Bio-sorption properties of *Sphagnum cymbifolium* (Moss) on methylene blue, bismark brown y, and indigo dyes by the batch process

*Idika, D .I[1]; Ogukwe, C .E[2]; Oguzie, E .E[2]; Aleshinloye, A .O[1]; Adewunmi, A[3].

[1]*Department of Basic Sciences, Chemistry Unit, Babcock University Ilishan, Remo. Ogun state.*
[2]*Department of Industrial Chemistry, Federal University Of Technology, PMB 1526, Owerri Imo state. Nigeria.*
[3]*Department of Basic Sciences, Biology Unit, Babcock University Ilishan, Remo. Ogun state.*

Corresponding author < idikad@babcock.edu.ng>

Abstract

The adsorption behavior of methylene blue dye, Bismarck Brown Y dye, and Indigo dye on to *Sphagnum cymbifolium* (Moss) 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 dyes adsorbed per unit mass of 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, and indigo dye, while a , pH of 4 was 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*, Sphagnum cymbifolium* , sem, adsorbent, batch process

1.0 Introduction

Bio-sorption can be defined as the abstraction of in-organic and organic species. This may include metals, dyes, and odour causing substances using live or dead biomass or their derivatives.

This can be achieved either through the batch or fixed bed techniques. But this work is based on achieving it through the batch process. Adsorption occurs as a result of agitation between the biomass and the dye solution. Such agitation can be achieved by the use of a shaker or magnetic stirrer.

Many industries such as plastics, dye stuffs and textiles use dyes to color their products and also consume substantial volumes of water. Due to their good solubility, synthetic dyes are common water pollutants. The presence of very small amount of dyes in water is highly visible and undesirable (Crini, G, 2006). Due to the negative undesirable effects of dyes in water, it becomes imperative that they should be removed from waste waters before they are discharged to the environment.

Adsorption techniques are effective and attractive for the removal of non-biodegradable pollutants (including dyes) from waste waters (Robinson etal, 2001). Most commercial systems use activated carbon as adsorbent to remove dyes from waste waters because of its excellent adsorption ability. But its widespread use is limited due to its high running cost.

Many low cost adsorbents including natural material adsorbent, and waste materials from industry and agriculture have been proposed by several workers (Amandurai etal, 2002). These materials do not require any expensive additional pre-treatment step, and could be used as adsorbent for the removal of dyes from solutions.

Robinson reviewed the current treatment technology including bio-sorption with proposed alternatives for the removal of dyes in textile effluents. On the other hand, a fresh water algae *Pithophora sp.* was studied by Kumar in finding out its bio-sorption properties on to malachite green (a cationic azo dye) (Kumar etal, 2005).

In this work, *Sphagnum cymbifolium* was used as the bio sorbent.

2.0 Materials and methods
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 etc.

The *Sphagnum cymbifolium* (moss) used in this work was obtained from ikorodu area of Lagos Nigeria and identified at the department of crop science at 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 measurements.

2.2 Characterization of the bio-sorbent
The surface structure and morphology of the *Sphagnum cymbifolium* (moss) 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) spectrometer employed for the elemental composition analysis.

The biomass sample was further characterized for their fundamental functional group 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.
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 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 super natant solution was analyzed for dye absorbance at 600nm for methylene blue dye, 320nm for Bismarck Brown Y dye, and 360nm for indigo dye respectively in a UV spectrophotometer. These test were carried out in triplicates and the mean values 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 our supernatant solution was analyzed for dye

absorbance in a UV spectrophotometer at the different wavelengths for methylene blue dye, Bismarck brown Y dye, and Indigo dye respectively.

2.3.2 Effect of pH on adsorption
Experiments were carried out by mixing 40mg of biomass in 90mg/L of different dye solutions at different pH range of (2-11). After three hours of agitations in a shaker at 250rpm, the samples were centrifuged. The supernatant solutions were analyzed in a UV spectrophotometer for the individual dyes.

2.3.3 Effect of initial dye concentration on adsorption.
Equilibrium experiments were performed by mixing 4omg of the sample with different dye concentrations (30-180mg/L). 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 UV spectrophotometer for the respective dyes.

2.3.4 Effect of temperature on adsorption.
Experiments were carried out by mixing 40mg of biomass in a 90mg/L dye solutions 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 UV spectrophotometer.

2.3.5 Effect of dissolved electrolytes (NaCl and CaCl$_2$ solutions)
Experiments were carried out by mixing 40mg of biomass in a 90mg/L dye solutions containing NaCl and CaCl$_2$ solutions. Two different electrolyte concentration, 0.10 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 UV spectrophotometer.

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

$$q_e = V (C_O-C_E)/M$$

where V = Volume of 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.
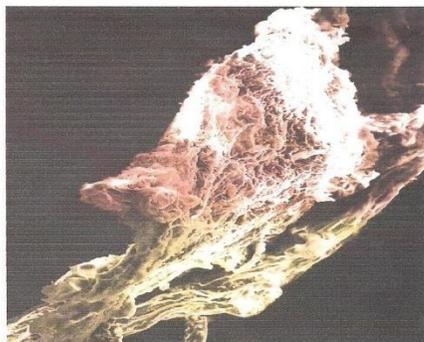
3.0 Results

Figure 3(a)
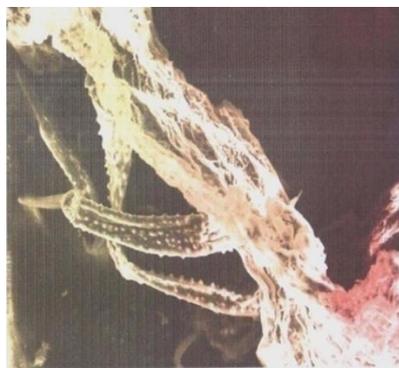SEM morphology of *Sphagnum cymbifolium* (X500)

Figure 3(b)
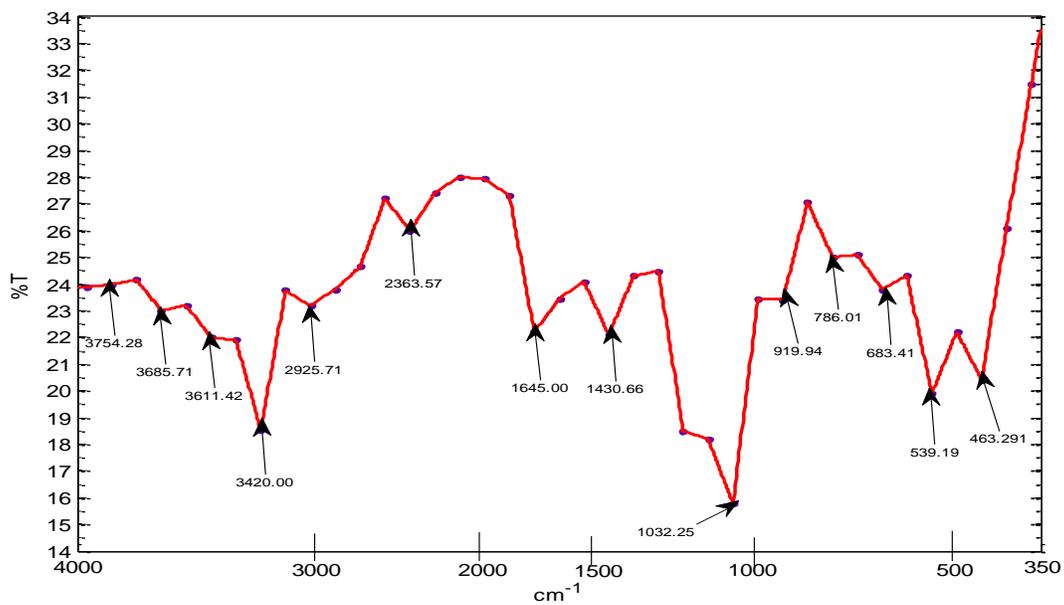SEM morphology of *Sphagnum cymbifolium* (x1000)

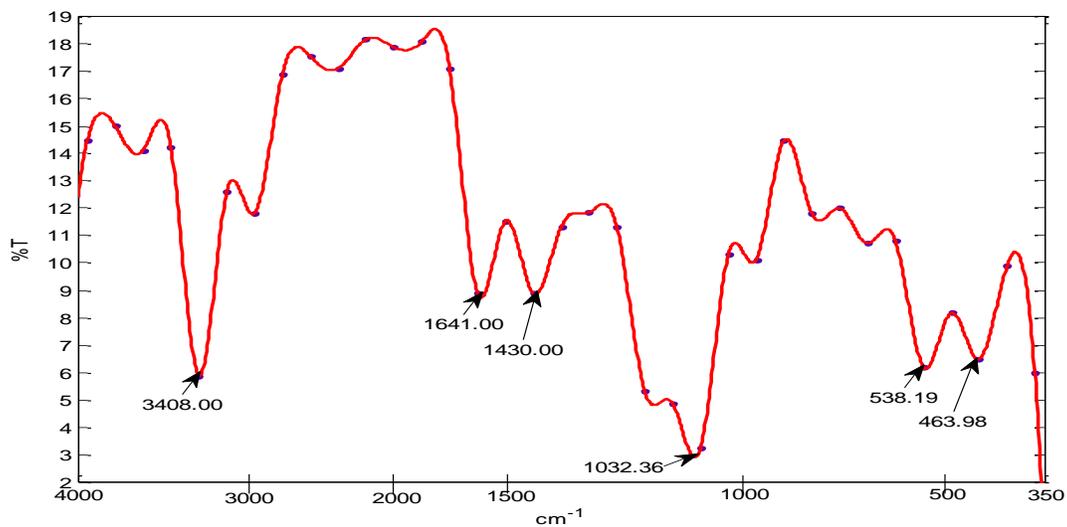Figure 3.1(a) FTIR Spectrum of *Sphagnum cymbifolium* before adsorption

Figure 3.1(b)   FTIR Spectrum of *Sphagnum cymbifolium* with methylene blue dye after adsorption
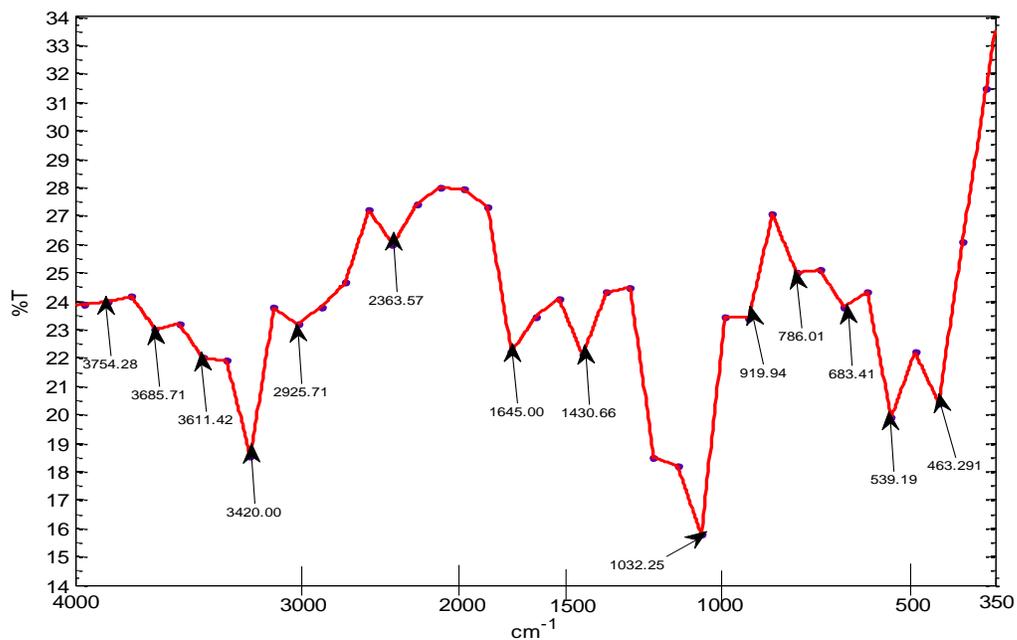
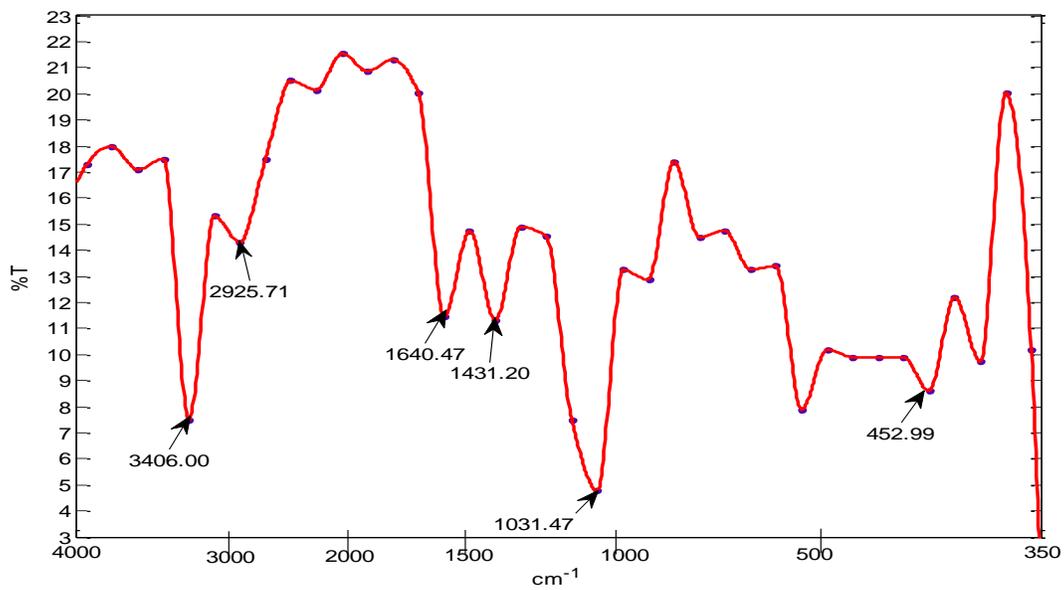Fig 3.2a FTIR spectrum of *Sphagnum cymbifolium* before adsorption

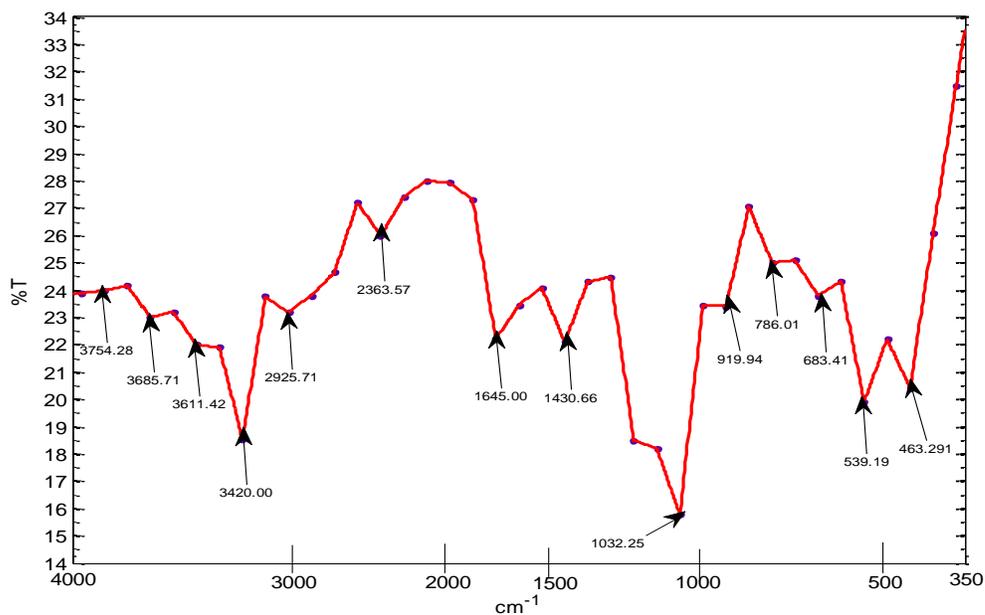Fig 3.2b FTIR spectrum of *Sphagnum cymbifolium* with Bismarck brown Y after adsorption

Fig 3.3a
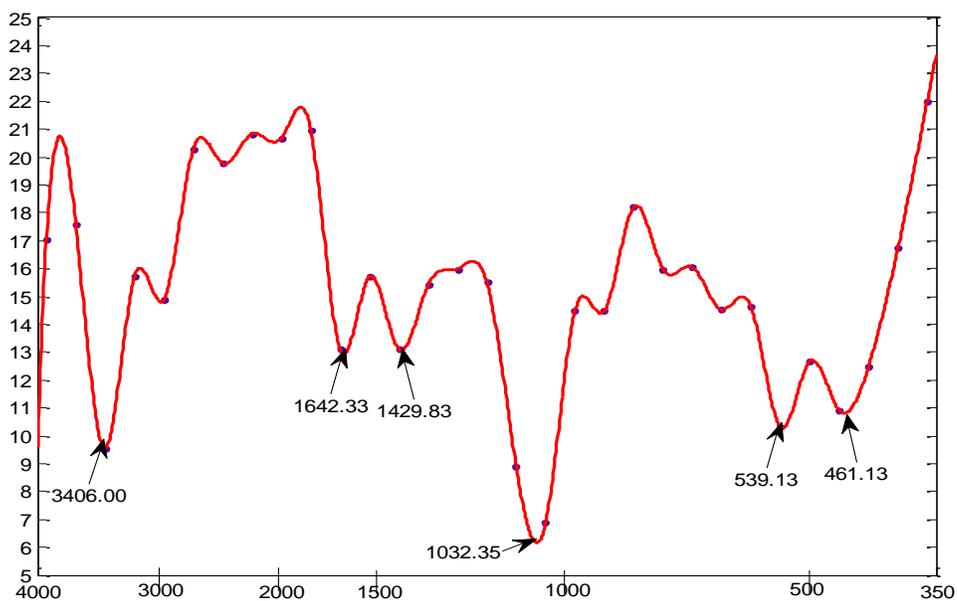FTIR spectrum of *Sphagnum cymbifolium* before adsorption

Fig 3.3b
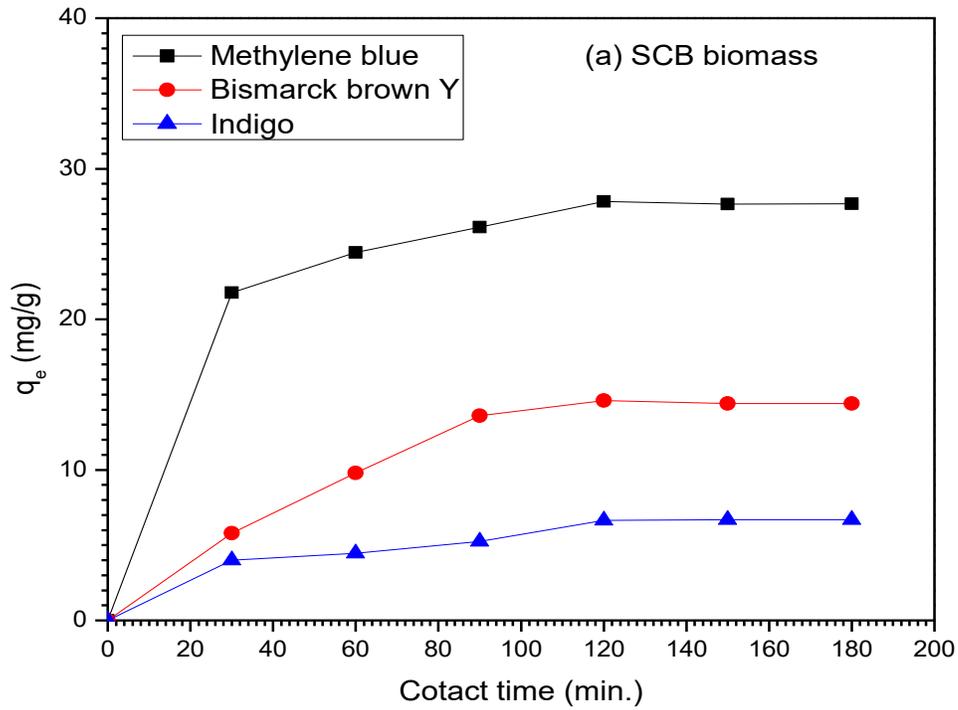FTIR spectrum of *Sphagnum cymbifolium* with indigo dye after adsorption

Fig 3.4
Effect of contact time on the adsorption capacity of *Sphagnum cymbifolium*
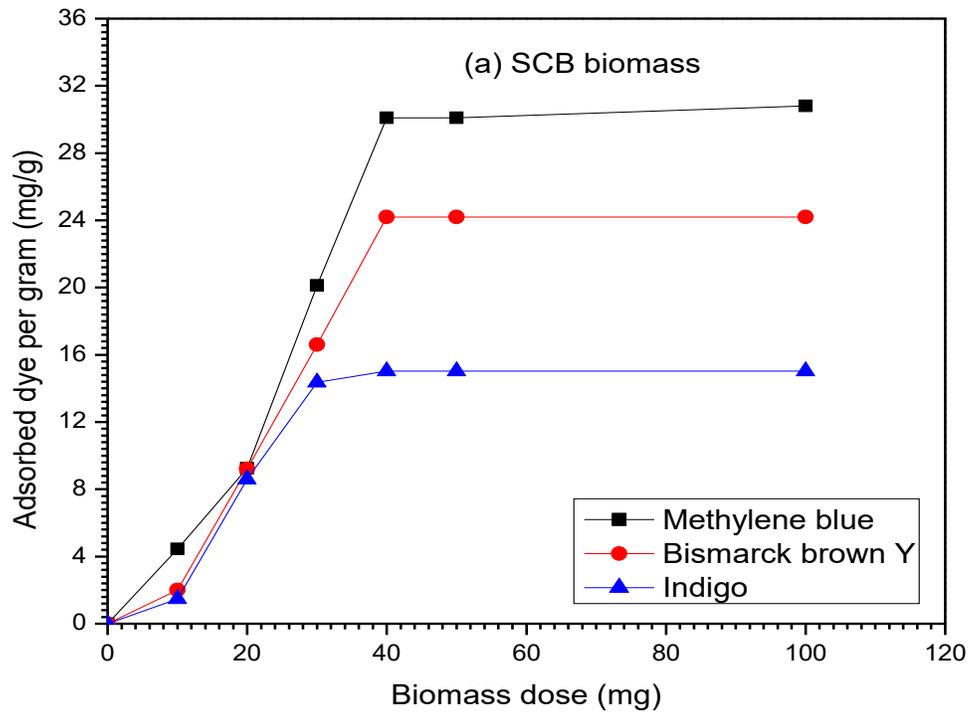
Fig 3.5
Effect of biomass dose on the adsorption capacity of *Sphagnum cymbifolium*
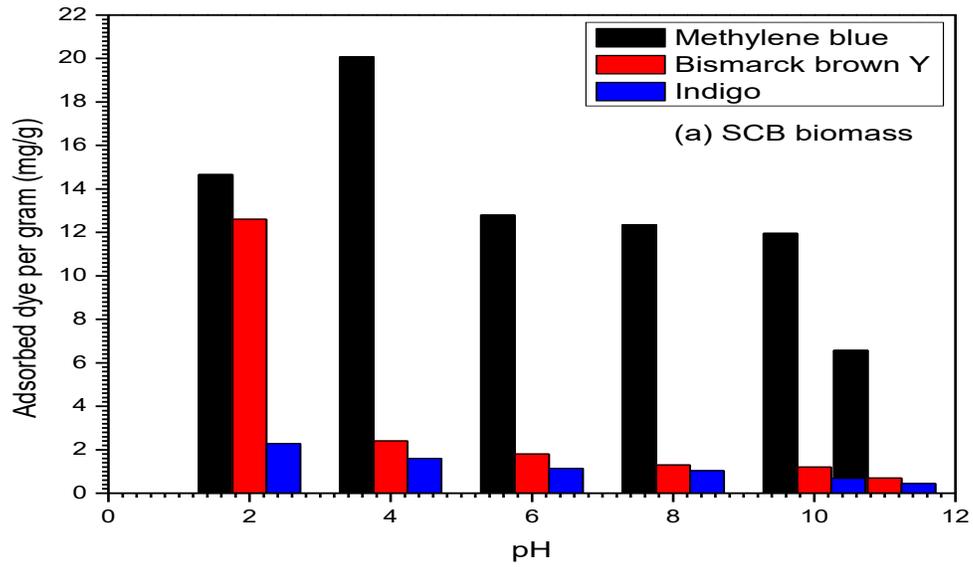
Fig 3.6
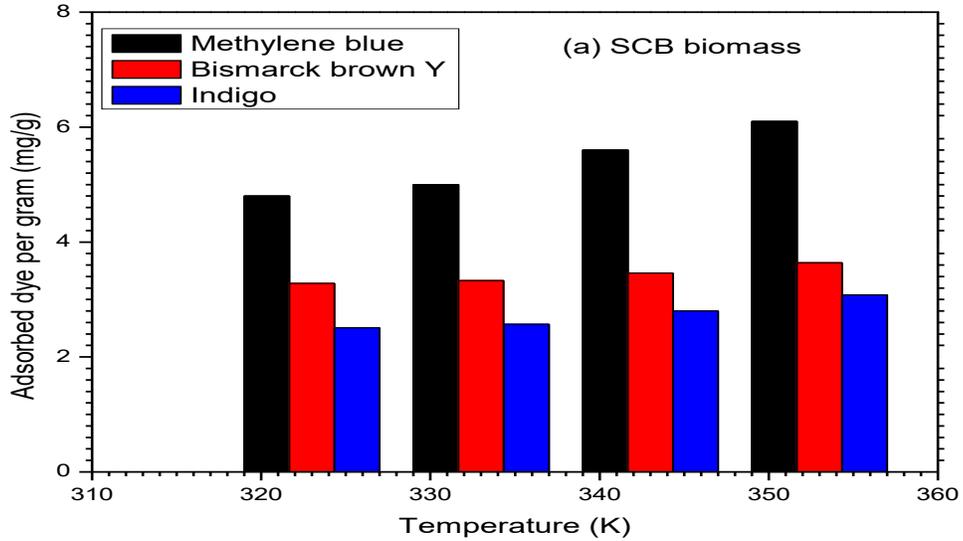Effect of pH on the adsorption capacity of *Sphagnum cymbifolium*

Fig 3.7
Effect of temperature on the adsorption capacity of *Sphagnum cymbifolium*

4.0 Discussion

The SEM micrographs of *Sphagnum cymbifolium* showed the presence of unevenly dispersed granules or cavities on the surface of the biomass. These cavities on the rough surface of the biomass provide sites where molecules of the dyes could be trapped thus giving rise to adsorption.

The FTIR Spectrum of *Sphagnum cymbifolium* before adsorption shown in figure 3.1(a) revealed 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 and benzene at < 1000nm.

Similar findings were reported by (chiou and HIP, 2004) for the characterization of the biomass *Padina parvonica..* The FTIR spectra of *Sphagnum cymbifolium* after adsorption were used to ascertain the functional groups which were responsible for the adsorption. Figures 3.1(b), 3.2(b) and 3.3(b) show the FTIR spectra of *Sphagnum cymbifolium* with methylene blue dye, Bismarck Brown Y dye, and Indigo dye respectively after adsorption.

The spectra showed prominent peaks at 3406nm (-OH, -NH), 1642nm and 1429nm which are characteristic of the –CO functional group which strongly predicts the presence of carboxylic acid group in the biomass with the adsorbed dye molecule. After the adsorption, there were some bond displacement of the original peaks indicating the functional groups that were responsible for the adsorption reactions. The displacements occurred at 2925.71nm and 2363.57nm which corresponds to these functional groups, C-H, C≡N, and C≡C.

Furthermore, although the intensity of the peaks greatly decreased after the adsorption, the functional groups on the biomass did not disappear totally during the biomass characterization after adsorption process. This indicates that the interaction of the dye molecules with the *Sphagnum cymbifolium* was merely a physical process.

In addition, the result of the finding indicated that the effect of changing the concentration of NaCl, and CaCl$_2$ from 0.10M to 0.20M on the adsorption process decreased the value of q$_e$ and the percentage removal efficiency of the biomass.

This could be attributed to the competitive effect between the dye ions and the cations from salt for sites available for the sorption process. Another reason could be that as the ionic strength increased, the activity (effective concentration) of the dyes and the active sites decreased, so the adsorptive capacity of the dye on to 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 etal, 2005), (Waranu Satigul etal, 2003). It was also observed that the percentage removal efficiency of the biomass 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 remained 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 concentrations, there is a very fast superficial adsorption on to 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 the q$_e$ value. Also, the results of the bio adsorption per gram adsorbent at different contact times showed a two staged kinetic behavior. A rapid initial adsorption over thirty minutes, followed by a longer period of much slower uptake as shown in figure 3.4. At the beginning of adsorption, the value of q$_e$ increased quickly, then 150 minutes later, the change became slow. Here, the reaction is assumed to have reached equilibrium.

On the other hand, increasing the temperature between 323-353K showed a corresponding increase in the value of q$_e$. This result implies that the adsorption here is endothermic in nature. This could be attributed to an increase in the pore size in the dye molecules (with increasing temperature), and an increase in the net negative charge existing on the biomass surface which promote electrostatic attraction of the positively charged dye molecules.

A similar situation has been reported by other researchers (Titilayo etal, 2008). According to the variation of temperature, the authors reasoned that the increase in temperature may partly point to the fact that the adsorbate adsorption was more chemical than physical, and the adsorption was endothermic in nature.

The rate of adsorption was also found to be dependent on pH. A pH of 2 favored a maximum

adsorption for Bismarck Brown Y dye and indigo dye respectively, while a pH of 4 favored the maximum adsorption of methylene blue dye. Several reasons may be activated 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 leaf particles may be negatively charged which engages the positively charged dye cations through electrostatic forces of attraction. Similar situations were reported by other researchers (Vennapusa etal, 2008).

4.1   Conclusion

From the experimental result, *Sphagnum cymbifolium* can be used as an adsorbent for the removal or treatment of dye waste waters especially the ones containing methylene blue dye, Bismarck Brown Y dye and indigo dye respectively. The rate of adsorption of these dyes, unto *Sphagnum cymbifolium* was found to be dependent on pH, contact time, dye concentration, biomass dose, biomass particle size, temperature, and presence of dissolved salts.

4.2   Acknowledgement

4.3 References

Crini ,G .,(2006) Non conventional low cost adsorbent   for dye removal. Journal of bio resour   Technol. 79 ,P. 1061-1085

Robinson , T., Mcmullan ,, G; Marchant .,R ;Nigam ,P .,(2001) Remediation of dyes in texile effluent; a critical review on current treatment technologies with proposed alternatives. Journal of bioresour Technol. 77, p. 247-255.

Vennapusa, R., etal (2008) surface energelics to access microbial adhesion on to fludized chromatography adsorbent. Journal of engineering life sciences 8, p.530.

Wang, S., etal (2004) the physical and surface chemical characteristics of activated carbon and adsorption of methylene blue from waste water. Journal of colloid inter. Sci. 284, p.440-446.

Khattri, S., Singh M., (1999) Adsorption of basic dyes from aqueous solution by natural adsorbent Indian journal of chem. Technol 6(2), P.2269-282.

Ghosh, D., Bhattacharya (2002) Adsorption of methylene blue on kaolinite. Journal of app. Clay sci. 20, P.295-300.

Amandurai, G., Janig, R., Lee, D; (2002) use of cellulose based waste waters for adsorption of dyes from aqueous solution. Journal of hazard matter, 392, P.263-274.

Akzu, Z., (2005) Application of bio-sorption for the removal of organic pollutants a review Journal of process Biochem. 40, P.887-1026.

Robinson, T., Chandran, B., Nigam, P; (200) Removal   of dyes from a synthetic dye effluent by bio-   sorption on apple penance and wheat straw.   Journal of water Res 36, P.2824-2830.

Hjorth, R., (1997) Expanded bed adsorption in industrial   bio-processing-   Recent development. Journal of trends in biotechnology 15(6), P.230.

Waranusatigul, P., etal (2003) Kinetics of basic dye (methylene) bio-sorption by giant duck weed (*Spirodela polyrrhiza*). Journal of environmental pollution, P.383-392.

Kumar, K., Savanesan, S, Ramanurhi, V; (2005) Adsorption of malachite green on to *Pitiphora sp*. A fresh water algae/Equilibrium and kinetic modelling. Journal of process Biochem 40, 2865-2872.

Vadivehan, V., Vanasat, K; (2005) Equilibrium kinetics, Mechanism and process design for

the sorption of methylene blue on to rice husk. Journal of colloid interf.sci. 286, 90-100.

Titilayo, B., Bagmibade, A., Nkiko, M., Ahmed, S., Ikotun, A., (2008) Kinetics and thermodynamic studies of adsorption of Malachite green on to unmodified and EDTA modified groundnut husk. Journal of Hazardous materials 15, 210-228.

Chiou, W., Mckay, G., (2004) Adsorption of anionic dyes in acid solution using chemically cross-linked beads. Journal of dyes and pigments 60, 69-84.