Adsorption equilibria of methylen blue dye from aqueous solutions by using activated carbon

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Abstract

In this study, activated carbon was prepared from coconut shell using sulfuric acid activation (CSAC). Removal of methylene blue (MB) dye from aqueous solution was performed using a batch technique for determination of the effects of initial pH, mass dosage, initial concentration and temperature. Adsorption of methylene blue (MB) was increased with increasing temperature, the maximum percentage removal of 73.14% (adsorption capacity 48.76 $mg.g^{-1}$), 77.07% (adsorption capacity 51.36 $mg.g^{-1}$), and 81.47% (adsorption capacity 54.31 $mg.g^{-1}$) for the temperature of 10 ^0C, 30 ^0C, and 55 ^0C respectively. Equilibrium data were mathematically modeled using the Langmuir, Freundlich, Fritz-Schelunder adsorption models to describe the equilibrium isotherms at different dye concentrations and temperatures, parameters of best-fit model were calculated and discussed. It was found that pH plays a major role in the adsorption process; adsorption capacity was influenced by the physical and surface chemical properties of carbon and the pH of the solution. Change in Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH) were also calculated, from the adsorption results were found the adsorption process was endothermic.

Key Words: Coconut shell, Methylen blue, Adsorption, Fritz-Schelunder model.

الخلاصة

في هذه الدراسة , تم تحضير الكاربون المنشط (CSAC) من قشور جوز الهند باستعمال حامض الكبريتيك كمادة محفزة. ازالة صبغة المثيلين الزرقاء من الحاليل المائية تمت من خلال طريقة الدفعات,التي استعملت لتحديد تاثير كل من الدالة الحامضية الابتدائية, وزن المادة المازة, التركيز الابتدائي وتاثير درجة الحرارة.

من خلال النتائج وجد بانه سعة الامتزاز تزداد مع ارتفاع درجة الحرارة, ان نتائج الامتزاز المستحصلة تمت معالجتها رياضيا باستعمال ايسوثرمات الامتزاز مثل لآنكماير, فرندلج, فرتس–سكلوندر, من خلال استعمال تراكيز مختلفة من المادة الممتزة ودرجات حرارية مختلفة, ثوابت المعادلات الايسوثرمية تم احتسابها ومن خلال معامل المطاوعة الخطية وجد بان النتائج العملية تطيع المعادلات اعلاه بصورة جيدة.

ايضا من خلال نتائج الامتزاز وجد بان تاثير الدالة الحامضية لها دورا مهما في عمليات الامتزاز, حيث وجد بان عملية الامتزاز تتاثر بالصفات الفيزيائية والكيميائية لسطح الكاربون وكذلك المحلول. ان التغييرات في الطاقة الحرة (ΔG) والانتروبي (ΔS) والانثالبي (ΔH) ايضا قد تم احتسابها, ومن خلال قيم الانثالبي وجد بان التفاعل هو ماص للحرارة.

الكلمات المفتاحية:الكاربون المنشط, , صبغة المثيلين الزرقاء, الامتزاز.

Introduction

Synthetic dyes have been increasingly used instead of natural dyes due to their ease of application, low cost of synthesis, stability and variety of color.[1, 2] Some of these dyes from wastewater effluents are toxic and even carcinogenic, highly colored and, the disposal of these wastes to receiving waters induces damage to the environment as they may significantly affect photosynthetic activity in aquatic life due to reduced light penetration. Color removal from these kinds of effluents is a major environmental problem due to the difficulty of treating such streams by convectional physical, chemical and biological treatment methods.[3-5]

These are generally synthetic and often contain aromatic rings, and hence many exhibit high resistance to biodegradation[6]. Methylene blue (MB) is a cationic dye widely used for dyeing of cotton, wool, and silk[7]. It is visible in wastewater at low concentration (1.0mg L^{-1}) which is undesirable, and can show toxic effects on living organisms[7]. Several physical and chemical treatment methods such as adsorption, oxidation or ozonation, biodegradation, coagulation/flocculation, and chemical precipitation have been used for the treatment of wastewater containing dyes[6, 8, 9]

Adsorption is one of the efficacious methods for removing pollutants from industrial wastewaters[10]. Due to high cost of commercial adsorbents, various agricultural waste materials have been widely examined for the preparation of low cost activated carbon such as tea industry waste[11], rice husk[12], cotton stalk[10], and sugar beet molasses[13].

Preparation of activated carbon is carried out by physical or chemical activation process. Physical activation method consists of two steps. The first step is carbonization and the second is activation with carbon dioxide or steam. Chemical activation is a single step process that activation is based on the decomposition of precursor with a chemical activator such as KOH,

K_2CO_3, NaOH, $ZnCl_2$, H_2SO_4 and H_3PO_4 at elevated temperatures.[2, 14-17]

In this study, activated carbon was produced from coconut shell by sulfuric acid activation method and Methylene blue (MB) adsorption ability of the prepared (CSAC) was examined in batch adsorption technique. Effective parameters such as initial pH of Methylene blue (MB) solution, activated carbon dosage, temperature, etc. were investigated. Methylene blue (MB) adsorption equilibrium, and thermodynamics were also evaluated.

Experimental part

Materials

Coconut shell where collected as a waste materials. The coconut shells were washed with water and dried at 105°C in a hot oven until it is completely dry. The dried coconut were crushed, sieved to size 2.0 to 2.5 mm and stored in airtight containers for further experimentation. Analytical grade MB supplied by Sigma-Aldrich, is used as adsorbate without further purification. The concentration of this dye is determined using a uv-visible spectrophotometer at 660 nm wavelength

Preparation of Coconut Shell Activated Carbon (CSAC)

10 g of dried coconut shell was impregnated with 50 mL of 60 %(v/v) H_2SO_4 solution, in an impregnation ratio of 3:1(wt. H_2SO_4: wt. Coconut shell). The H_2SO_4 soaked sample was left overnight and the excess water is evaporated in an oven at 100°C to ensure complete removal of the H_2SO_4 on to the coconut shell powder. The acid soaked samples are semi-carbonized in a hot air oven at a preset furnace temperature of 500°C for 2 h under a self-generated atmosphere. After activation, the samples were washed repetitively with distilled water to remove residual acid. The product was finally air dried at 105°C, before been manually ground to a fine powder and sieved to a size below 75 µm, which are utilized for product characterization.

Adsorption studies

Methylene Blue with a molecular formular of $C_{16}H_{18}ClN_3S$ was used without further purification. The chemical structure of MB is shown in Figure 1. The stock solution was prepared by dissolving appropriate amount of MB in distilled water. The stock solution was diluted to obtain the initial MB concentrations used in the sorption experiments.

To study the effect of MB concentration on color removal, 0.075 g of (CSAC) was added to each 100 mL of MB solution pH (5.6). The initial concentrations of the dye solution tested were 10, 20, 30, 40, 50, 60 and 75 mg/L and the experiments were carried out at three temperatures 10 ^{0}C, 30°C, and 55 ^{0}C for 60 min.

To examine the effect of temperature on the adsorption process, the temperature of the adsorbate solution was controlled at 10°C, 30 ^{0}C and 55°C. The effect of CSAC dosage on the adsorption process was investigated by varying the CSAC dosage of Methylene blue (MB) solution was varying from 0.02 to 0.2

gm in 100 mL of aqueous solution of MB 50 $mg.L^{-1}$, at pH 5.6.

The effect of pH on the adsorption process was investigated by varying the pH of Methylene blue (MB) solution from 2.05–11.2. The pH of the solution was controlled with 0.1 M HCl and 0.1 M NaOH solution as per required pH value. The flasks were then removed from the shaker, 3 cm^3 of reaction mixture was collected and centrifuged (4000 rpm, 15 minutes), the supernatuant was measured at maximum wavelength of Methylene blue MB (660 nm) using a UV/vis spectrophotometer.

The samples were centrifugal for two times prior to analysis in order to minimize interference of the carbon fines with the analysis. The amount of adsorption at equilibrium, qe (mg/g), was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L), and m is the mass of dry adsorbent used (g).

also the percentage of dye removed (*R*%) from solution was calculated using the following equation

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

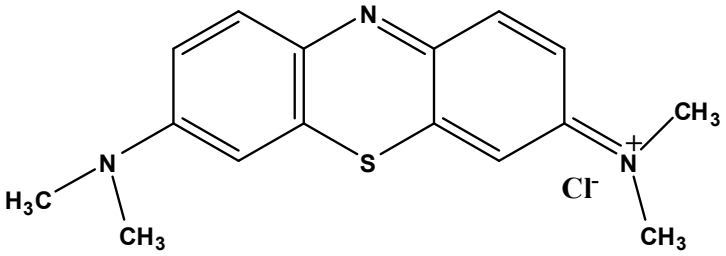

Figure 1: Chemical Structure of Methylene Blue.

Results and Discussion

Effect of pH

The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of different pollutants. Change of pH affects the adsorptive process through dissociation of functional groups of the adsorbent surface active sites. This subsequently leads to a shift in reaction

kinetics and equilibrium characteristics of adsorption process.

Therefore the pH of the solution appears to be a strong factor affecting the adsorption characteristics of Methylene blue (MB) onto CSAC as it controls the electrostatic interaction between CSAC and the Methylene blue (MB) molecules.[18, 19]

In this study, impact of pH has been investigated by adjusting pH of the dye solutions from 2 to 11. In the conducted experiments, 0.075g activated carbon has been added into 100mL of 50mg/L dye solution. Samples have been shaken for 60min in 200rpm agitation speed at 30 ^{0}C, the obtained results are given in Fig. 2.

Initially, it seems increasing the pH of the dye solution (pH 2.2 – 4) yields an increase the adsorption capacity of CSAC (Fig. 2), but decrease in adsorption of Methylene blue (MB) ions was observed as the pH increases (pH 4 – 6). With further increase in pH, adsorption again significally decreased and continuously till the pH of 11 Fig. 2).

At strongly acidic media remarkable electrostatic attraction exists between the positively charged surface of the used adsorbent and anionic dye molecules[19], this is due to zero point charge effect of the surface and also ionization state of methylen blue dye, because the surface will have high positive charge density, and, under these conditions, the uptake of methylene blue (MB) would be quite low because of electrostatic repulsion, then after pH 6, the percentage of removal will decrease. Beyond pH 7, the adsorption gradually highly decreases because of surface saturation.[20]

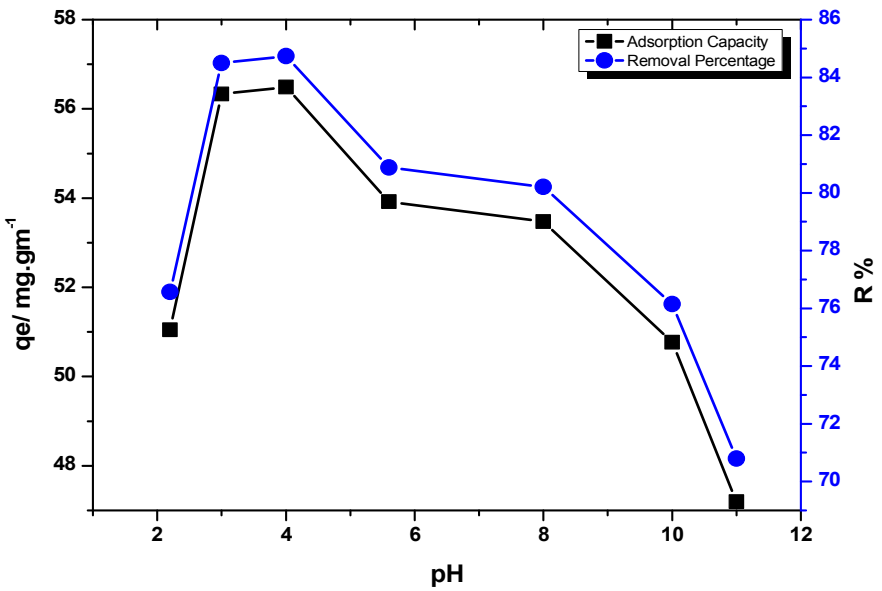

Figure 2: effect of pH on the adsorption of Methylene blue (MB) by the surface of CSAC. (mass dosage 0.75 gm.L^{-1}, Temp. 30 C, dye cocnetration 50 ppm, agitation rate 200 rpm, time of agitation 1 hr.)

Effect of Mass dossage

In order to provide quantitative adsorbate uptake determination of ideal adsorbent dosage is demanded. Commonly increasing adsorbent dosages improve adsorption efficiencies. This can be explained by the increase of surface area where the adsorption takes place .

Under the conditions of pH of dye solution (pH 5.6), C_0 of 50 mg/L, and contact time of 60 min., the effect of dose of activated carbon (obtained at the optimum conditions) on the percentage removal and adsorption capacity of methylene blue (MB) is shown in Fig. 3.

It is apparent that the percentage removal of methylene blue (MB) was increased by increasing the activated carbon dose. This was the reason that the number of available adsorption sites was increased by increasing the adsorbent dose[21-23].

When the activated carbon dose was 2 g/L, the removal percentage of MB can reach 96.3%, and in vise-versa for the adsorption capacity will be (21.3 mg.g^{-1}). Increases in the percentage of dye removal with increases of adsorbent masses could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption, as already was reported in the literatures.[24-26]

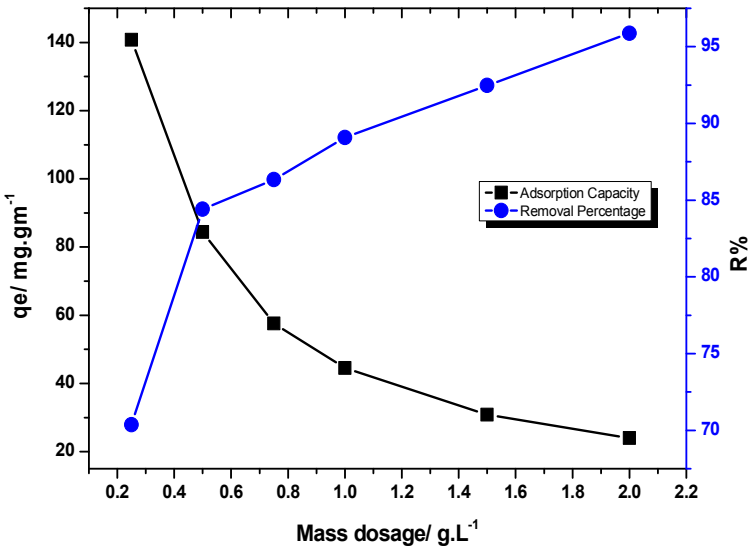

Figure 3: effect of mass dosage on the adsorption of MB onto the surface of CSAC. (pH of solution 5.6, Temp. 30 C, dye concentration 50 ppm, agitation rate 200 rpm, time of agitation 1 hr.)

Effect of Temperature

To examine the effect of temperature, the CSAC 75 mg, was added to the MB solutions (100 mL) at the initial concentration of 50mg L^{-1} pH (5.6) and then these suspensions were shaked for 60 min at over a range of temperatures 10°C, 30°C, and 55°C. The temperature dependence of the adsorption process is a complex phenomenon. Temperature rise affects the solubility, molecular interaction, and chemical potential of the adsorbate, the latter being a controlling factor for adsorption. In these experiments, the adsorption of MB on the adsorbents was analyzed at three different temperatures as shown in Figure 4.

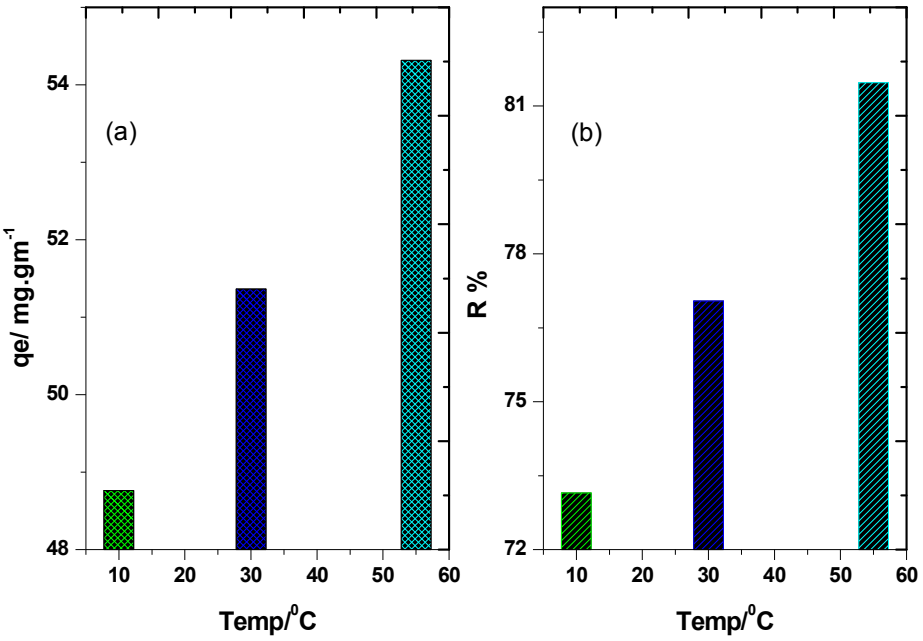

Figure 4: effect of temperature dosage on the adsorption of MB by the surface of CSAC, a)adsorption capacity, and b)percentage of removal % (pH of solution 5.6, mass dosage 0.75 gm.L^{-1}, dye concentration 50 ppm, agitation rate 200 rpm, time of agitation 1 hr.)

It is clear from figure 4, the uptake of dye increases with the increase with increasing temperature. The maximum percentage removal of 73.14% (adsorption capacity 48.76 mg.g^{-1}), 77.07% (adsorption capacity 51.36 mg.g^{-1}), and 81.47% (adsorption capacity 54.31 mg.g^{-1}) for the temperature of 10 ^{0}C, 30 ^{0}C, and 55 ^{0}C respectivelly was obtained at normal pH of dye, this fact may be due to increasing of MB mobility with the increasing of temperature [14]

On the other hand, if temperature has the reverse effect on the solubility, then both the side effects will act in the opposite direction and adsorption may increase or decrease depending on the predominant factor.[20]

Thermodynamic study

The thermodynamic parameters, including the free energy changes (ΔG^0), standard enthalpy changes (ΔH^0) and the entropy changes (ΔS^0) associated with the adsorption process, can be used to deduce the adsorption mechanism. They can be calculated by the dependence of thermodynamic equilibrium constant (K_s) on temperatures[27]:

$$\Delta G^0 = -RT\ln K_s \quad (3)$$

$$\ln K_s = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4)$$

The thermodynamic equilibrium constant (K_s) for the adsorption of MB on CSAC can be calculated using the equation[28]:

$$K_s = \frac{q_e}{C_e} \times \frac{v_1}{v_2} \quad (5)$$

where v_1 is the activity coefficient of the adsorbed solute, and v_2 is the activity coefficient of the solute in equilibrium suspension. The ratio of activity coefficients was assumed to be uniform in the dilute range of the solutions[28]. As the concentration of the dye in the solution approached zero, the activity coefficient approached unity and Equation. (5) will be:

$$\lim_{C_e \to 0} \frac{Q_e}{C_e} = K_s \quad (6)$$

The values of K_s determined from Figure 5, by plotting ln qe/Ce versus Ce and extrapolating to Ce = 0 [28]. The calculated values of K_D and the correlation coefficients are listed in Table 1.

According to Equation. (3), the values of ΔG^0 were calculated and listed in Table 1. The values of ΔG^0 of (dye /CSAC adsorption systems) are negative, which indicates the spontaneous adsorption processes. Moreover, the increase in the absolute value of ΔG^0 with increasing temperature indicates that higher temperatures facilitated the adsorption.

The value of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the van't Hoff plot (Equation. (4)) of $\ln K_s$ against $1/T$, respectively (**Figure not shown**), and the results are listed in Table 1. The positive value of ΔH^0 indicates that the adsorptions processe are endothermic. When attraction between adsorbates and an adsorbent took place, the change in standard enthalpy was caused by various forces, including van der Waals, hydrophobicity, hydrogen bonds, ligand exchange, dipole–dipole interactions and chemical bonds.

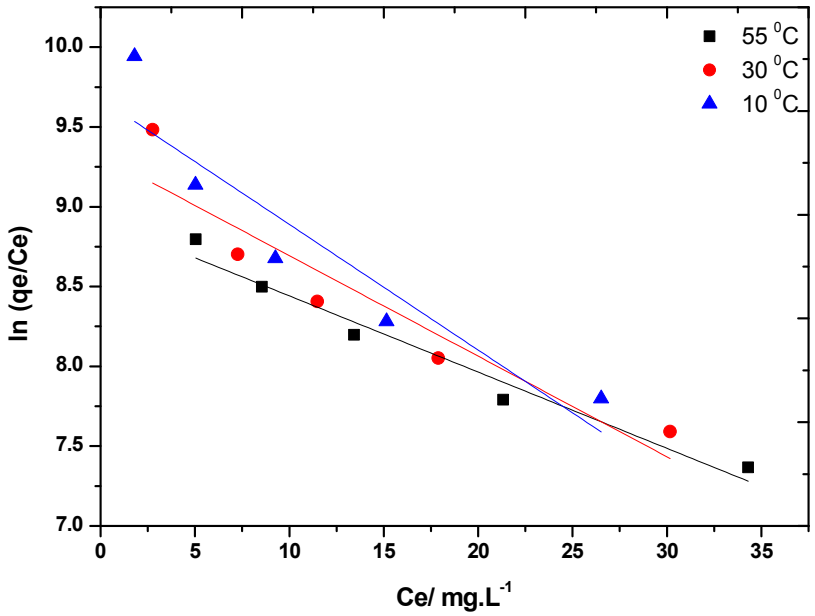

Figure 5: Linear plots for determination of equilibrium constant (K_s) values at different temperatures.

Table 1: Thermodynamics parameters for adsorption of MB dye by CSAC surface.

Temp./ K	K_s	SE	R^2
283	8.91922	0.09638	0.95871
303	9.32299	0.21700	0.98864
328	9.67642	0.25222	0.98102
Temp/ K	**ΔG^0/ kJ.mol^{-1}**	**ΔH^0/ kJ.mol^{-1}**	**ΔS^0/ J.K.$^{-1}$mol^{-1}**
283	-4.9175	1.395	23.13
303	-5.5823		
328	-5.9740		

Equilibrium study for adsorption of methylene blue (MB)

The adsorption isotherm describes how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. It can provide qualitative information on the nature of the solute–surface interaction at constant temperature. [21]

Equilibrium studies have been performed at three different temperatures and data were fitted to three different adsorption isotherm models viz., Langmuir[29], Freundlich[30], and Fritz-Schelunder adsorption isotherm models [31]. Results are shown in figure 6, the values of equilibrium constants are found out and shown in Table 2.

Separation factor or equilibrium parameter (R_L), as determined using the following equation:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (4)$$

R_L is an essential characteristics of Langmuir isotherm model[32-34]. In Fig. 7, R_L have been plotted against initial concentration at three different temperatures viz., 10 °C, 30 °C and 55 °C. It is evident

from the figure that in all the cases R_L lies in the range of zero to one, ($0 < R_L < 1$).

This indicates that adsorption of Methylene blue (MB) on CSAC is favourable at the operating conditions being studied. The decrease in R_L values with increase in initial concentration of Methylene blue (MB) points out that removal is more favourable at higher initial concentration which is in conformity with the observation made by Dutta et al. [17].

The results found fitted to Freundlich model. The magnitude of the exponent, $1/n$, gives an indication of the favourability of adsorption. Value of $n > 1$ represents favourable adsorption condition [35].

The Fritz -Schelunder model fitted the experimental data better than Langmuir and Freundlich models, indicating the adsorption of methylene blue (MB) onto the adsorbent tended to multilayer adsorption. The R^2 of the three models descend in the order of: Fritz -Schelunder> Freundlich > Langmuir.

The maximum removal capacity of CSAC derived from coconut shell for Methylene blue (MB) is found to be 61.7 mg/g as evident from the value of *qmax*, Langmuir adsorption isotherm model parameter. This value is compared to those obtained in the literature for activated carbons prepared from various agricultural wastes (Table 3). It can be seen from this (Table 3) that the prepared activated carbon can be classified as one of the effective adsorbents for this purpose.

Table 2: Experimental constants for the adsorption isotherms models under study.

Isotherm models	Parameters	Temp./283 K	Temp./303 K	Temp./328 K
Langmuir $q_e = \frac{K_L q_{max} C_e}{1 + K_L C_e}$	q_{max}	51.7680	51.7465	55.1642
	K_L	1.3400	3.8714	4.8762
	R^2	0.9125	0.8162	0.8094
Fruendlich $q_e = K_F C_e^{1/n}$	K_F	24.5188	30.090	33.437
	1/n	0.2408	0.2073	0.2076
	R^2	0.9514	0.9569	0.9637
Fritz-Schelunder $q_e = \frac{K_L q_{max} C_e}{1 + q_{max} C_e^n}$	K_L	25.3784	16.8744	17.9117
	qm	45.116	45.8742	57.5273
	n	0.8483	0.8247	0.8249
	R^2	0.9750	0.9546	0.9645

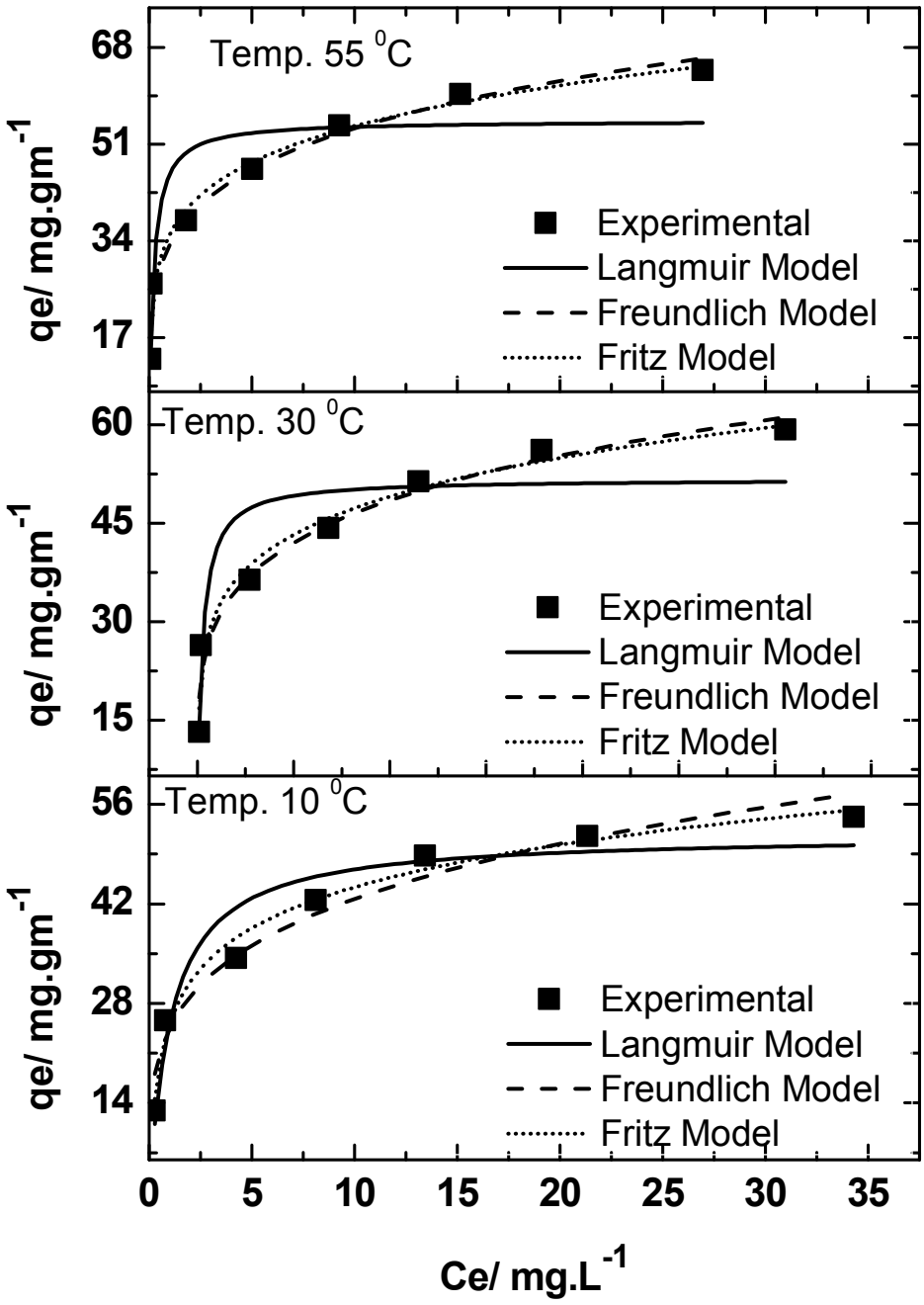

Fig. 6. Comparison of different isotherm models for MB adsorption onto (CSAC) in the presence of different temperatures.

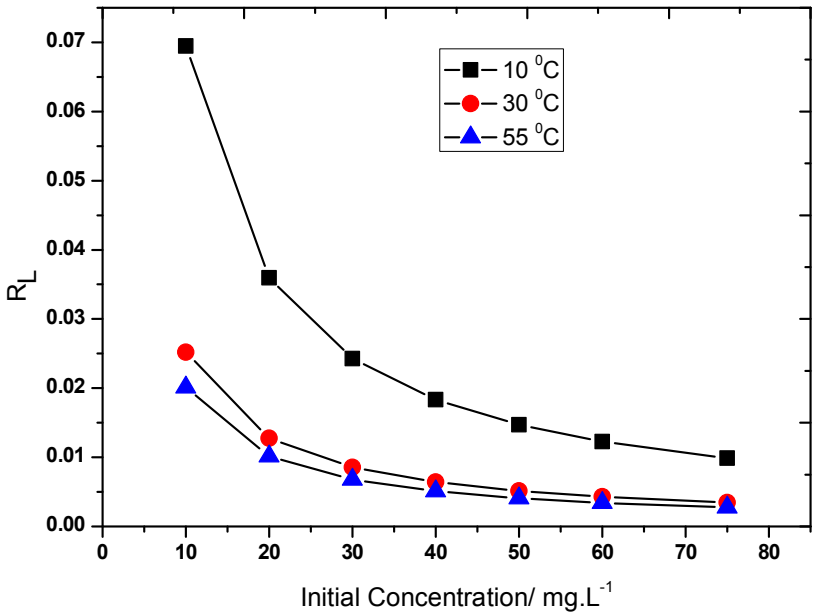

Figure 7: Separation factor or equilibrium parameter (R_L) behaviour with different initial concentrations, at different temperatures.

Table 3. Comparison of MB maximum adsorption capacity onto activated carbon prepared from various precursors.

Activated carbon	Activator	Maximum capacity ($mg.g^{-1}$)	Ref.
Coconut shell	H_2SO_4	61.7	This study
Sunflower cake-carbon	H_2SO_4	16.43	[2]
Citrus fruit peel-carbon	H_3PO_4	25.51	[17]
Apricot stones-carbon	$ZnCl_2$	4.11	[16]
Wood apple rind-carbon	H_2SO_4	40.00	[15]

Conclusions

Sulfuric acid has been used as an activator for preparation of activated carbon from coconut shell. Maximum MB adsorption capacity of 61.7 mg/g was obtained at operating conditions of 5.6 pH value, 0.75 g/L adsorbent dose and 60 min. contact time. Equilibrium adsorption data of MB onto CSAC were well represented by Fritz-Schelunder isotherm model with R^2 value of 0.9750. The calculated thermodynamic parameters, namely ΔG, ΔH, and ΔS showed that adsorption of MB onto CSAC was spontaneous and endothermic under examined conditions.

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