table of comparison between the batch and the fixed bed technique. The result shows that the fixed bed technique favored a better adsorption of methylene blue dye on to Cedrus libani over the batch process. However, the result fluctuated with the Bismarck brown Y and indigo. It was equally observed that fixed bed technique is more rapid than the batch process.

4. Conclusion

Successful bio-sorption can be achieved through the fixed bed process. The percentage removal efficiency of methylene blue dye on to Cedrus libani is better than that in batch process. The fixed bed process was found to be a faster bio-sorption process compared with the batch process. It is therefore recommended that the use of this technique should be adopted in recent adsorption-based researches.
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