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THERMODYNAMIC ADSORPTION STUDIES OF ACTIVATED CARBON FROM COCONUT SHELL USING METHYL ORANGE DYE

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ABSTRACT

The present work evaluates the prepared coconut shell activated carbon (CSAC) using chemical activation as an adsorbent in removing Methyl orange (MO) dye from aqueous solution. Batch Adsorption experiments were conducted to determine the effectiveness of the CSAC as an adsorbent. The maximum adsorption capacity of 3.0 mgg^{-1} and the maximum %Removal of 99.8 were attained at optimum conditions of 6 gL^{-1} adsorbent dosage, contact time of 80 min, and at temperature of 330 K. the results obtained from enthalpy (ΔH° = 46.4 KJ/mol) and Gibb's free energy of adsorption ΔG° = -3.62KJ/mol, -5.03 KJ/mol, -6.65 KJ/mol and -8.59 KJ/mol at 300 K, 310 K, 320 K and 330 K respectively, which concluded that, thermodynamic parameters show the adsorption process was exothermic, spontaneous and feasible in nature. The examination of the experimental data accord with Langmuir adsorption isotherm.

Keywords: Activated carbon, Zinc chloride, Methyl orange, Adsorption, Kinetic, Thermodynamic

INTRODUCTION

Due to the introduction of this industrial waste dye into water bodies, both the environment and human health are at risk. This effluent mainly contains a lot of organic matter, inorganic matter, heavy metals, and toxic dyes. When non-treated effluent is released directly into a natural water source, the photosynthetic process in aquatic environments may be negatively impacted. (Hynes *et al.,*2020). Also, Climate change and the rapid increase in world population have had a substantial impact on water quality, causing a growing freshwater problem on a global scale. Although environmental contamination is unavoidable, it can be regulated using a variety of pollution-control measures (Wong *et al.*,2019)

A dye is a colorful substance that can be either natural or manufactured and contains at least one color-bearing group (chromophore) and color-helping group (auxochrome), which are repulsive and unwelcome in wastewater (Lin *et al.,* 2017). generally, organic and inorganic dyes that are released directly into rivers without any preparation have a range of negative effects. One of the major characteristics of dyes is they can expose color easily in the water due to the availability of chromophore compounds in their structure. Methyl Orange is one of the very common water-soluble azo dyes (commonly known as a pH indicator) that is extensively used in several industries including the textile, paper, printing, and food industries and mostly discharged in industrial wastewater (Malviya *et al.,* 2015). Methyl orange is available in generic form with common side effects which include abnormal urine or stool color, mild bladder irritation, dizziness, headache, increased sweating, nausea, vomiting, abdominal pain, diarrhea, upset stomach, frequent urination, or stomach cramps. The effluents from industrial activities are considered to be most significant source of water contamination, among many others (Ikram *et al.*,2020). Activated carbon was found to be a potent and effective adsorbent for the removal of dye from an aqueous solution, according to the results of the current study. (Hussain *et al,* 2023). Due to its high adsorption capacity, activated carbon is typically the favored adsorbent for the removal of contaminants (Enenebeaku *et al.,* 2016). Zhang *et al.,* (2016) were able adsorbed and/or removed 90.9% methyl orange model dye using a synthesized nano-ZnO/chitosan composite membrane (ZnOCTF). using batch adsorption technique, Hussain et al., (2023) also synthesized activated carbon from ginger bread plum (GBPA) which thermodynamically feasible, endothermic and spontaneous in nature. In this research, activated carbon derived from coconut shell was utilized to remove methyl orange dye from aqueous solution. The effect of experimental parameters on the efficiency and adsorption capacity were investigated using batch experimental methods. Thermodynamic parameters for the adsorption of methyl orange onto CSAC was studied together with Langmuir isotherm model.

MATERIALS AND METHODS

Materials

All the reagents used in this research were of analytical and used further purification. Preparation of stock and other working solutions were done by double distilled water.

Sample Collection and Adsorbent Preparation

The adsorbent was produced according to the procedure adopted by Husaini et al (2023); Bae et al., (2014) with a little modification. The coconut shell material was gotten from local area within Kaduna city and it was weighed and recorded. then soaked in a 0.5 M of NaOH solution and left for 24hrs to remove all impurities such as mud, dirt and ash percent in coconut shell during harvesting and processing. The shell has been properly washed with deionized water until neutral pH. Dried in oven at 110 ^{0}C for twenty-four hours. The sample has been impregnated with $ZnCl_2$ in 1:2 ratios. 60g of $ZnCl_2$ dissolved in 540 ml distilled water and mixed with the dried sample in 1:2 $ZnCl_2$ to dried sample impregnation ratio. The mixture stands for 24h at room temperature. Then evaporated to dryness at 110 ^{0}C for 24 h in an oven. Some quantity weighed in to a crucible and heated at 480 ^{0}C in a muffle furnace. (Bae *et al.,* 2014).

Preparation of Dye Solution

Preparations of stock solution of methyl orange were carried out by dissolving 1g of methyl orange (MO) dye in 1000 ml of distilled water in order to get 1g/L concentration according to the standard method of preparation. The serial dilution was carried out to prepare solutions with concentrations of 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L.

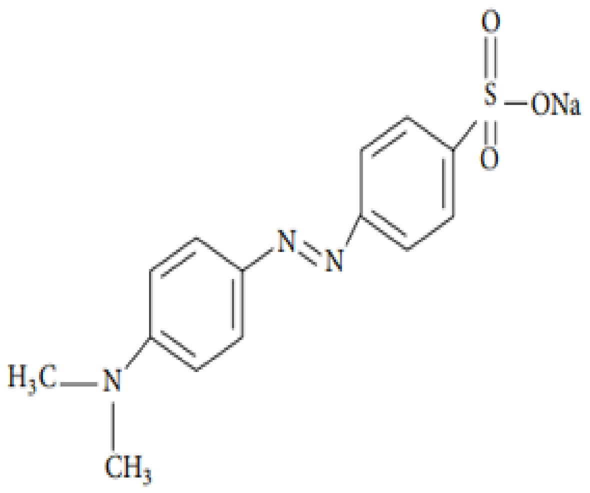


Figure 1: Structure of Methyl orange

Standard Calibration Curve of Adsorbate

Dyes solutions in water were prepared with concentrations 2.0 mg/L, 4.0 mg/L, 6.0 mg/L, 8.0 mg/L and 10.0 mg/L and their Percentage absorbance were found out by UV spectrophotometer (λmax =464 for MO). The concentration of residual methyl orange was measured using UV-visible spectrometer. A calibration graph was plotted between absorbance and concentration of dye solution to obtain absorbance-concentration profile.

The equation of the graph was used to calculate the concentrations for various % absorbance.

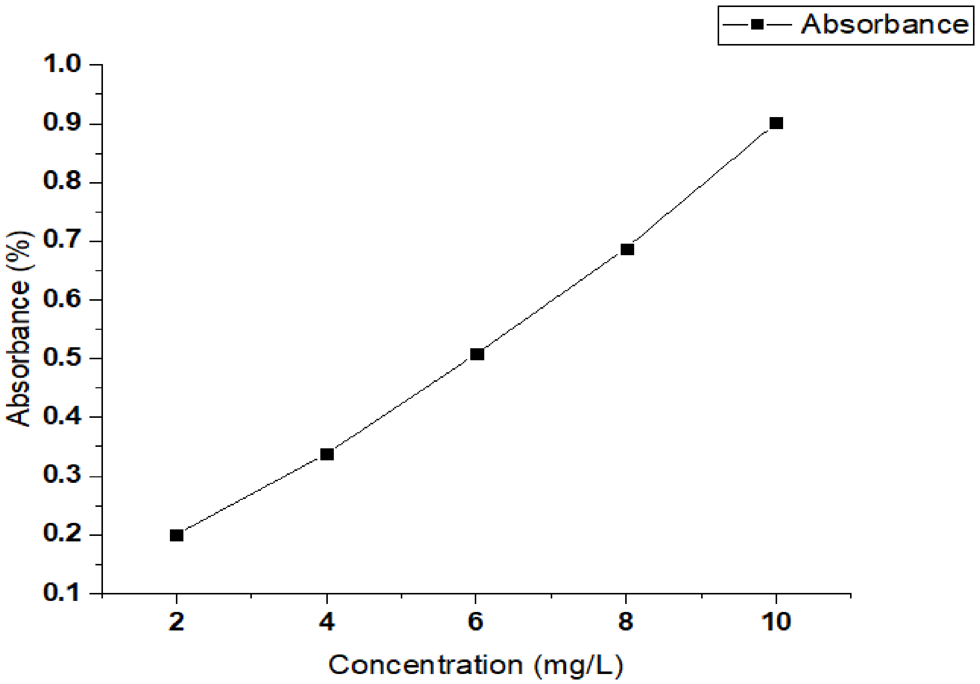


Figure 2: Standard calibration curve of different dye concentrations

Batch Adsorption Experiment

The batch adsorption was studied to identify some experimental parameters like contact time, temperature and isotherm model. This was achieved by transferring 100 ml dye solution in a beaker containing a magnetic stirrer with 0.2 g activated carbon stirred for a contact time of 80 minutes to achieve equilibrium. The dye percentage removal can be calculated as follows:

$$\%Removal = \frac{C_O - C_e}{C_O} \times 100 \quad -- \quad (1)$$

Where, Co and Ce (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

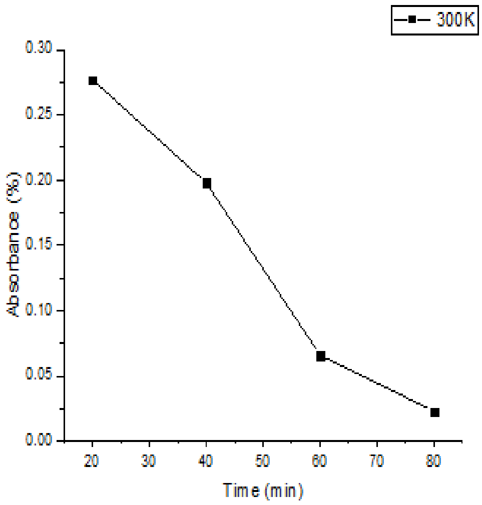
The amount of adsorption equilibrium (q_e) was calculated by;

$$q_e = \frac{(c_0 - c_e)v}{w} \quad --- \quad - (2)$$

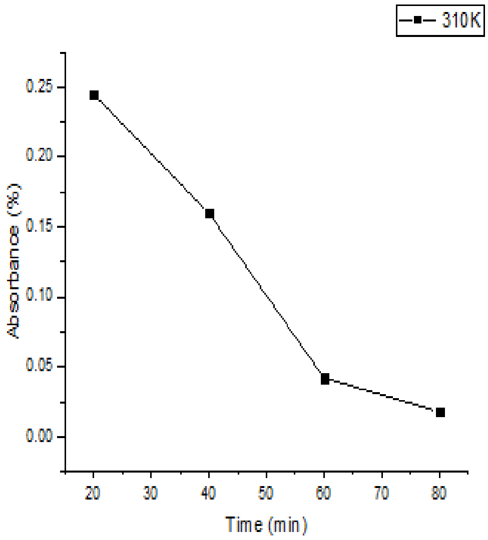
where; qe is the adsorption capacity of methyl orange dye adsorbed onto the activated carbon, Co and Ce (mg/L) are the concentrations of methyl orange dye at initial and at any time respectively, W (g) is the mass of dry adsorbent used, and V (ml) is the volume of methyl orange dye solution.

Effect of Temperature

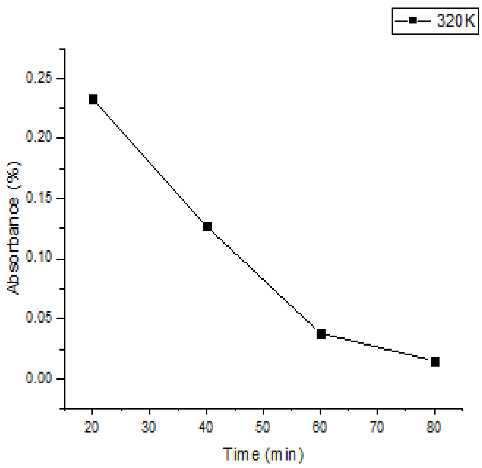
Four (4) solutions of dye were prepared (same concentration 6 mg/L) 100ml of the dye solutions was transferred into the four 500 ml beakers and were stirred on a magnet stirrer (RPM =160) with 0.2 g of activated carbon at different temperatures 300 K, 310 K, 320 K and 330 k for 80 minutes to achieve equilibrium. An aliquot was picked every 20 minutes to know the time at which equilibrium is obtained. Their % absorbance were calculated using spectrophotometer (λmax=464nm).



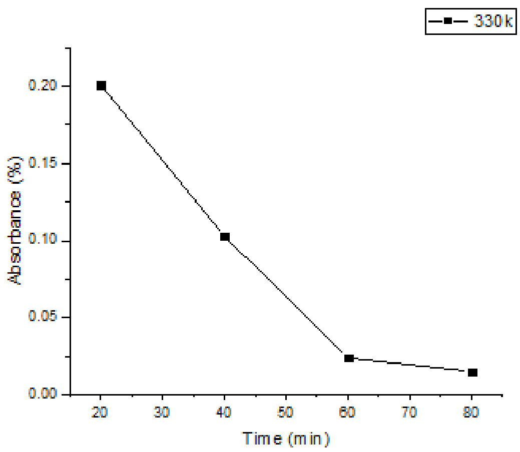
(a)



(b)



(c)



(d)

Figure 3: Effect of time on absorbance at different temperatures; (a) at 300 k, (b) at 310 K, (c) at 320 K and (d) at 330 K.

Figure 3 indicates the relationship between percentage absorbance and contact time at different temperatures whereby all the results a, b, c and d show a decrease in absorbance with the increase in time. With (a) having the highest percentage at least temperature (300 K) and minimum time (20 mins) and (d) with the least absorbance value occurring at highest temperature (330 K), this also be ascertain from Figure 4.

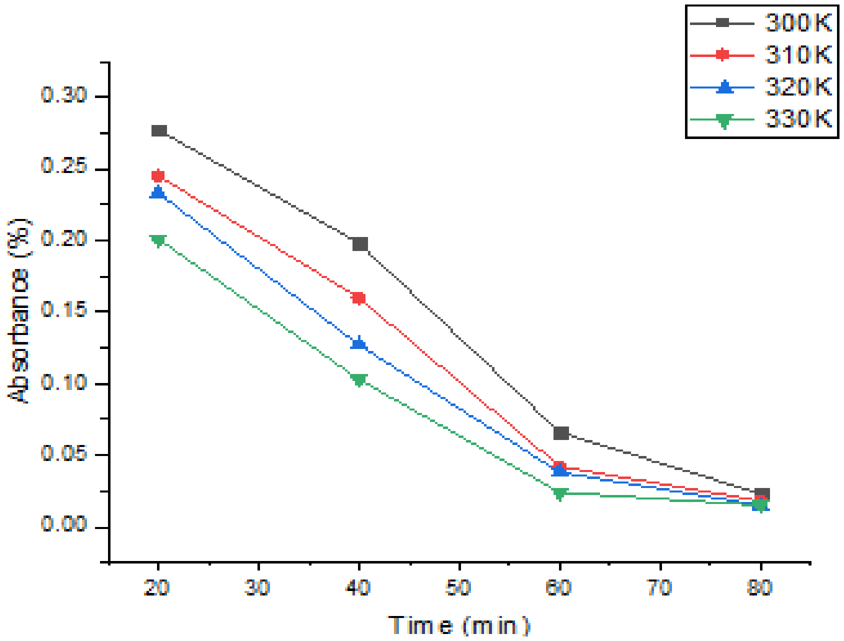


Figure 4: Comparative variation of absorbance at different temperature.

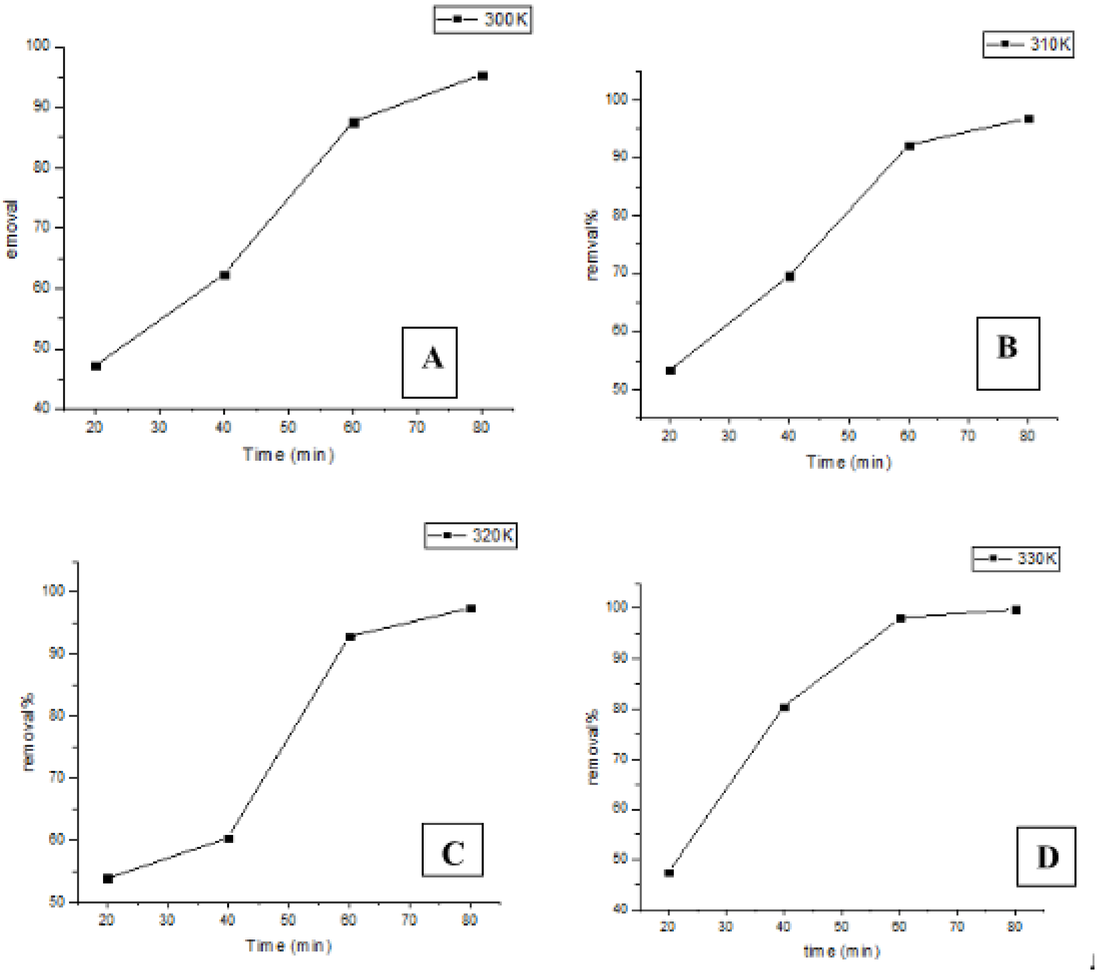


Figure 5: Effect of temperature and time on % removal at equilibrium (a) at300 K, (b)at 310 K, (c) at 320 K and (d) at 330 K.

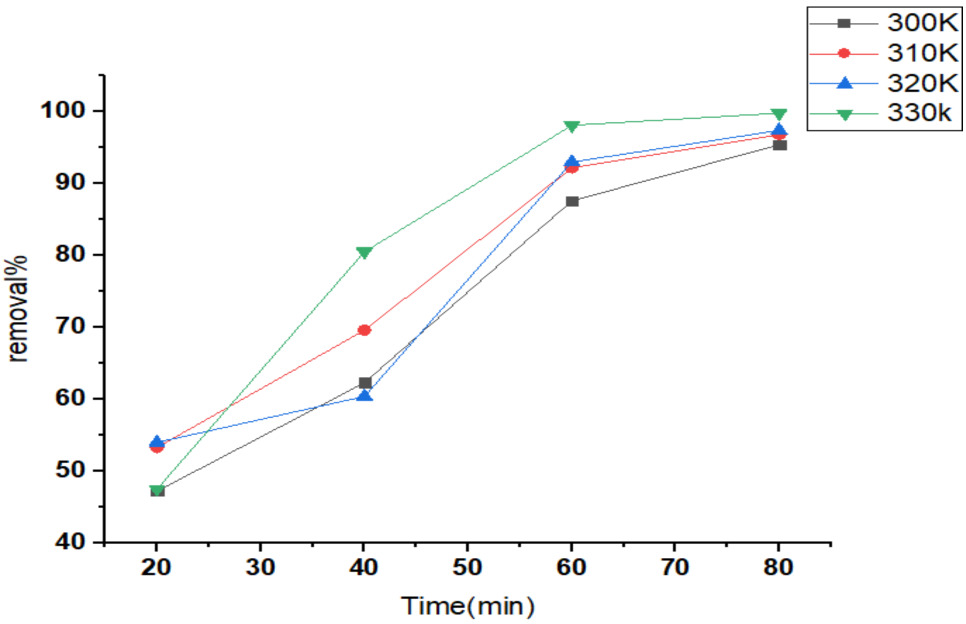
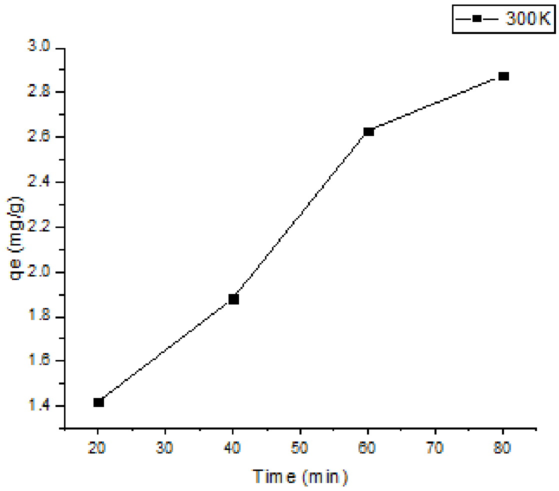
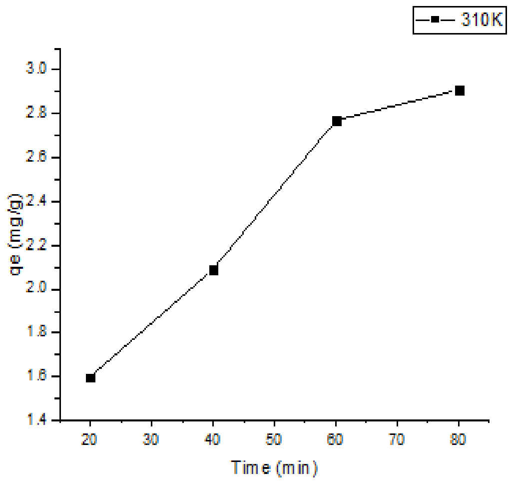


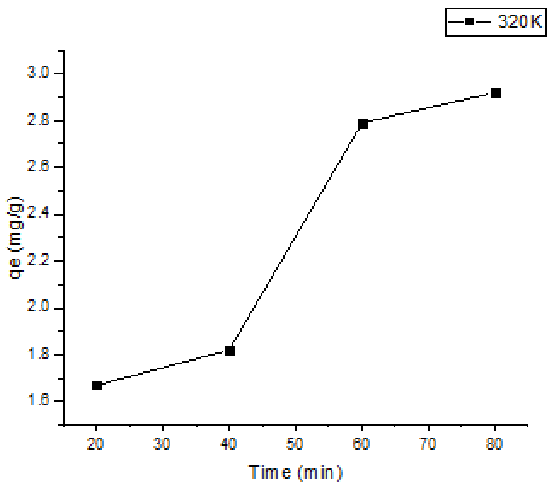
Figure 6: Comparative variation of temperature and time on % removal at equilibrium %Removal of dye.



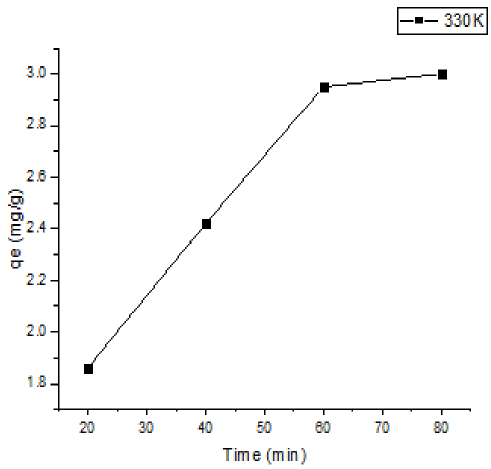
(A)



(B)



(C)



(D)

Figure 7: Effect of temperature and time on adsorption capacity

The adsorption capacity increases with increase in contact time and temperature figure 7(d) has the highest adsorption capacity at 330 K while figure 7(a) with least value at 300 K, this can also be seen from figure 8 below.

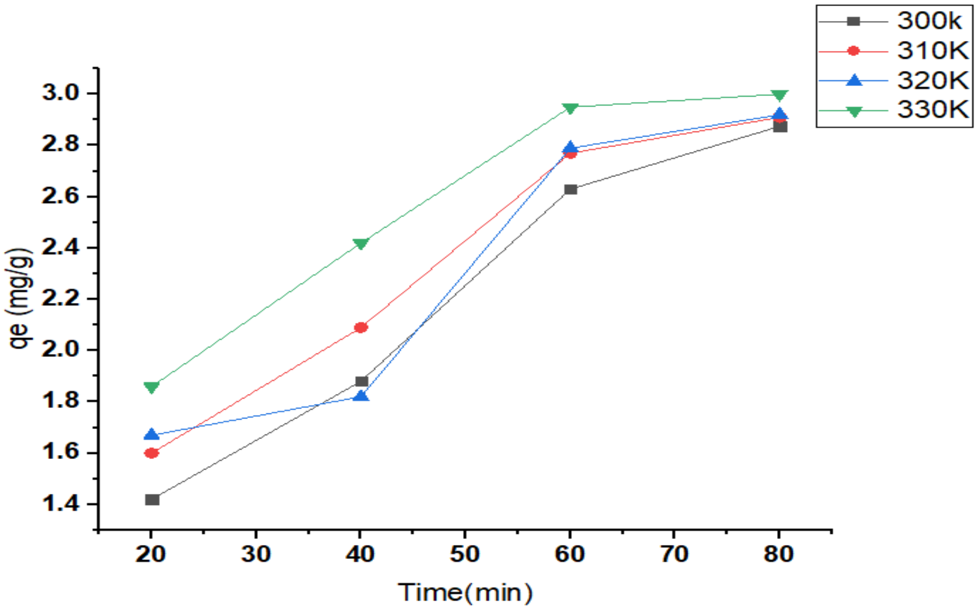
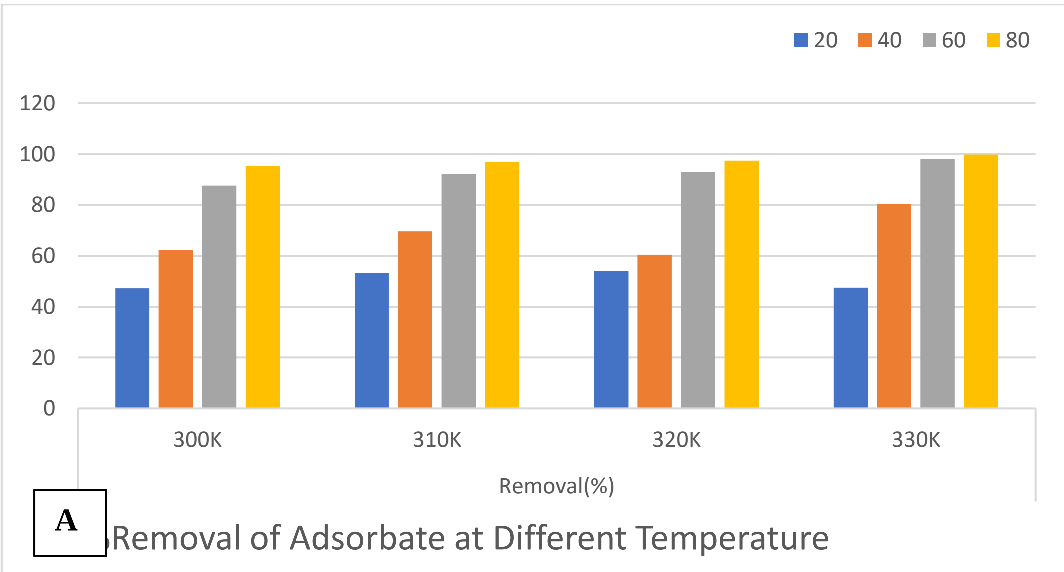


Figure 8: Comparative adsorption capacity of adsorbent at different temperatures

Effect of temperature on removal of dye solution was studied with initial concentration of methyl orange (6 mg/L) and with 0.2 g of prepared activated carbon from coconut shell, the temperatures were varied in the range of 300 K, 310 K, 320 K and 330 K. From figures (2, 3, 4 ,5 ,6, 7 and 8) the results indicated that the adsorption capacity and percentage removal increase with increase in temperature. This can be ascribed by the fact that with increase in temperature there is increase in the mobility of the large dye ions (Kurniawan, 2011). The molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface



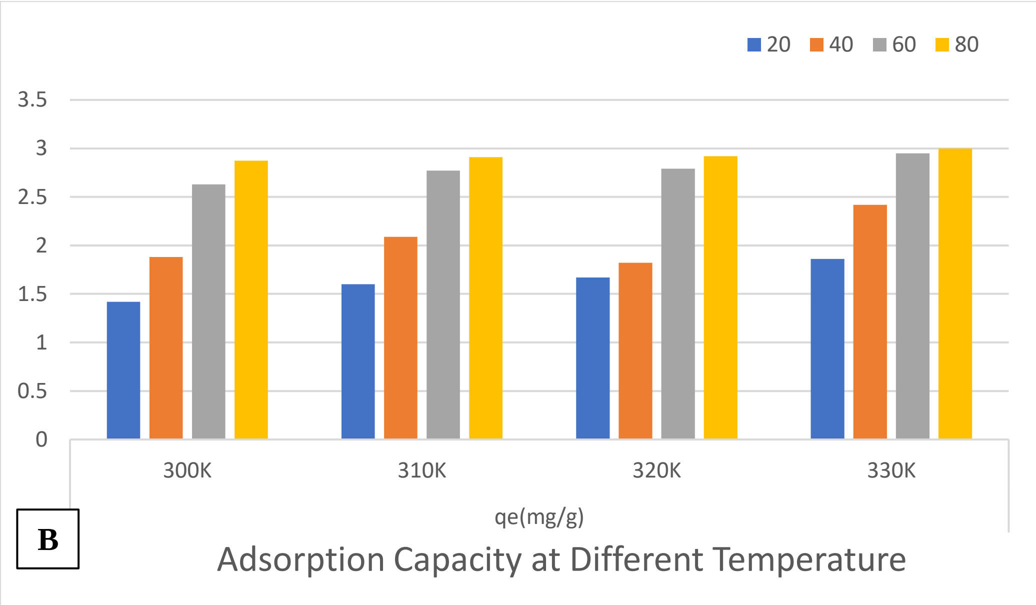


Figure 9: A bar chart representing (a) %removal of MO (b) adsorption capacity of adsorbent.

Langmuir Isotherm

Among the different isotherm models, we can studied the Langmuir model only by examination of the isotherm parameters based on linear regression coefficient (R^2) of the Langmuir model at different temperatures 300 K, 310 K, 320 K and 330 K. R^2 at 320 K (0.995) emerges as the best fitting followed by 330 K and lastly (0.970) at 300 K. The essential characteristics of the Langmuir isotherm Fig (5, 6, 7 and 8) and table 1. Usman et al., (2022).

Table 1. Adsorption Isotherm Studies (Langmuir Isotherm)

Langmuir constants	Temperature			
	300 K	**310 K**	**320 K**	**330 K**
Q_o(mgg^{-1})	0.74	0.67	0.61	0.54
b(L/mg)	4.27	7.04	12.2	22.9
R^2	0.970	0.977	0.995	0.984
R_L	0.04	0.02	0.01	0.007

Husaini *et al.*, (2023)

Thermodynamic Adsorption Studies

Values of thermodynamic parameters including change in the enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), are the actual indicators for practical application of a process. In the present work, the effect of temperature on adsorption was studied at four different temperatures (300 K, 310 K, 320 K and 330 K) at 6 mg/L concentrations of the dye. ΔG, ΔH and ΔS were calculated from the slope and intercept of the linear plot of ln b vs. 1/T using equation 3.

$$ln\, ln\, b = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \text{-----} \quad (3)$$

$$\Delta G^o = \text{-RT}b\text{) --} \quad (4)$$

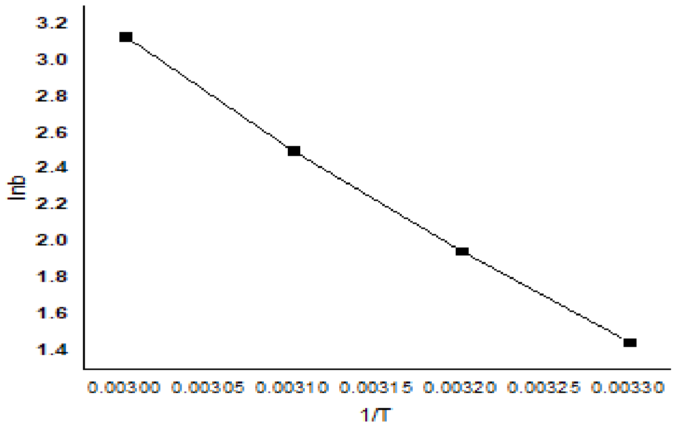


Figure 10: thermodynamic adsorption graph

The Gibbs free energy (ΔG) values were evaluated and other thermodynamic parameters including enthalpy change (ΔH) and ΔS were determined using the plot presented in Fig. 10. As shown in Table 2, the negative value of ΔG indicates the spontaneous process. The positive value of ΔH indicates that the adsorption is an endothermic process. In this study, the value of ΔH (46.4 kJ/mol) suggests the physisorption of the adsorbate onto CSAC, because ΔH is below 80 kJ/mol, (Husaini *et al.*,2023).

Table 2: Thermodynamic Studies

Adsorbate	Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/Mol/K)	R^2
MO	300	-3.62	46.4	0.1650	0.9973
	310	-5.03			
	320	-6.65			
	330	-8.59			

CONCLUSION

This study revealed that coconut shell-activated CSAC was an effective adsorbent for MO removal from aqueous solutions. The batch adsorption parameters such as temperature were effective in the adsorption process. The equilibrium sorption phenomena were found to be well described by the Langmuir isotherm model. The values of ΔG°, ΔS° and ΔH° from thermodynamic analysis indicated the feasibility.

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