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Column adsorption studies for Methylene blue dye removal from aqueous solution using Rubber seed husk activated carbon

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ABSTRACT

This work studied the adsorption of MB dye onto activated carbon prepared from rubber seed husk using adsorption column. The activated carbon was characterised with FTIR and SEM and was used to study both batch and column adsorption of MB dye. Effect of dosage (0.02g, 0.05g, 0.08g, 0.11g, 0.14g, 0.17g, 2g), temperature (303K, 313K, 323K, 333K), and time (0-240mins) on the batch adsorption was studied. Effect of bed height (2.5mm, 5mm, 7.5mm, 10mm), pH(2, 4, 6, 8), initial dye concentration (20mg/l, 50mg/l, 80mg/l, 110mg/l) and flow rates (3ml/min, 5ml/min, 8ml/min, 10ml/min) on the breakthrough curve was studied. FTIR analysis revealed the presence of some functional groups that can enhance adsorption. SEM analysis confirmed sharp and distinct pores for the adsorption. It was observed that increase in flow rate form 3ml/min to 10ml/min reduced the breakthrough time from 170minutes to 50minutes. Increase in bed height from 2.5mm to 10mm increased the exhaustion time from 80 minutes to 170minute. Increase in initial dye concentration from 20mg/l to 110mg/l decreased the breakthrough time from 170minutes to 70minutes. It can be concluded that effective activation of rubber seed husk recorded high MB dye removal efficiency and it can be used to study breakthrough time for the adsorption process.

KEYWORDS: *Adsorption Column, Activated carbon, Rubber seed husk, MB dye*.

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I. INTRODUCTION

Dye is a major pollutant extruded by many Industries all over the world especially textile, paper, printing, leather, food, cosmetics etc which extensively use dyes to color their final products [1]. The presence of dyes in textile effluents is highly visible; it affects the aesthetics and the transparency of the water and the solubility of gases in the receiving bodies [2].

Various conventional methods are applied for the removal of dyes from wastewater but adsorption is worth mentioning among all [1]. The activated carbon is one of the versatile adsorbents because of its large surface areas and highly porous structures. The activated carbon which is widely used can be fully employed in fixed bed columns [3]. Due to high cost of conventional adsorbents, researchers have been directed to the use of alternative adsorbents like waste biomass.

The objective of the operation of adsorption column is to reduce the concentration of adsorbate (dye) so that it does not exceed a predefined value.

The ideal breakpoint time would be the column operation time required to obtain an output effluent with a true color of up to 75mg/l according to indices recognized by Resolution n^{o} 357 of 17th March 2005 of Conselho Nacional do Meio Ambience [4], the Fedral Government Agency which establishes the conditions and standards for effluent discharges [2].

The aim of this work is to study the ability of rubber seed husk in removing Methylene blue dye from aqueous solution using column process.

II. METHODS

The rubber seed husk was be obtain from rubber factory at Benue State, it was washed several times using de-ionized water to remove all traces of impurities, oil, dirt, dust, etc. then dried in the sun for 72 hours to remove excess water until constant weight was obtained.

Preparation of rubber seed activated carbon

Activated carbon was prepared from rubber seed using thermal heating in a furnace followed by chemical activation with potassium hydroxide. The method was according to the work done by Ejikeme et. al 2015 [5]with slight modification. Dried rubber seed was ground and screened to the desired mesh size of 1 – 2mm. The carbonization process was performed by loading a known quantity of the precursor into a vertical furnace, and the temperature was ramped from room temperature to 800^{o}C. The char produced was soaked in 6N KOH solution with impregnation ratio of (1.5: 1) defined as the volume of activating agent solution per weight of char. The mixture was then dehydrated in an oven for one hour to remove moisture. It was taken back to the furnace but at this time, the temperature was increased to 850°C.

The resultant activated carbon was washed repeatedly with 0.1MHCl and distilled water until PH 6-7 was reached in the residual liquid.

Preparation of Methylene blue dye solution

Methylene blue dye of commercial purity was used without further purification. The dye stock solution of concentration of 1000 mg/L was prepared by dissolving desired quantity of dye in distilled water. The experimental solutions of different initial concentrations were obtained by diluting the dye stock solution.

Adsorption column study

A glass column of 1.2 cm i.d. and 12.5 cm length was used for the column study. The column was packed with activated carbon pellets followed by a layer of glass beads on both the sides to provide uniform flow of solution. To avoid entrapping of air bubbles inside the activated carbon pellets, the particles was soaked in appropriate amount of water and agitated until no air bubbles were detected in the solution. Dye solution of three different concentrations (10, 15 and 20 mg/L) was percolated downward through the varying bed height (2.5–10mm) at a desired flow rates of 5, 10 and15 mL/min. The samples were collected at various intervals of time and analyzed using an UV–Vis spectrophotometer.

The adsorption kinetics models were determined using first order, second order, pseudo first order, pseudo second order and intra particle diffusion.

Characterisation of Activated carbon

The surface functional groups and structure were studied by fourier transform infrared spectroscopy [Buck 530 IR]. The FTIR spectra of the raw material and activated carbon were scanned at a wavelength of 600– 4000nm to obtain its spectra lines.

III. RESULTS AND DISCUSSION

Characterisation of Activated Carbon

Table 1 below shows the properties of the activated carbon used in this study. High surface area suggested high and well developed adsorption sites. The iodine number equally suggested that the micropore capacity was also high. These pointers show that the adsorption process will be favourable.

The SEM analysis (Figure 1) revealed sharp and distinct pores which confirmed effective activation and suggested that high adsorptive capacity will be recorded during the adsorption study. FTIR (Figure 2) confirm the presence of some functional groups that are necessary for the adsorption of MB dye on the activated carbon.

Parameters	Units	Activated carbon
Bulk Density	g/ml	0.58
Ph	-	6.9
Surface Area	m^2/g	832.1
Iodine number	mgI_2/g	458.3
Ash	%	3.6
Volatile matter	%	9.8
Fixed Carbon	%	80.8

Table 1. Physiochemical properties of rubber seed activated carbon

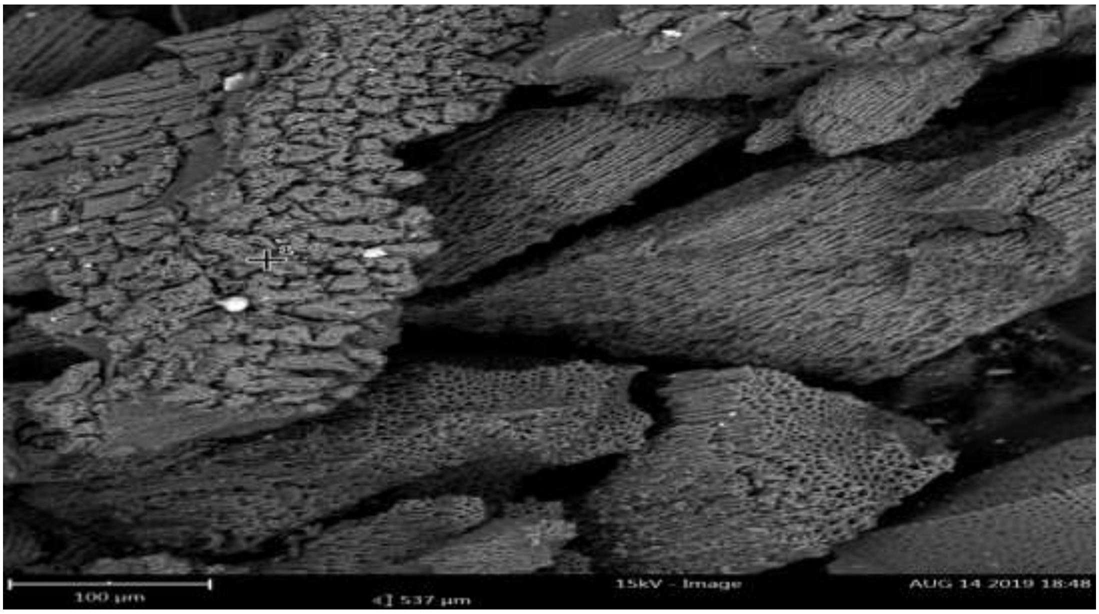

Figure 1. SEM analysis of rubber seed activated carbon

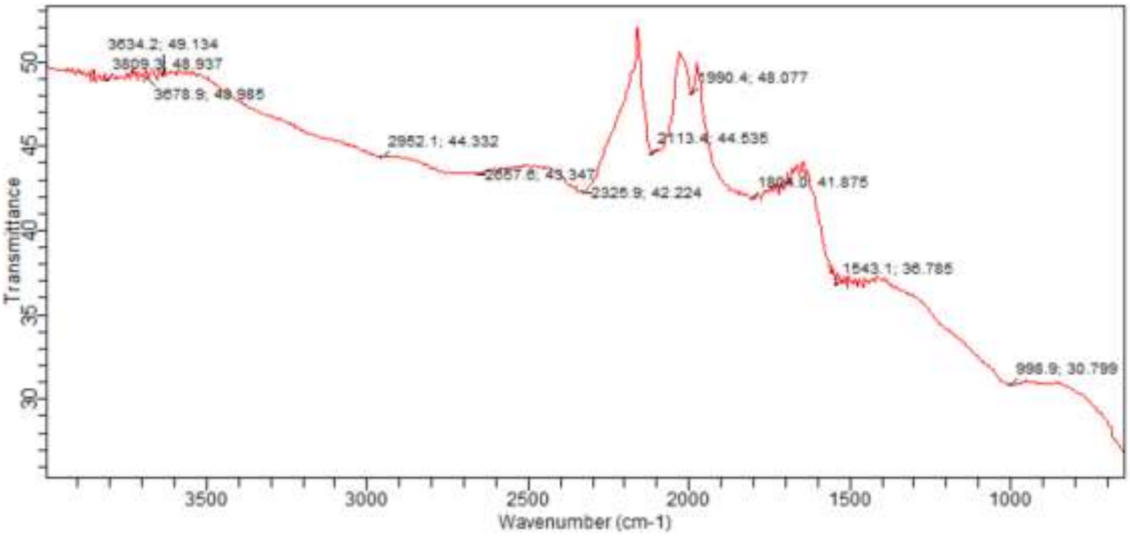

Figure 2. FTIR analysis of rubber seed activated carbon

Effect of time on the batch adsorption of MB dye

Figure 3 shows the effect of time on the batch adsorption of MB dye on rubber seed activated carbon. It was studied at initial concentrations of 20mg/l, 50mg/l, 80mg/l and 110mg/l for time interval of 0-240mins. It was observed that adsorptive capacity was rapid initially and reached equilibrium after about 200mins. There was two parts on the graph, the first was the instantaneous one where the dye adsorption was rapid and the second was the slow part where the adsorption of dye was sluggish and finally the adsorption reached equilibrium [6].

The initial rapid phase can be attributed to the large number of vacant sites on the surface of the activated carbon while the slow stage can be attributed to the repulsive forces between the adsorbed molecules on the activated carbon and bulk solution.

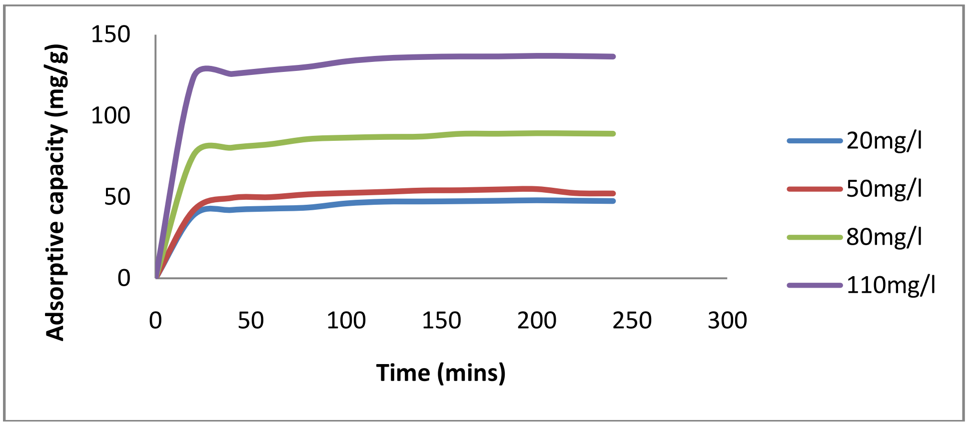

Figure 3. Effect of time on the batch adsorption of MB dye

Effect of dosage on the batch adsorption of MB dye

Figure 4 shows the effect of dosage of activated carbon on the adsorption of MB dye. It was studied at different initial dye concentrations and the dosage interval of 0-2g. It was observed that increase in activated carbon dosage increases the removal efficiency due to the increase in surface areas and availability of active sites [7], but adsorptive capacity decreases with increase in dosage. The decrease recorded on the graph can be attributed to the increase in the viscosity of the solution as a result of increase in dosage which inhibited the diffusion of dye molecules to the surface of the activated carbon [8].

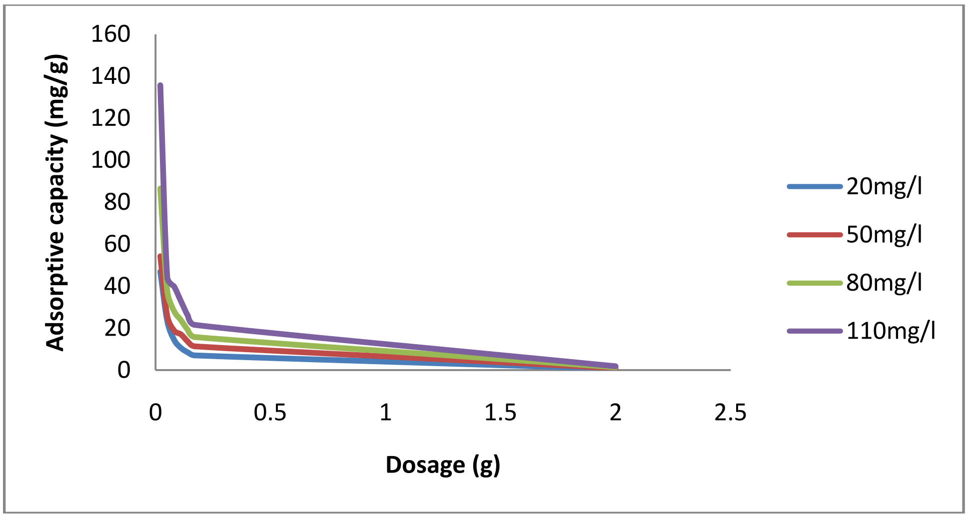

Figure 4. Effect of dosage on the batch adsorption of MB dye

Effect of temperature on the batch adsorption of MB dye

Figure 5 shows the effect of temperature on the adsorption of MB dye. It was studied at various initial dye concentration and temperature intervals of 303-333K. It was observed from the graph that increase in temperature decreased the adsorptive capacity of the activated carbon. This suggested the exothermic nature of the adsorption process. The decrease can be attributed to the tendency of the dye molecules to escape from the activated carbon after adsorption at higher temperature thereby favouring desorption process.

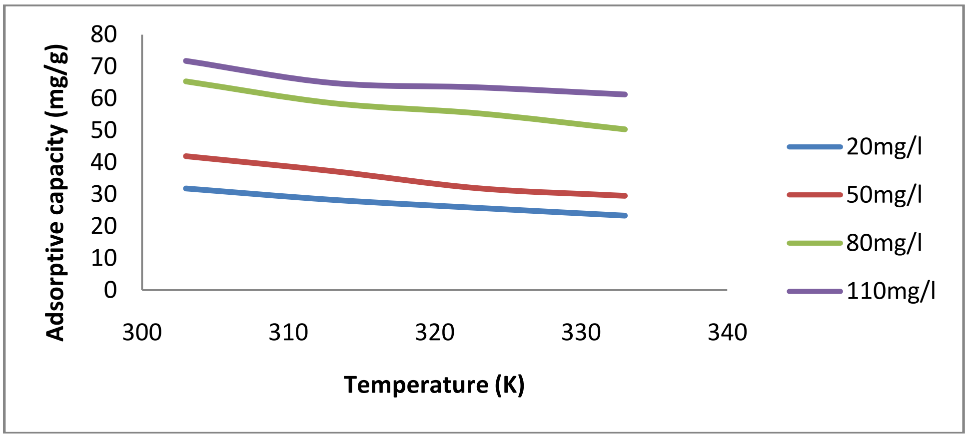

Figure 5. Effect of temperature on the batch adsorption of MB dye

Effect of flow rates on the column adsorption of MB dye

Figure 6 shows effect of flow rates on the adsorption of MB dye. To obtain the breakthrough time, different times were considered form 0 to 170mins. The flow rates were 3ml/mins, 5ml/mins, 8ml/mins and 10ml/mins. It was observed that increase in flow rate led to faster breakthrough. At lower flow rate, there was enough contact time between the activated carbon and the MB dye solution which resulted to higher removal efficiency. At higher flow rates, there was no sufficient contact time between the activated carbon and MB dye solution which resulted to the dye molecules leaving the column unadsorbed before equilibrium occurred.

Faster saturation was observed at higher flow rates due to increase in the rate of mass transfer onto unit bed height.

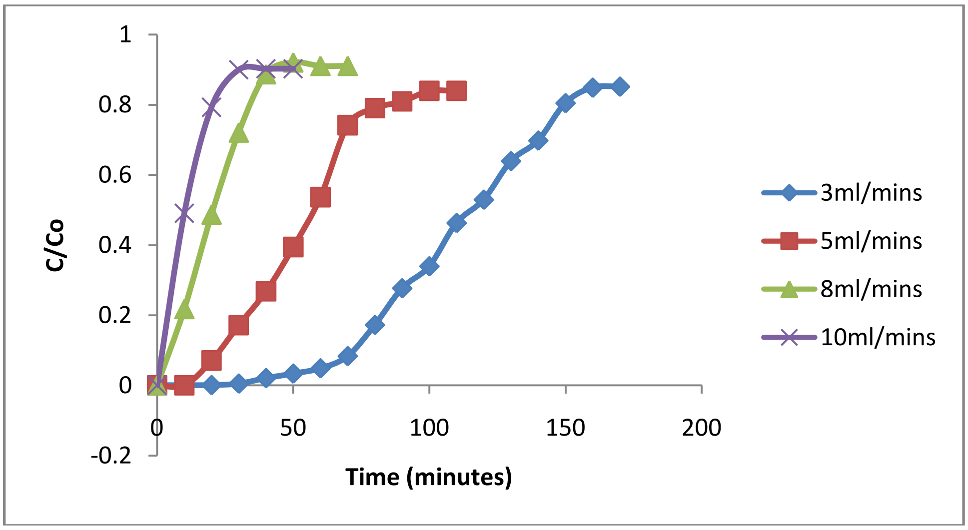

Figure 6. Effect of flow rate on the column adsorption of MB dye

Effect of initial dye concentration on the column adsorption of MB dye

Figure 7 shows the effect of initial dye concentration on the column adsorption of MB dye. The adsorption was done at a constant flow rate and different initial dye concentrations of 20mg/l, 50mg/l, 80mg/l, and 110mg/l at various time intervals of 0-150mins. It was observed that the breakthrough time was reduced as the concentration of dye was increased. Breakthrough time occurred faster as the concentration increased. Lower concentration gave rise to slower mass transfer. A decreased initial concentration gave an extended breakthrough curve since the lower concentration gradient caused a slower transport due to reduced diffusion coefficient and mass transfer coefficient.

The reduced breakthrough curve at higher concentration can equally be attributed to the saturation of active sites of the carbon at high initial dye concentration.

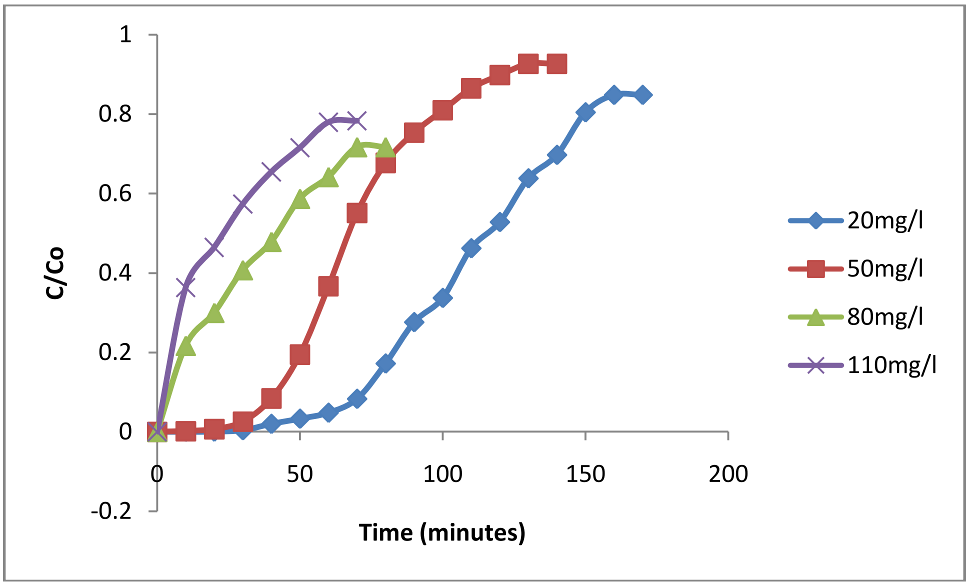

Figure 7. Effect of initial dye concentration on the column adsorption of MB dye

Effect of pH on the column adsorption of MB dye

Effect of pH was studied at pH of 2, 4, 6, and 8 as shown on figure 8. It was studied at constant flow rate and bed height. pH plays a major role on the adsorption of dye. Dye exists in an ionic form the aqueous solution. As charged species, their degree of adsorption on activated carbon is influenced by the surface charge on the activated carbon which in turn is affected by solution pH. The result reveals that the ion exchange activity between the dye and activated carbon is more at pH of 6. The breakthrough time occurred faster at high acidic and basic conditions which implied that neutral pH is more favourable for the adsorption process.

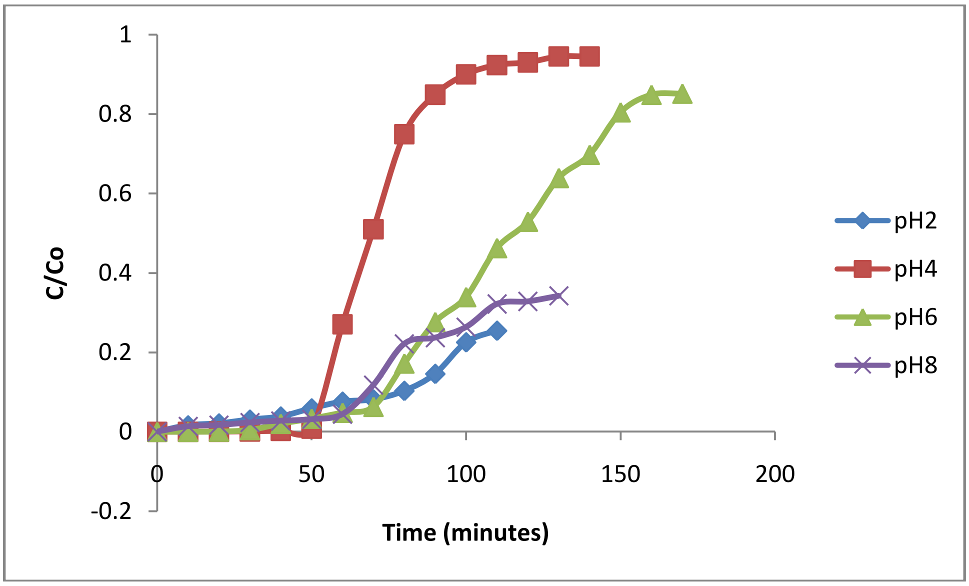

Figure 8. Effect of pH on the column adsorption of MB dye

Effect of bed height on the column adsorption of MB dye

Effect of column height was studied at the height of 2.5mm, 5mm, 7.5mm and 10mm at constant flow rate and pH (Figure 9). It was observed that increase in bed height increased the exhaustion time and extended the breakthrough curve. Increase in bed height provided more contact time for the activated carbon and the MB dye, therefore increasing the removal efficiency. Increase in bed height increased the amount of activated carbon on the column thereby increasing the surface area necessary for the adsorption. Higher bed height resulted in a decrease in the solute concentration in the effluent at the same time.

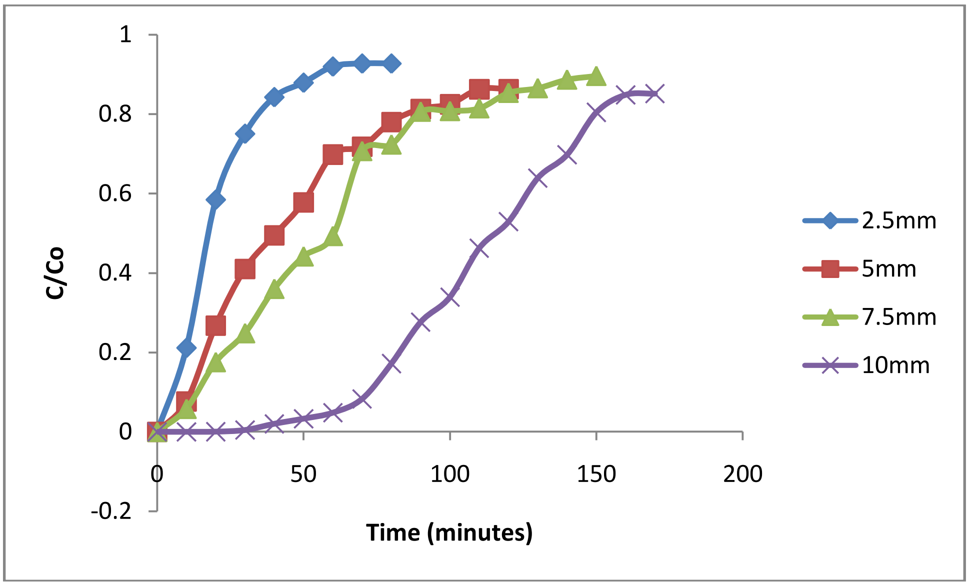

Figure 9. Effect of bed height on the column adsorption of MB dye

Equilibrium study for adsorption studies

The equilibrium data were fitted to Langmuir, Freundlich, Temkin, and Redlich-Peterson models. Table 2 shows the correlation coefficients for the fitted data.

The Langmuir constants were obtained from the slope and intercept of linear plot of Ce/qe versus Ce. It was observed that the Langmuir constant obtained decreased with the increase in temperature. This observation suggested exothermic nature of the process. All the fitted models had high correlation coefficients greater than 0.9. The data fitted more to freundlich model based on the highest correlation coefficient.

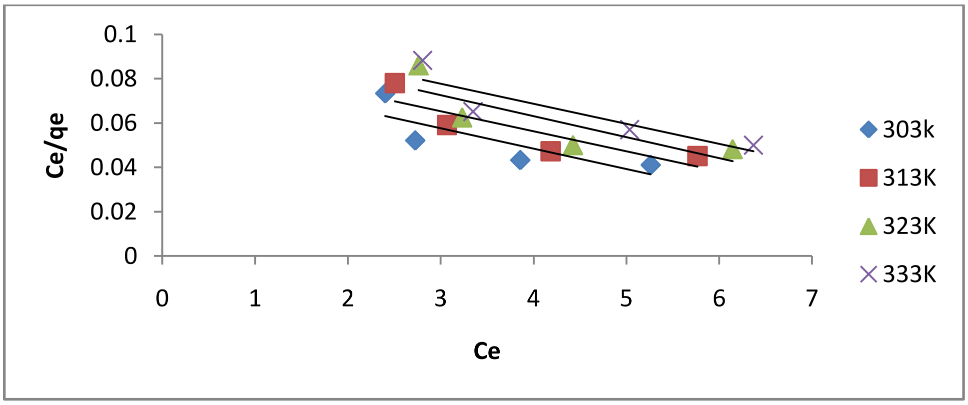

Figure 10. Langmuir plot for the adsorption process

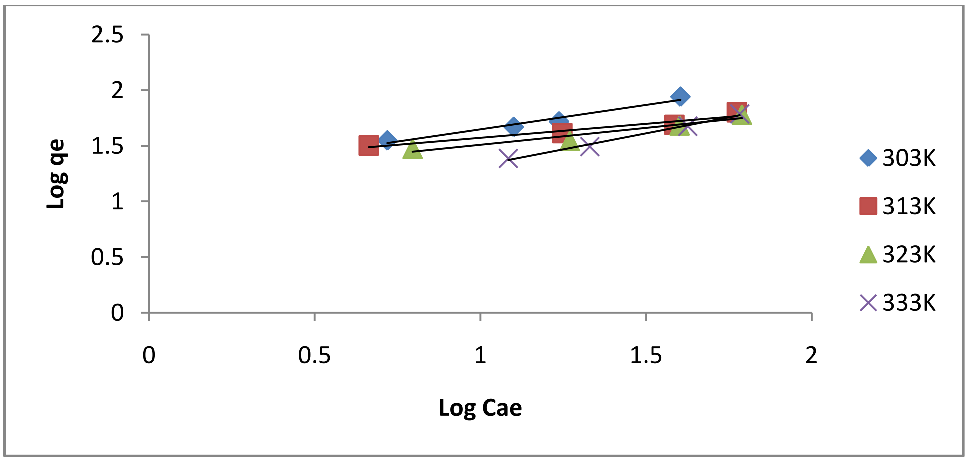

Figure 11. Freundlich plot for the adsorption of MB dye

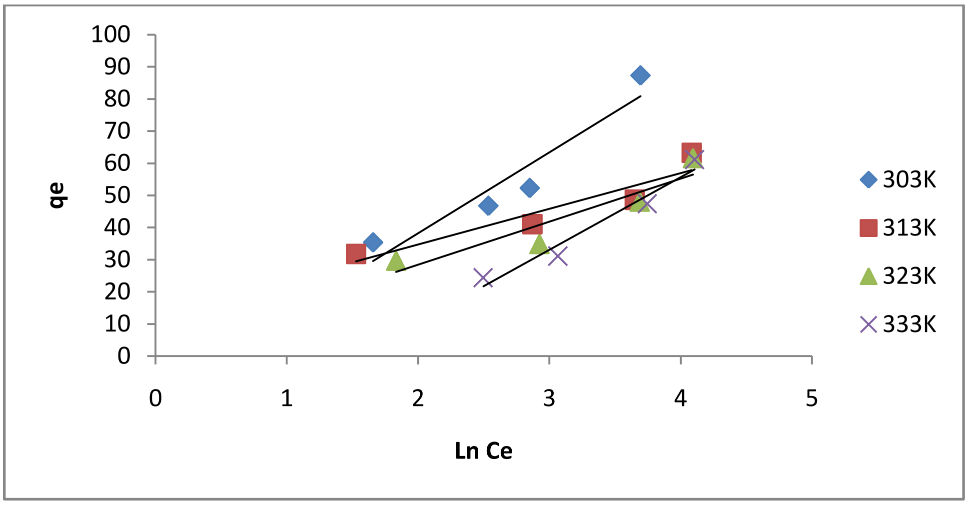

Figure 12. Tempkin plot for the adsorption of MB dye

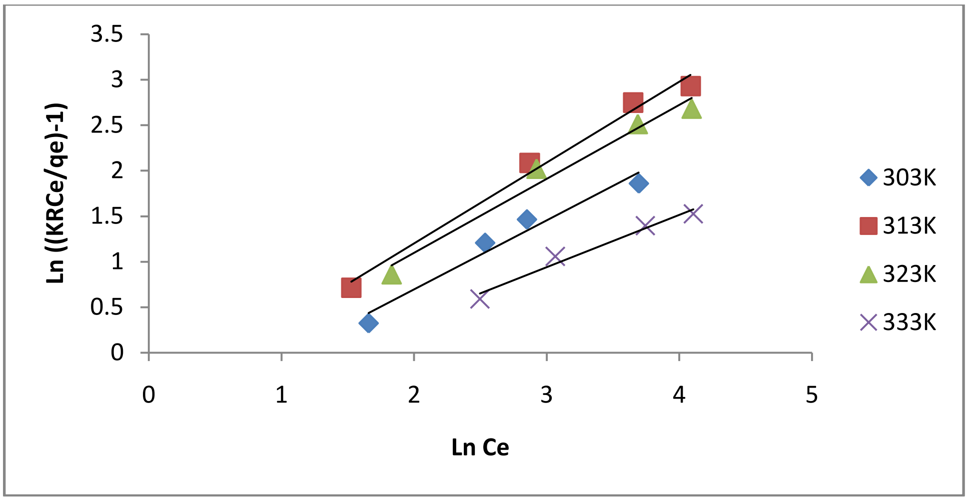

Figure 13. Redlich-Peterson plot for the adsorption of MB dye

Temperature(K)	303	313	323	333
		Langmuir		
R^2	0.9506	0.9645	0.9046	0.9555
		Freundlich		
R^2	0.9761	0.9753	0.9929	0.9979
		Temkin		
R^2	0.9472	0.9316	0.9517	0.9773
		Redlich-Peterson (R-P)		
R^2	0.9762	0.9749	0.9927	0.998

Table 2. Isotherm data for batch adsorption of MB dye

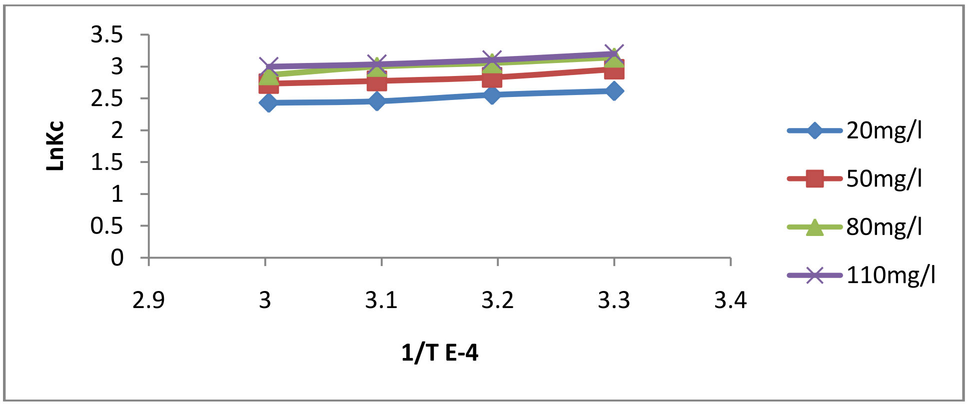

Figure 14. Thermodynamic plot for adsorption of MB dye

The adsorption process had negative values for enthalpy and enthropy. This suggested the process as exothermic in nature, feasible and spontaneous, while the positive value recorded for enthropy confirmed the process to had increase disorder. The magnitude of Gibb's free energy suggested the process to be physical in nature.

Initial Conc.(mg/l)	-ΔH (KJ/mol)	-ΔS (J/mol.K)	-ΔG(KJ/mol)			
			303K	313K	323K	333K
20.0	23.150	86.55	6.061	5.329	4.624	3.664
50.0	28.361	78.619	4.909	3.651	2.965	1.762
80.0	26.923	75.70	3.531	2.543	1.643	0.716
110.0	21.659	70.876	2.110	1.699	0.918	0.525

Table 3. Thermodynamic data for the adsorption of MB dye

IV. CONCLUSION

Activated carbon was successfully prepared from rubber seed husk for removal of Methylene blue dye from aqueous solution using both batch and column studies. It was observed that time, dosage and temperature had effect on the batch adsorption studies. Freundlich isotherm model fitted the batch adsorption process properly due to the high correlation coefficient. The adsorption process was feasible, spontaneous and exothermic in nature. It was equally observed that column adsorption studies depend on the column bed height, initial dye concentration and flow rates. The breakthrough time increased with increase in bed height, while increase in flow rates and initial dye concentration decreased the breakthrough time.

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