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Abstract- Objective: One of the major objectives of this research work is to expand the field of application of natural biomass for the treatment of dye based industrial effluents. It is also aimed at studying the effect contact time, initial dye concentration, pH, temperature, dissolved salts on the bio-sorption properties of sphagnum cymbifolium(moss) on to methylene blue dye by the batch process.

Methods: The biomass was characterized by scanning electron microscopy (SEM) in order to examine the surface morphology of the biomass. The screened biomass samples were characterized at 1000 x magnification, 500 x magnification and 200 x magnification for their surface morphologies, This was done using a scanning electron microscope (FEI – inspect/ OXFORD INSTRUMENTS – X- MAX), which was equipped with an energy dispersive X- ray (EDAX) spectrophotometer employed for elemental composition analysis. It was equally characterized with Fourier transformed infrared spectroscopy (FTIR) spectrophotometer (Perkin – Elmer, England) in the wavelength range of 350 – 4000nm.

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Results: Results for the biomass surface morphology obtained through the scanning electron microscopy (SEM) showed the presence of pores. These pores represented sites where dye molecules could be trapped in the course of the adsorption. The results from the Fourier Transformed spectroscopy (FTIR) after adsorption show that C-H, C≡H, and C≡C, functional groups were responsible for the adsorption. The adsorption of methylene blue dye was found to be dependent on contact time, biomass dose, pH, temperature and effects of dissolved salts.

Conclusion: From the results obtained, it is clearly seen that methylene blue can absorb onto *sphagnum cymbifolium*(moss). It was equally discovered that all these variables contact time, biomass dose, pH, temperature and the presence of dissolved salts affected the rate of adsorption of methylene blue onto *sphagnum cymbifolium*(moss). In each of the analyses, three different experiments were performed, and the mean values respected with their standard deviations.

Keywords: bio-sorption, sphagnum cymbifolium, batch process, sem.

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I. Introduction

Bio-sorption can be defined as the abstraction of organic and in-organic species. This may include dyes, metals, and odor causing substances using live or dead biomass or their derivatives. The above can be achieved either through the batch or fixed bed technique.

But, this research work is aimed at achieving it through the batch process.

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 a magnetic sterner.

Synthetic dyes which include a wide range of aromatic water soluble dispersible organic colorants are used extensively in textile industries. Effluents containing synthetic dyes not only produce visual pollution, but also are hazardous to ecological systems and public health.

Conventional treatments of dye containing effluents are either in effective, costly, complicated or have sludge disposal problems [1].

Robinson *etal* [2] reviewed the current treatment technologies including bio- sorption with proposed alternatives for the removal of dyes in textile effluents.

Due to the increasing stringent restriction on pollutant contents of industrial effluent. Due to the increasing stringent restriction on pollutant contents of industrial effluents, it becomes very important to remove dyes from waste water before they are discharged the environment many low cost adsorbents including natural materials from industries and agriculture have been proposed by several workers [3, 4].

Some researchers reported the use of plant leaf biomass to adsorb heavy metals from solutions [5-7]. Limited work was reported on the bio-sorption of cationic azo dyes and other reactive dyes on fresh water algae [8, 9].

This work is carried out with the view of expanding the field of application of natural biomass for the treatment of dye waste waters, and also determine the adsorption capacity of *sphagnum cymbifolium* (moss) on to methylene blue dye. Since such an indepth study has not been done on this biomass, the results obtained from the work will add to the expansion of knowledge in this area.

II. Materials and Methods

The methylene blue dye used in these investigations were obtained from qualikem laboratory, owerri Nigeria. Other necessary laboratory, Owerri Nigeria. Other necessary laboratory chemicals used were equally obtained from this laboratory.

The sphagnum cymbifolium (moss) used was obtained from ikorodu area in Lagos, Nigeria which is located within the following coordinates 6.6194°N and 3.5105°E. This 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/005/16.

The biomass was washed severally with distilled water to remove any dirt from it. The washed biomass was air dried for ten days until a 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 micro sized sieves and stored in air tight containers ready for adsorption.

The methods and techniques employed in these determinations are the standard methods which have been used by other researchers [10, 11].

III. 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 morphology. This was done using scanning electron microscopy (SEM) (FEI- Inspect oxford instrument-x-max) which was equipped with an energy dispersive x-ray (EDAX) spectrophotometer 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 (FTIR) spectrophotometer (Perkin- Elmer, England) in the wave length range of 350-4000nm using KBr powder and fluk a library for data interpretation.

a) *Effect of Contact Time*

Experiments were carried out by mixing 40mg of the biomass in a dye solution of 90mg/L. Agitations were made using a shaker at the range of 30-180 minutes at 250rpm. After the shaking, the sample was taken and centrifuged. The left out solution was analyzed for dye absorbance at 600nm in au.v spectrophotometer. These tests were carried out in triplicates and mean values with their standard deviations reported.

b) *Effect of biomass dose*

Experiments were carried out by mixing biomass of different doses (10-100mg) with a dye solution of concentration 90mg/L. Agitations were made for three hours in a shaker at 250rpm. The left out solution was centrifuged and subsequently analyzed in au.v spectrophotometer at 600nm.

c) *Effect of ph*

Experiments were carried out by mixing 40mg of the biomass in a 90mg/L dye solution at different pH range (2-11). After three hours of agitation in a shaker at 250rpm, the samples were centrifuged. The left out supernatant solution was analyzed in au.v spectrophotometer for dye absorbance at 600nm.

d) *Effect of dissolved calcium chloride*

Experiments were carried out by mixing 40mg of the biomass in a 90mg/L dye solution with varying amount of dissolved calcium chloride (0.10-0.20M). After three hours of agitation in a shaker at 250rpm, the samples were centrifuged and the left out supernatant solution analyzed for dye absorbance in au.v spectrophotometer at 600nm.

e) *Effect of temperature*

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 agitation in the hot plate at 250rpm, the samples were centrifuged, and the super natant solution analyzed for dye absorbance in au.v spectrophotometer at 600nm.

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

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

Where V= volume of samples 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.

IV. Results and Discussion

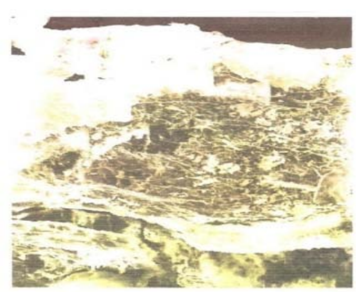

Fig. 1: SEM morphology of Sphagnum cymbifolium (moss) (X250)

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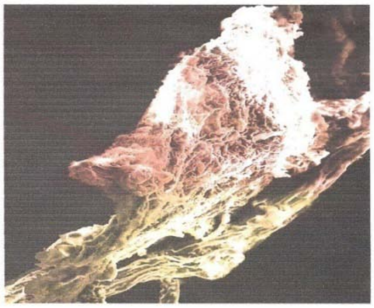

Fig. 2: SEM morphology of Sphagnum cymbifolium (moss) (X500)

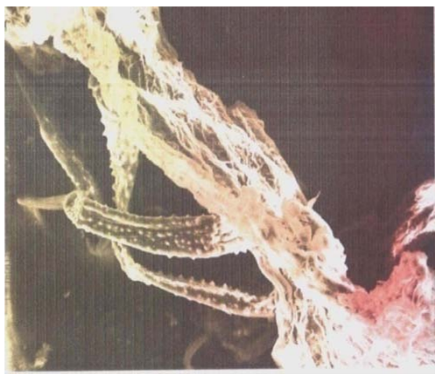

Fig. 3: SEM morphology of Sphagnum cymbifolium (moss) (X1000)

The SEM micrographs of Sphagnum cymbifolium (moss) shown in figure 1,2, and 3 above reveals 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. Similar cavities on biomass surface have been indicated by other researchers [12].

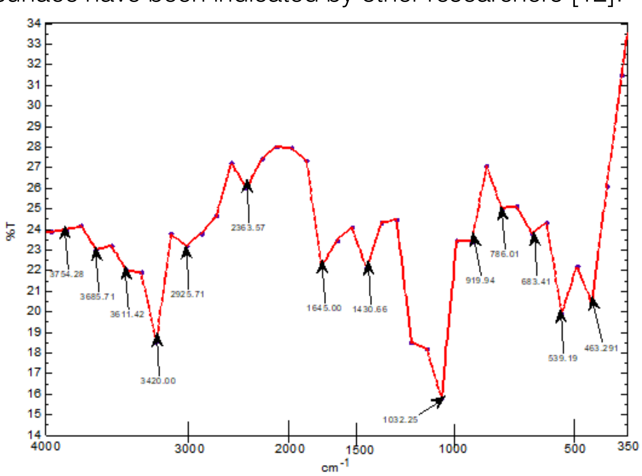

Fig. 4: FTIR Spectrum of Sphagnum cymbifolium (moss) before adsorption

The FTIR spectrum of Sphagnum cymbifolium (moss) before adsorption shown in figure 4 revealed the presence of five major functional groups. The functional groups include O-H or N-H at 3420nm, C-H at 2925.74nm, 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 PadinaParvonica.

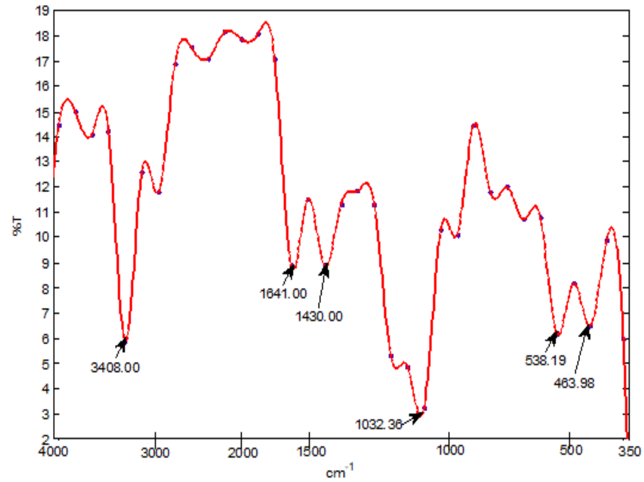

Fig. 5: FTIR Spectrum of Sphagnum cymbifolium (moss) after adsorption.

The FTIR spectrum of Sphagnum cymbifolium (moss) after adsorption as shown in figure 5 above was used to ascertain the functional groups that were responsible for the adsorption reaction.

The spectrum showed prominent peaks at 3406nm (-OH, -NH), 1642nm and 1429nm which are characteristic of the –CO functional group which strongly predict 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 correspond 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 the adsorption. This indicates that the interaction of the dye molecules with the *sphagnum cymbifolium* was merely a physical process.

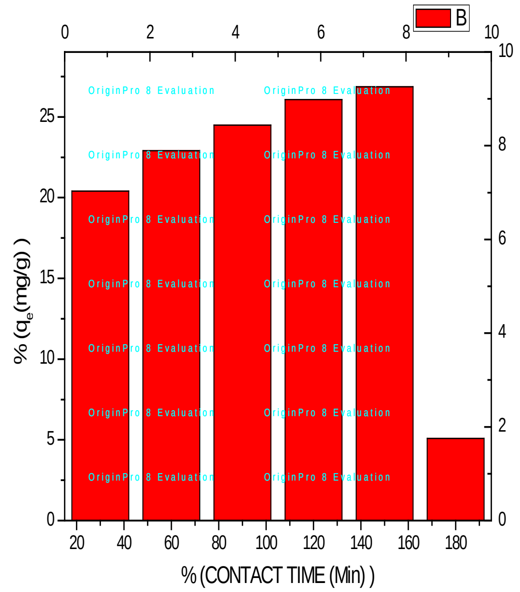

Fig. 6: Effect of contact time on adsorption.

As could be seen from figure 6, a two stage kinetic behavior is observed. A rapid initial adsorption over thirty minutes, followed by a longer period of much slower uptake as could be seen from figure 6 above. At the beginning of the 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.

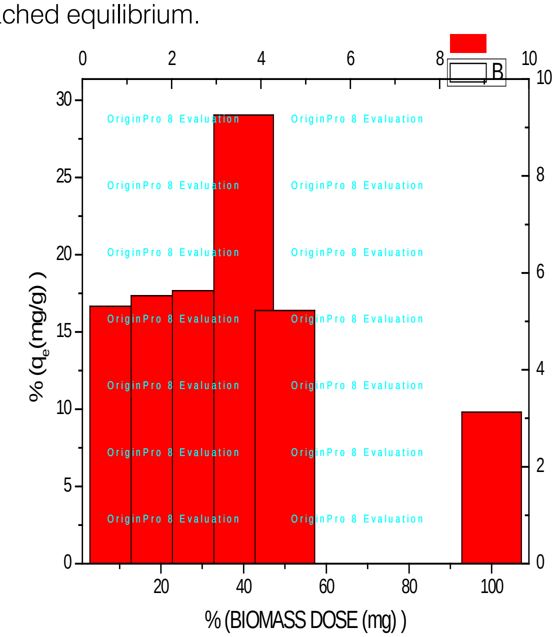

Fig. 7: Effect of biomass dose on adsorption

It was observed that the percentage removal efficiency of the biomass increased significantly when the biomass increased significantly when the adsorbent dose increased from (10-40mg). The value of qe 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 concentration, there is a fast superficial adsorption onto the adsorbent surface than when the adsorbent dose is lower. Thus, with increasing the adsorbent dose, the amount of dye adsorbed per unit mass of the adsorbent is reduced. A similar trend was previously reported by other researchers [13, 14].

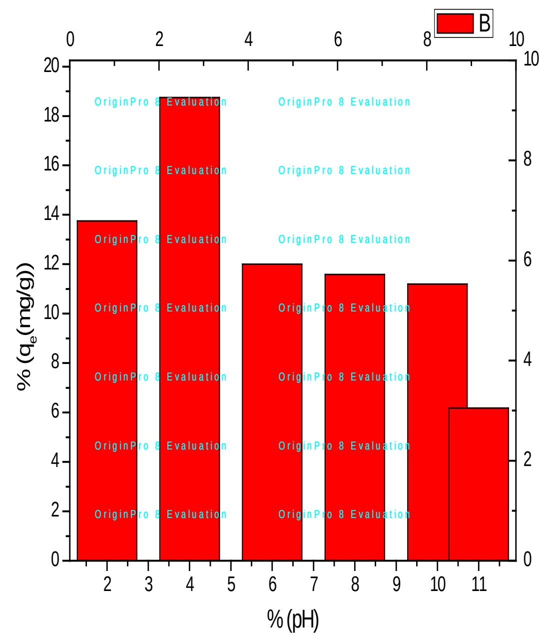

Fig. 8: Effect of pH on adsorption.

The rate of adsorption was found to be dependent on pH. A pH of 4 favored the maximum adsorption of the dye onto the biomass as could be seen in figure 8. 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 solution. At very low pH values, the surface of the adsorbent would be surrounded by hydrogen ions which compete with dye ions binding sites of the sorbent. At high pH values, the surface of the leaf particles may be negatively charged which engaged the positively charged dye cations through electrostatic forces of attraction. Similar situation were reported by other researchers. (vennapusaetal 2008).

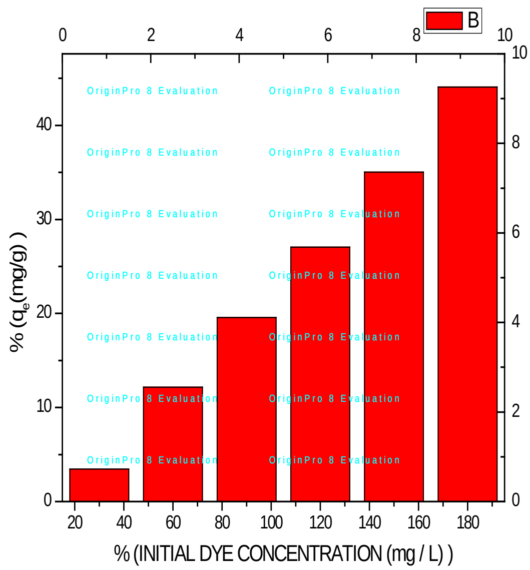

Fig. 9: Effect of initial dye concentration

As could be seen from the figure 9, the equilibrium uptake increased with the increase of initial dye concentration at the range of experimental considerations. This is as a result of the increase in the driving force from the concentration gradient. In the same conditions, if the concentration of the dye in solution was bigger, the active sites of the biomass will be surrounded by much more dye ions. The process of adsorption would carry out more sufficiently. So, the values of q_e increased with the increasing of initial dye concentrations. Other studies have revealed the same pattern of result about initial dye concentration. (vennapusaetal 2008).

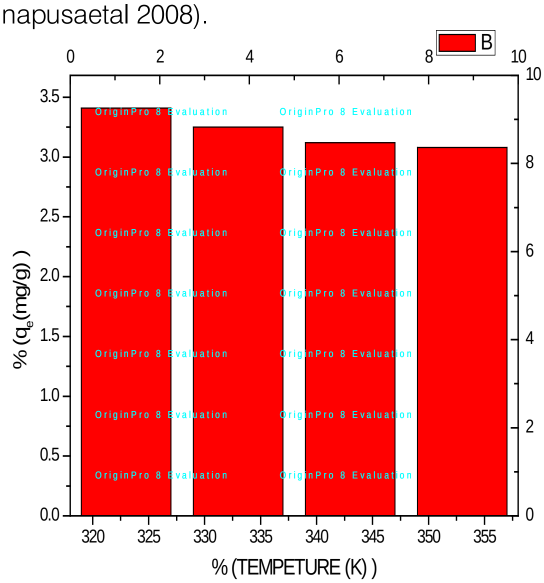

Fig. 10: Effect of temperature

Figure 10 shows the effect of temperature on adsorption. It was observed that the value of q_e decreased with increase temperature. This could suggest that the adsorption process may be a physical process. A similar trend was observed by other researchers.

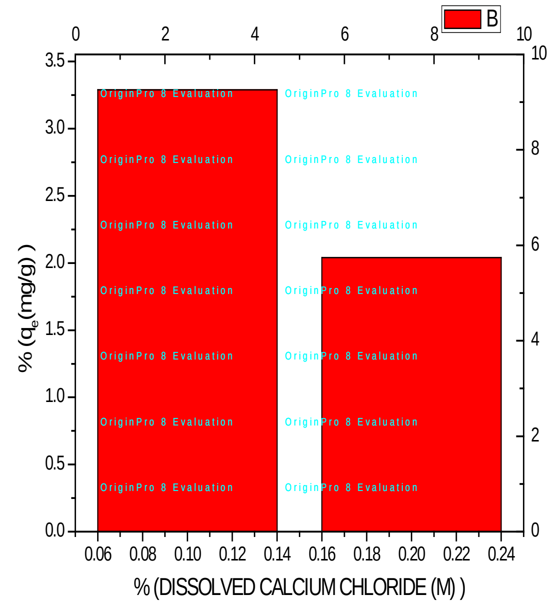

Fig. 11: Effect of dissolved salt on adsorption.

Figure 11 shows the effect of dissolved calcium chloride on q_e. The waste water containing dye has commonly higher salt concentration. The effects of ionic strength are of some importance in the study of dye adsorption onto biomass. It was seen that the increase in salt concentration resulted in the decrease of the values of q_e, and the percentage removal efficiency. This trend indicated that the adsorbing efficiency decreased when calcium chloride concentration increased in the dye solutions. This could be attributed to the competitive effect between the ions and the cations from the salts for sites available for the salt increased from 0.10m to 0.20m, the q_e values decreased to lower values.

V. Conclusions

From the experimental results, *sphagnum cymbifolium* (moss) could act as a good bio-sorbent for the removal of methylene blue dye in aqueous solutions. It was equally observed that lower pH value favored the adsorption of methylene blue dye onto the biomass. The values of q_e were found to be dependent on the solution pH, biomass dose, contact time, salt concentration and initial dye concentration.

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