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RESEARCH ARTICLE

EXPLORING THE BIOSORPTION OF METHYLENE BLUE DYE ONTO ACID TREATED SUGARCANE BAGASSE

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ABSTRACT

The potential of acid treated sugarcane bagasse (ATSB) to remove methylene blue (MB), an azo-cationic dye, from waste waters was explored. Surface characterization of the biomass before and after MB sorption was achieved using FTIR spectrophotometer. The ATSB had surface functional groups, -OH, N-H, -C=O, -C-OH, SiO₂ and C-halogen that were involved in removing MB from solution. Batch equilibrium sorption experiments were performed under optimized pH, contact time, biosorbent dosage and varying MB initial concentrations. The Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halsey adsorption isotherms were used to describe equilibrium data generated from the effect of MB initial concentration. The equilibrium data fitted the isotherms in the order: Langmuir > Freundlich = Halsey > Dubinin-Radushkevich (D-R) > Temkin with R² ranging from 0.9957 to 0.9621. The Langmuir isotherm based separation factor, R_L, (0 < R_L < 1) and the Freundlich's adsorption intensity, n, (1/n < 1) indicated sorption favorability between MB and ATSB with the Langmuir sorption capacity of 64.9351 mg/g. The Freundlich and Halsey isotherms pointed to the surface heterogeneity that the ATSB comprised of both macropores and micropores. The energy of sorption, E_D and b_T parameters, derived from the D-R and Temkin isotherms respectively indicated that the biosorption was endothermic and physical ion-exchange in nature. ATSB can be used to remove MB from waste waters. However there is need to explore the effects of metal ions, anions and other dyes on the removal of MB by ATSB.

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INTRODUCTION

Synthetic dyes are widely used in a number of industrial processes such as textile, carpet, leather, paper, printing, food, cosmetics, petroleum, solvent, rubber, plastic and photography (Chowdhury and Saha, 2012). The effluents from these industries can cause local environmental problems by significantly affecting photosynthetic activity in aquatic life because of the reduced light penetration (Shih, 2012). Among the different classes of dyes, azo-cationic dyes have been reported to be the most toxic. Elmorsi (2011) highlighted that many azo dyes and their intermediates have toxic effects on environment and human health due to their carcinogenicity and visibility. Incomplete degradation of these dyes by bacteria results in production of some carcinogenic and harmful amines. Methylene Blue (MB) belongs to this group of dyes. Methylene blue is a basic thiazine (cationic) dye with the chemical name tetramethylthionine chloride. It has a characteristic deep blue color in the oxidized form and the reduced form, leukomethylene blue is colorless (Malash and Ei-Khaiary, 2010). Methylene blue dye is one of the most important basic dyes as a result of its wide applications that include coloring paper, hair colorant, dying cotton, wools and coating for paper stock (Aksu and Kabasakal, 2004). Its chemical structure is shown in Fig 1. The chemical structure shows the presence of aromatic amines that are carcinogenic, causes liver, bladder, intestine and skin cancer and allergy in humans (Han *et al.*, 2006). Acute human exposure to methylene blue may cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis (Rafatullah *et al.*, 2009). Hence the removal of this dye from wastewaters is a priority. The current strategies to remove dyes from

industrial effluents include membrane technologies, biological treatment, ozonation, physicochemical methods, adsorption, chemical precipitation, flocculation, photolysis and ion pair extraction (Aravindhan *et al.*, 2009; Ong *et al.*, 2011). These methods require considerable start-up costs and cannot meet increasingly stringent effluent-color standards. The adsorption process has been demonstrated to be relevant when compared to other techniques for water reuse. It has very low initial cost, easy operation, flexible, simple, minimum sludge generation and the possibility of recovery of sorbate and the regeneration of the biosorbent for reuse (Volesky, 2000).

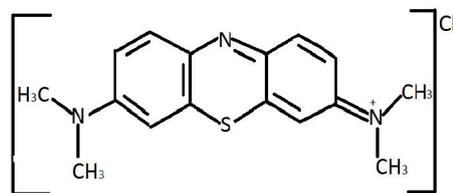


Fig 1. Chemical structure of Methylene Blue dye

Several low-cost adsorbents have been investigated for their potential to remove to MB dye. These include rubber seed shell (Oladoja, 2008); Miswak leaves (Elmorsi, 2011); rice husk (Shih, 2012); carbonized plant leaf powder (Gunasekar and Ponnusami, 2012); treated saw dust (Bello *et al.*, 2010); treated and untreated rice hulls (El-Maghraby and El-Deeb, 2011); raw sugarcane bagasse (Sharma and Kaur, 2011); propionic acid activated sugarcane bagasse (Said *et al.*, 2012) and water hyacinth roots (Low *et al.*, 1995) to mention a few. Sugarcane bagasse is found in large quantities as a byproduct of sugar production at Chiredzi Sugar Production Company in Zimbabwe. An average of 2.7 million tons of sugarcane was produced in 2010 (Bernard, 2011) implying that a huge amount of sugarcane

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bagasse was eventually produced. The bagasse is always a problem in most cities and towns in Zimbabwe as people feed on the sugarcane and dump the bagasse anywhere. Finding a better use for this abundant and renewable waste material is important in order to minimize the environmental impacts caused by inadequate disposal of these wastes (Raymundo *et al.*, 2010). Crude agricultural by-products have generally low sorption capacities (Hema and Arivoli, 2000) hence there is need to chemically pretreat them with either bases or acids. Mahamadi and Nharingo, (2007) reported that chemical treatment of the sorbents is important to remove any previously adsorbed substances that may interfere with the sorption process. It chemically modifies the surface, prevents fouling of the sorbent and prolongs its life span and hence increases the number of its sorption-desorption cycles. The research focused on the equilibrium isotherm study of the removal of Methylene Blue dye by the sulphuric acid treated sugarcane bagasse (ATSB).

MATERIALS AND METHODS

Sampling and treatment of sugarcane bagasse

Sugarcane bagasse (SB) was collected from Kudzanai Bus Terminus of Gweru city, Zimbabwe. The bagasse was collected into a plastic bag using a plastic sweeper and was washed several times with tap water to remove dust. It was then soaked in distilled water for 48 h and then dried for 24 h at 100 °C. The bagasse was treated with sulphuric acid according to Abdullah *et al.*, (2005). The dried sugarcane bagasse was mixed with concentrated sulphuric acid in the ratio of 1:1 and heated in a Clifton GB 004 muffle furnace for 24 h at 150 °C. The dried material was washed with distilled water followed by soaking in 1% sodium bicarbonate solution to remove residual acid. The biomass was then dried in an oven at 105 °C for 24 h and sieved to 250-500 µm. The biomass was stored in polythene bags and was heated overnight at 105 °C before use.

Preparation of sugarcane bagasse sample for FTIR analysis

The Fourier Transform Infrared was used to identify the characteristic functional groups on the sugarcane bagasse. Three samples were prepared: (a) sample of untreated sugarcane bagasse (b) sample of the acid treated adsorbent before the biosorption process and (c) sample after the biosorption process. To obtain the observable adsorption spectra the sugarcane bagasse samples were separately ground to very fine powders and then dried at 150 °C overnight. 0.005 g of each of the separate three powders was each mixed with 0.500 g of KBr (spectroscopic grade) with additional grinding. Discs were prepared in a manual hydraulic press at 10 tons for a pressing time of 1 min. The Dig lab Merlin Fourier Transform Infra-Red spectrophotometer (model 2000) was used in the scanning of the sugarcane bagasse in the range 4000 cm⁻¹ – 400 cm⁻¹ (Tsai *et al.*, 2000).

Preparation of Methylene blue adsorbate

Methylene blue (1.0 g) of analytical grade was weighed and dissolved in 1000 mL of distilled water to form a stock solution of concentration 1000 mg/L. From the 1000 mg/L stock solution, 10 ml were pipetted into a 100 mL volumetric flask and distilled water was added to the mark to make a concentration of 100 mg/L. Serial dilution of the 100 mg/L stock solution was done in preparation of instrument calibration standards and all MB concentrations that were used in this research.

Batch experiments

In order to have a clear picture of the effect of different parameters on the adsorption of the dye, experiments were carried out at different initial pH, contact time, dosages and different initial dye concentrations. The experiments were carried out as described below.

Effect of Initial pH of the medium on sorption of Methylene blue by ATSB

Solutions of the dye (100 mL of 30 mg/L MB) were transferred into separate 250 ml Erlenmeyer flasks. The pH was adjusted to 2, 3, 4, 5,

6, 7, 8, 10 and 12 using 0.1 M HCl and 0.1 M NaOH solutions (Ashokar and Inamdar, 2010). ATSB (0.4 g) was added into each Erlenmeyer flask and the mixtures were placed on the rotary shaker operated at 150 rpm at a temperature of 25 ± 2 °C for 24 h. The samples were vacuum filtered using whatman No. 1 filter paper before analysis by OHAUS-Germany UV-VIS spectrophotometer (model UV1800) at a wavelength of maximum absorption of 660 nm.

Effect of contact time on the biosorption of Methylene blue

Batch adsorption studies were conducted at different contact times (5, 10, 15, 20, 30, 40, 60, 80, 100, 120, 150, and 180 min) by taking initial concentration of dye 60 mg/L with 0.4 g adsorbent dose of ATSB in 100 mL dye solution of MB, at the determined optimum pH of 6, flask shaking rate of 150 rpm and a temperature of 25 ± 2 °C. Replicate analysis of the residual MB was done at each predetermined time by UV-VIS spectrophotometer. The equilibrium time was 80 minutes and 100 minutes was used for subsequent experiments to ensure that equilibrium was achieved.

Effect of adsorbent dosage on the sorption of MB

The adsorption of methylene blue by ATSB was studied by changing the quantity of adsorbent in the range 0.1 to 1 g in 100 mL of 60 mg/L solution of MB at a temperature of 25 ± 2 °C and a pH of 6. The flasks were placed on a shaker at 150 rpm for 100 minutes. The optimum dosage was found to be 0.6 g / 100 mL of MB solution.

Effect of initial dye concentration on MB sorption

The effect of the initial dye concentrations on the amount of MB adsorbed was examined under optimum conditions by contacting 0.6 g samples of ATSB with 100 mL of MB solution of different initial concentrations ranging from 5 to 60 mg/L at pH 6. The experiments were conducted at a temperature of 25 ± 2 °C, a constant flask shaking rate of 150 rpm for a contact time of 100 minutes. The samples were vacuum filtered and appropriately diluted before analysis.

Analysis of MB and data treatment

Spectrophotometric measurements of MB concentration were done at the wavelength of maximum absorption of 660 nm. The calibration standards of MB in the linear dynamic range of 5 to 30 mg/L were used to calibrate the OHAUS-Germany UV-Visible spectrophotometer. The lower limit of correlation of determination (R²) of 0.99 was used to ensure linearity. The initial and equilibrium concentrations of the dye in solution were measured and the amount of MB adsorbed on the ATSB was calculated from the mass balance equation 1 given below:

$$Q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

The percentage removal was calculated using equation 2.

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \quad (2)$$

Where C_i and C_e are the initial and equilibrium concentrations of MB in mg/L respectively, Q_e is the amount of MB adsorbed at equilibrium in mg/g, V is the volume of the MB solution (L) and m is the mass of the acid treated sugarcane bagasse in grams.

RESULTS AND DISCUSSION

Characterization of the sugarcane bagasse

The FTIR spectra of natural, treated and MB-loaded ATSB in the range 400-4000 cm⁻¹ were recorded to obtain information on the effect of treatment and the nature of the functional groups that were involved in the sorption of MB. The results are presented in Table 1. The results show that both untreated and acid treated sugarcane bagasse were composed of many functional groups that form active

Table 1. FTIR bands of the natural, acid treated and MB loaded sugarcane bagasse

| Band cm^{-1} | Natural SB | ATSB | ATSB with MB | Inferences | Reference |
|-----------------------|-----------------|-----------------|--------------|---|-----------------------------------|
| 3600-3200 | Broad band | Broad band | Broad band | N-H, O-H vibrations | Kamsonlian <i>et al.</i> , (2011) |
| 2920 | Weak sharp band | - | - | -OH bonded to CH_3 -group | Shih (2012) |
| 1640 | Strong band | Strong band | Strong band | C=O stretch $\text{uC}=\text{C}$ aromatic | Kamsonlian <i>et al.</i> , (2011) |
| 1260 | Weak sharp band | - | - | Si-C stretch | Suyamboo and Perumal (2012) |
| 1200 | - | Strong band | Weak band | C-OH -polysaccharides | Yuvaraja <i>et al.</i> , (2011) |
| 1060 | - | Strong band | - | C-OH stretching vibrations | Suyamboo and Perumal (2012) |
| 1040 | Strong band | - | - | -C-C- stretching | Sen <i>et al.</i> , (2010) |
| 880-840 | - | Weak sharp band | - | SiO_2 typical structures. | Shih (2012) |
| 580 | Broad band | Strong band | - | C-halogen bonds. | Mwangi <i>et al.</i> , (2011) |
| 500-400 | Broad band | - | - | O-Si-O bending | Shih (2012) |

sites for the adsorption of methylene blue. The treatment resulted in the decrease in % transmittance of the biomass, shifting or disappearance of bands at 2920, 1260, 1040 and $500\text{-}400\text{ cm}^{-1}$ and creation of new bands at 1200, 1060 and $880\text{-}840\text{ cm}^{-1}$ assigned in Table 1. Analysis of the ATSB and ATSB loaded with MB dye revealed the significant increase in % transmittance on MB loaded biomass, band broadening and weakening and the disappearance of some bands. This pointed to the involvement of the biomass surface functional groups in the sorption process. The functional groups involved included; -OH/N-H, -C=O, C-OH, SiO_2 and the C-halogen bonds. Similar results were reported by Abdel-Ghani and Elchaghaby, (2007); Sen *et al.*, (2010); Yuvaraja *et al.*, (2011) and Kamsonlian *et al.*, (2012).

Effect of pH on the removal of MB

Fig 2 shows that as the pH was increased from 2 to 6, there was gradual increase in the uptake of MB by ATSB. Further increase in pH beyond pH 6 resulted in decrease in the amount of MB removed by the sorbent. At low pH, minimum sorption of the dye was observed due to the presence of high concentration of H^+ ions that competed effectively with MB (cationic) dye molecules (Elmorsi, 2011). As the pH of the system increased to pH 6, the number of negatively charged sites on ATSB surface increased and the number of positively charged sites decreased. Hsu, (2008) reported that negatively charged surface sites on the adsorbent favors the adsorption of the cationic dye because of electrostatic attraction. The decrease in MB sorption beyond pH 6 may not be attributed to electrostatic interaction between sorbent and sorbate and hence other forms of interactions were involved. Gunasekar and Ponnusami (2012) got similar results on the effect of pH on the sorption of MB by carbonized plant leaf powder.

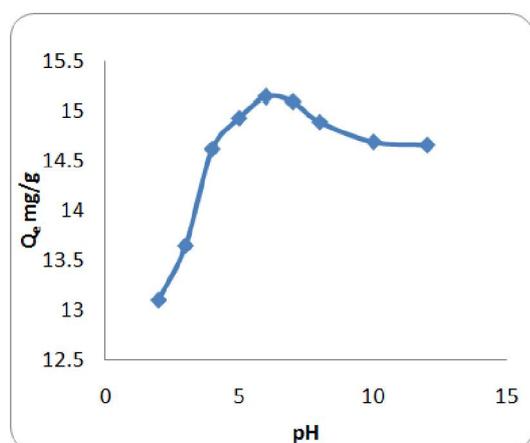


Fig 2. Effect of pH on biosorption of MB

Effect of contact time

The effect of contact time was investigated using initial dye concentration of 60 mg/L with sorbent dosage of 0.2 g at pH 6, $25\text{ }^\circ\text{C}$ temperature and agitation rate of 150 rpm over a period of 180 minutes. Fig 3 shows that the adsorption was rapid at the initial stages

and gradually decreased with time until it became constant after 80 minutes. The ATSB sites were unoccupied at the initial stages allowing the biosorption rate to be fast as a result of a higher diffusion of MB from the bulk solution to the sorbent sites (Viraraghavan and Ramakrishna, 2000). The biosorption sites progressively diminished with time as they got occupied resulting in reduced diffusion gradient and hence the rate of sorption decreased with time until it reached zero (equilibrium point) at 80 minutes. The contact time of 100 minutes was used throughout the study to ensure that equilibrium was reached.

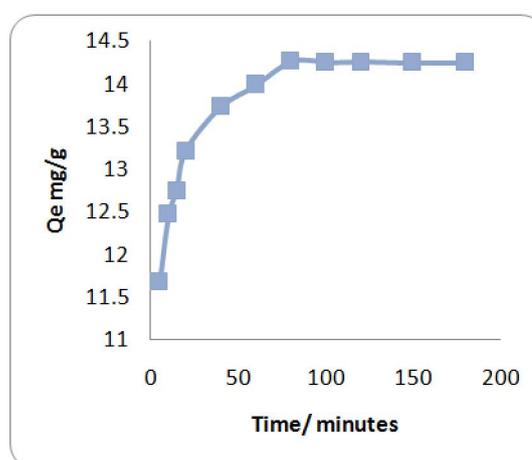


Fig 3. Effect of contact time on biosorption of MB

Effect of adsorbent dosage

The effect of ATSB dosage on the removal of methylene blue is shown in Fig 4.

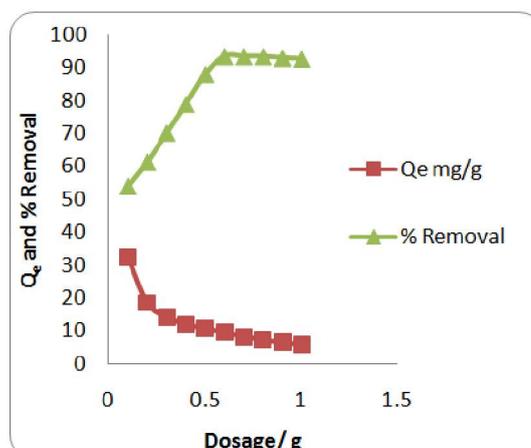


Fig 4. Effect of ATSB dosage on biosorption of MB

The amount of dye sorbed at equilibrium, Q_e , decreased with ATSB dosage. Based on the calculation of Q_e in equation 1, the observed trend was attributed to the rapid increase in the dosage (m) that

outweighed the gradual increase in the mass of MB dye adsorbed on the surface of the biosorbent [$V(C_i - C_e)$]. Rajamohan (2009) argued that the decrease in Q_e may be due to solute transfer rate to the adsorbent surface getting splitted as the adsorbent dosage increased. Percentage removal was also used to evaluate the effect of dosage on MB sorption. Fig 4 shows that % removal increased with increasing ATSB dosage up to a dosage of 0.6 g after which it became constant. The increase in adsorption of MB dye with adsorbent dosage was due to the availability of more adsorption sites on bagasse surface for adsorption. Ashoka and Inamdar (2010) attributed the increase in adsorption with dosage to the increase in surface area and the pores available for the sorption process. This occurred until the amount of MB in solution became limiting and hence no further increase in % removal of dye was observed beyond this point.

Effect of Initial MB concentration

The effect of initial MB concentration was investigated under optimum conditions of pH 6, 100 minute contact time, and ATSB dosage of 0.6 g/ 100 mL of MB solution at a temperature of 25 ± 2 °C. Fig 5 shows that with increasing initial MB concentration, the amount of dye removed by ATSB increased almost linearly with $R^2 = 0.9977$ (Result not shown). Diffusion of MB from the bulk solution to the biosorbent surface increased with increase in diffusion gradient with each increase in MB initial concentration. The linearity between Q_e and C_i implied that significant removal of MB from solution would occur beyond the 60 mg/L limit in the research (Said *et al.*, 2012). The result shows that the ATSB has high affinity for the sorption of MB even at higher concentrations than those investigated. However the removal efficiency decreased with initial concentration. This was the case when rice hulls were used to remove MB from aqueous solution by El-Maghraby and El-Deed (2011).

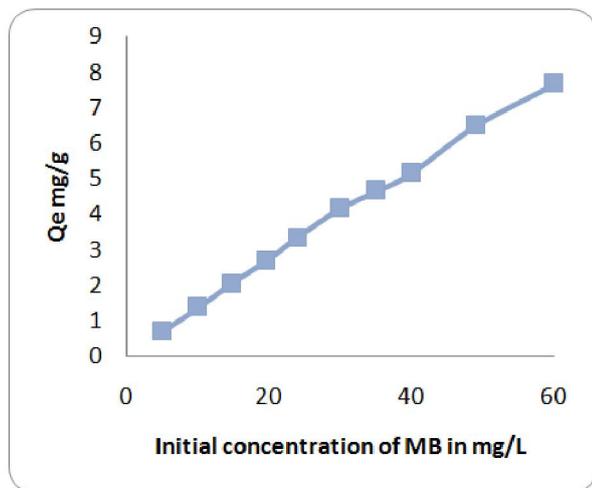


Fig 5. Effect of MB concentration on its sorption

Adsorption Equilibrium Isotherms

Analysis of adsorption isotherms is of fundamental importance to describe how adsorbate molecules interact with the adsorbent surface. Equilibrium studies determine the nature of the adsorbent surface, sorption favorability, sorption energetics and the possible mechanisms of adsorbate-adsorbent interactions through the evaluation of sorption parameters. The Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halsey isotherms were used to describe equilibrium data.

Langmuir Isotherm

The Langmuir adsorption isotherm model is based on the following assumptions:

- The biosorbent has a homogenous surface of identical sites that are equally available and energetically equivalent,

- Each site carries an equal number of adsorbed molecules and
- no interaction between adsorbate molecules occurs (Shih 2012).

The linearized form of the Langmuir adsorption isotherm is presented below:

$$\frac{1}{Q_e} = \frac{1}{bQ_m C_e} + \frac{1}{Q_m} \quad (3)$$

Where C_e (mg/L) is the equilibrium concentration of the dye, Q_e is the amount of MB adsorbed at equilibrium (mg/g), b is the adsorption energy of the treated sugarcane bagasse adsorbent and Q_m is the maximum sorption capacity of the dye (mg/g). The plot of $1/Q_e$ against $1/C_e$ gives $1/Q_m$ as the y-intercept and $1/bQ_m$ as the gradient from which the model parameters are derived.

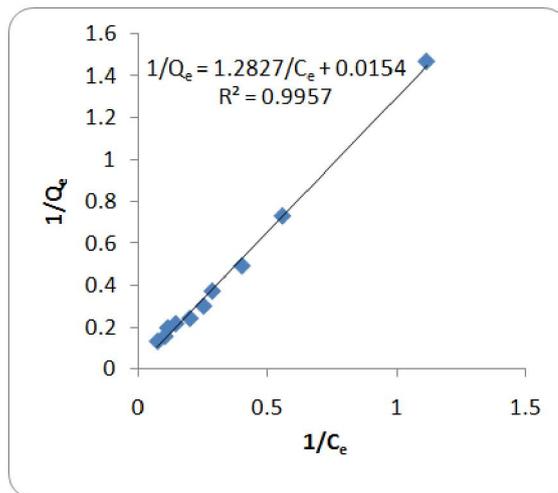


Fig 6. Linearized Langmuir plot of MB sorption onto ATSB

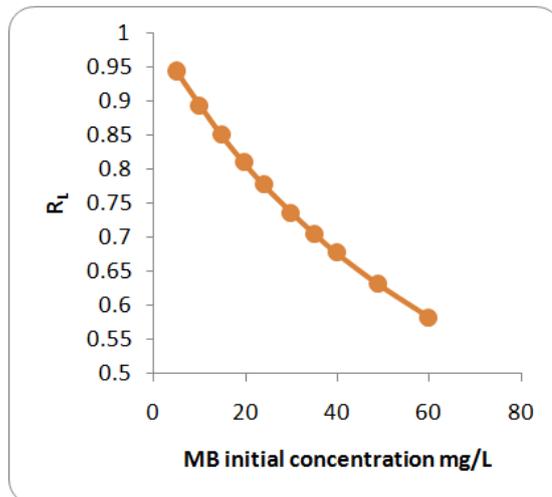


Fig 7. R_L against MB initial concentration

The Langmuir plot in Fig 6 shows that the adsorption isotherm describes the sorption of MB dye onto ATSB with R^2 of 0.9957. The value is very close to unity indicating the applicability of Langmuir isotherm model in describing the sorption process. The magnitude of Q_m , a measure of maximum sorption capacity corresponding to complete monolayer coverage, is very high (Table 2) compared to those of other sorbents used in the removal of MB from waste waters (Sen *et al.*, 2010). This shows that ATSB is among the good sorbents with high potential to sorb MB. The favorability of the adsorption process was checked for using the dimensionless constant, R_L , related to the Langmuir model. R_L is defined as shown in relationship 4.

$$= \frac{1}{1 + bC_i} \quad (4)$$

Table 2. Adsorption isotherm parameters for MB sorption onto ATSB

| Langmuir parameters | | | Freundlich parameters | | | Temkin parameters | | |
|---------------------|-------|--------|-----------------------|--------|--------|-------------------|--------|--------|
| Q_m mg/g | b | R^2 | Kf | 1/n | R^2 | K_T | b_T | R^2 |
| 64.9351 | 0.012 | 0.9957 | 0.8611 | 0.8695 | 0.9786 | 0.7812 | 0.8354 | 0.9621 |

Where b is the Langmuir constant related to the apparent energy of sorption and C_i is the initial dye concentration (Horsfall and Spiff, 2005). The meaning of the magnitudes of the separation factor was reported by Oladoja *et al.* (2009) as follows: when $R_L > 1$ sorption is unfavorable, sorption is linear when $R_L = 1$, when $R_L = 0$ irreversible sorption occurs and when R_L is in the range $0 < R_L < 1$ sorption is favorable. Fig 8 shows that sorption was favorable at all initial MB concentrations investigated. However, sorption was more favorable at higher initial concentrations than at the lower ones implying that high concentrations of MB in waste waters may not limit its sorption onto ATSB (Mahamadi and Nharingo, 2010).

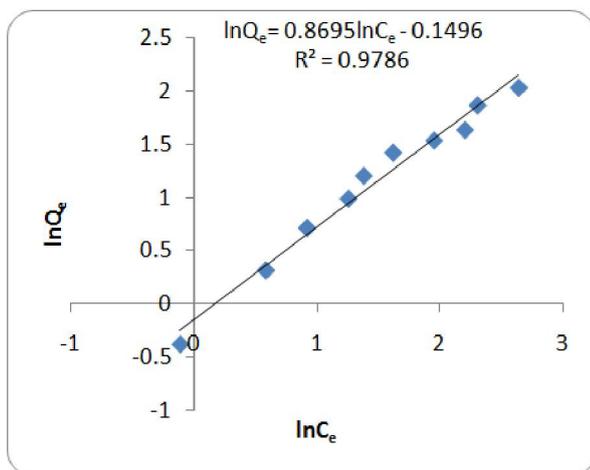


Fig 8. Linear Freundlich plot of MB sorption onto ATSB

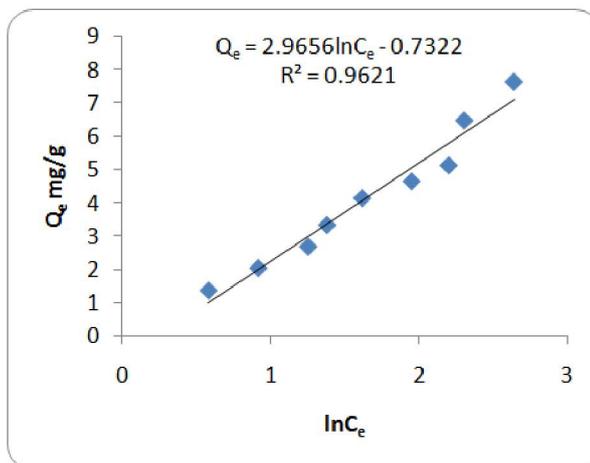


Fig 9. Linear Temkin plot of MB onto ATSB

Freundlich isotherm

This is monolayer isotherm model that assumes the heterogeneity of the surface on which adsorption occurs (Sen *et al.*, 2010). The linearized form of the isotherm can be expressed as:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

Where K_f and n are constants indicating adsorption capacity and adsorption intensity respectively (Uddin *et al.*, 2007). K_f and $1/n$ are obtained from the plot of $\ln Q_e$ against $\ln C_e$ as the intercept and gradient respectively. Fig 8 shows the Freundlich plot with a fairly high correlation of determination, $R^2 = 0.9786$. Table 2 shows that the

$1/n$ was in the range $0.1 < 1/n < 1$ that pointed to the sorption favorability as reported by Cengiz and Cavas (2009), Oladoja *et al.*, (2008) and Said *et al.*, (2012). Sharma and Kaur (2011) reported that the adsorption intensity, $1/n < 1$, implies heterogeneous surface of the biosorbent with minimum interactions between the adsorbed molecules. This was the case for the adsorption of MB onto ATSB in this research.

Temkin isotherm

The Temkin isotherm was tested on the equilibrium data to evaluate the heat of sorption and the indirect adsorbate-adsorbate interactions on the adsorption process. The linearized Temkin adsorption isotherm is presented as equation (6):

$$Q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (6)$$

Where T is the absolute temperature, R is the universal gas constant, K_T is the equilibrium binding constant and b_T is related to the heat of sorption (Samarghandi *et al.*, 2009). Fig 9 shows the plot of Q_e against $\ln C_e$. It yielded a fair fitness to the equilibrium data with R^2 of 0.9621. This meant that the more energetic sorption sites were occupied by MB molecules before the less energetic ones (Abdel-Ghani and Elchaghaby, 2007). Table 2 shows the adsorption isotherm parameters. The constant b_T was determined as 0.835 kJ/mol and the equilibrium binding constant of 0.7812 L/g. The variation of adsorption energy was very low and positive showing that the adsorption process was physisorption and endothermic in nature.

Dubinin-Radushkevich isotherm (D-R)

The characteristic porosity of the biomass and the apparent energy of adsorption were estimated using the D-R adsorption isotherm model (Igwe and Abia, 2006 and Itodo and Itodo, 2010). The linear form of the D-R isotherm is expressed as:

$$\ln Q_e = \ln Q_D - 2B_D RT \ln(1 + 1/C_e) \quad (7)$$

Where Q_e is the amount of MB dye adsorbed at equilibrium (mg/g), Q_D is the adsorption capacity (mg/g), B_D is a constant related to the adsorption energy, R is the ideal gas constant, T is the temperature in K and C_e is the MB equilibrium concentration in mg/L. A plot of $\ln Q_e$ against $\ln(1+1/C_e)$ gives B_D as the gradient and Q_D as the intercept.

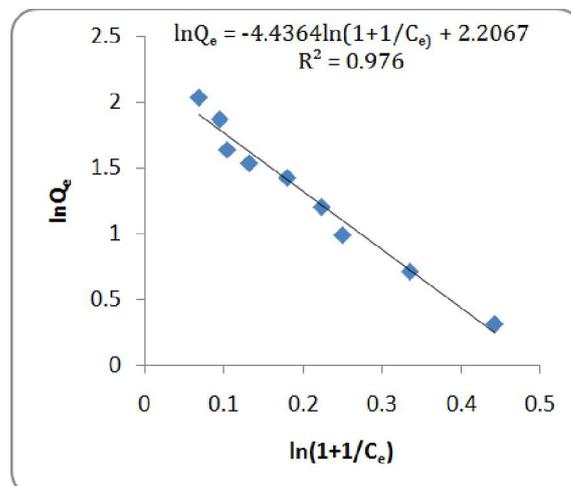


Fig 10. Linearized D-R plot of MB sorption onto ATSB

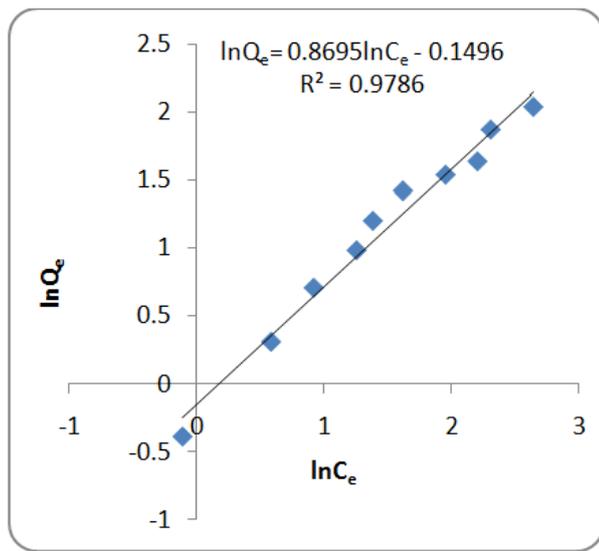


Fig 11. Linearised Halsey plot of MB sorption

Table 3. D-R and Halsey isotherm parameters for MB sorption onto ATSB

| D-R | | | | Halsey | | |
|--------|-----------------|---|--------|--------|---------|--------|
| E_D | Q_D (mg/g) | B_D (mol ² kJ ⁻²) | R^2 | K_H | n | R^2 |
| 0.7473 | 9.0857 | 0.8953 | 0.9760 | 1.1878 | -1.1501 | 0.9786 |

Fig 10 shows the linear plot of the D-R isotherm. The R^2 of 0.976 pointed to the fitness of the isotherm model in describing the equilibrium data. The deduced model parameters in Table 3 show that the maximum sorption capacity ($Q_D = 9.0857$ mg/g) is much smaller than the Langmuir maximum sorption capacity ($Q_m = 64.9351$ mg/g). It is evident in this research that $Q_m \gg Q_D$ which is the opposite of what Itodo and Itodo (2010) reported from the sorption of atrazine onto activated carbon derived from sheanut shells. It can therefore be concluded that the relationship between Q_m and Q_D depends on the nature and amount of the sorbate and the sorbent used.

The mean free energy, E_D , was estimated from the B_D constant using the relationship:

$$E_D = \frac{1}{\sqrt{2B_D}} \quad (8)$$

Table 3 shows that the mean free energy was found to be 0.7473 kJ/mol. The sign and magnitude of E_D indicated that the sorption process was endothermic and physisorption in nature. Atkins (1999) reported that the enthalpy of physisorption gives typical values in the region less than 20 kJ/mol and monolayer chemisorption enthalpy in the range of 200 kJ/mol. The sorption energy was very low and hence implied a physisorption mechanism. Mall *et al* (2005) in Oladoja *et al.*, (2009) reported similar findings during the sorption of Congo red and Orange green onto mesoporous fertilizer plant waste carbon. Itodo and Itodo (2010) reported E_D value of 0.8111 kJ/mol in the removal of atrazine by sheanut shells activated carbon. The sorption of MB by hen feathers involved energy (E_D) that varied with temperature from 13.52 to 15.67 kJ/mol (Chowdhury and Saha, 2012).

Halsey adsorption isotherm

The isotherm predicts multilayer adsorption and fitting of equilibrium data to the model suggests the heteroporosity of the adsorbent surface (Oladoja *et al.*, 2008). The linear form of the isotherm is expressed as:

$$\ln Q_e = 1/n \ln K_H - 1/n \ln C_e \quad (9)$$

Where K_H and n are the Halsey adsorption isotherm constant and exponent respectively (Samarghandi *et al.*, 2009). Fig 11 and Table 3 show the linear plot and parameters of the Halsey adsorption isotherm respectively. The equilibrium data fitted well to the model ($R^2 = 0.9786$) confirming multilayer sorption and the surface heterogeneity of the acid treated sugarcane bagasse. The biosorbent comprised of both macropores and micropores (Oladoja *et al.*, 2009) and can be successfully used for the sorption of MB dye.

Conclusion

The abundant, readily available sugarcane bagasse, treated with concentrated H_2SO_4 , was successfully used for the removal of Methylene Blue dye from aqueous solutions. The optimum conditions were determined as a pH of 6, 80 minute contact time and a biomass dosage of 0.6 g/100 mL of dye solution. The equilibrium data generated was best described by the Langmuir isotherm ($R^2 = 0.9957$). The equilibrium data also fitted to the Freundlich, Temkin, Dubinin-Radushkevich and Halsey adsorption isotherms with R^2 values of 0.9786; 0.9621; 0.9760 and 0.9786 respectively. The separation factor, R_L , derived from the Langmuir isotherm and the adsorption intensity, n , from the Freundlich isotherm confirmed sorption favourability. The Temkin and Dubinin-Radushkevich isotherms revealed that the sorption of MB onto ATSB was an endothermic process that was of a physical ion-exchange in nature. The Halsey isotherm model suggested that multilayer sorption took place on a heterogeneous surface comprising of macro and micropores.

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