Iranian Journal of Chemistry and Chemical Engineering (IJCCE)

Preparation and diagnosis of activated carbon from hydrothermally carbonized sucrose as an adsorber for the removal methyl red dye from aqueous synthetic solutions

Mustafa, Raqeeb Mohammed*+, Al-Obaidi, Omar B., Ismael, S. Mahmood

Department of Chemistry, College of Education, Al- Iraqia University, Baghdad, IRAQ

Al-Mamoori, Ahmed

Department of Chemical Engineering, College of Engineering, Al-Nahrain University, Baghdad 10072, IRAQ

** Corresponding author: mustafa.r.mohammed@aliraqia.edu.iq*

ABSTRACT

In this work, activated carbon derived hydrothermally carbonized sucrose material was synthesized, chemically activated with KOH, and then utilized as an adsorbent material for removal of methyl red (MR) dye from wastewater. The physiochemical characteristics of the activated carbon (AC) were analysed employing scanning electron microscopy (SEM)coupled with energy dispersive spectroscopy (EDX), and N_2physisorption measurements to characterize and assess the physical features, morphology, elemental analysis, and specific surface area. The obtained AC showed high specific surface area (2306.31 m^2/g). The capability of activated carbon to remove MR dye from aqueous solutions has also been investigated. The impact of initial concentration, adsorbent dose, temperature, and contact time on the adsorption capacity was examined to determine the adsorption isotherm. Maximum adsorption capacity (52.29mg/g for 90 mg/L) and fast adsorption kinetic (98 percent saturated within 5 min) were obtained. The numerical data fitted well with the pseudo-second-order kinetic model (R^2=0.98). The Freundlich and Langmuir adsorption isotherm models were also examined. The adsorption thermodynamics demonstrated that MR adsorption by AC was spontaneous and endothermic process.

.

KEYWORDS: *Activated carbon, adsorption, adsorbent, sucrose, methyl red*

INTRODUCTION

Due to the expansion of industry, agriculture, growth of global population, and rising the usage of chemicals[1], the environmental pollution has become one of the most serious and genuine challenges of the modern world[32]. The contamination of water resources with synthetic dyes and pigments is highly paramount important regarded this pollution. Most industrial areas such as cosmetics, leather, textile, and food employ dyes and pigments as colors of products[2]. When industrial wastewater is released into various water systems[3], it endangers human health and the environment [4]. These dyes are recognized by their intricate aromatic structure, which makes them highly resistant to biodegradation[5].These liquid wastes are highly harmful to the environment and living organisms[3] as they have toxic, mutagenic, and carcinogenic properties [6]. In addition, they disrupt light transmission and biological metabolism processes, resulting in the destruction of aquatic communities in the ecosystem [2]. Some of the most common techniques for treating dye waste that utilized in water treatment are photo catalysis, ozonation, coagulation[7], flocculation[8], membrane, nanoparticle, and adsorption [4].Among these technologies proposed to remove dyes is adsorption which is considered to be one of the easiest and most efficient methods [9]. Activated carbon has been demonstrated to be a highly effective adsorbent. Activated carbon has been demonstrated to be a highly effective adsorbent. [8]. In this work sucrose was used after its chemical activation with KOH to produce activated carbon with a significant surface area. The capacity of the sucrose-activated carbon to remove MR from synthetic aqueous solutions was explored. Chemical activation provides some advantages such as faster activation with only one activation step, lower activation temperatures, larger yields, and hence higher atom economy, resulting in high specific surface area and micro porosity. On the other hand, chemical activation has a number of drawbacks, including the high cost of activating chemicals[10]. The production of tiny mesoporous to ultra-microspores occurs when activated carbon chemically treated, such as carbon fibers, carbon nanofibers, carbons produced from carbide, carbon nanotubes, fibers aerogels, and graphene. The present work aims to diagnose activated carbon produced from hydrothermally carbonized sucrose, study the effect of several factors (contact time, adsorbent loading, dye concentration, temperature, and pH) on the adsorption process, and obtain the adsorption isotherm and adsorption kinetics of methyl red dye on the prepared AC adsorbent.

EXPERIMENTAL SECTION

Materials

Chemical reagents used in this investigation are shown in table (1). The chemical structure of the dye methyl red (MR) is depicted in Figure 1. It has a molecular weight of 269.3 g/mol.

Table1: Table1: Chemical reagents used in this study

Chemicals	*Chemical symbol*	*Origin*
Activated carbon	*AC*	*Prepared in the laboratory*
MR	$C_{15}H_{15}N_3O_2$	*DC company*
Distilled water	H_2O	*Laboratory*
Potassium hydroxide	*KOH*	*CDH*
Sucrose	$C_{12}H_{22}O_{11}$	*On market*
Sulfuric acid	*92%* H_2SO_4	*BDH*

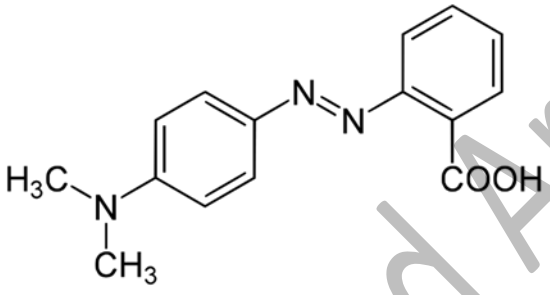


***Fig. 1**: The chemical structure of (MR) dye*

Instrumentation

Laboratory equipment used in this study is shown in table (2):

Table2: Laboratory equipment used in this study

Equipment name	Type	Origin
UV-Vis spectrophotometer Spectroscan-60 DV	Biotech engineering	Greece
Quartz cell	The thickness of 1cm	China
Centrifuge	PLC-03	Taiwan
Shaker	Shaking water bath	Germany
Sensitive balance	Iso	Germany
Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)	Bioenergy	Germany
Oven	LSIS-B2V/EC55	Germany
Autoclave	Teflon-lined stainless-steel autoclave	Germany
Nitrogen atmosphere furnace	Horizontal quartz furnace tube in a nitrogen atmosphere	Germany

Adsorbate preparation

1000 mg/Lof methyl red dye stock solutions was prepared. Thenthe desired concentrations (20-90 mg/L) was obtainedby diluting the stock solution.

Preparation of activated carbon

Two steps were engaged to prepare activated carbon including: (a) hydrothermally carbonized of sucrose at 453.15K and (b) Chemical activation by potassium hydroxide KOH. In a typical preparation, 100g of sucrose was dissolved in 40 ml distilled water and placed in a Teflon-lined stainless-steel autoclave inside a convection oven at 453.15 K for 24 h. The product was then filtered and washed with distilled water three times, and then dried overnight in the oven at 393.15 K. The char was mixed with KOH in a 1:4 mass ratio and burned at 873.15 K for 3 h in a horizontal quartz furnace tube in a nitrogen atmosphere, then washed with H_2SO_4 (0.05N) and distilled water for chemical activation. The carbon was then dried for 1 h at 353.15 K in the oven.

Adsorption capacity batch and dye removal efficiency

250 ml of Erlenmeyer flasks supplemented with 0.05 g of activated carbon dosage, batch adsorption investigations were carried out using an MR dye solution with varied concentrations of 30, 60, and 90 mg/L. After each 10 minutes, samples were withdrawn from the shaking water bath and the supernatant was separated by a centrifuge for 10 minutes at 3000 rpm. The dye concentrations were obtained by measuring the absorbance using UV- spectrophotometer device at a wavelength of 430nm and the solution adsorption was recorded.

Adsorption process study

50 ml of MR dye solution was placed in the shaker and kept with different contact times, onset times, concentrations, and temperatures to conduct adsorption kinetic experiments. The adsorption uptake and removal efficiency of methyl red by activated carbon can be expressed by formula (1) and (2)[11]:

$$qe = \frac{V*(Co-Ce)}{m} \quad \text{(1)}$$

$$\%R = \frac{(Co-Ce)}{Co} * 100 \quad \text{(2)}$$

Where:

q_e = Adsorption capacity of MR dye

% R = Removal efficiency of MR dye

C_o and C_e = Concentration of MR dye solution before and after adsorption experiments in mg/L

V= Solution volume of methyl red in L

m= Mass of activated carbon in g

RESULTS AND DISCUSSION

EDX and SEM Analysis

EDX (elemental analysis) and SEM images of the prepared activated carbon (AC) are shown in Figure 2 and Table3, respectively. The decrease in oxygen content of the as-synthesized AC adsorbent is due to polymerization and carbonization processes that happened during the hydrothermal process, which resulted in reduction in the number of functional groups due to diverse reactions such as dehydration.

The morphology of the AC was studied using a scanning electron microscope (SEM), which reveals distinctive characteristics. In the case, however, sucrose-derived AC as depicted in Figure 3, the observed morphology exhibits large sized pieces with sharp edges, along with numerous cages and cavities. These features are typical of microporous solids, which possess a vast internal network of interconnected pores [10] .

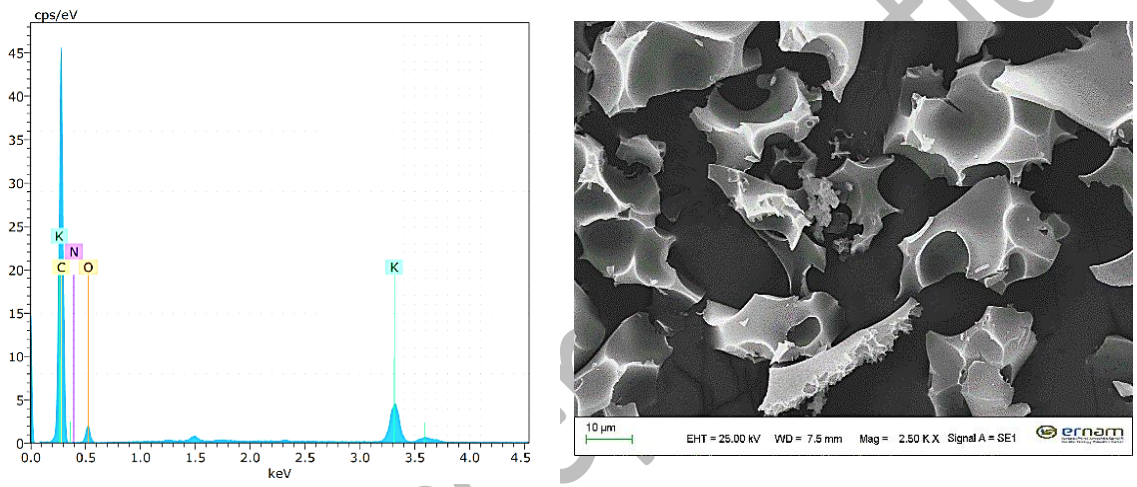


Fig. 2: EDX and SEM images of the prepared AC

Table 3: The elements composition of the AC

Estimated phases and element composition of AC	K Weight %	N Weight %	O Weight %	C Weight %
	2.88	3.96	15.89	77.26

N_2 physisorption and BET Specific Surface Area

Figure 3displays N_2adsorption/desorption isotherm curve at 77K under liquid N_2 atmosphere. The BET specific surface area of the prepared AC based sucrose was2306.31 m^2/g. The adsorption isotherms of AC showed mixed of Type I and Type II isotherm characteristics at extremely low relative pressure p/p^0 and extremely high relative pressure p/p^0, implying the presence of microspores and mesoporous below than 2 nm and between 2–50 nm, respectively, according to IUPAC classification.[12]

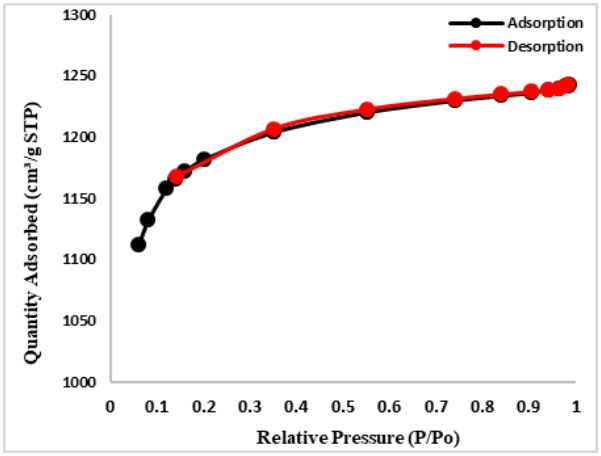


Fig.3: Nitrogen adsorption/desorption isotherms of the AC

Effect of equilibrium time

The equilibrium time of the MR dye adsorption on the activated carbon surface is a significant aspect that affects adsorption performance. The obtained results show that the adsorption process presented sharp uptake in the first few minutes and then flattened to marginal decrease in the remaining time up to120min. Figure 4 shows the removal percentage of methyl red dye versus the contact time of the activated carbon which was achieved at 30 min with 0.05 mg/g, corresponding to a removal rate of 98 %. The substantial initial adsorption capacity may be caused due to the abundance of active sites on the adsorbent surface, but when these sites are gradually filled, the adsorption capacity drops. According to the previous findings, the MR adsorption reaction on activated carbon is an endothermic process [4].

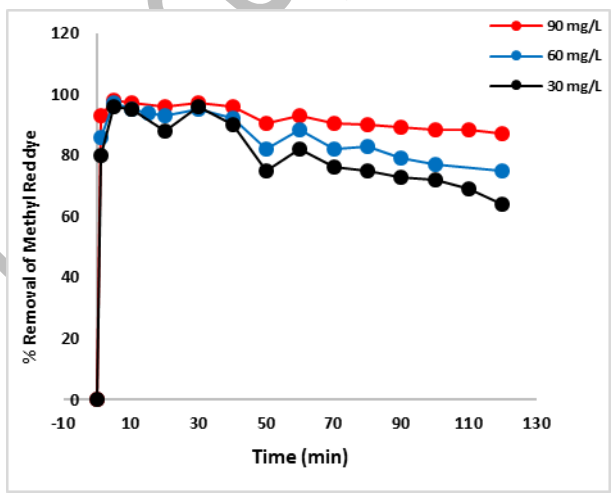


Fig.4: Effect of the AC contact time on the removal of methyl red dye.

Effect of AC doses

The effect of different activated carbon doses from (0.05 to 0.4g) on the aqueous solution of MR dye at temperature 298.15 K with a constant concentration (90 mg/L) was examined. The results show that the adsorbent amount of 0.05 g is enough to achieve an optimal methyl red dye removal rate of 99.97%, which is attributed to the overlapping the surface area that MR dye can use accumulating or aggregation, resulting in the elongation of the diffusion length leading to pathways and active sites during adsorption as shown in Figure 5[14].

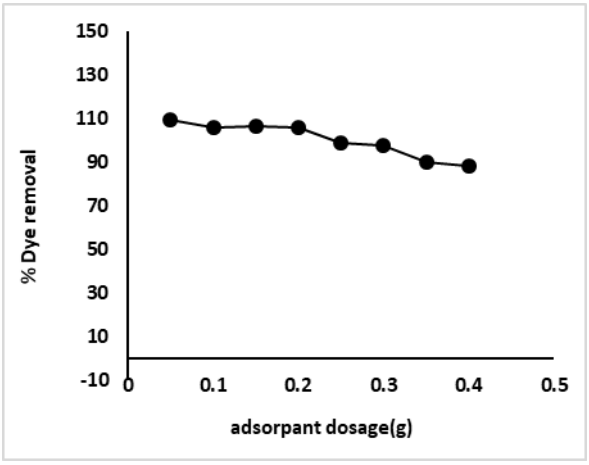


Fig.5: Effect of the AC doses on MR dye adsorption

Effect of the initial dye concentration

Figure 6 shows the influence of initial MR dye concentrations. It can be seen that when the initial concentrations were increased, the removal efficiency of MR dye was increased. Increasing dye concentration enhances the driving force necessary to overcome all MR mass transfer resistances between the aqueous and solid phases because the adsorbent has more dye molecules available for adsorption as the dye concentration rises, resulting in a higher equilibrium adsorption capacity [15].

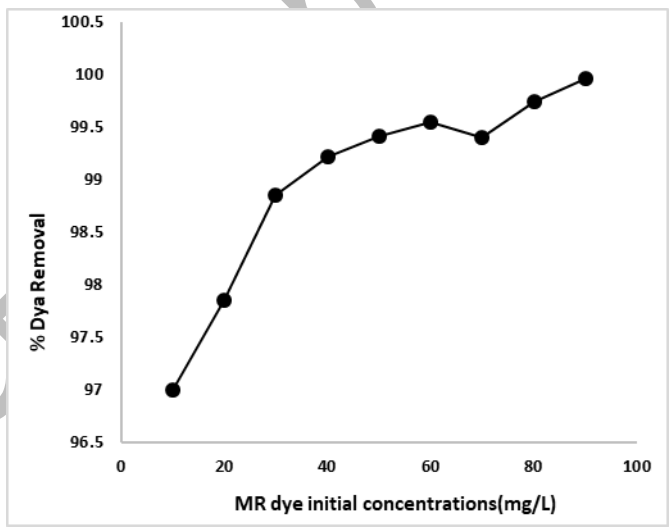


Fig.6: Effect of the MR dye concentrations on AC adsorption

Effect of temperatures

The temperature effect on methyl red adsorption was examined at 293.15, 303.15, and 313.15 K. The removal ofmethyl red on the AC adsorbent versus temperature has been plotted in Figure 7. The dye adsorption process at higher temperatures may increase the MR dye's intraparticle diffusion rate into the pores of the activated carbon, which may explain why there is an increase in adsorption capacity. The mobility of molecules generally increases with increasing temperature, which causes the dye molecules to diffuse and penetrate through the activated carbon's porous structure more quickly. The increased diffusion and penetration may lead to a greater adsorption capacity. According to these findings, the MR adsorption reaction on activated carbon is an endothermic process[13].

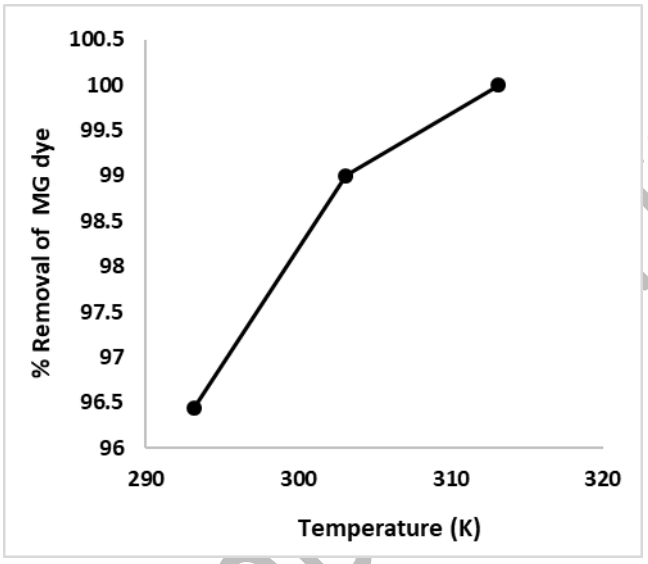
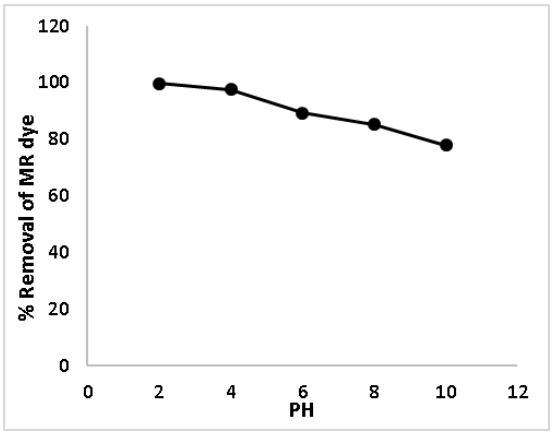


Fig.7: Effect of temperatures on MR dye removal percentage

Effect of pH

Dye solutions with a 90 mg/L concentrationswereprepared with a different range of pH values from 2 to 10 at room temperature in order to study the effectof pH on the adsorption uptake and the removal percent of methyl red onto activated carbon. 0.5 g of the adsorbent was mixed with 100 ml of each solution throughout the contact duration. At pH 2, adsorption was found to be the optimum condition. Increased pH levels lead to decrease the removal percentage and adsorption capacity because, at these pH levels, the over The overabundance of hydroxyl ions in the solution compete with the anionic groups of the methyl red dye for adsorption sites on the adsorbent surface. abundance of hydroxyl ions in the solution compete with the anionic groups of the methyl red dye for adsorption sites on the adsorbent surface. As the adsorbent surface is more positively charged at low pH levels and the solution's negative charges are reduced, the methyl red dye's anions are more attracted when the pH level is low[14].



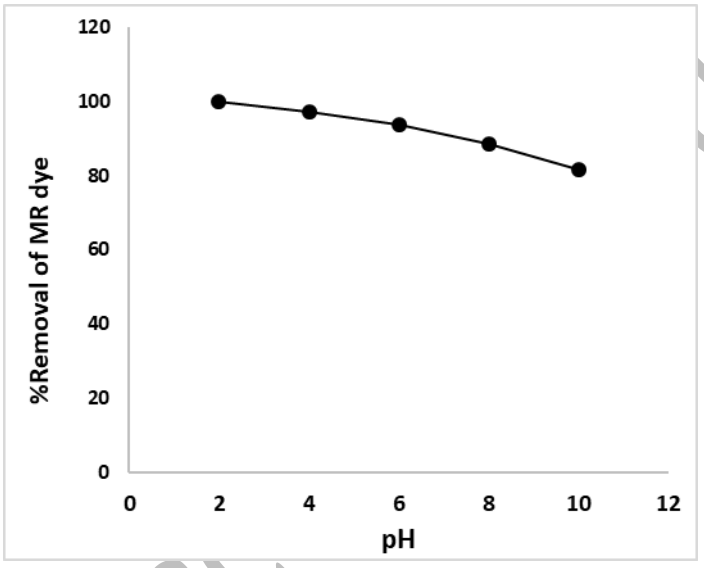


Fig.8: Effect of pH on MR adsorption onto AC

Adsorption isotherm study

In order to understand the interaction between the concentration of MR dye in the bulk solution and that on the surface of the AC powder, Langmuir and Freundlich isotherm models of adsorption were applied[14].

Langmuir isotherm model equation (3) is[15] :

$$\frac{Ce}{qe} = \frac{1}{qm\ KL} + \frac{Ce}{qm} \quad \text{..... (3)}$$

Where:

K_L: Langmuir constant isotherm,

q_m: maximum adsorption monolayer capacity,

C_e:denotes the equilibrium concentration in milligrams per litter (mg/L),

q_e : equilibrium amount of dye adsorbed on the AC.

The factor of separation R_L can determine the adsorption process's favourability[16], which is computed using equation (4)[17].

$$RL = \frac{1}{1+KL\ Ci} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where R_L values provide significant information about adsorption, R_L=1 for linear adsorption, R_L=0 for irreversible adsorption, 0<R_L<1 for favourable adsorption, and R_L>1 for unfavourable adsorption, Ci: is the initial concentration of Adsorbate[20]. According to Freundlich model, adsorption occurs on heterogeneous surfaces with varied affinities. The linear form of Freundlich model is written as shown in equation(5)[18].

$$\log qe = \ln K_f + \frac{1}{n} \log Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where K_f and n refer to Freundlich constants that represent adsorption capacity and intensity (strength) of adsorption respectively[16]. The importance of n is as follows n=1 (linear), n<1 (chemical adsorption), and n>1 (physical adsorption)[22].

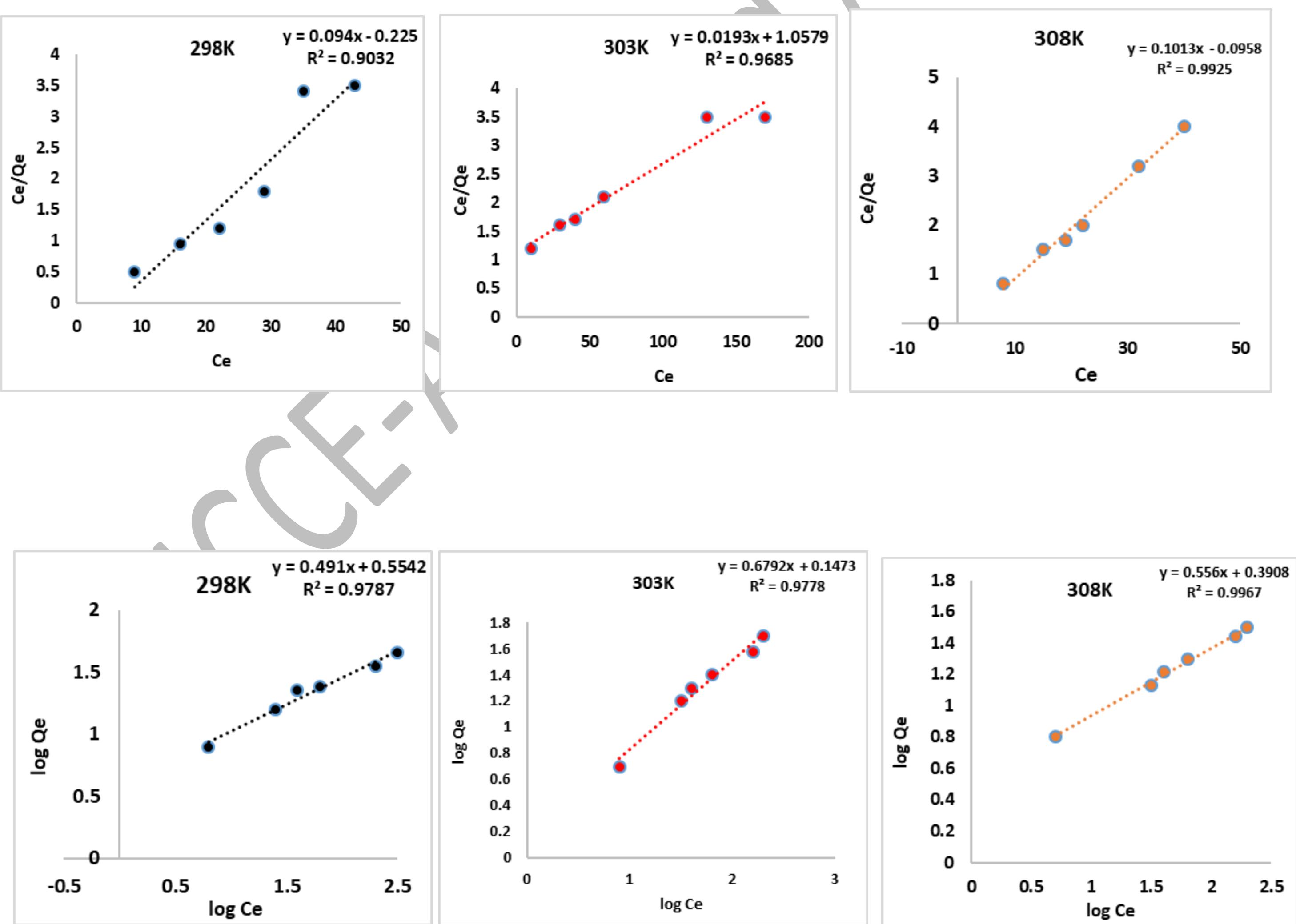


Fig.10: Freundlich isotherm models chart

Table 4: ***Isotherm constants of MR dye adsorption onto activated carbon***

	Parameters	293.15 K	303.15 K	313.15 K
Langmuir model	Q_{max} (mg/g)	49.33	51.82	52.29
	K_L(L/mg)	0.02	0.018	0.016
	R^2	0.9032	0.9685	0.9911
	R_L	0.31	0.37	0.40
Freundlich model	K_F (mg/g)	3.91	1.49	4.51
	n	2.03	1.78	1.79
	R^2	0.9787	0.966	0.9967

As it's clear from the linear Langmuir and Freundlich diagrams, the computed adsorption constants, are shown in (Fig. 9 and 10). At 313.15 K ,the correlation coefficients were clear, and the Freundlich model (R^2 = 0.9967) suited the adsorption data better than the Langmuir model (R^2 = 0.9911). The findings indicate that MR dye adsorption from the aqueous phase on the AC surface may occur in a complicated heterogeneous way rather than a homogenous monolayer. According to the Freundlich isotherm model theory, the heterogeneous AC surface could contain different adsorption sites, and the affinities of these adsorption sites to the MR dye are variable [33].

Table 5 shows the adsorption of MR on different types of adsorbents. Sucrose-based activated carbon showed good adsorption capacity for MR compared with other adsorbents reported in the literature.

T***able 5: Comparison of the different adsorbents' dye-adsorption capabilities***

Adsorbents	q_m (mg/g)	Reference
activated carbon derived from sucrose	52.29	This study
activated carbon derived from custard apple	171.23	[23]
Annona squamosa shell activated carbon with phosphoric acid	434.78	[24]
Pistachio shell-derived activated carbon	0.430	[25]
Activated Carbon Derived from Agricultural waste	64.9	[26]
activated carbon prepared from date pits	434	[27]
corncob activated carbon	107.52	[28]
Swietenia mahagoni bark activated carbon	6.07	[29]

Adsorption kinetic study

The adsorption kinetic of MR dyes on AC was investigated using two kinetic models, pseudo-first-order and pseudo-second-order kinetic models, to examine the chemical methods and potential rate-limiting processes. The pseudo-first-order model"Figure 11 (A)" was unable to provide satisfactory fit to the experimental data due to the nonlinearity and poor R^2 value of the plot of ln (q_e-q_t) vs. t. In Figure 11 (B), the pseudo second order kinetic model provided a substantially better correlation fit for the dye adsorption data due to its outstanding linearity and high R^2 correlation values indicating the chemisorption is the rate-limiting step in the MR adsorption on the AC surface. Furthermore, there was a good agreement between the estimated and actual q_e values, suggesting that the pseudo-second-order kinetics of MR dye adsorption by AC powder was followed. The theoretical and experimental equilibrium adsorption capacity, the pseudo-second-order rate constant, k_2, and the initial adsorption rate, q, are all summarized in Table 6. Figure 11 shows the t/q_t vs. time plot [15].

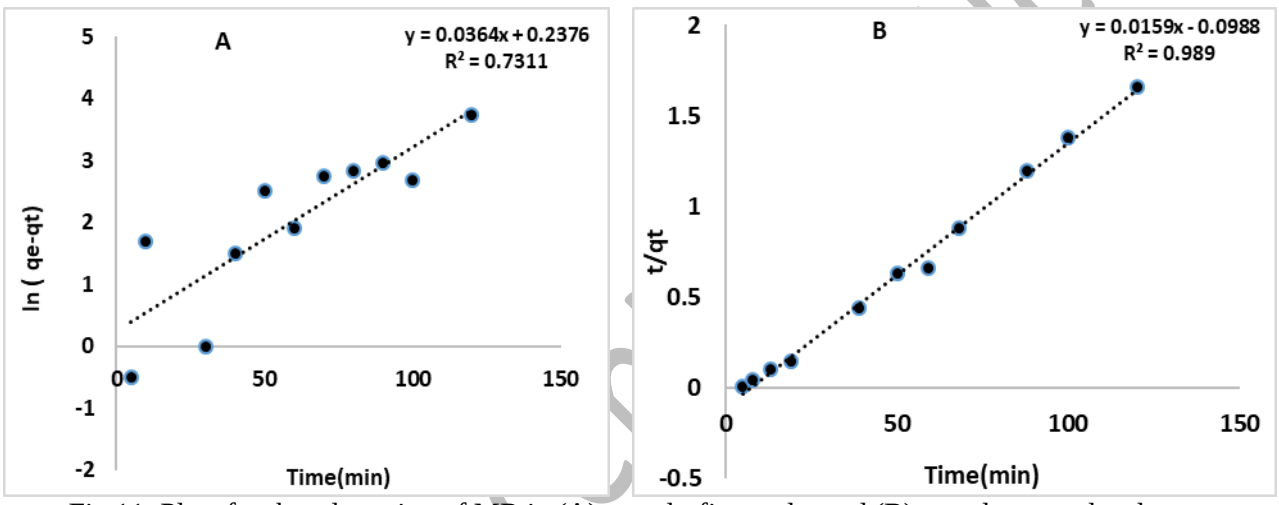


Fig.11: Plots for the adsorption of MR in (A) pseudo-first-order and (B) pseudo-second-order

Table 6: Kinetic parameters and statistical test of MR dye adsorption on to AC

Pseudo first order Model			Pseudo second order Model			adsorption capacity
q_e mg/g	K1 (1/min)	R^2	K_2 (g/mg min)	q_e theo mg/g	R^2	q_e mg/g
1.26	0.0003	0.73	8.38	62.89	0.98	89.17

Thermodynamics study of the adsorption

The study of the adsorption mechanism can be evaluated based on the thermodynamic parameters: Gibbs free energy (ΔG°), Enthalpy (ΔH°) and Entropy (ΔS°) .Table 7 shows the thermodynamic parameters for the adsorption of MR dye[25]. The Van't Hoff equations were used to calculate quantities such as enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°)[26].

$$\Delta G° = \Delta H° - T\Delta S° \ldots\ldots\ldots\ldots\ldots (6)$$

$$\Delta G° = -RT \ln K \ldots\ldots\ldots\ldots\ldots (7)$$

$$K_{ads} = \frac{qe}{Ce} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where: R is gas constant and T is absolute temperature, q_e is dye concentration on the solid at equilibrium, and C_e denotes the equilibrium concentration

As seen below Van't Hoff equation is expressed [31]:

$$lnK = -\frac{\Delta H°}{R} . \frac{1}{T} + \frac{\Delta S°}{R} \ldots\ldots\ldots\ldots (9)$$

The thermodynamic equilibrium constant (K) must be determined by plotting q_e/C_e versus C_e and extrapolating to zero q_e[30].

The negative values of ΔG° demonstrate that the mechanism of MR dye adsorption from the aqueous solutions show feasible and spontaneous nature of the process. According to these findings, increasing the temperature leads to improve the adsorption process [27].The endothermic property of the MR dye adsorption onto activated carbon is confirmed by the positive value of ΔH°.The increase in randomness at the solid-liquid interface throughout the adsorption process may be noticed by the positive value of ΔS° that represents activated carbon's affinity for MR dye[18].

Table 7: Thermodynamic parameters of MR dye adsorption onto activated carbon.

T (K)	ΔG° (KJ. /mol)	ΔH° (KJ. /mol)	ΔS° (J.mol. /K)	R^2
293.15	-257.83	1842.78	7.16	0.84
303.15	-284.31			
313.15	-402.26			

CONCLUSION

Activated carbons derived from sucrose using hydrothermal carbonation and subsequent chemical activation by KOH have been prepared and tested for removal of MR dye aqueous synthetic solutions. The results showed that the dye removal is more effective in acidic solution. A pseudo-second-order equation was used to describe the reaction kinetics. Equilibrium isotherm data fitted well to the Freundlich isotherm model better than the Langmuir isotherm models at 313.15 K. Various thermodynamic characteristics, such as changes in enthalpy, entropy, and the Gibbs free energy, were also determined, demonstrating the adsorption's spontaneous characteristic of the process. More importantly, activated carbon which is widely used adsorbent can be synthesized from the waste containing sucrose and check how much it is used instead of sucrose, which is considered to be of high cost.

Acknowledgements

The researchers extend gratefully to the Al-Iraqia University, College of Education, Department of Chemistry, and Research Laboratory for their cooperation with the present research work.

CONFLICT OF INTEREST

The authors claim that there is no conflict of interest

AUTHOR CONTRIBUTIONS

MUSTAFA R. MOHAMMED conducted the experiment, OMAR B. AL-OBAIDI and ISMAEL, S MAHMOOD conducted the calculations, MUSTAFA R. MOHAMMED, OMAR B. AL-OBAIDI, ISMAEL, S. MAHMOOD and AHMED AL-MAMOORI wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

REFERENCES

[1] Osasona, I., Kanuhor, U. B.,Characterization and utilization of sulphuric acid and bitter leaf extract activated carbon from rice husk for Zn(II) adsorption, Indones. J. Chem., 21: 318–331 (2021).

[2] Mohammed, M. R., Abass, A. M., Preparation and characterization of low cost adsorbents for the remove of methylene blue dye from aqueous solution by using adsorption technology, *Int. J. Pharm. Res.*, **12**: 1–11 (2020).

[3] Khelifi, O., Mehrez, I., Younsi, M., Nacef, Affoune, A. M., Adsorption du méthylorange sur un biosorbant à base de noyaux de mangue. *Larhyss J.*, **36**:145–156 (2018).

[4] Purnaningtyas, M. A. K., Sudiono, S., Siswanta, D., Synthesis of activated carbon/chitosan/alginate beads powder as an adsorbent for methylene blue and methyl violet 2b dyes, *Indones. J. Chem.*, **20**: 1119–1130 (2020).

[5] Kamatchi, C., Arivoli, S., Prabakaran, R., Thermodynamic, Kinetic, Batch Adsorption and Isotherm Models for the Adsorption of Nickel from an Artificial Solution Using Chloroxylon Swietenia Activated Carbon,

Phys.Chem. Res., **10**: 315–324 **(**2022).

[6] Yilmaz, E., Sert, E.,Atayal, F. S., Synthesis, characterization of a metal organic framework: MIL-53 (Fe) and adsorption mechanisms of methyl red onto MIL-53 (Fe), *J. Taiwan Inst. Chem. Eng.*, **65**: 323–330 (2016).

[7] Africana, K., Azedarach, M., Shell, G., Removal of Methylene blue by adsorption using Tribulus terrestris activated carbon, *Int. J. Adv. Chem. Sci. Appl.*, **3**: 1–5 (2015).

[8] Khelifi, O., Nacef, M., Chelaghmia, M. L., Affoune, A. M., Mehrez, I., Laksaci, H., Equilibrium, mechanism, and mass transfer studies of Nickel(II) adsorption by sewage sludge-derived activated carbon,

Iran. J. Chem. Chem. Eng., 40: 1675–1682 (2021).

[9] Abrar, M., Optimization of PB(II) adsorption onto Australian pine cones-based activated carbon by pulsed microwave heating activation, *Iran. J. Chem. Chem. Eng.*, **36**: 115–127 (2017).

[10] Shi, Y., Zhang, X., Liu, G., Activated Carbons Derived from Hydrothermally Carbonized Sucrose: Remarkable Adsorbents for Adsorptive Desulfurization, *ACS Sustain. Chem. Eng.*, **3**: 2237–2246 (2015).

[11] Al-Tameemi, M. S. M., Mohammed, M. R., Al-Sadoon, A. A. T., Study the Ability of Saccharomyces cerevisiae to Remove Methyl Green Dye from Water as a Pollutant Agent,

J. Chem. Health Risks, **12:** 93–104(2022).

[12] Liakos, E. V., Rekos, K., Giannakoudakis, D. A., Mitropoulos, A. C., Kyzas, G. Z., Carbonaceousadsorbents derived from agricultural sources for the removal of pramipexole pharmaceutical model compound from synthetic aqueous solutions, *Processes*, **9**: 253 (2021).

[13] Barmaki Z., Aghaie H., Seif A., Monajjemi M., Kinetic and Thermodynamic Study of Chromium Picolinate Removing from Aqueous Solution onto the Functionalized Multi-Walled Carbon Nano Tubes, Iran. J. Chem. Chem. Eng (IJCCE), 40(3): 765-779 (2021).

[14] Enenebeaku, C. K., Okorocha, N. J., Enenebeaku, U. E., Ukaga, I. C., Adsorption and Equilibrium Studies on the Removal of Methyl Red from Aqueous Solution Using White Potato Peel Powdering.

Lett. Chem. Phys. Astron, 72: 52–64 (2017).

[15] Wang, G., Luo, Q., Dai, J., Deng, N., Adsorption of dichromate ions from aqueous solution onto magnetic graphene oxide modified by β-cyclodextrin, *Environ. Sci. Pollut. Res.*, **27**: 30778–30788 (2020).

[16] Conrad, E. K., Nnaemeka, O. J., Uchechi, E. E., Basil, A., Veronica, O. O., Cynthia, O. E., Emeka, O. E.,Adsorption of Congo Red Dye from Aqueous Solution Using Agricultural Waste,

IOSR J. Appl. Chem., **9**: 39–51(2016).

[17] Geçgel, Ü., Üner, O., Gökara, G., Bayrak, Y., Adsorption of cationic dyes on activated carbon obtained from waste Elaeagnus stone,*Adsorpt. Sci. Technol.*, **34**: 512–525 (2016).

[18] Conrad, E.K., Nnaemeka, O.J., Chris, A.O., Adsorptive Removal of Methylene Blue from Aqueous Solution Using Agricultural Waste: Equilibrium, Kinetic and Thermodynamic Studies,

Am. J. Chem. Mater. Sci., **2**(3)**:**14-25 (2015).

[19] Boudouara, K., Ghelamallah, M., Khemliche, H. N., Adsorption of Methyl Red from Aqueous Solutions by Algerian Bentonite Clay,*2nd Int. Congr. Energy Effic. Energy Relate. Mater. (ENEFM2014), Springer Proc.*

Energy, 203–209 (2015)

[20] Jale, B. N., Achra, G., Adsorption of Indigo Carmine Dye onto Physicochemical-Activated Leaves of Agave AmericanaL, *Iran. J. Chem. Chem. Eng.*, **40**: 1154-1066 (2021).

[21] Khelifi, O., Nacef, M., Affoune, A. M., Nickel (II) adsorption from aqueous solutions by physico-chemically modified sewage sludge, *Iran. J. Chem. Chem. Eng.*, **37**: 73–87 (2018).

[22] Al-Sadoon A. A.T., Mohammed M.R., Al- Tameemi M. S. M., Adsorption of Remove Methyl Green Dye from Wastewater by Using Fava Bean Peel Waste: Kinetic and Thermodynamic Studies,

AIP Conf. Proc., **2591**(1):030060–1–030060–11(2023).

[23] Tu, N. T. T., Thanh, T. S., Quy, P. T., Ha, T. T. M., Thu, P. T. K., Bich, N. H., Soп, L. V. T., Nguyen, V. T., Nhiem, D. N., Lieu, P. K., Khieu, D. Q., Trinary Component Adsorption of Methylene Blue, Methyl Orange, and Methyl Red from Aqueous Solution Using TiO_2/Activated Carbon, Adsorption, Ads. *Sci. Tech*., 1–17**.** (2023).

[24] Khan, E. A, Khan, T. A, Adsorption of methyl red on activated carbon derived from custard apple (Annona squamosa) fruit shell: Equilibrium isotherm and kinetic studies. *Mol. Liq.*, **249**: 1195–1211 (2018).

[25] A. A. Attia, B. S. Girgis, and S. A. Khedr, "Capacity of activated carbon derived from pistachio shells by H3PO4 in the removal of dyes and phenolic," *J. Chem. Tech. Bio*., **78** (6): 611–619 (2003).

[26] Ariyanto, E., Juniar, H., Sari, E. L., Marindah, R., Adsorption Studies of Methylene Blue and Methylene Red on Activated Carbon Derived from Agricultural waste: Rubber (Haveabrasiliensis) Seed Powder, *The 5th Sriwij. Int. Semin. Energy Environ. Sci. Technol.*, **1**: 153-157 (2014).

[27] Mahmoudi, K., Hosni, K., Hamdi, N., Srasra, E., Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits-A comparative study, *Korean J. Chem. Eng*., **32**: 274–283 (2015).

[28] Abollé, A. , Urbain, K. Y. , Ollo, K. , Tchonrontcha, K. Y., Rodrigue, K. A., Adsorption of Methyl Orange on Corncob Activated Carbon: Kinetic, Equilibrium, and Thermodynamic Studies,

Earthline J. Chem. Sci., **8**: 205–224 (2022).

[29] Ghosh, G. C., Chakraborty, T. K. , Zaman, S. , Nahar, M. N., Kabir, A. H. M. E., Removal of methyl orange dye from aqueous solution by a low-cost activated carbon prepared from mahagoni (Swietenia mahagoni) Bark,

Pollution, **6**:171–184 (2020).

[30] Khan, E. A., Shahjahan, Khan, T. A., Adsorption of methyl red on activated carbon derived from custard apple (Annona squamosa) fruit shell: Equilibrium isotherm and kinetic studies, *J. Mol. Liq*., **249**:1195–1211

(2018).

[31] Belgacem, A., Ould Brahim, I., Belmedani, M., Hadoun, H., Removal of Methyl Green Dye from Aqueous Solutions Using Activated Carbon Derived from Cryogenic Crushed Waste Tires,*Iran. J. Chem. Chem. Eng.*, **41**:207–219 (2022).

[32] Al-Mamoori, A., Hameed, M., Saoud, A., Al-ghamdi, T., Al-Naddaf, Q., ALwakwak, A. A., Baamran, K., Development of Sodium-Based Borate Adsorbents for CO_2 Capture at High Temperatures,

Ind. Eng. Chem. Res.,**62**(8): 3695-3704 (2023).

[33] Obaid, S. A., Langmuir,twntyseven Freundlich and Tamkin Adsorption Isotherms and Kinetics For The Removal Aartichoke Tournefortii Straw From Agricultural Waste, *J. Phys.: Conf. Ser.*, **1664**: 012011 (2020).