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Evaluation on the Impact of Flow Rate and Bed Height on the Fixed Bed Adsorption of Methylene Blue Dye, Bismarck Brown Y Dye, and Indigo Blue Dye on to *Cedrus Libani* (Elizabeth Leaf) Biomass

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ABSTRACT

The impact of flow rate and bed height on the adsorption behavior of methylene blue, Bismarck brown y, and indigo dyes on to *Cedrus libani* was investigated. The biomass was characterized by scanning electron microscopy as well as Fourier transformed infrared spectroscopy before and after adsorption to ascertain the functional groups responsible for the adsorption. The amount of dye adsorbed per unit mass of the biomass (q_e) was calculated and was found to be dependent on the variables investigated within the experimental range. It was discovered that increase in bed height and flow rate increased the value of the dye adsorbed on to the biomass. The results obtained show that methylene blue dye adsorbed more onto the biomass, while indigo dye adsorbed at the least level.

Keywords: *Bio-sorption, Cedrus libani, SEM, Adsorbent, Fixed bed, Dye.*

1. Introduction

Bio sorption can be defined as the abstraction of organic and inorganic species including metals, dyes and odor causing substances using live or dead biomass or their derivatives. This process can be achieved either through the batch or fixed bed technique. The batch process of adsorption occurs as a result of agitation between the biomass and the dye solution, such agitation is normally provided by a shaker or magnetic stirrer.

On the other hand, fixed bed adsorption process are ubiquitous throughout the chemical process industries [1]. Separation in a fixed bed is virtually in all practical cases an unsteady state rate controlled process. Adsorption only occurs in a particular region of the bed known as the mass transfer zone which moves the bed.

This is practically achieved by allowing the dye solution to pass through the column containing the biomass from down of the column to the top by the use of a peristaltic pump. The removal of dyes from solutions has been attempted in the past, using such techniques as advanced oxidation process, nano filtration and reverse osmosis membrane [2,3]. In recent times, the use of bio-sorption technique for the removal of dye contaminants from solution has been found to be superior to other techniques based on simplicity of design and operation [4]. Activated charcoal is widely employed as an adsorbent. However, the use of activated charcoal is restricted due to high cost. This has resulted in attempts by various workers to prepare low cost alternative adsorbents [5].

Adsorption techniques are effective and attractive for the removal of non-biodegradable pollutant (including dyes) from waste waters [6]. Many low cost adsorbent and waste materials from industries and agriculture have been proposed by several researchers [7]. These materials do not require any expensive additional pre-treatment step and could be used as adsorbent for the removal of dyes from solutions.

An investigation was carried out on the kinetics and thermodynamic studies of adsorption of malachite green on to un modified and Ethylene di amine tetra acetic acid modified groundnut husk, using the batch technique [8].

This work is carried out with the view of expanding the field of application of natural biomass for the treatment of dye wastewaters and also to determine the adsorption capacity of *Cedrus libani* (Elizabeth leaf) on Methylene blue, Bismarck brown Y, and Indigo dyes respectively. Since such an in-depth comparison has not been done on this biomass, the results obtained from this work will add to the expansion of knowledge in this area.

2. Materials and Methods

2.1. Material Preparation

The methylene blue dye, Bismarck brown y dye, and indigo dye used in these investigations were obtained from qualikem laboratory, Owerri, Nigeria. Other materials obtained here include analytical grade sodium hydroxide pellets, concentrated hydrochloric acid, distilled water etc.

The *Cedrus libani* (Elizabeth leaf) used in this work was obtained from ikorodu area of Lagos, Nigeria which is located within the following coordinates 6.6194°N, and 3.5105°E. The sample was identified at the department of crop science at the Federal university of technology, Owerri, Nigeria with the voucher specimen number of FUT/CR/002/15. The biomass was washed severally with distilled water to remove any dirt from it. The washed biomass was air dried for 10 days until constant weight was obtained. The biomass was grinded with a new sonic domestic blender to avoid any form of contamination. It was screened using 600-800 micron sized sieves and were stored in air tight containers ready for adsorption measurement. The methods and techniques employed in these determinations are the standard methods which have been used by other researchers [8].

2.2. Characterization of the Bio-Sorbent

The surface structure and morphology of the *Cedrus libani* was characterized at 1000× magnification, 500× magnification and 250× magnification respectively for their surface morphology using a scanning electron microscopy. This was done using (FEI- Inspect oxford instrument x-max SU9000 Model) which was equipped with an energy dispersive x-ray (EDAX) spectrometer employed for elemental composition analysis.

The biomass sample was further characterized for their fundamental functional groups before and after adsorption experiment using a Fourier Transformed Infrared spectrophotometer (FTIR – IRSpirit Shimadzu model) (Perkin Elmer, England) in the wavelength range of 350-400nm using KBr powder and fluka library for data interpretation.

2.3. The Fixed Bed Setup

The fixed bed was set up by packing wire gauze, glass wool, glass beads, glass wool, biomass, and glass wool in that order in a graduated condenser. Then a dye solution of a known concentration and pH pressurized from down to top where a known amount of bio-sorbent is placed with a peristaltic pump (CHEM- TECH Model X030- XB-AAAA365, China) from there, a sample is collected for analysis in a UV spectrophotometer (CAMSPEC M 106 Model. England) by monitoring the absorbance changes at wavelength of maximum absorbance already determined for methylene blue dye (600nm), Bismarck brown y dye (320nm) and indigo dye (350nm) respectively.

The variables investigated here include the effect of bed height and flow rate.

2.4. Effect of Flow Rate on Adsorption

Experiments were carried out at different flow rate of 20 m^3/s, 30 m^3/s and 40 m^3/s while keeping constant a bed height of 1 cm, 40 mg biomass dose, 90 mg/L dye solution and a pH of 4 for methylene blue dye and a pH of 2 for Bismarck brown y and indigo dyes as earlier determined as the best pH of maximum adsorption. The dye solution was subjected to pass through the column already prepared using the peristaltic pump. The samples collected were subjected to U.V analysis for absorbance measurements. Subsequently, the absorbance values were converted to concentration by the use of Beer Lamberts law. Similar experiment were carried out in triplicates and the mean values reported.

2.5. Effect of Bed Height on Adsorption

Experiments were carried out at different bed heights of 4 cm, 5 cm and 6 cm were considered while keeping constant a flow rate of 10 m^3/s, 90 mg/L dye solution, pH of 4 for methylene blue dye and a pH of 2 for both Bismarck brown y and indigo dyes as earlier determined as the best pH of maximum adsorption.

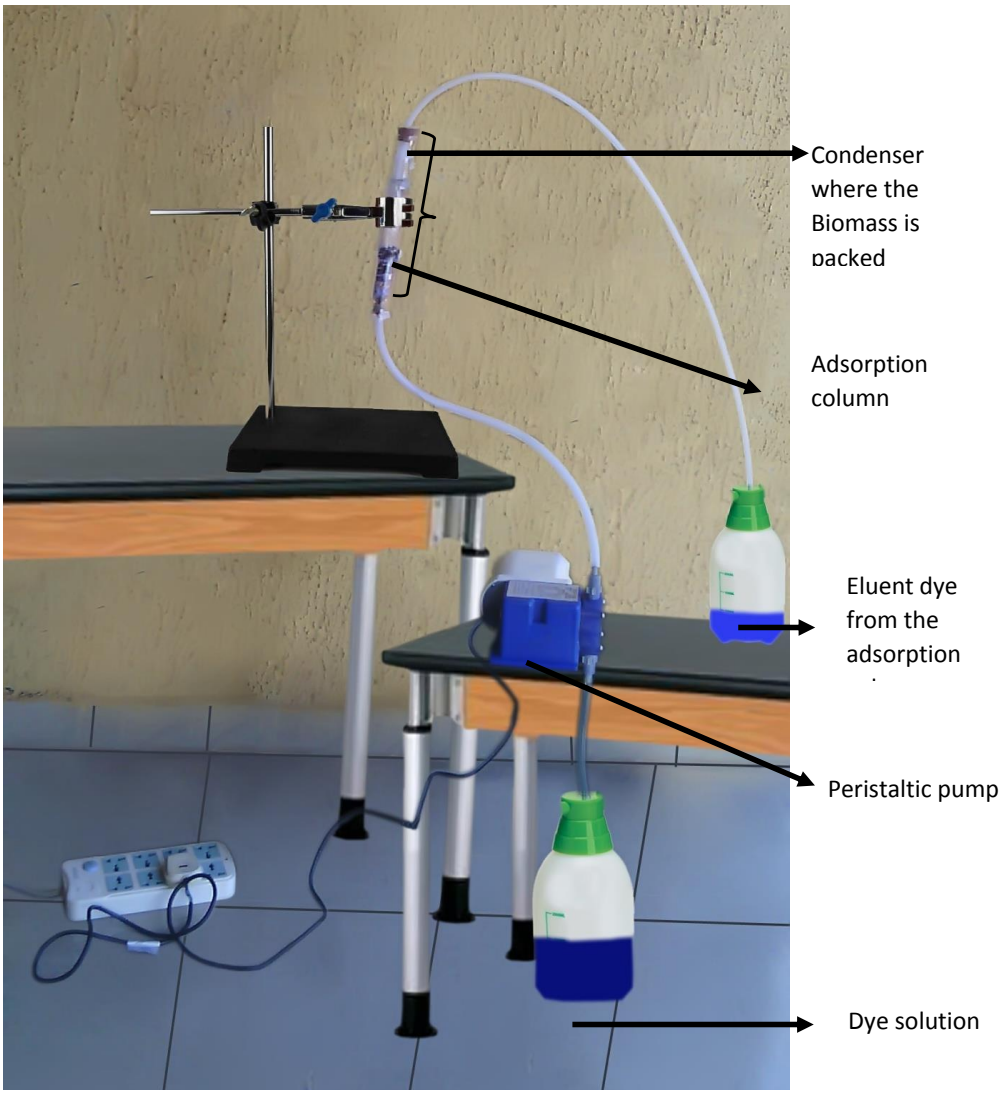

Fig.1. Fixed bed technique apparatus

The dye solution was subjected to pass through the column already prepared using the peristaltic pump. The samples collected were subjected to U.V analysis for absorbance measurements. Subsequently, the absorbance values were converted to concentration by the use of Beer Lambert's law. Similar experiments were carried out in triplicates and the mean values reported.

NOTES: The amount of dye adsorbed per gram biomass (q_e) was calculated using the expression below.

$$q_e = V (C_o - C_e) /M \qquad (1)$$

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 Discussions

The SEM micrographs of *Cedrus libani* revealed the presence of unevenly dispersed cavities on the surface of the biomass. These cavities provide sites where the molecules of the dyes could be trapped in the course of adsorption. The SEM micrographs of 500× and 1000× magnifications are shown in figures 2 and 3 respectively.

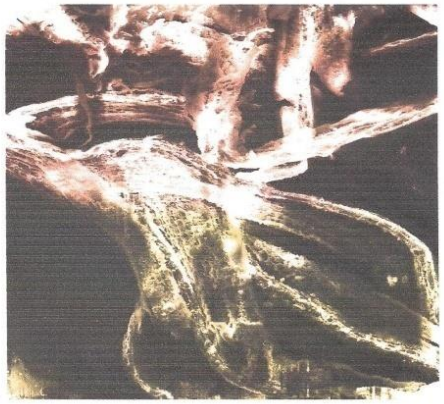

Fig.2. SEM morphology of *Cedrus libani* (×500)

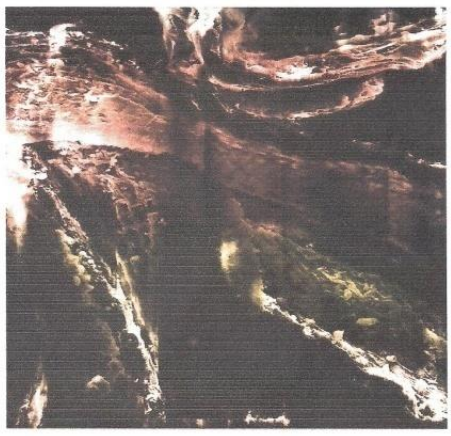

Fig.3. SEM morphology of *Cedrus libani* (×1000)

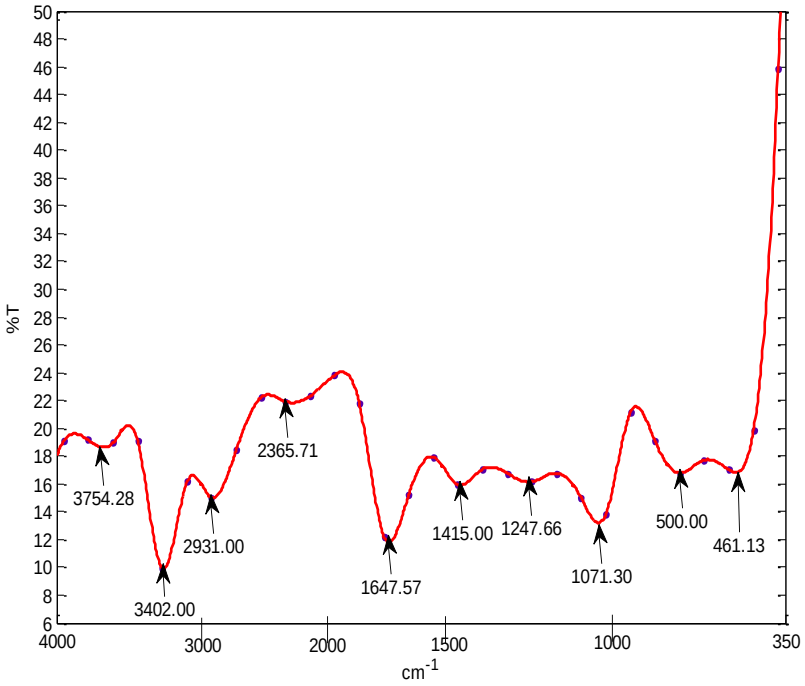

Fig.4. FTIR Spectrum of *Cedrus libani* before adsorption

The FTIR spectrum of *Cedrus libani* shown in figure 4 reveals the presence of five major functional groups. The functional groups include O-H or N-H at 3420 nm, C-H at 2925.71 nm, C≡N, C≡C at 2363.57 nm, C=O, C=C at 1645 nm. As could be seen, the *Cedrus libani* spectra (scanned between 350-400 nm) revealed broad peaks around 3420 nm which lie well between 3200-3600 nm. This corresponds to the presence of OH functional group o the surface of the biomass[10]. Other prominent peaks were observed around 1645 nm and 1430 nm and are due to carbonyl (C=O) stretching from aldehydes or ketones[9]. The peaks observed around 1031 nm was attributed to the C=O stretch due to primary alcohol. The combination of these functional groups arising from the OH and CO suggest the occurrence of carboxylic functional group.

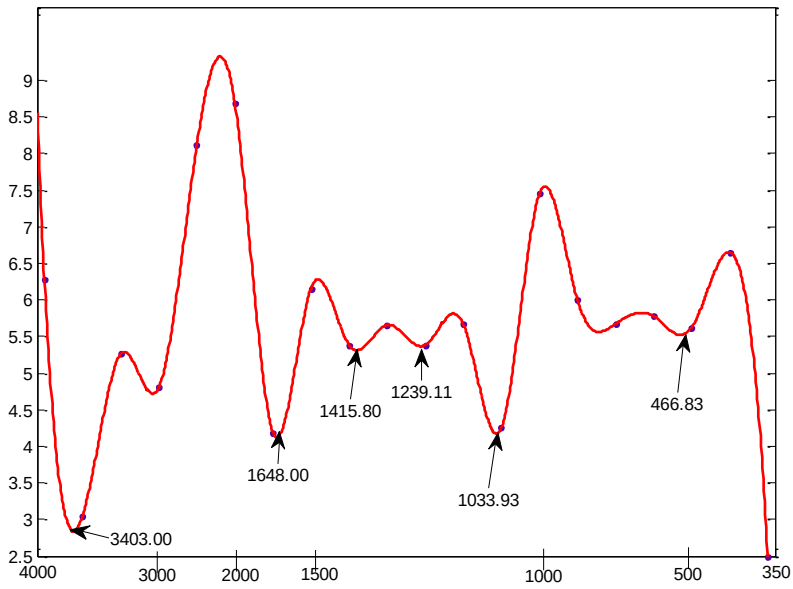

Fig.5. FTIR Spectrum of *Cedrus libani* with methylene blue dye after adsorption

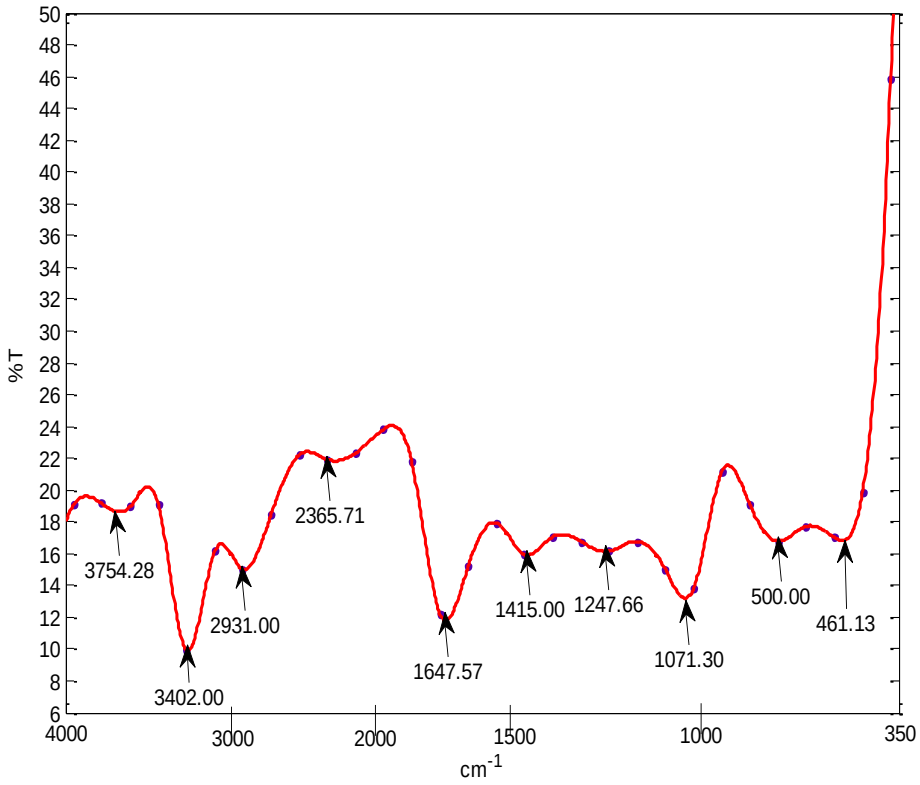

Fig.6. FTIR Spectrum of *Cedrus libani* before adsorption

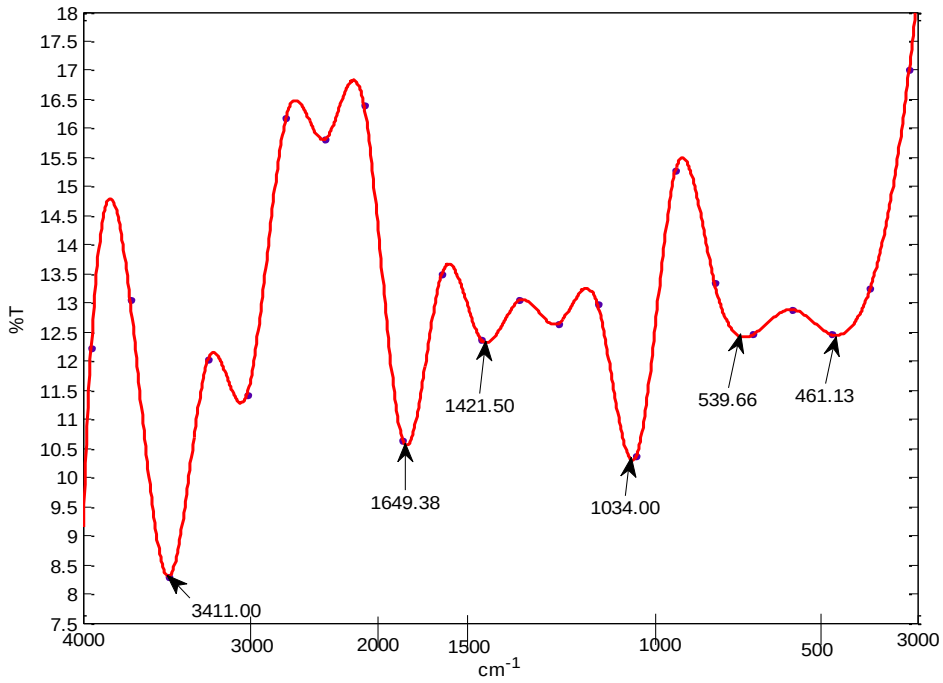

Fig.7. FTIR Spectrum of *Cedrus libani* with Bismarck brown y dye after adsorption

After the adsorption process as shown in figures 6, 8, and 10, there were depressions of the original peaks as shown in figures 5, 7 and 9 respectively. From the depressions observed, we can determine the functional groups that were actually responsible for the adsorption reaction. The displacements occurred at 2931.00 nm and 3265.71 nm 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 adsorption process. This indicates that the interaction of the dye molecules with *Cedrus libani* was indeed a physical process [1].

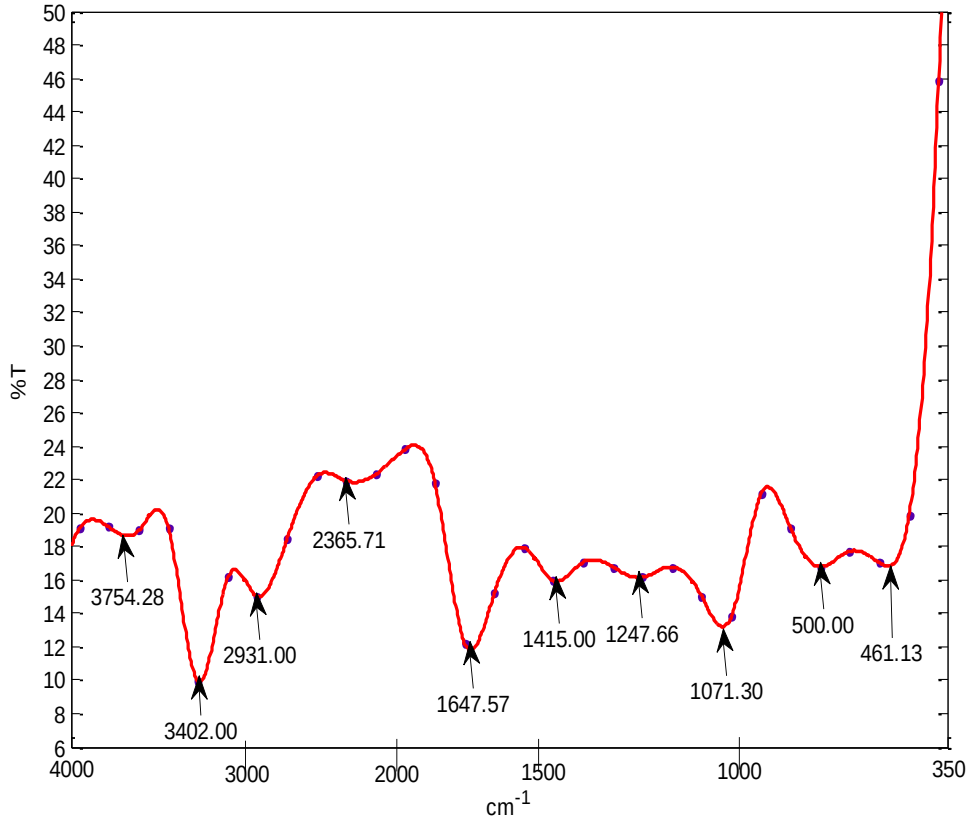

Fig.8. FTIR Spectrum of *Cedrus libani* before adsorption

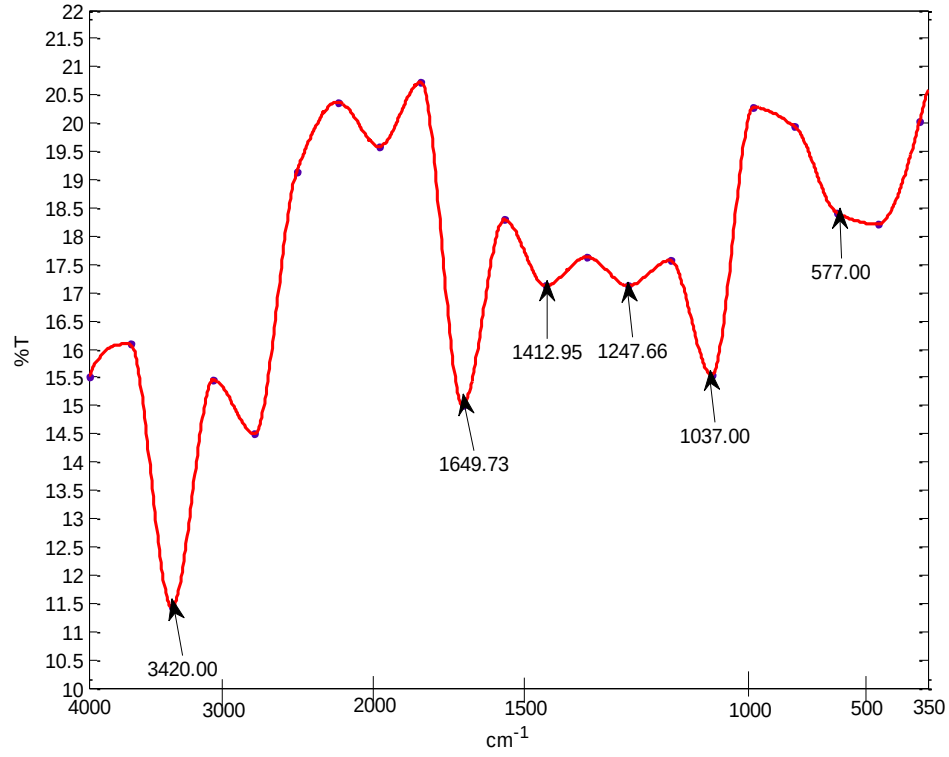

Fig.9. FTIR Spectrum of *Cedrus libani* with Indigo dye after adsorption

Table 1. Effect of Flow Rate on the Fixed Bed Adsorption of Methylene Blue Dye, Bismarck Brown Y Dye and Indigo Dye on to *Cedrus Libani*

Flow rate (m^3/s)	**20**	**30**	**40**
Methylene blue dye q_e (mg/g)	8.40	11.30	13.64
Bismarck brown Y dye q_e (mg/g)	4.71	8.80	9.78
Indigo dye q_e (mg/g)	2.80	6.46	8.00

As could be seen from table 1, increase in the flow rate caused a corresponding increase in the q_e values for the biomass within the range of experimental consideration. A similar effect was reported by other researcher [11].

This could be attributed to the increase in the force of interaction between the dye solution and the biomass surface area. Methylene blue dye was the most adsorbed, while indigo dye was the least adsorbed.

Table 2. Effect of Bed Height on the Fixed Bed Adsorption of Methylene Blue Dye, Bismarck Brown Y Dye and Indigo Dye on to *Cedrus Libani*

Bed height (cm)	**4**	**5**	**6**
Methylene blue dye q_e (mg/g)	5.15	20.35	24.62
Bismarck brown Y dye q_e (mg/g)	8.20	11.00	15.00
Indigo dye q_e (mg/g)	5.66	12.91	14.86

Table 2 shows the effect of bed height on to the quality of each dye adsorbed on to the adsorbent. The q_e values for the biomass increased with increase in bed height within the range of experimental considerations. The result indicates that longer the bed height, the higher the q_e values. A similar situation has been reported in a similar investigations [12]. This could be due to the longer time of interactions between the biomass and the dye solutions. Methylene blue dye was adsorbed more while indigo dye was the least in these considerations.

4. Conclusion

The findings of this research vividly showed that the two variables- flow rate and bed height can affect the adsorption properties of Cedrus libani on to methylene blue dye, Bismarck brown y dye and Indigo dye respectively. Increase in flow rate and bed height gave rise to a corresponding increase in the q_e value of the adsorbent. Figures 2 and 3 show pores in the morphology of the Cedrus libani. These pores are the sites where the dye molecules are trapped in the course of the adsorption. Additionally, figures 5, 7, and 9 showed some

depressions in the wavelength of adsorption of the dyes, which is indicative of the fact that adsorption has taken place.

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Declarations

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Competing Interests Statement

The authors declare no competing financial, professional and personal interests.

Consent for publication

Authors declare that they consented for the publication of this research work.

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