



Adsorption Thermodynamics of Some Basic Dyes Uptake from Aqueous Solution using *Albizia lebbek* Shells

Ibrahim, M. B. and Umar, A.

Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria

Email: mbibrahim.chm@buk.edu.ng, alaminusk@gmail.com

ABSTRACT

The efficiency of *Albizia lebbek* shell for the adsorption of auramine yellow (AY), basic malachite green (BMG) and basic violet (BV) dyes from aqueous solution has been studied in a batch system. The effects of contact time, adsorbent dosage, initial dye concentration, solution pH and temperature have been investigated and the optimum conditions were determined. Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) were studied and the values were $-53,475.648 \text{ Jmol}^{-1}$, $-138.345 \text{ Jmol}^{-1}\text{K}^{-1}$ and $-11,557.125 \text{ Jmol}^{-1}$ respectively for the adsorption of auramine yellow and $-12,6730.302 \text{ Jmol}^{-1}$, $-389.012 \text{ Jmol}^{-1}\text{K}^{-1}$ and $-8,859.648 \text{ Jmol}^{-1}$ respectively for the adsorption of basic malachite green indicating exothermic, non-spontaneous and feasible processes for AY and BMG at tested low and high temperatures of 303k and 323k. However, the enthalpy, entropy and free energy changes' values for the adsorption of basic violet were $19,030.746 \text{ Jmol}^{-1}$, $83.639 \text{ Jmol}^{-1}\text{K}^{-1}$ and $18,335.371 \text{ Jmol}^{-1}$ respectively indicating endothermic, spontaneous and infeasible process at 303k but feasible at 323k. Surface characterization of the adsorbent based on scanning electron microscopy (SEM) were studied before and after adsorption, and the results indicate that the adsorbent could be effective due to its large number of external cavities on the surface. Therefore, *Albizia lebbek* shells could serve as an effective adsorbent for the removal of organic colorants from textile wastewater prior to disposal since it has 94.2, 72.4 and 85.3% adsorption efficiency values for the removal of AY, BMG and BV respectively.

Keywords: Adsorption, *Albizia lebbek* Shells, Basic Dyes, Thermodynamics

INTRODUCTION

Local pollution of lakes and rivers has occurred from a variety of sources such as sewage, effluents, agricultural wastes and waters used for mineral processing and industrial works (Bowen, 1979). Textile dyeing industry is known to be one of the major contributors to environmental pollution (Christie, 2007). It is estimated that approximately 40, 000 tones of dyes out of roughly 450, 000 tonnes in total production are not used but discharged into waste waters (Marsh and Rodriguez-Reinoso, 2006).

Dye concentrations in watercourses higher of 1 mg/L caused by the direct discharges of textile effluents, treated or not, can give rise to public compliant. High concentrations of textile dyes in water bodies stop the Re-oxygenation capacity of the receiving water and cutoff sunlight, thereby upsetting biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae (Zaharia *et al.*, 2009).

Traditional and conventional techniques usually employed for the treatment of dye wastewater consist of biological, physical and chemical methods most of which are becoming inadequate due to large variability of the

composition of dye wastewaters. In other words, most of these techniques are often ineffective, expensive, complicated, time-consuming and require highly-skilled personnel especially when the levels of dissolved dye adsorbates are in the range of 1 - 100 mg/L (Liu *et al.*, 2012). Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design and operation, and insensitivity of toxic substances (Tong *et al.*, 2010).

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent (Khattri and Singh, 2009). The factors affecting the adsorption process are: surface area, nature and initial concentration of adsorbate, solution pH, temperature, interfering substances and nature and dose of adsorbent (Grassi *et al.*, 2012). Separation-Adsorption is used as a separation process in many chemical as well as bio chemical industries to separate gaseous or liquid mixtures. Designing

adsorption equipment like fixed bed adsorbers, gas drying, pressure swing adsorption etc., chromatography requires knowledge of adsorption (NPTEL, 2003).

Agro-waste Materials are waste materials from forest and poultry industries. They are available in large quantities and may have potential as a sorbent due to their physico-chemical properties and low cost. They contain various organic compounds such as lignin, cellulose and hemicellulose with polyphenolic groups that might be useful for binding dyes through different mechanisms. Examples are sawdust, wood, hen feather, sheep wool, corn cob, rice husk, coir pith, rice bran, wheat bran etc (Crini, 2005).

Albizia lebbek known as English women tongue is a perennial plant found in many different part of the world especially Asian and west African countries. The genus *Albizia* comprises almost 150 species. *Albizia lebbek* is a large, erect, unarmed, deciduous spreading tree usually planted in tropical and subtropical regions of Asia and Africa (Sharma and Dubey, 2015). The shells (pods) of *Albizia lebbek* are pale straw to light brown at maturity, narrow-oblong, 15-26 x 3-5 cm, papery, leathery, and flat not raised or constricted between seeds. The seeds are brown, flat, orbicular or elliptic, 8-10 x 6-7 mm; transversely placed with 6-12 in each pod.

Sivakumar *et al.* (2012) studied the adsorption of total dissolved solids and sulphate in the electroplating industry effluent using *Albizia lebbek* pod powder in a batch method. 100 mg/L was found to be the optimum adsorbent (slurry) concentration and the equilibrium data were found to be fitted well with pseudo-second order kinetic model than that of other models. Ahmed and Theydan (2014) utilized *Albizia lebbek* seed pods for the preparation of activated carbon by microwave assisted KOH activation. The surface

area, micropores volume and mesopores volume of the carbon (KAC) were 1824.88m²/g, 0.645cm³/g and 0.137cm³/g respectively. The effects of process variables represented by radiation time, radiation power and impregnation ration on the yield and methylene blue (MB) uptake of such carbon were studied. The experimental kinetic data were well described by the pseudo-second order model, and Langmuir isotherm gave the best fit with a maximum adsorption capacity of 381.22mg/g. Raju *et al.* (2012) investigate the biosorption performance of *Albizia lebbek* pods powder for the removal of lead from aqueous solution in a batch process. The kinetic study showed that biosorption of lead followed pseudo-second order kinetics. Thermodynamic data revealed the endothermic nature of the biosorption as ΔH (9.1581 Jmol⁻¹) is positive, irreversible nature of biosorption as ΔS (14.8438 Jmol⁻¹K⁻¹) is positive and spontaneity of biosorption as indicated by negative ΔG ($\Delta G = -4488.5194$ Jmol⁻¹). Therefore, the aim of this work is to study the adsorption thermodynamics for the removal of auramine yellow, basic malachite green and basic violet dyes from aqueous solution using *Albizia lebbek* shells.

The sample dyes (Auramine Yellow, Basic Malachite Green and Basic Violet) were chosen based on their availability, low cost and wider applicability to textile, leather, plastic and paper industries. International Agency for Research on Cancer included Basic yellow 2, Basic Green 4 and Basic Violet 3 among chemicals for which there is sufficient evidence of carcinogenicity in experimental animals (IARC, 1987) due to their bio-transformation to reactive species in target organs of both rats and humans (Martelli *et al.*, 1998). The dyes are produced in large quantities and have wavelengths of maximum absorption at 430, 620 and 580nm respectively (Allen *et al.*, 1992).



Fig. 1: Structure of Auramine Yellow

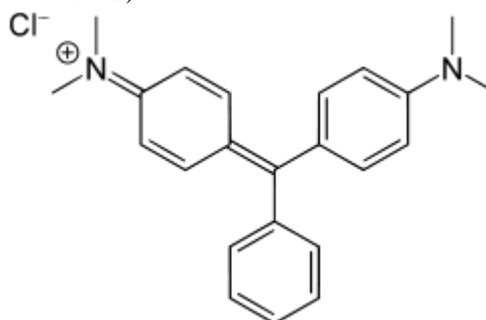


Fig. 2: Structure of Basic Malachite Green

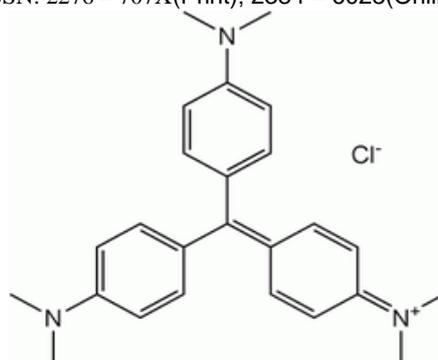


Fig. 3: Structure of Basic Violet

Stock solution of each was prepared by dissolving 1.0g of the dye in 1000 cm³ volumetric flask containing some distilled water and was then made to the mark. Intermediate stock and other lower concentrations of the dye solutions were prepared by appropriate dilution using dilution formula. In each case 2.0 mg/L solutions were used for the analysis of wavelength of maximum absorption (λ_{max}) and 2.0 – 10.0 mg/L solutions were used in establishing calibration curves.

MATERIALS AND METHODS

Albizia lebbek plant (common name; Flea tree), locally called Albiziya belongs to the family *Fabaceae* of Kingdom Plantae. The shells were sampled in a clean polythene bag within Bayero University Kano old campus and identified by the Plant Science Department of the university with Herbarium Accession Number BUKHAN 0187. It was then air-dried, ground into powder, sieved, soaked in distilled water (to percolate possible color component) and washed severally with distilled water until colorless filtrate was obtained. The residue after filtration was dried in an oven at 105°C for 6 hours, and was then stored in a cleaned well labeled and air tight container at room temperature without further treatment for surface characterization and biosorption studies (Ibrahim and Sani, 2014).

$$q_e = \frac{C_o - C_e}{w} \times V \quad (1)$$

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

Where q_e is the equilibrium adsorption capacity in mg/g, C_o and C_e are the initial and final (equilibrium) concentration in mg/L respectively, w is the adsorbent weight in grams, V is the volume of solution in dm³.

BATCH ADSORPTION STUDIES

Batch adsorption technique was used to study the effect of solution pH, contact time, adsorbent dosage, initial dye concentration, and temperature on the adsorption processes. The experiments were carried out in a 120cm³ sample bottles by mixing 0.2g of approximately 35 μ m diameter adsorbent with 100cm³ of 10mg/L dye solutions and agitated at 250rpm in a mechanical isothermal orbital shaker (LONOVO Labotec) for a period of 5 – 240 minutes at different time intervals. The samples were then removed, filtered and filtrates were investigated for residual dye concentrations using UV-visible spectrophotometer (Aquarius CECIL CE7200 7000 SERIES) at pre-determined wavelengths of 430, 620 and 580 nm for AY, BMG and BV dye solutions respectively. Absorbance values were converted to concentrations using absorptivity (gradient) obtained from the established linear regression equations.

Equations (1) and (2) were used to evaluate the equilibrium adsorption capacity and percentage removal respectively (Ibrahim and Sani, 2014) while (3) and (4) are the Van't Hoff and Arrhenius equations used to estimate the thermodynamic properties of the adsorption processes (Laidler, 1987).

RESULTS AND DISCUSSION

Adsorption experiments were carried out to evaluate the optimum working conditions by varying the operation parameters such as contact time (5 – 240 min), adsorbent dosage (0.2 - 1.0 g), initial dye concentration (10 – 100 mg/L), pH (3.0 – 10.00), and temperature (30 – 50 °C) and the optimum conditions were arrived at as recorded in Table 1.

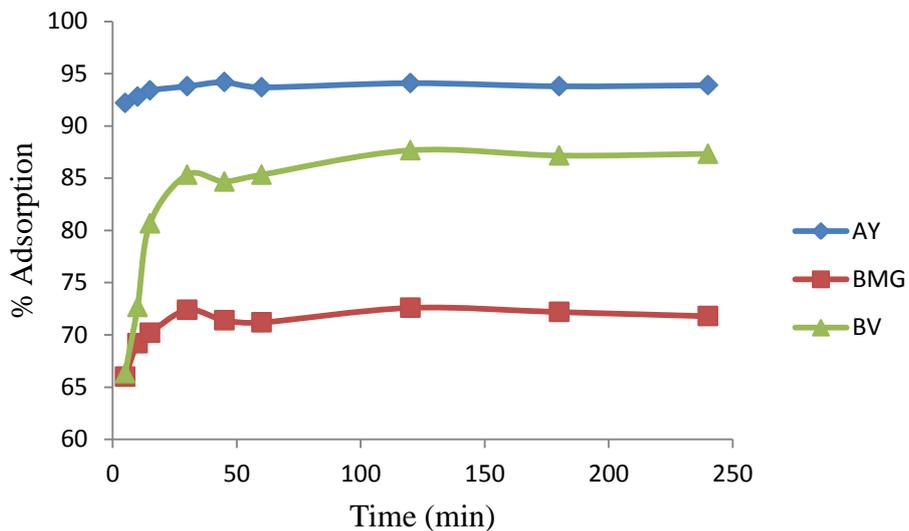


Fig. 4: Effect of Contact Time on Adsorption of AY, BMG and BV onto *Albizia lebeck* Shells

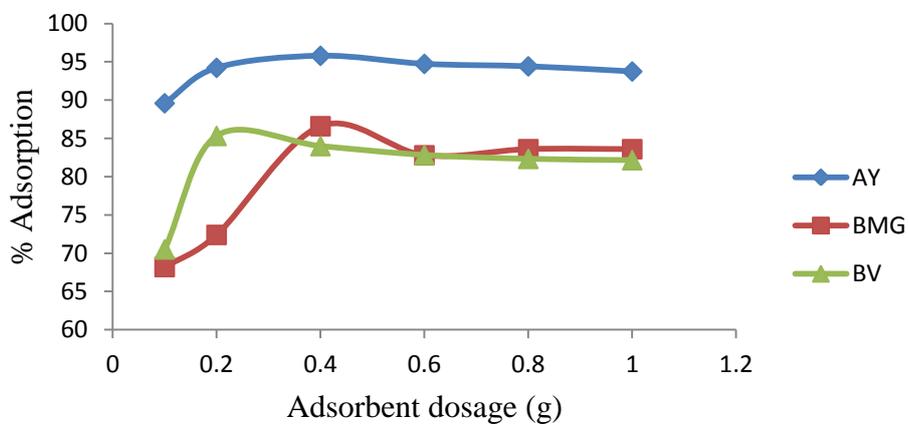


Fig. 5: Effect of Adsorbent Dosage on Adsorption of AY, BMG and BV onto *Albizia lebeck* Shells

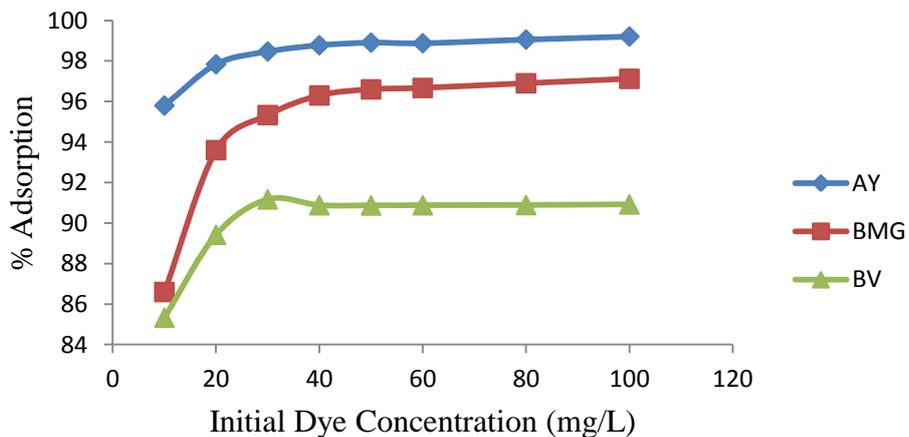


Fig. 6: Effect of Initial Dye Concentration on Adsorption of AY, BMG and BV onto *Albizia lebeck* Shells

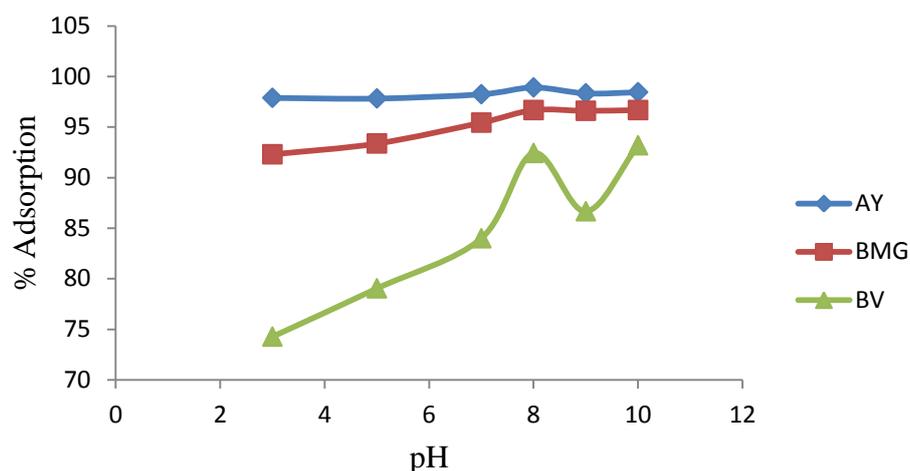


Fig. 7: Effect of Solution pH on Adsorption of AY, BMG and BV onto *Albizia lebbek* Shells

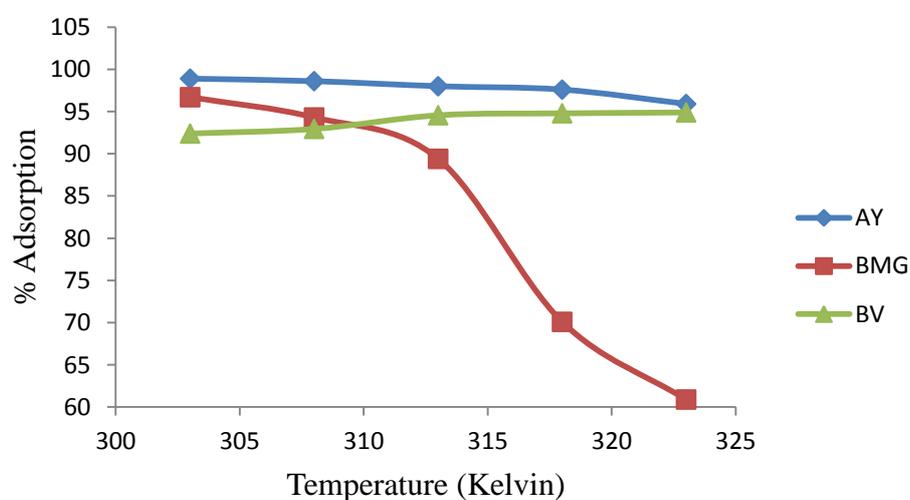


Fig. 8: Effect of Temperature on Adsorption of AY, BMG and BV onto *Albizia lebbek* Shells

Table 1: Optimum Conditions for the Adsorption of AY, BMG and BV onto *Albizia lebbek* Shells

Dyes	Time (min)	w (g)	C ₀ (mg/L)	pH	Temp. (K)
A Yellow	45	0.4	50	8.00	303
BM Green	30	0.4	60	8.00	303
B Violet	30	0.2	35	8.00	323

Thermodynamics of Adsorption

Thermodynamic properties of the adsorption processes for removal of AY, BMG and

BV were assessed using Van't Hoff's plots as presented in Fig. 9. Thermodynamic parameters evaluated from the plots are presented in Tables 2.

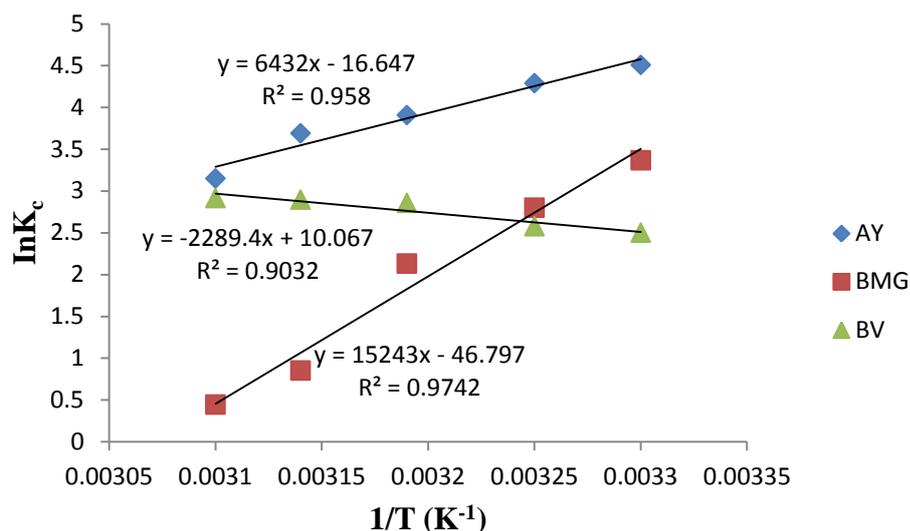


Fig. 9: Van't Hoff's Plots for Adsorption of AY, BMG and BV onto *Albizia lebbek* Shells

Table 2: Thermodynamics parameters for the Adsorption of AY, BMG and BV

Basic Dyes	ΔH (J/mol)	ΔS (J/molK)	ΔG (J/mol)	
			303K	323K
A Yellow	-53,475.648	-138.345	-11,557.125	-8,790.213
BM Green	-12,6730.302	-389.012	-8,859.648	-1,079.426
B Violet	19,030.746	83.639	18,335.371	-7,984.651

Scanning electron microscope (SEM) images of *Albizia lebbek* shell before and after adsorption of AY, BMG and BV are presented in Figs. 10, 11, 12 and 13 respectively. SEM images

could be used to establish whether pore diffusion and other morphological changes on the adsorbent surface take place.

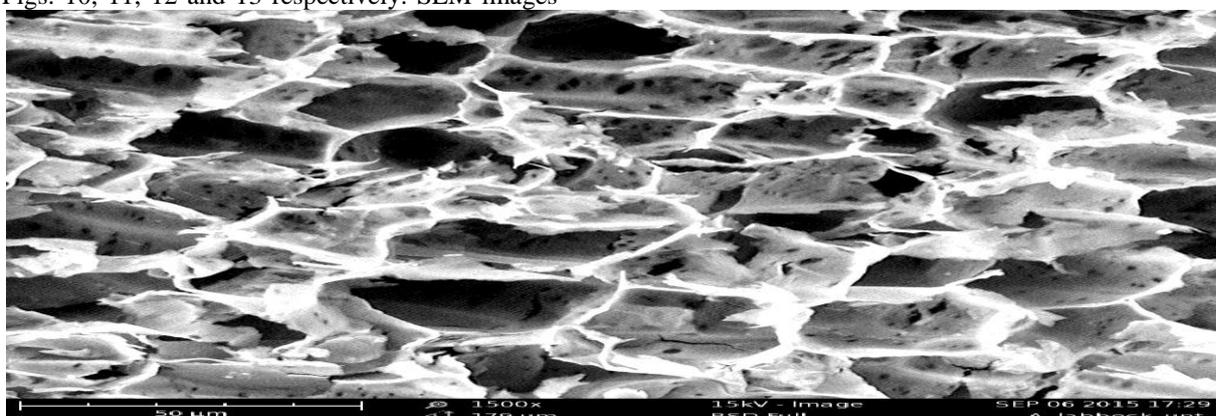


Fig. 10: SEM Image of *Albizia lebbek* Shells Prior to Adsorption

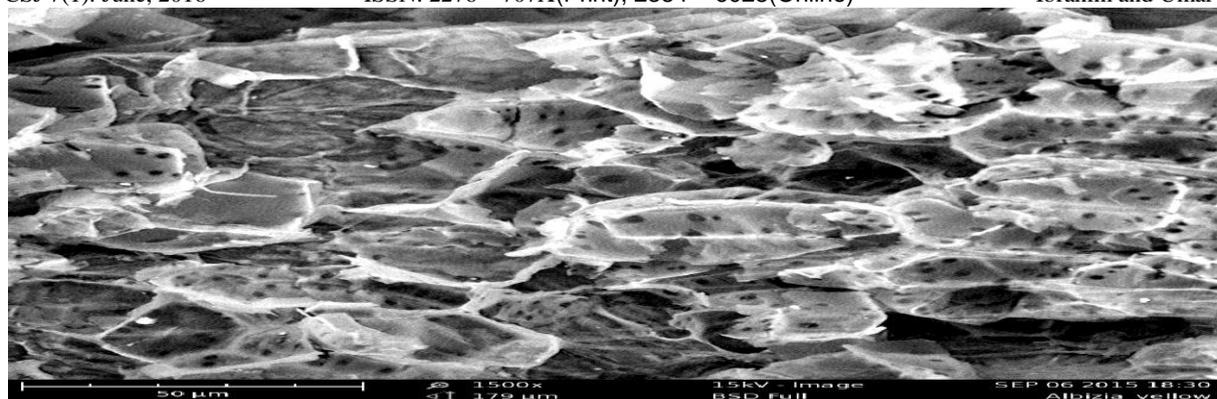


Fig. 11: SEM Image of *Albizia lebeck* Shells after Adsorption of Auramine Yellow



Fig. 12: SEM Image of *Albizia lebeck* Shells after Adsorption of Basic Malachite Green

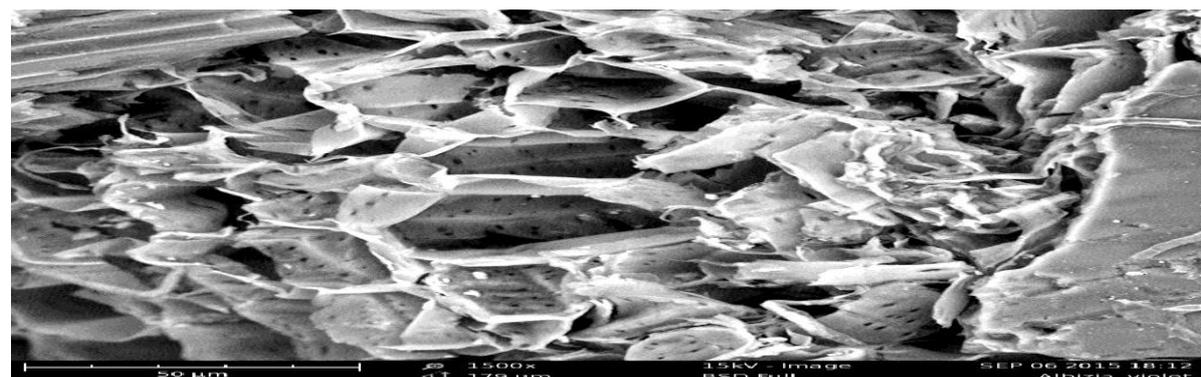


Fig. 13: SEM Image of *Albizia lebeck* Shells after Adsorption of Basic Violet

Effect of Contact Time

Experiment were conducted to find out the effects of contact time on the adsorptive removal of AY, BMG and BV by *Albizia lebeck* shells and the results are shown in Fig. 4. The maximum amount of AY, BMG and BV are adsorbed at equilibration time of 45, 30 and 30 minutes respectively. The rapid nature of the adsorptions could be attributed to nature of sorbate-sorbent interaction and large cavities on the adsorbent surface (Selvarani, 2000).

Effect of Adsorbent Dosage

The effects of adsorbent dosage on the removal of AY, BMG and BV have been studied. Fig. 5 represents the plots of amount of adsorbent

against percentage adsorption. It can be seen that as the dose of the adsorbent increases, extent of adsorption increases since there will be more active sites at higher sorbent dose before equilibrium is attained (Selvarani, 2000).

Effect of Initial Dye Concentration

Fig. 6 shows the effects of increase in dye concentration on the removal of AY, BMG and BV. The results showed that increase in the initial dye concentration increases the removal of the dyes due to increase in collision frequency between the dye molecules and the adsorbent particles before reaching equilibrium where 98.9% AY, 96.6% BMG and 91.2% BV were adsorbed (Anandan and Janakiram, 2013).

However, the process became feasible at high temperature of 323K.

Effect of pH

The effects of pH on the removal of AY, BMG and BV have also been investigated and the results are presented in Fig. 7. The pH values were measured using pH meter (Jenway 3320) and varied with 0.1 M NaOH and 0.1 M HCl. The optimum pH for the dyes removal were found to be around 8.00 since the dyes have cationic species which will have greater electrostatic attractions towards the negatively charged adsorbent surface at basic pH (Anandan and Janakiram, 2013).

Effect of Temperature

The effects of temperature on the adsorption of AY, BMG and BV are shown in Fig. 8. The results indicate that the adsorptions of AY and BMG are higher at low temperature suggesting exothermic processes. However, adsorption of BV is maximal at higher temperature indicating that the process is endothermic.

The differences in the optimum conditions for the removal of the dyes from aqueous solution using *Albizia lebbbeck* shells could be due to the nature, structure, basicity and purity of the adsorbate molecules (ions). These observations compare closely to those of Tahir *et al.*, (2008), Gaikwad and Kinldy, (2009) and Hossaini and Rahman, (2013) on their work on remediation of basic dyes (malachite green and methylene blue) using household used black tea as adsorbent, auramine dye adsorption on *Psidium guava* leaves and removal of basic violet 10 from neutral aqueous solution by adsorption on used black tea leaves respectively.

Van't Hoff's Plots

Linear plot of natural logarithm of the equilibrium constants ($\ln K_c$) against the reciprocal of the corresponding temperatures ($1/T$) from equation 3 were used to estimate the enthalpy, entropy and Gibb's free energy changes of the adsorption process. For an endothermic reaction, the slope is negative and so as the temperature increases, the equilibrium constant increases, where as the slope of an exothermic reaction is positive and so as temperature increases, the equilibrium constant decreases (Jean, 2015).

Table 2 shows that, adsorptions of auramine yellow and basic malachite green were found to be exothermic due to negative values of enthalpy changes (ΔH). This is also because of the decrease in adsorption with temperature (Jean, 2015). The processes were also found to be non-spontaneous and feasible due to negative values of ΔS and ΔG at tested low and high temperatures of 303K and 323K respectively. On the other hand, positive values of ΔH , ΔS and ΔG made the adsorption of basic violet to be endothermic, spontaneous and non-feasible respectively (Jean, 2015). This is also because percentage (%) adsorption was increasing with temperature.

Scanning Electron Microscopy

Fig. 10 shows the image of *Albizia lebbbeck* shells prior to the adsorption process. The morphological image revealed that the adsorbent could be a good adsorbent due to the large number of cavities and high porosity on its surface. Figs. 11, 12 and 13 displayed the irregular distribution of the dye molecules on the surface of the adsorbent after adsorptions of auramine yellow, basic malachite green and basic violet dyes onto *Albizia lebbbeck* shells. Most of the cavities are covered especially that used for the removal of basic violet dye as shown in Fig. 13. The images revealed clearly the differences in the morphology of the adsorbent before and after adsorptions. These changes in the morphologies are in good agreement with the literature for various materials (Al-Ghouti *et al.*, 2003; Saha *et al.*, 2010; and Ashish *et al.*, 2013).

CONCLUSION

The adsorptions of Auramine yellow (AY), Basic malachite green (BMG) and Basic violet (BV) dyes from aqueous solutions using *Albizia lebbbeck* shells adsorbent were studied at optimum conditions. Thermodynamic parameters such as ΔH , ΔS , ΔG were all evaluated and the values indicate feasible processes at 323K for all the dyes. Therefore, *Albizia lebbbeck* shells can serve as cheap, readily available, non-toxic and potential adsorbent for the removal of basic dyes particularly AY, BMG and BV from aqueous solution.

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