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Removal of Methylene Blue from Aqueous Solution by Dehydrated Maize Tassels

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Abstract

Maize tassels are agricultural wastes that are abundant. They were used to prepare Dehydrated Maize Tassels for methylene blue adsorption. Dehydrated Maize Tassels were produced by mixing maize tassels and concentrated sulphuric acid for 24 hours. The adsorption studies of methylene blue from aqueous solution using maize tassels was studied in the range of 1–5 mg dm^{-3} initial methylene blue concentration, at different temperatures, different adsorbent dosages and at varied contact times. The adsorption was determined spectrophotometrically at 660nm. Adsorption increased with increase in adsorbate dosage. Increase in initial methylene blue concentration resulted in increased adsorption. Maximum adsorption occurred at pH of 6.8, temperature of 25°C, and contact time of 20 minutes. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption equilibrium. The data fitted well into the Langmuir isotherm. The maximum adsorption capacity obtained was 99.84%.

Keywords: Dehydrated maize tassels, methylene blue, adsorption, Langmuir isotherm.

Introduction

Recently there has been a gradual interest in dyes and dye removal or treatment[1]. Dyes and pigments are highly visible material. Colour is not only unpleasant in a water body but it interferes with light penetration and reduces photosynthetic action[2]. Methylene blue (MB), a cationic dye, is not regarded as acutely toxic, but it has various harmful effects. MB is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns, if inhaled it can cause rapid problems in breathing while ingestion can cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia. Methylene blue is a compound consisting of dark green crystals or crystalline powder, having a bronze-like luster. An alternative approach to addressing the problem of colour in textile dyeing effluent has involved the development of effluent treatment methods to remove colour. Several methods have been used for the removal of dyes from the aquatic environment, including physical, chemical, and biological processes. These methods inevitably add to the cost of the overall process and some present the complication associated with the possible toxicity of degradation products[3]. Among these methods, adsorption is a widely used method for dye removal from wastewaters[4]. Activated carbon has ability to remove a large variety of compounds from contaminated water, but the disadvantage is that it's very expensive. There is need to develop low cost adsorbents, that are renewable and readily available. Maize tassel is the male inflorescence of the maize plant that forms at the top of the stem. It is discarded by local communities in Zimbabwe in large quantities with the rest of the plant once the cobs have been harvested. The obvious advantage of using maize tassels is the lower costs involved as well as the relative abundance of these agricultural wastes and by-products in nature. There are various conventional methods of removing dyes including chemical precipitation, coagulation, membrane filtration, electrolysis and oxidation[5]. However these methods are not economical and are often unable to adequately reduce contaminants concentrations to desired levels. In contrast, an adsorption technique is by far the most versatile and widely used[5]. Several studies on the removal of methylene blue on various types of these non-conventional materials have been reported. Rajeshwarisivaraj and co-workers[6] have studied the adsorption on a cassava peel, and Janos and co-workers on fly ash[7]. Garg and co-workers[8] have used Indian rosewood sawdust, Kadirvelu and co-workers[9] used various agricultural wastes such as cotton hulls, coconut tree sawdust, sago waste, maize cobs and banana piths, Chaudhary and coworkers[10] used a chromium waste sludge[11]. The objective of this study is to investigate the ability of dehyhydrated maize tassel in the removal of methylene blue. A survey of literature reveals that maize tassels have not been used for removal of methylene blue from aqueous solution.

Material and Methods

Preparation of Dehydrated Maize Tassels: The maize tassels were collected from a local Bindura farm. The maize tassels were first cut into 10cm pieces and washed to remove dust particles. They are then dried overnight at 50^0C, ground and sieved to retain 20-40 mesh fractions. The Dehydrated Maize Tassels (DMTs) were prepared by mixing the maize tassels and concentrated sulphuric acid in the ratio 1:2. The mixture was manually stirred at the beginning to contact maize tassels well with the acid. This was left for 24hrs to ensure complete dehydration. At the end of the dehydration process, sufficient distilled water was added to the mixture before filtering through Whatmann filter paper by using a water pump. The process was repeated until the final pH of the filtrate was about 2.5. The dehydrated material were rinsed with distilled water and dried for 24hours in an oven at 80^0C. The adsorbent was then stored in a closed bottle which was placed in a desiccator to prevent moisture uptake. The adsorbent was later used in adsorption studies.

Preparation of Stock Solution: Stock solution was prepared by dissolving 1.178g of methylene blue hydrochloride three hydrate of spectroscopic grade with M_r of 373.90 (MERCK Laboratory Supplies) in 1 litre of de-ionized water. The test solutions were prepared by diluting the stock solutions to the desired concentrations. The concentrations of solutions varied in the range 1-5mg/L.

Adsorption Studies: This method involves agitating Erlenmeyer flasks of 1L on a mechanical shaker at 150rpm. These flasks contain different amounts of DMT ranging from 0.5-2g and 500mls of MB solutions at the desired concentration. Temperature and pH were kept constant. Samples of $10cm^3$ were taken from the mixture during stirring at predetermined time intervals for determining the residual concentration in the medium.

Analysis: The concentration of residual colour of MB in the adsorption media was determined spectrophotometrically using Evolution 300 UV/Vis Spectrophotometer (Thermo Fischer Scientific, Waltman, MA, USA). The absorbance of the colour was read at 660nm.

Determination of Parameters: Effect of initial MB concentration: The initial MB concentration was varied from 1mg/L; 2mg/L; 2.5mg/L and 5mg/L at room temperature and constant pH of 2.5. Initial MB concentration provides an important driving force to overcome all mass transfer resistance.

Effect of Contact Time: Adsorption was measured at contact times of 1; 5; 10; 15; 20; 25; and 30minutes. All work was conducted at room temperature. The pH was kept constant at 2.5. Initial MB concentration was 2.5mg/L and adsorbent mass was 1g.

Determination of Equilibrium Parameters: For isotherm studies, a series of flasks containing 100ml MB solution of concentration 2.5mg/L were prepared. 0,2g DMT was added to each flask and then the mixtures were agitated at varying temperatures of 25; 35; and 45^0C for 72hours. The pH of the solution was kept constant at 2.5.

Effect of adsorbent Dosage: The adsorbent masses that were used were 0.5g; 1,0g; 1.5g; and 2g whilst holding the MB concentration constant at 2,5mg/L. Temperature and pH were also kept constant with temperature at room temperature and pH at 2.5.

Effect of pH on MB Adsorption: The pH was adjusted in the range 1.5-12 by adding 0.5M H_2SO_4 or 0.5M NaOH. Initial MB concentration was kept constant at 2.5mg/L. The analysis was performed at room temperature.

Characterization of DMT: The powder DMT were placed in an oven and dried at 80^0C for 1 hour to drive off moisture. The dry powder was placed on the FT-IR machine (Thermo Scientific NICOLET 6700 FTIR) and the spectrum was run at wavelengths from 400-4000nm. The machine made use of Attenuated Total Reflectance (ATR) accessory which requires little to no sample preparation.

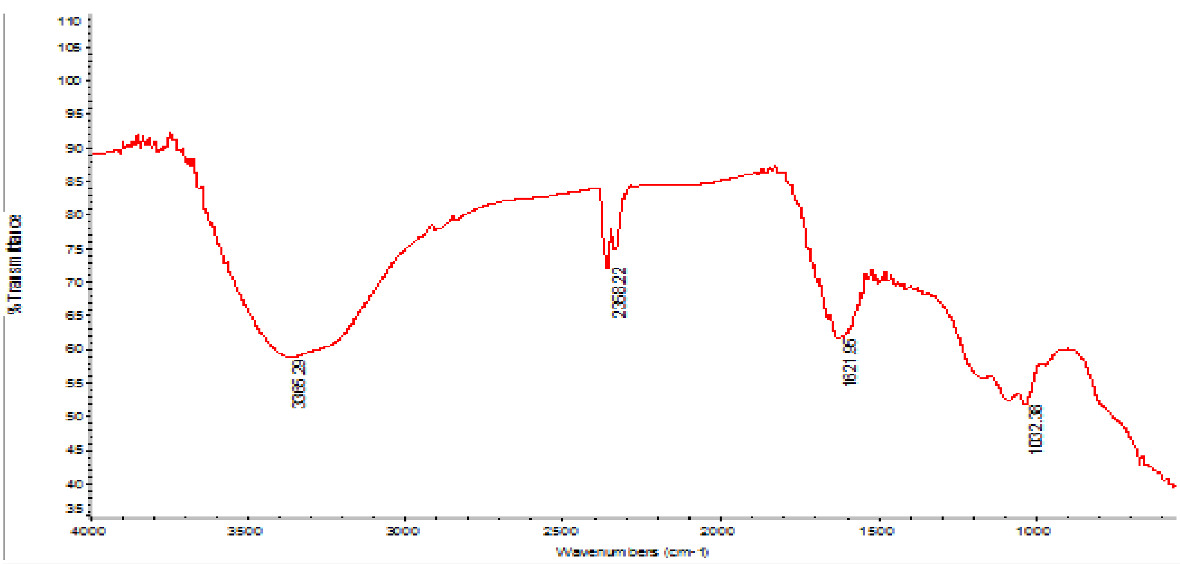

Figure-1
FT-IR Spectra for DMT

Results and Discussion

Table 1
FT-IR SPECTRA BANDS

BANDS	ASSIGNMENT
3365.29	O-H stretch vibration bonded[12,13,14]
1621.95	-C=O stretch with conjugate aromatic ring[15, 12]
1032.38	C-O or C-H stretching vibrations[12,16,17]

Ft-IR Characterization of Dehydrated Maize Tassels: The FTIR spectra of dehydrated maize tassels are shown in (figure-1). From this table I it can be suggested that methylene blue adsorption occurs via interaction between tertiary amines of methylene blue and the functional group of dehydrated maize tassels i.e. hydroxyl (-OH) group.

Adsorption Studies: The percentage removal of methylene blue dye was calculated using equation (1)[5]:

$$\%sorption = \left[(C_o - C_e)/C_o \right] \times 100 \frac{n}{r\left(n-r\right)} \quad (1)$$

Where C_o and C_e are the dye concentrations before and after adsorption

For adsorption isotherms, the adsorption capacity of methylene blue adsorbed per gram adsorbent (mg/g) was calculated using equation (2) below:

$$q = \left(C_o - C_e\right) V/W \quad (2)$$

Where C_0 and C_e is the initial and at any time (t) concentration (mg/L) of methylene blue dye in the solution, V the volume (L) of solution and W is the weight (g) of the adsorbent. For the equilibrium conditions in these equations, C_e (equilibrium concentration) and q_e (adsorbed methylene blue dye at equilibrium) must be written instead of C_t and q. C_e and q_e have the same unit with Ct and q, respectively[18].

Effect of pH: The effect of pH was investigated from pH 3 to pH 10 at initial MB concentration of 2.5mg/L and adsorbent dosage of 1.0g. The results obtained (figure-2) showed that pH 6-7 had highest adsorption further increase or decrease had a negative effect on dye adsorption[19]. pH increased due to increased electrostatic attraction between methylene blue cation and dehydrated maize tassels functional groups such as hydroxyl group (-OH). The solution pH is one of the most important factors that control the sorption of dyes on sorbent material. The initial pH influences the kinetics of sorption because the proton concentration decreases when the initial pH increases, and then the dye molecules have more chance to react with the active sites on the adsorbent surface because of a lower proton competition[20]. Since the dye solution is not buffered, a change in pH of the dye solution is expected during the sorption process. So both initial and equilibrium pH was measured. The final pH is higher than the initial pH for the bio sorption of methylene blue. This indicates competitive sorption of H^+ ions during the bio sorption of methylene blue[20]. The data fitted in the Langmuir isotherm (figure-3), with R^2 value of 0.9999.

Effect of Adsorbent Dosage: The effect of adsorbent dosage was investigated using adsorbent dosages which ranged from 0.5 to 2.0g. This was investigated at the optimum pH 2.5 and the results showed that as the adsorbent dosage increased the adsorption capacity also increased. The maximum adsorption capacity was observed for the 2g adsorbent dosage as shown by figure-4. According to a study by Dash and co-workers,[3] it is obvious as with increasing dosage amount the active sites for adsorption of methylene blue dye increases which results in an increase in removal efficiency. The sorption of methylene blue increased with an increase in sorbent dosage. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increased dose of the sorbent[14, 20, 21]. The adsorption data fitted well into the Langmuir isotherm with R^2 value of 0.9992 (figure-5).

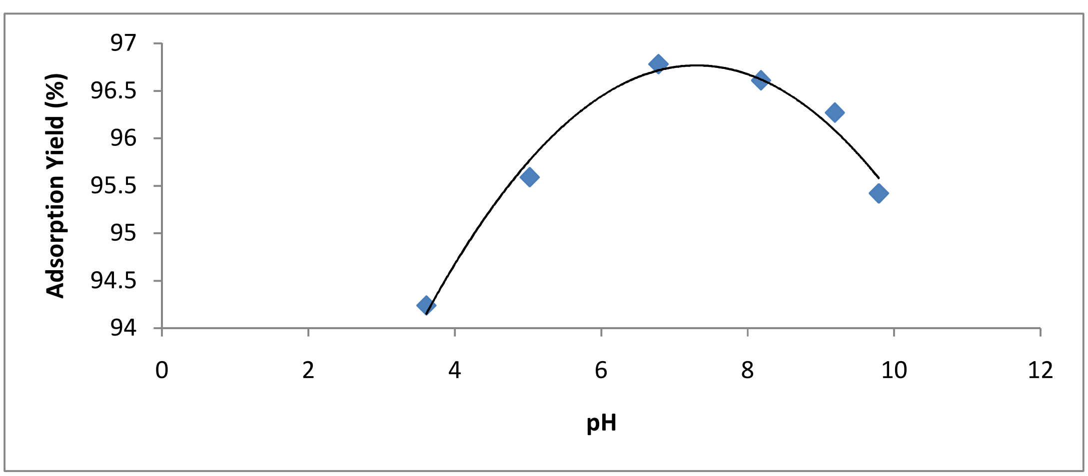

Figure-2
Plot for the effect of pH against adsorption yield

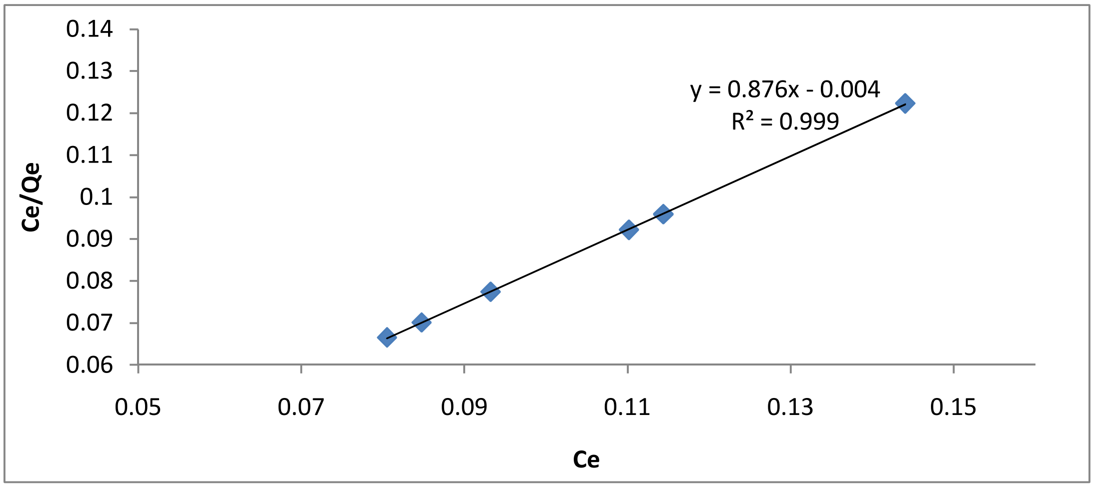

Figure-3
Langmuir adsorption isotherm for the effect of pH

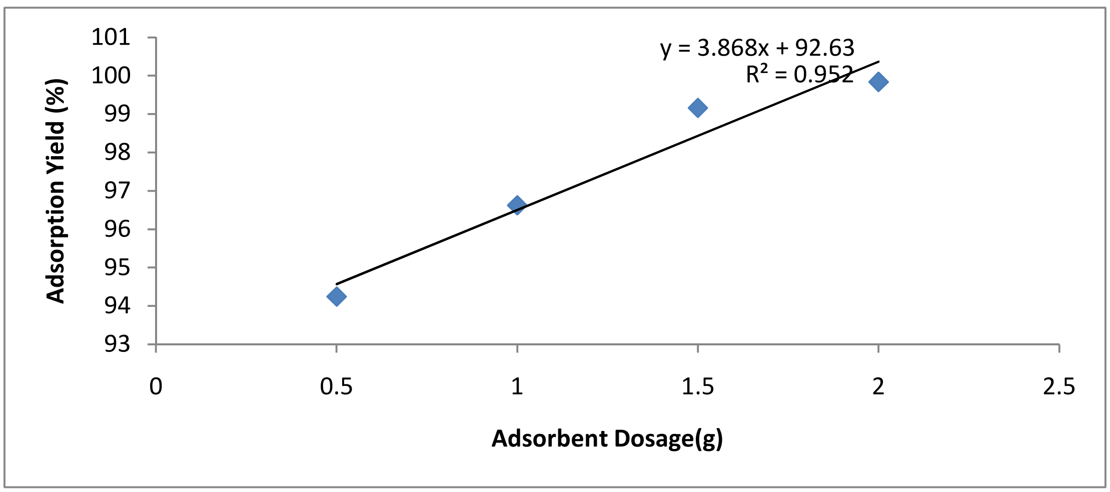

Figure-4
Plot of adsorbent dosage against adsorption yield

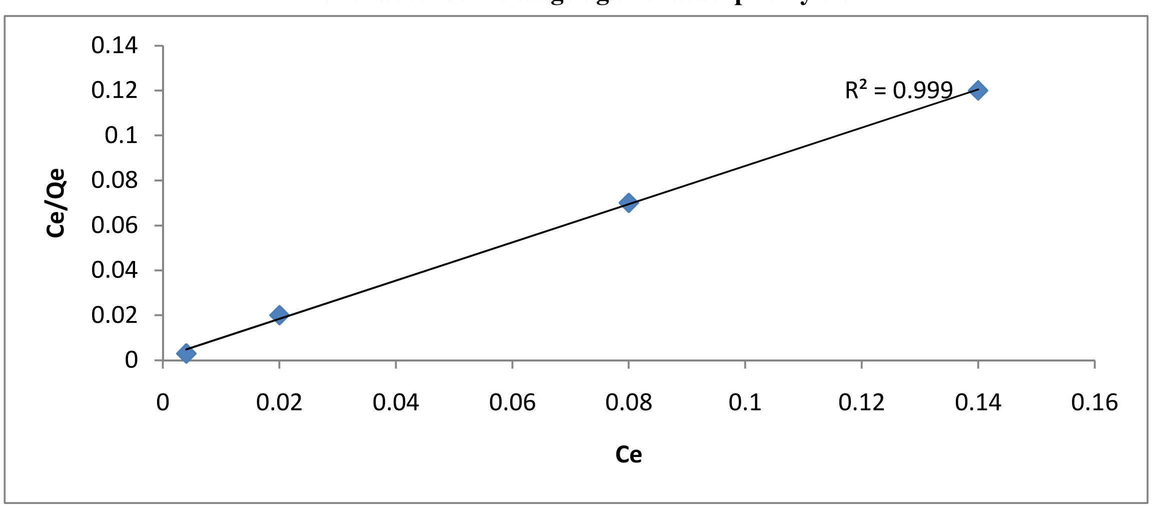

Figure-5
Langmuir adsorption isotherm for the effect of adsorbent dosage

Effect of Contact Time: This effect was investigated at pH 2.5 and an adsorbent dosage of 1.0g. The effect of contact time can be seen from figure-6. It is clear that the extent of adsorption is rapid in the initial stages due to the increased number of vacant sites on the adsorbent. It becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 20minutes from the start of adsorption process. The mechanism of adsorption process takes place in three steps, firstly, the molecules of dyes reach the boundary layer, then they diffuse to the surface of adsorbent and finally they diffuse to the porous structure of adsorbent[22]. It was observed that the rate of removal of MB dye increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material[5]. The adsorption data fitted well the Langmuir isotherm (R^2=0.9984), figure-7.

Effect of Temperature: Results indicate that the adsorption capacity of dehydrated maize tassels onto methylene blue increased with temperature (figure-8). According to Dash and Mishra[3], this may be a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface as temperature increase. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling large dyes to penetrate further. This agrees with what Shehata[22] and Abechi[21] found that increasing the temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer. It also increases the internal pores of the adsorbent particle. Increase of adsorption due to temperature implies that the adsorption process is endothermic in nature. The adsorption data fitted well into the Langmuir isotherm (figure-9) with R^2 value of 0.9997
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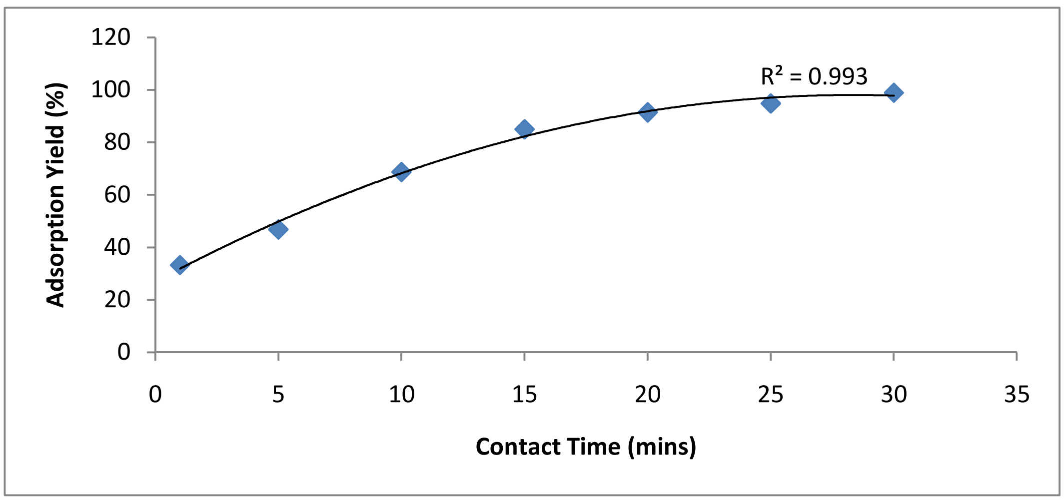

Figure-6
Graph for the effect of contact time against adsorption yield

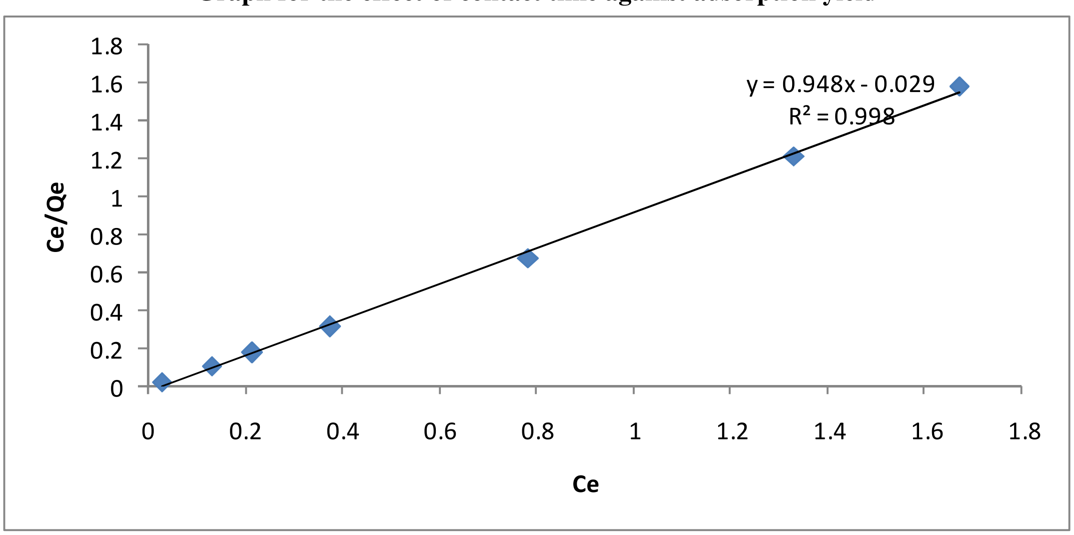

Figure-7
Langmuir adsorption isotherm for the effect of contact time

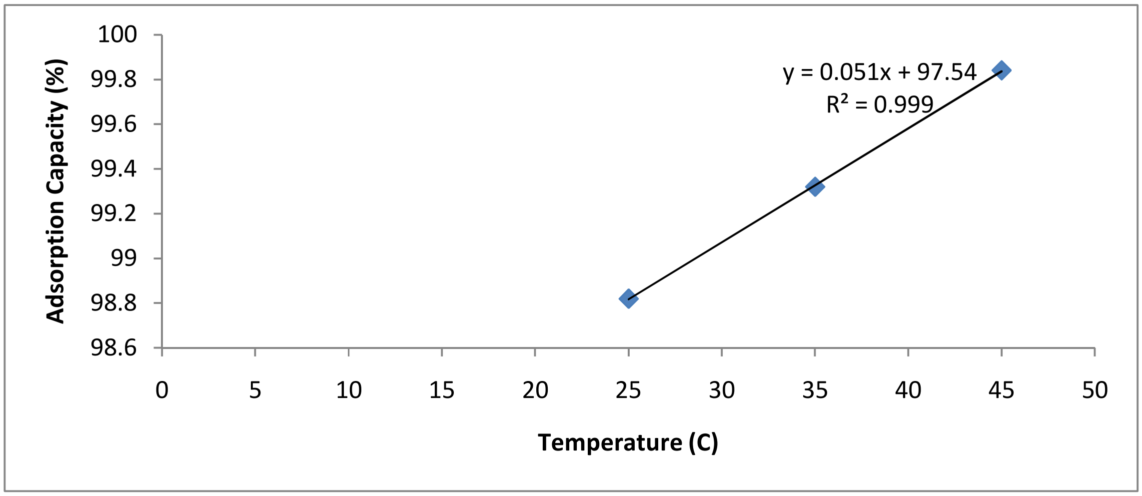

Figure-8
Plot of the effect of temperature against adsorption yield

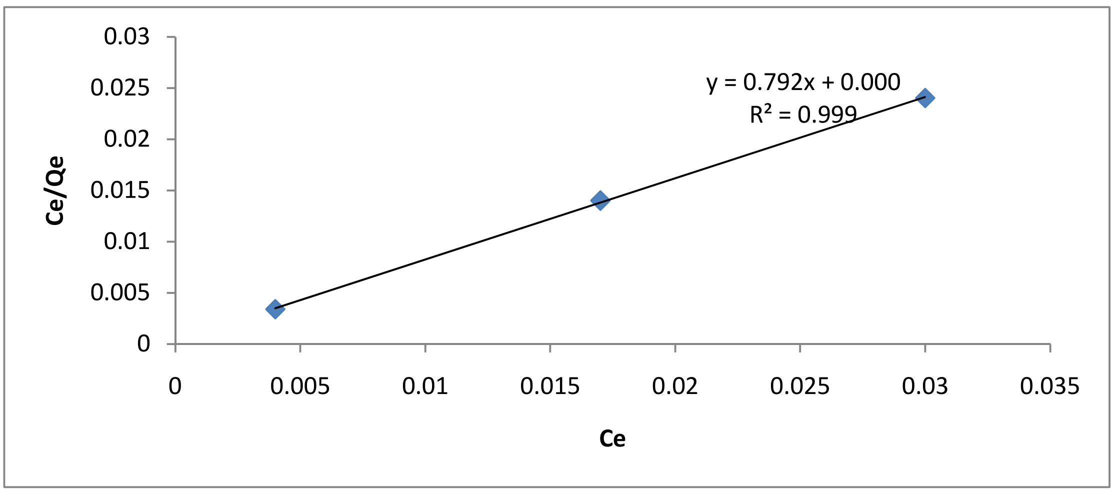

Figure-9
Langmuir adsorption isotherm for the effect of temperature

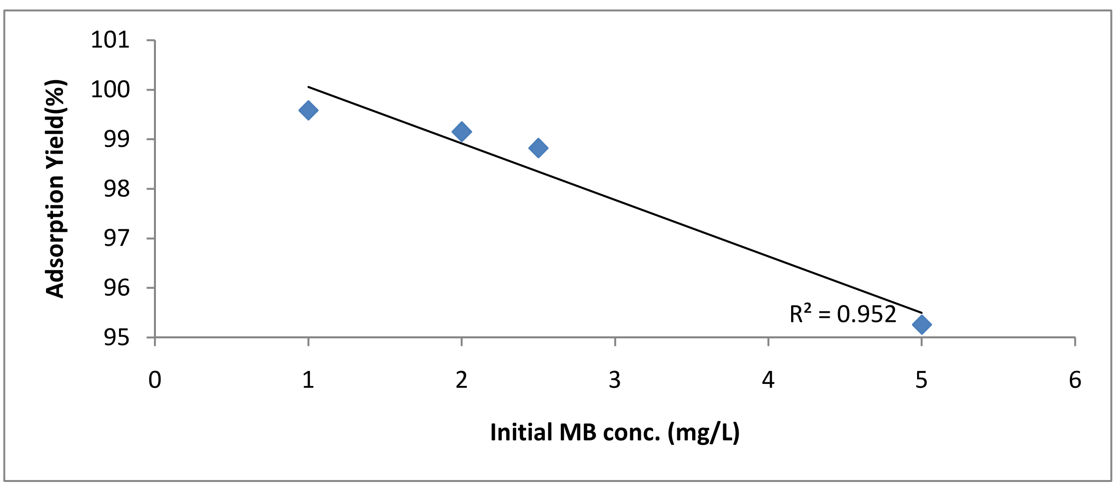

Figure-10
Plot of initial MB concentration against adsorption yield

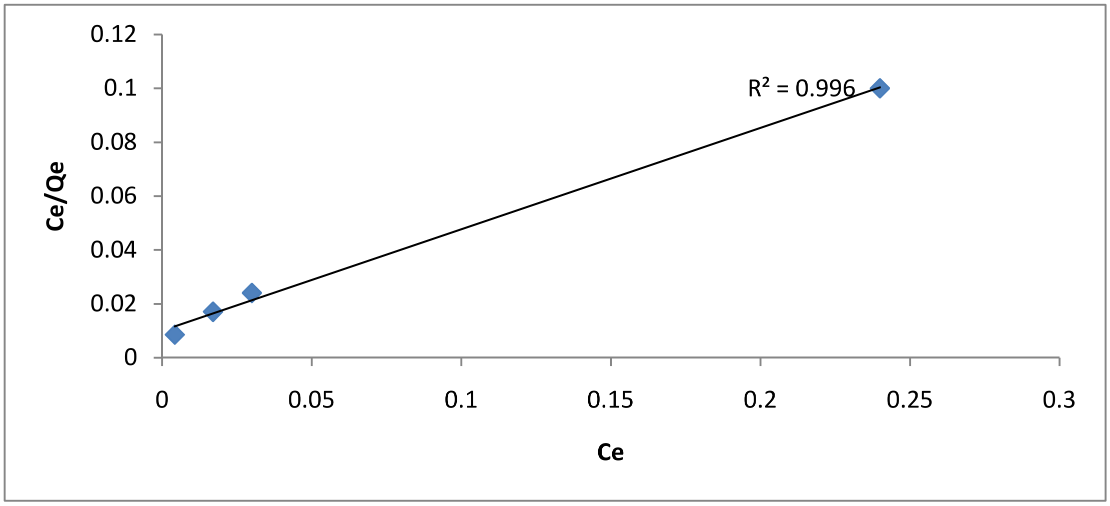

Figure-11
Langmuir adsorption isotherm for the effect of initial MB concentration

Effect of Methylene Blue Initial Concentration: The results of sorption of methylene blue by dehydrated maize tassels at various initial concentrations of 1; 2; 2.5 and 5mg/L with contact time and adsorbent dosage of 1g is shown in Figure 10. Results obtained were in agreement with findings by Zhang[14], and Hamdaoui and Chiha[20] in that the percentage sorption of methylene blue decreased with the increase in the dye concentration at the contact time (figure-11). Results from this study show that the adsorption process is highly dependent on the initial concentration of the dye in solution[5]. The data was fitted well the Langmuir isotherm (figure-11), R^2 0.9968

Conclusion

Dehydrated maize tassels proved to be a novel adsorbent for the removal of methylene blue from aqueous environment. The process of adsorption had an optimum pH of 6.8; adsorbent dosage required was 1g at a temperature of 25°C and contact time of 20 minutes. Adsorption of methylene blue increased with increase in intial MB concentration and adsorbent dosage. The data fitted well into the Langmuir absorption isotherm and not the Freundlich adsorption The R^2 ranged from 0.9968 to 0.9999. This suggests the monolayer adsorption of methylene blue onto dehydrated maize tassels.

References

1. Mohammed M.A., Shitu A. and Ibrahim A., Removal of Methylene Blue Using Low Cost Adsorbent: A Review, *Research Journal of Chemical Science.,* **4(1)**, 91-102 **(2014)**

2. Gong R, Jin Y, Chen J, Hu Y, and Sun J., Removal of basic dye from aqueous solution by sorption on phosphoric acid modified rice straw, *Dyes Pigm.*, **73**, 332–337 **(2007)**

3. Dash R., and Mishra P., Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. Hazard. Mater,* **B112 ,** 269–278 **(2010)**

4. Bhattacharyya K.G. and Sharma A., Kinetics and thermodynamics of Methylene Blue adsorption on Neem (Azadirachta indica) leaf powder, *Dye. Pigment.*, **65**, 51–59**(2005)**

5. Keivani M.B., Zare K., Aghaie H. and Ansari R., Removal of methylene blue dye by application of polyaniline nano composite from aqueous solutions, *Journal of Physical and Theoretical Chemistry of Islamic Azad University of Iran*, **6(1)**, 50 – 56 **(2009)**

6. Rajeshwarisivaraj S., Sivakumar S., Senthilkumar P. and Subburam V., Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution, *Bioresour. Technol.*, **80**, 233–235 **(2001)**

7. Janos P., Buchtova H., and Ry´znarova M., Sorption of dyes from aqueous solution onto fly ash, *Water Res.*, **37**, 4938–4944 **(2003)**

8. Garg V.K., Amita M., Kumar R. and Gupta R., Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood sawdust : A timber industry waste, *Dyes Pigments*, **63**, 243–250 **(2004)**

9. Kadirvelu K., Kavipriya M., Karthika C., Radhika M., Vennilamani N. and Pattabhi S., Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, *Bioresour, Technol.*, **87**, 129–132 **(2003)**

10. Chaudhary A.J., Ganguli B. and Grimes S.M., The use of chromium waste sludge for the adsorption of colour from dye effluent streams, *J. Chem. Technol. Biotecnol*., **77**, 767–770 **(2002)**

11. Pavan F.A., Mazzocato A.C. and Gushikem Y., Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent, *Bioresource Technology.*, **99**, 3162–3165 **(2008)**

12. Adel A.M., El –Wahab Z.H.A., Ibrahim A.A. and Al–Shemy M.T., Characterization of microcrystalline cellulose prepared from lignocellulosic materials, Part I. Acid catalyzed hydrolysis, *Bioresource Technology*., **101**, 4446–4455 (**2010**)

13. Kumar K.V. and Kumaran A., Removal of methylene blue by mango seed kernel powder, *Biochem. Eng. J.*, **27**, 83–93 **(2005)**

14. Zhang Z., O'Hara I.M., Kent G.A. and Doherty W.O.S., Comparative study on adsorption of two cationic dyes by milled sugarcane bagasse, *Industrial Crops and Products*., **4**, 41-49 **(2013)**

15. Cyran M.R., Association and Structural Diversity of Hemicelluloses in the Cell Walls of Rye Outer Layers : Comparison between Two Ryes with Opposite Bread making Quality, *Journal of Agriculture and Food Chemistry*., **55**, 2329-2341 **(2007)**

16. Wilson R.H., Smith A.C., Kacurakova M., Saunders P.K., Wellner N. and Waldron K.W., *Plant Physiology*., **124**, 397-405 (**2000**)

17. Schulz H. and Baranska M., Identification and Quantification of valuable Plant Substances by IR and Raman Spectroscopy, *Vibrational Spectroscopy.*, 43, 13-25 (**2007**)

18. Muchanyereyi N., Chiripayi L., Shasha D. and Mupa M., Adsorption of Phenol from Aqueous Solution Using Carbonized Maize Tassels. *British Journal of Applied Science and Technology*. , **3(3)**, 649-661 **(2013)**

19. Annadurai G., Juang R.S., and Lee D.J.: Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials*, **92**(**3**),263-274 **(2002)**

20. Hamdaoui O. and Chiha M., Removal of Methylene Blue from Aqueous Solutions by Wheat Bran; *Acta Chim. Slov.,* **54**, 407–418 **(2007)**

21. Abechi E.S., Gimba C.E., Uzairu A, and Kagbu J.A., Kinetics of adsorption of methylene blue onto activated carbon prepared from palm kernel shell, *Archives of Applied Science Research*., **3** (**1**),154-164 **(2011)**

22. Shehata A.M.A., Removal of Methylene Blue Dye from Aqueous Solutions by Using Treated Animal Bone As A Cheap Natural Adsorbent, *International Journal of Emerging Technology and Advanced Engineering*., **3**(**12**), 507-513 (**2013**)