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Evaluation of Bio-Sorption Properties of *Cedrus Libani* (Elizabeth Leaf) on Methylene Blue Dye, Bismarck Brown Y Dye and Indigo Dye by the Batch Process

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Abstract:
The adsorption properties of methylene blue dye, Bismarck brown Y dye, and Indigo dye on Cedrus libani(Elizabeth leaf) was investigated as a function of contact time, initial dye concentration, biomass dose, pH, dissolved salts, biomass particle size and temperature.
The biomass was characterized by scanning electron microscope (SEM), as well as Fourier Transformed Infrared Spectroscope (FTIR) before and after adsorption in order to determine the functional groups responsible for the adsorption. The amount of the dye adsorbed per unit mass of the biomass (q_e) was calculated and found to be dependent on all the variables investigated. Optimal pH of 2 was determined for the adsorption of Bismarck brown Y dye and Indigo dye, while a pH of 4was determined as the optimal pH for the methylene blue dye. 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, sem, adsorbent, batch process*

1. Introduction

Bio sorption which involves the sequestering of organic, and inorganic species including dyes, metals, and other odor causing substances using live or dead adsorbents can be achieved through the batch process. In recent times, this has also been achieved through the fixed bed process.

Synthetic dyes which include a wide range of aromatic water soluble dispersible organic colorants are used extensively in textile, ink, and paint industries. Effluents containing synthetic dyes do not produce visual pollution only, but also are hazardous to ecological system and public health (Low etal, 1995).

Conventional treatment of dye containing effluents are either ineffective, costly, complicated or have sludge disposal problems (Han etal, 2006). Thus, there is a need for a continuous search for a cheaper and environmentally friendly methods for the treatment of such effluents. Thus, many low cost adsorbents including natural adsorbents, and waste materials from industries and agriculture have been proposed by several workers (Amadurai etal, 2002). As expected, these materials do not require any expensive additional pretreatment step, and so could be used as adsorbents for the removal of dyes from dye waste waters.

Some researchers reported the use of plant leaf biomass to adsorb heavy metals, dyes etc. from solutions (Wang etal, 2004). This work investigated the adsorption of Methylene blue dye, Bismarck brown y dye and Indigo dye unto *Cedrus libani*, (Elizabeth leaf).

2. Experimental

2.1. Material Preparations

The Methylene blue dye, Bismarck brown Y dye, and the 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, distilled water, sodium chloride, calcium chloride etc.

The *Cedrus libani*used in this work was obtained from Ikorodu, Lagos, Nigeria and identified at the department of crop science at the Federal university of technology, Owerri, Nigeria. The biomass was washed severally with distilled water to remove any dirt from it. The washed biomass was air dried for ten 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 600-850 micron size sieves and were stored in air tight containers ready for adsorption measurement.

2.2. Characterization of the Bio Sorbent

The surface structure, and morphology of *Cedrus libani* was characterized at 1000 X magnification, 500 X magnification and 250 X 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 composition analyses.

The biomass sample was further characterized for their fundamental functional groups before and after adsorption experiment using Fourier Transform Infrared (FTIR) spectrophotometer (Perkin Elmer, England) in the wave length range of 350-400nm using KBr powder and Fluke library for data interpretation.

2.3. Effect of Contact Time on Adsorption

Experiments were carried out by mixing 40mg of the biomass in a dye solution of 90mg/L of Methylene blue, Bismarck brown y dye, and Indigo dye respectively. 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 adsorbance at 600nm for Methylene blue dye, 320nm for Bismarck brown Y dye, and 360nm for indigo dye respectively in a U.V spectrophotometer. These tests were carried out in triplicates, and the mean values were reported.

2.3.1. Effect of Biomass Dose on Adsorption

Experiments were carried out by mixing biomass of different doses (10-100mg) with different dye solutions of concentration 90mg/L. Agitations were made for three hours in a shaker at 250rpm. The left out supernatant solution was analyzed for dye absorbance in a U.V spectrophotometer at the different wavelength for Methylene blue dye, Bismarck brown Y dye, and Indigo dye respectively.

2.3.2. Effect of Ph on Adsorption

Experiments were performed by mixing 40mg of biomass in 90mg/L of different dye solutions at different pH range of (2-11). After three hours of agitation 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 Initial Dye Concentration on Adsorption

Equilibrium experiments were performed by mixing 40mg of the sample 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 respective samples.

2.3.4. Effect of Temperature on Adsorption

Experiments were carried out by mixing 40mg of biomass in a 90mg/L dye solution in a vessel placed in a magnetic hot plate. This was done in batches with the aid of a thermometer for the proper monitoring of the temperature. The temperature range was between (323-353K). After three hours of agitations in the hot plate at 200rpm the samples were centrifuged and the supernatant solution analyzed for dye absorbance in a U.V spectrophotometer.

2.3.5. Effect of Dissolved Electrolytes (Nacl and $Cacl_2$ Solutions)

Experiments were carried out by mixing 40mg of the biomass in a 90mg/L dye solution containing NaCl, and $CaCl_2$ solutions. Two different electrolyte concentrations, 0.10M, and 0.20M were employed for each electrolyte. After three hours of agitation in a shaker at 250rpm, the samples were centrifuged, and the supernatant solutions analyzed for dye absorbance in a U.V spectrophotometer.

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

$q_e = V (Co – C_e) / M$

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

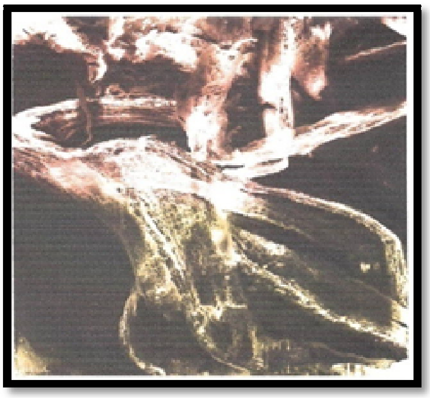

Figure 1: SEM Morphology of Cedrus Libani (X500)

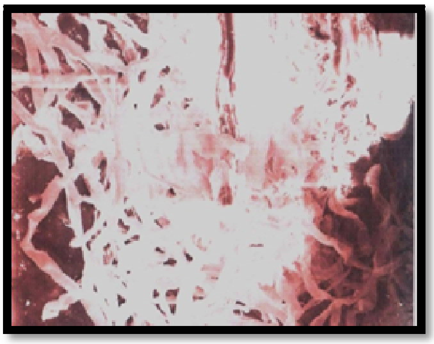

Figure 2: SEM Morphology of Cedrus Libani (X1000)

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 (X500), and (X1000) magnifications are shown in figures 1and 2respectively.

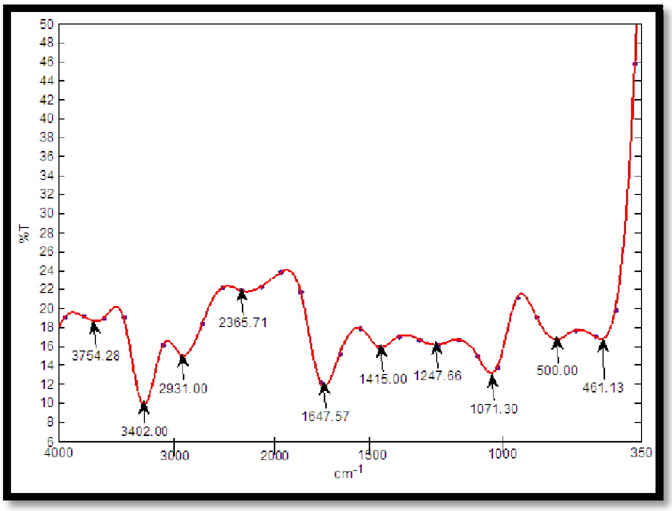

Figure 3: FTIR Spectrum of Cedruslibani before Adsorption

The FTIR spectrum of *Cedrus libani* showed in figure 3reveals the presence of five major functional groups. The functional groups include O-H or N-H 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 etal, 2013, Eman etal 2013). Other prominent peaks were observed around 1645nm and 1430nm and are due to carbonyl (C=O) stretching from aldehydes or ketones as reported by Dotto (2013). The peaks observed around 1031nm 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.

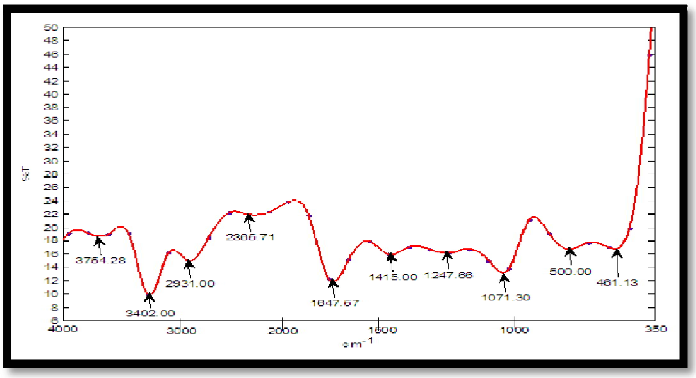

Figure 4: FTIR Spectrum of Cedruslibani before Adsorption

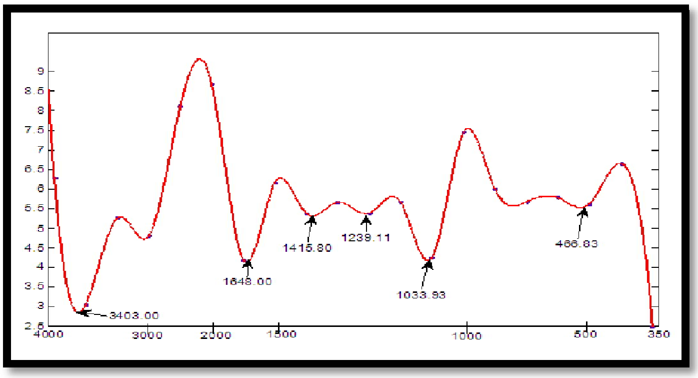

Figure 5: FTIR Spectrum of Cedruslibani with Methylene Blue Dye after Adsorption

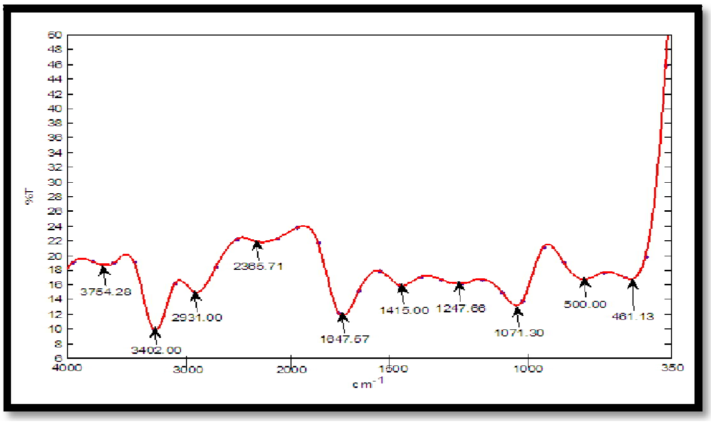

Figure 6: FTIR Spectrum of Cedruslibani before Adsorption

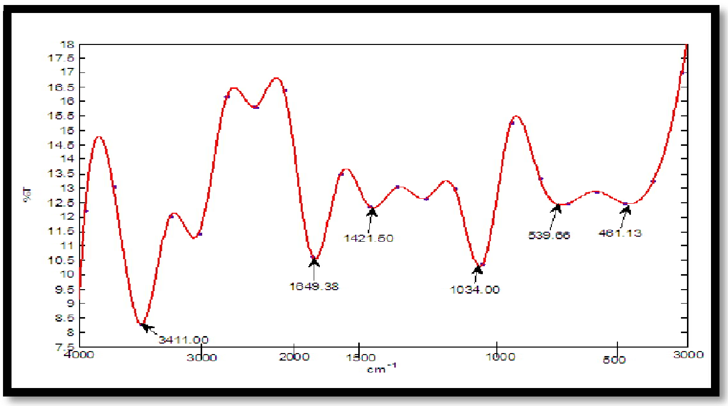

Figure 7: FTIR Spectrum of Cedruslibani With Bismarck Brown Y Dye after Adsorption

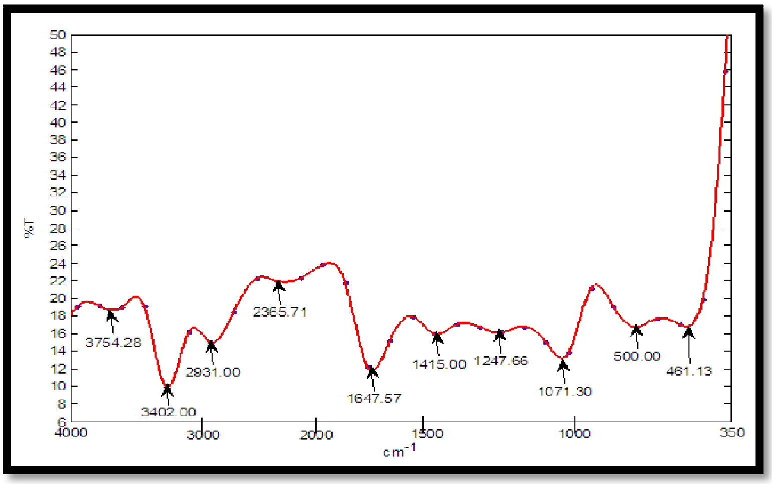

Figure 8 FTIR Spectrum of Cedruslibani before Adsorption

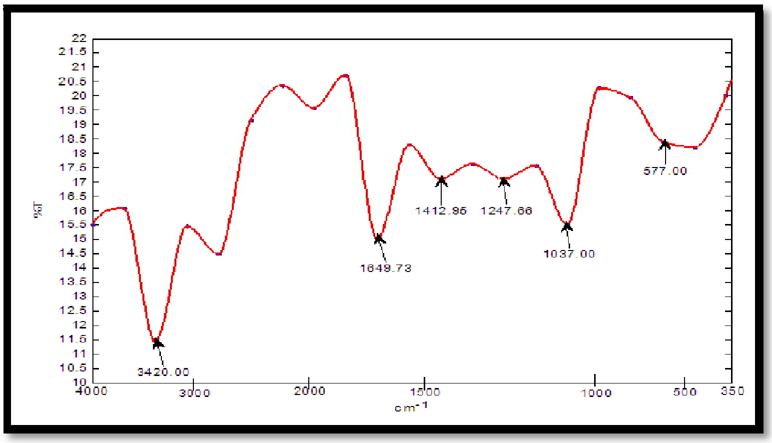

Figure 9: FTIR Spectrum of Cedruslibani with Indigo Dye after Adsorption

After the adsorption process as shown in figures 6 7, 9 respectively. There were depressions of the original peaks as shown in figure 4of the original peaks indicating the functional groups that were actually responsible for the adsorption reactions. The displacements occurred at 2931.00nm, and 3265.71nm 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 the dye molecules with *Cedrus libani*was indeed a physical process.

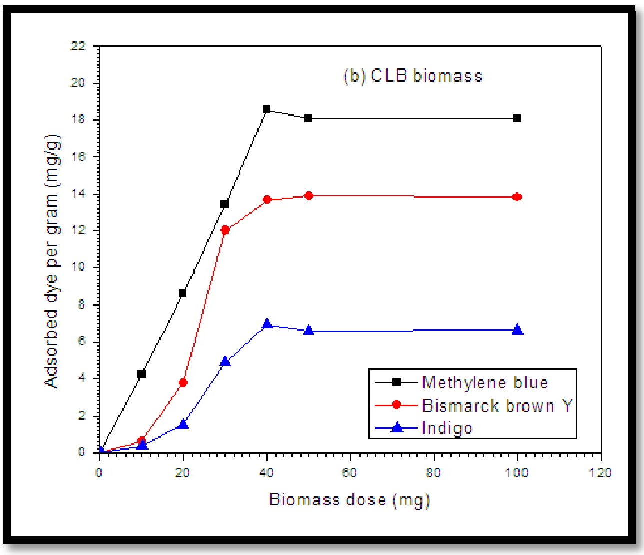

Figure 10: Effect of Biomass Dose on Adsorption with Cedrus Libani

As could be seen on figure 3.4, the percentage removal efficiency of the adsorbent increased significantly when the adsorbent dose increased from 10-40mg. The value of q_e decreased marginally when the adsorbent dose increased from 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 unto 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 the q_e value. A similar effect was previously reported (Wang etal 2004, Waranusatigul etal 2003).

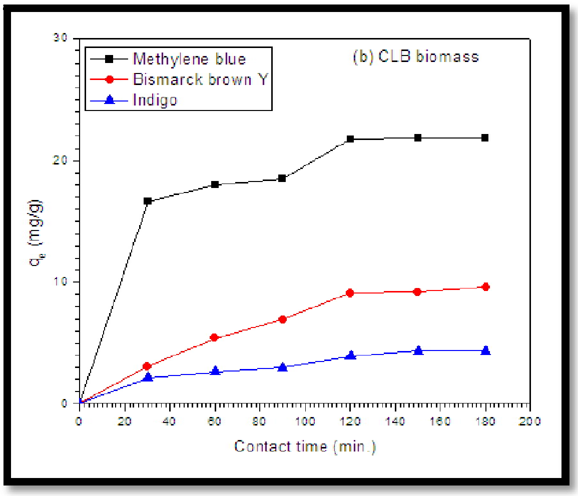

Figure 11: Effect of Contact Time on Adsorption with Cedrus Libani

Figure 11shows the result of the bio-sorption per gram adsorbent at different contact times. It shows a two stage kinetic behavior, a rapid initial adsorption over thirty minutes, followed by a longer period of much slower up take as shown in the figure above. At the beginning of adsorption the values of q_e increased quickly, then after 150 minutes, the change became slow. Here, the reaction is assumed to have reached equilibrium. Similar findings were reported by other researchers (Titilayo etal, 2008). The authors reasoned that greater adsorption sites resisted during the initial exposure periods, and that equilibrium was established by the repulsive force between the solute molecules on the biomass surface and the bulk phase.

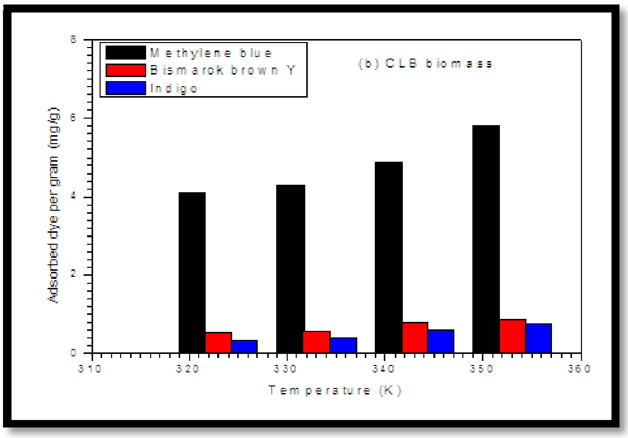

Figure 12: Effect of Temperature on the Adsorption Capacity of Cedrus Libani

Increasing the temperature between 323-353K showed a corresponding increase in the value of q_e. This shows that the adsorption of the dyes unto the biomass is endothermic in nature. This could be attributed to an increase in the pore size of the dye molecules with increasing temperature. It could also be as result of the increase in the net negative charge existing on the biomass surface which promote electrostatic attraction of the positively charged dye molecules. According to the variation in temperature, it could be reasoned that the increase in sorptive removal of the dye with increase in temperature may partly point to the fact that the adsorbent adsorption was more endothermic than exothermic.

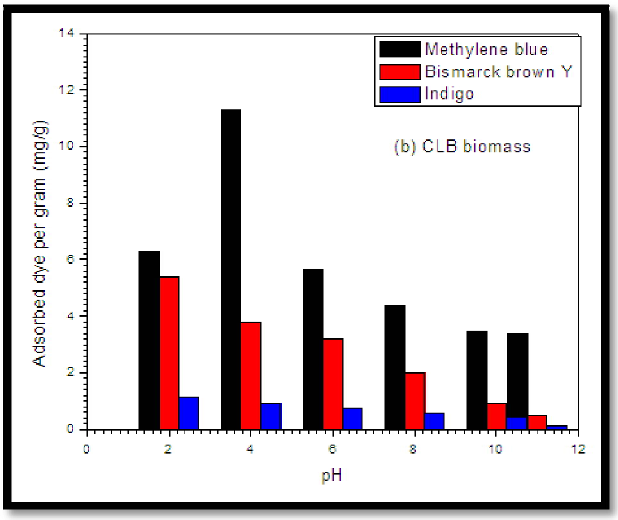

Figure 13: Effect of Ph on Adsorption with Cedrus Libani

The rate of adsorption was also found to be dependent on pH. As could be seen from figure 13a pH of 2 favoured a maximum adsorption for Bismarck brown Y dye, and Indigo dye respectively. Whereas a pH of 4 favoured the maximum adsorption of methylene blue dye unto the biomass. 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 will be surrounded by hydrogen ions which compete with the dye ions binding site of the sorbent. At high pH values, the surface of the biomass particles may be negatively charged which engages the positively charged dye cations through electrostatic force of attraction. Similar situation was reported by other researchers (Vannapusa etal, 2008).

NaCl	$CaCl_2$			
	0.10 M	0.20 M	0.10 M	0.20 M
q_{MB} (mg/g)	3.90	1.40	2.48	1.15
q_{BB} (mg/g)	3.64	0.46	2.57	0.34
q_{IN} (mg/g)	2.83	0.36	2.20	0.15

Table 1: Effect of Dissolved Electrolytes on Adsorption with Cedrus Libani

Also, the result of the findings indicate that the effect of changing the concentration of sodium chloride and calcium chloride from 0.10M to 0.20M on adsorption of the dye molecule unto the biomass decreased the value of q_e and the percentage removal efficiency. This could be attributed to competitive effect between the dye ions and the cations from the salt for sites available for the sorption process. Another reason could be that as the ionic strength increase, the activity (effective concentration) of the dyes and active sites decreased, so the adsorptive capacity of the dye unto the 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 molar concentration. Similar findings have been reported by other researchers (Vadivehan, V., Vasanth, K., 2005).

4. Conclusion

From the experimental results, *Cedrus libani*can be usefully employed in the treatment in of dye waste waters especially the ones containing Methylene blue dye, Bismarck brown Y dye, and Indigo dye. The rate of adsorption of this dyes on to *Cedrus libani* was found to be dependent on pH, contact time, dye concentration, biomass dose, temperature, and presence of dissolved salts. The percentage removal efficiency of Methylene blue dye unto the biomass was the highest, while Indigo dye was the least.

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