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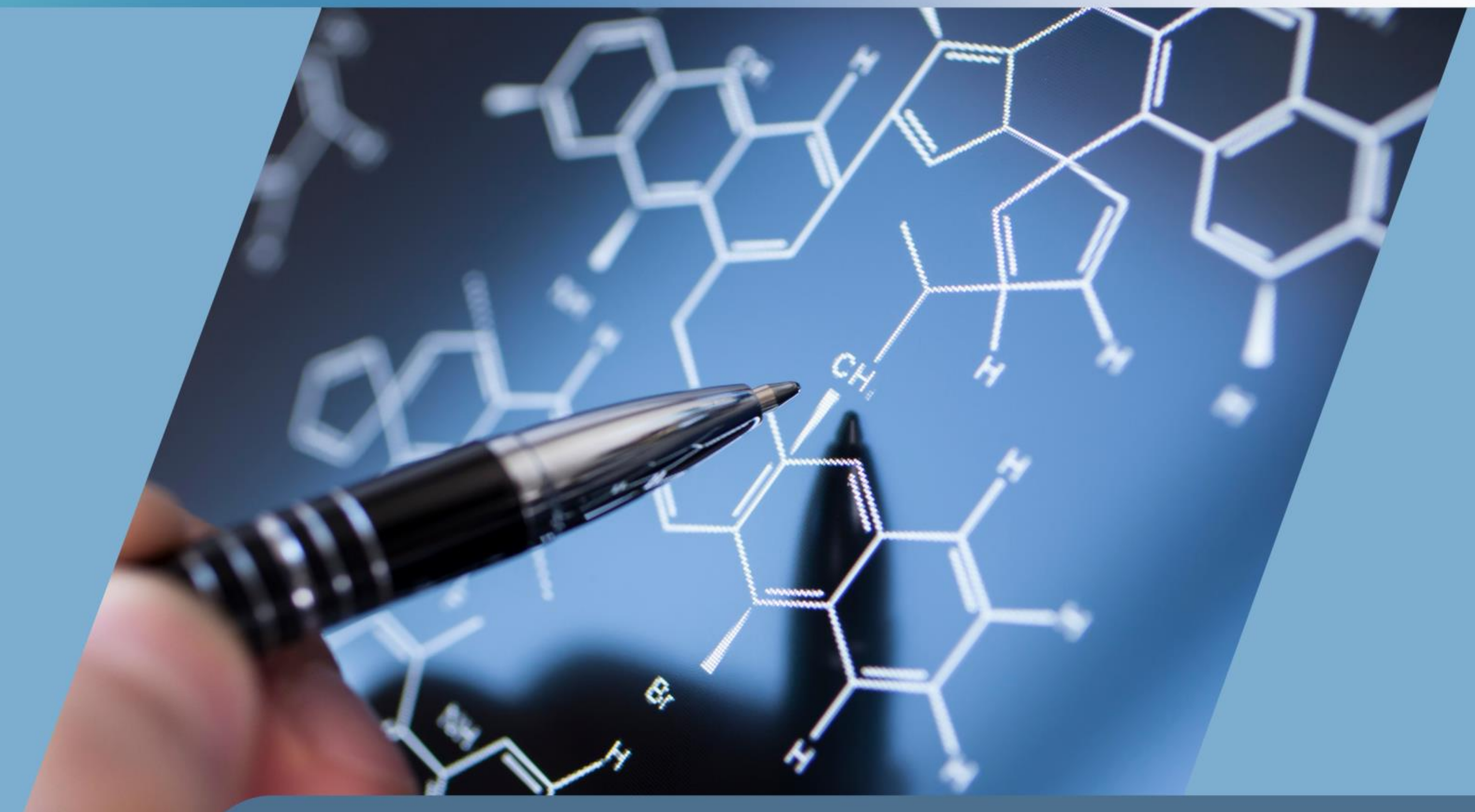

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Efficient Removal of Methylene Blue Dyes from Aqueous Solutions Using Various Charcoal Adsorbents: A Comparative Thermodynamic and Isotherm Study of Olive, Pine, and Commercial Activated Carbon

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ABSTRACT

In this study, the effectiveness of various types of charcoal, including pine, olive, and commercial activated carbon, as adsorbents for removing methylene blue dye from water is evaluated. The study was conducted by preparing aqueous solutions containing methylene blue dye and using the three types of charcoal as adsorbents. The main factors affecting the adsorption process were determined through laboratory experiments, which included varying temperature, contact time, pH, and the quantity of charcoal to optimize the dye removal process. Additionally, isotherm studies and thermodynamic analysis of the reaction were conducted. The results demonstrate the successful removal of methylene blue dye by all three types of charcoal, with maximum adsorption capacities of 346.02 mg/g, 283.28 mg/g, and 406.50 mg/g for commercial activated carbon, olive charcoal, and pine charcoal, respectively. The ΔH results indicate that the adsorption process for pine charcoal and activated carbon was physical, while it was chemical for olive charcoal. This research highlights the efficiency, cost-effectiveness, and sustainability of the adsorption process using charcoal as a promising solution for reducing dye pollution in water sources, contributing to the development of sustainable water purification strategies.

1 Introduction

The extensive use of synthetic dyes in the textile industry has led to the generation of colored wastewater, contributing to the pollution of water bodies and posing a significant environmental concern. Colored wastewater contains various organic and hazardous substances, which not only endanger aquatic life but also pose risks to public health (Ramakrishna & Viraraghavan, 1997). Synthetic dyes, known for their non-biodegradability and resistance to heat, light, and chemicals, exacerbate water contamination, potentially causing mutagenic, carcinogenic, or toxic effects (Almeida & Chemosphere, 2014). This pollution threatens the sustainability of ecosystems and compromises the availability of clean water resources for communities.

In addition to environmental pollution resulting from the dye industry, communities around the world face various environmental challenges arising from the use of chemicals, biological, and physical factors (Goudarzi & Mahvi, 2021). Pollution encompasses not only colored wastewater from industries but also air pollution caused by industrial emissions and volatile organic compounds, as well as soil pollution from the disposal of solid and hazardous wastes (Sarwar et al., 2020; Hahladakis & Iacovidou., 2020; Kim et al., 2017; Gyawali & Techato 2020).

Pollution is considered one of the most significant environmental challenges facing humanity in the modern age, adversely affecting the environment, human health, and animal life. Among the effects of environmental

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pollution are increased rates of chronic diseases such as asthma and respiratory diseases, deterioration of water quality affecting access to clean and potable water, and negative impacts on biodiversity and ecosystem stability (Landrigan et al., 2018; Prüss-Ustün et al., 2016; Patz et al., 2014)

Conventional wastewater treatment methods such as precipitation, coagulation, and filtration, while effective, are often time-consuming and expensive, limiting their widespread application (Crini, 2005). Therefore, addressing the issue of synthetic dye removal from wastewater requires exploring alternative, cost-effective solutions. Adsorption, a process involving the attachment of pollutant molecules to the surface of a material, particularly activated carbon, has emerged as a promising approach for the treatment of organic contaminants (Khettaf et al, 2016).

Moreover, the utilization of plant waste, such as seeds and roots, as eco-friendly and cost-effective adsorbents for dyes, has gained significant attention (Seow & Lim., 2016; Verma & EnviManag., (2016); Hassaan & El Nemr, 2017). Furthermore, the recent emphasis on producing activated carbon from agricultural and food waste offers a sustainable solution to address this environmental challenge (Aboushaloa et al., 2022; Alardhi et al., 2020; Maghni et al., 2017; Aboushloa & Etorki, 2015). Therefore, this study aims to assess the adsorption effectiveness of methylene blue onto olive, pine, and commercially produced activated carbon surfaces.

In this study, the adsorption capacity and efficiency of the three types of activated carbon, namely olive charcoal, pine charcoal, and commercially produced activated carbon, will be evaluated for the removal of methylene blue from wastewater. The findings of this research will contribute to the development of efficient and sustainable methods for dye removal, potentially leading to reduced environmental pollution and improved water quality.

2 Materials and Methods

2.1 Coal Preparation: Three coal samples (olive coal, pine coal, and commercial activated carbon) underwent drying at 105°C for 8 hours, followed by grinding and sieving for particle size standardization.

2.2 Effect of Initial Concentration on Adsorption Capacity: To establish the optimum initial concentration for dye (MB) adsorption, concentrations ranging from 5 to 25 ppm were prepared for olive coal, pine coal, and commercial activated carbon. After adding the coal, adsorption was measured following a 30-minute incubation.

2.3 Effect of Weight on Adsorption Capacity: The study explored the impact of coal weight (0.1-1.5 grams) on dye (MB) adsorption by assessing seven different weights for each type of coal at concentrations of 10, 10, and 25 ppm. Adsorption measurements were conducted after a 30-minute incubation.

2.4 Effect of Contact Time on Adsorption Capacity: Investigating the influence of contact time, olive coal and pine coal (0.4 grams each) and commercial activated carbon (0.1 grams) were added to dye solutions (10, 10, and 25 ppm). After a 30-minute incubation, adsorption was measured.

2.5 Effect of Temperature on Adsorption Capacity: The impact of temperature on adsorption capacity was evaluated by exposing olive coal and pine coal (0.4 grams each) and commercial activated carbon (0.1 grams) to dye solutions (10, 10, and 25 ppm) at different temperatures (25, 30, 40, and 70°C) for 30 minutes. Adsorption measurements were conducted after filtration.

Equations for Adsorption: The amount adsorbed (Qe) onto the silicon surface was determined using the following equation:

$$Q = \frac{Ci - Ce}{w} \times v \qquad (1)$$

The removal efficiency (% Removal) was calculated as:

$$\%\text{Removal} = \frac{Ci - Ce}{Ce} \times 100 \qquad (2)$$

Adsorption Isotherm Models: The Langmuir isotherm model, applicable to monolayer adsorption, is represented by:

$$Ce/\,Qe = 1\,/qmax\ Ce + 1/\ q\ maxb \qquad (3)$$

where qmax is the maximum adsorption capacity (mg/g), and b is the adsorption energy (L/mg).

The Temkin model, considering the adsorption as a chemical process, is expressed as:

$$Qe = \frac{RT}{b}\ln(A) + \frac{RT}{b}\ln(Ce) \quad (4)$$

Where $B = \frac{RT}{B}$ (5)

Freundlich adsorption isotherm is calculated by:

$$\ln(Qe) = \ln(Kf) + \frac{1}{n}(Ce) \quad (6)$$

where Kf and n are proportional constants reflecting adsorption capacity and intensity.

These equations provide a foundation for evaluating the adsorption performance of the studied materials under various conditions. (Aboshaloa et al.,2022)

3 Results and Discussion

3.1 Effect of Initial Concentration: The influence of the initial concentration of methylene blue (MB) dye on the adsorption ratio was investigated using three types of charcoal (olive, pine, commercial) at different dye concentrations (5, 10, 15, 20, 25 ppm), as illustrated in Figure 1.

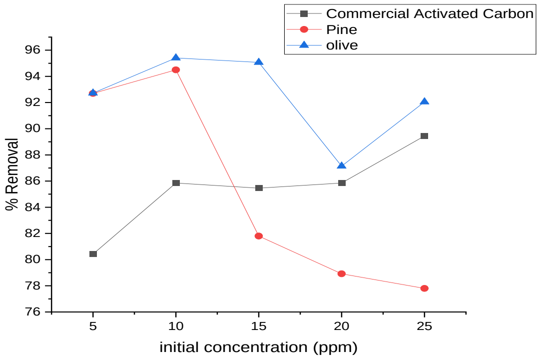

Figure (1) Effect of initial concentration (ppm) on Adsorption Process

The results demonstrate that the adsorption ratio for olive charcoal peaks at 10 ppm (95.41%), pine charcoal at 10 ppm (94.5%), and commercial activated charcoal at 25 ppm (89.45%). These findings align with previous studies (Rahman, et al., 2012; Li et al., 2016). suggesting an overall trend of increased adsorption rates with higher dye concentrations. The variation in optimal concentrations for each charcoal type emphasizes the need for tailored adsorption conditions based on specific adsorbent characteristics. Increased competition between dye molecules for scarce active sites on the charcoal surface or saturation of adsorption sites could be the cause of the plateau or minor decline in adsorption effectiveness at higher doses.

3.2 Effect of Weight on Adsorption Capacity: The impact of weight on the adsorption process of MB dye was explored using different weights of the three types of charcoal (0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.5 g), as depicted in Figure 2.

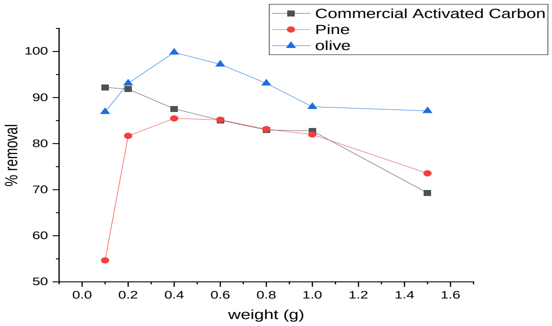

Figure (2) Effect of Weight (g) on Adsorption

Process results indicate that the adsorption rate for olive charcoal and pine charcoal is optimal at 0.4 g, with removal ratios of 99.8% and 85.4%, respectively. Commercial activated charcoal demonstrates the highest adsorption rate at 0.1 g, with a removal ratio of 92.2%. These outcomes align with a prior study (Aboushloa & Etorki, 2015). that identified the best dye adsorption rate at 0.3 g.

3.3 Effect of Contact Time on Adsorption Capacity: The influence of contact time on the adsorption process of MB dye was studied using three types of charcoal at different shaking times (10, 20, 30, 40, 50, 60, 90, 120 min), as presented in Figure 3.

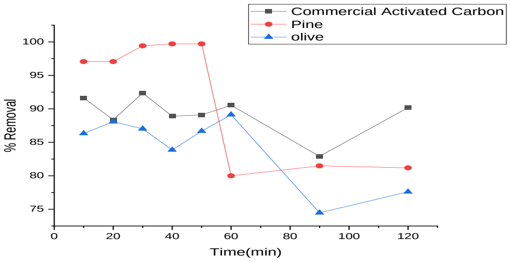

Figure (3) Effect of time(min) Values on Adsorption Process

Results indicate that the best adsorption rate for olive charcoal was observed at a contact time of 60 minutes (89.1%), while pine charcoal demonstrated optimal adsorption at 40 minutes (99.42%). Commercial activated charcoal displayed the highest adsorption rate at 30 minutes (92.63%). These findings align with previous studies (Pathania et al., 2017; Rahman, et al, 2012; Li et al., 2016) reporting optimal shaking times for dye removal ranging from 30 to 60 minutes.

3.4 Effect of pH on Adsorption Capacity: The adsorption process of MB dye was influenced by the pH of the solution, adjusted using dilute solutions of sodium hydroxide and oxalic acid, over a pH range of 1 to 12, as illustrated in Figure 4.

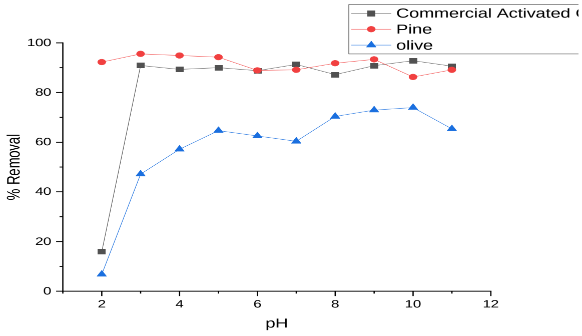

Figure (4) Effect of pH Values on Adsorption Process

Results showed that the highest adsorption rates for olive charcoal and commercial charcoal were observed at pH 10, with removal ratios of 73.93% and 92.8%, respectively. Pine coal exhibited the maximum adsorption rate at pH 3, with a removal ratio of 95.57%. These findings are consistent with previous studies (Pathania et al., 2017; Rahman, et al, 2012; Kumar et al., 2011). which reported higher adsorption rates in basic media. However, another study (Li et al, 2016) reported higher adsorption rates at pH 3, consistent with the results for pine coal.

3.5 Effect of Temperature on Adsorption Capacity: The effect of temperature on the adsorption process of methylene blue dye was investigated over a temperature range of 25-70°C, as shown in Figure 5.

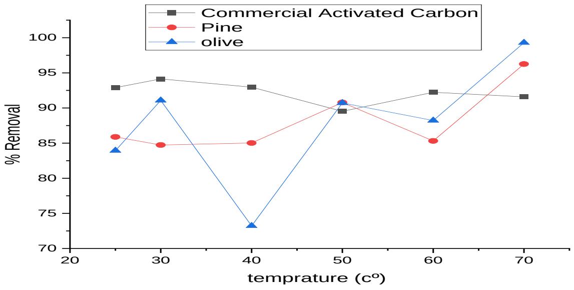

Figure (5) Effect of Temperature (c°) on Adsorption Process

The highest adsorption ratios for olive charcoal and pine charcoal were observed at 70°C, with removal ratios of 99.29% and 96.26%, respectively. For commercial activated charcoal, the highest adsorption rate was observed at 30°C, with a removal ratio of 94.14%. These results are consistent with previous studies (Rahman, et al, 2012; Kumar et al, 2011; Li et al, 2016; Aarfane et al., 2014). reporting an increase in adsorption rates with increasing temperature.

3.6 Isotherm Adsorption: Adsorption models, including Langmuir, Freundlich, and Temkin, were applied to the methylene blue dye, and the results are presented in Table 1. The isotherm of olive coal is also shown in the table1. Figures 6, 7 and 8 shows Langmuir, Freundlich and Temkin models.

Table (1) shows the isotherm of olive coal

Olive coal isothermates						
Isotherm models	Correlation Parameter					
Langmuir	Intercept 0.00353	Slope 0.00301	qmax(mg/g) 283.2861	AT 1.17257	RL 0.07857	R2 083665
Freundlich	Intercept 2.18097	Slope 0.87486	1/n 0.87486	Kf 151.6945	R2 0.79086	
Temkin	Intercept 168.814	Slope 108.26033	Pt (j mol-1) 108.26033	CT (j mg-1) 1.55933	R2 0.97174	

3.7 Isotherm Langmuir, Freundlich, Temkin for olivecoal

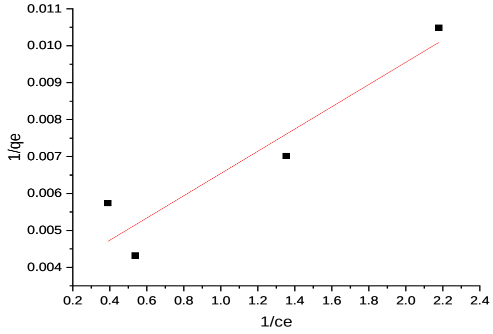

Figure (6) shows the Langmuir model

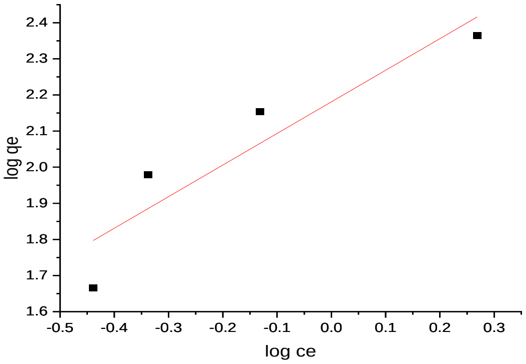

Figure (7) shows Freundlich model

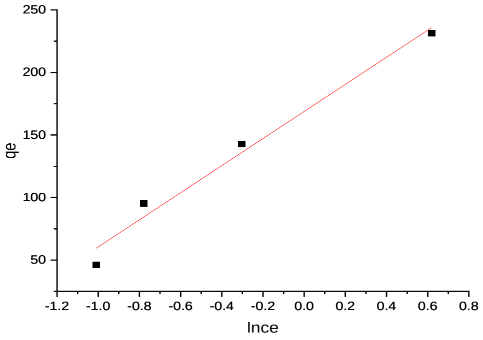

Figure (8) shows Temkin model of olive charcoal

Table (2) shows pine coal isotherm

Coal pine isothermate						
Isotherm models	Correlation Parameter					
Langmuir	Intercept 0.00246	Slope 0.00268	qmax(mg/g) 406.50406	AT 0.917910	RL 0.09824	R^2 0.70906
Freundlich	Intercept 2.24475	Slope 0.4006	1/n 0.4006	Kf 175.69119	R^2 0.68938	
Temkin	Intercept 194.27847	Slope 74.83377	Pt (j mol-1) 74.83377	CT (j mg-1) 2.596133	R^2 0.81187	

3.8 Isotherm Langmuir, Freundlich, Temkin for pine coal

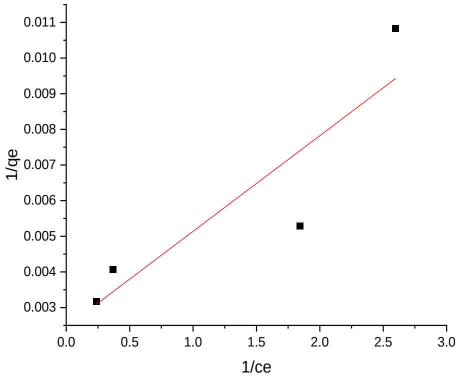

Figure (9) shows the Langmuir model

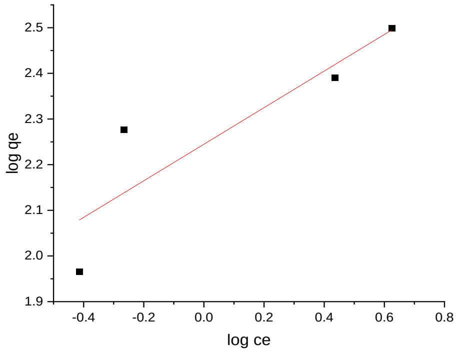

Figure (10) shows the Freundlich model

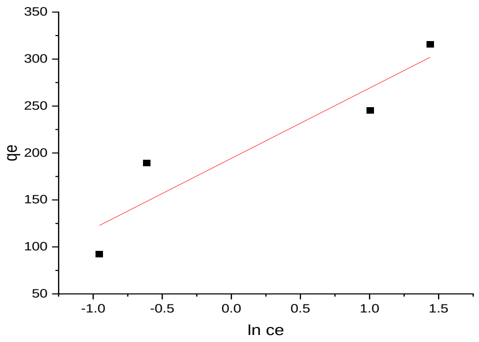

Figure (11) shows the Temkin model of pine charcoal

Table (3) shows the isotherm ate of commercial activated coal

Isothermate of commercial activated charcoal						
Isotherm models	Correlation Parameter					
Langmuir	Intercept 0.00289	Slope 0.01431	qmax(mg/g) 346.0207	AT 0.20195	RL 0.24698	R^2 0.93817
Freundlich	Intercept 1.95537	Slope 1.44764	1/n 1.44764	Kf 90.23395	R^2 0.92448	
Temkin	Intercept 84.51345	Slope 239.44749	Pt (j mol-1) 239.44749	CT (j mg-1) 0.35295	R^2 0.98687	

3.9 Isotherm Langmeier, Freundlich, Temkin Commercial Activated Coal

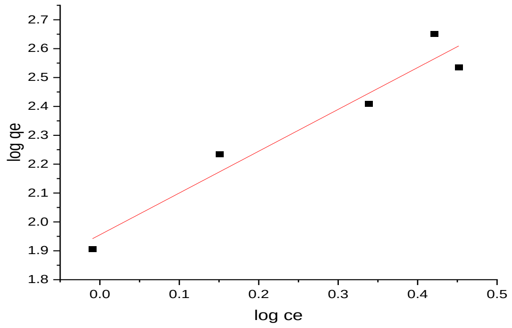

Figure (12) shows the Langmuir model

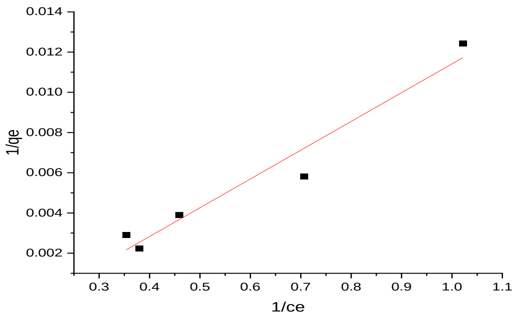

Figure (13) shows the Freundlich model

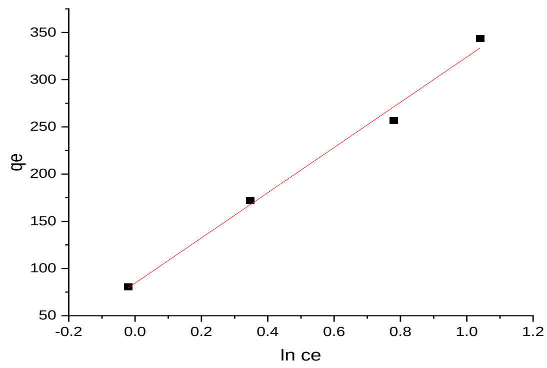

Figure (14) shows a model of Temkin isotherm

3.10 Thermodynamic functions of olive coal,

R^2 values of 0.97, 0.81, and 0.98 were found, respectively, when the Langmuir model was used to the adsorption of MB dye on the three forms of carbon (commercial activated charcoal, olive charcoal, and pine charcoal). The Temkin model was found to be most applicable to commercial activated charcoal and olive charcoal, but not to pine charcoal. The adsorption of MB dye on the three different forms of carbon (commercial activated charcoal, olive charcoal, and rosin charcoal) was found to have a correlation coefficient R^2 of 0.79, 0.68, and 0.92 for the Freundlich model. The results show that the Freundlich model is most applicable to commercial activated charcoal, while it is not suitable for olive charcoal or pine charcoal. The adsorption of methylene blue dye on the three different forms of carbon was also studied using the Temkin model; R^2 values of 0.97, 0.81, and 0.98 were found for commercial activated charcoal, olive charcoal, and pine charcoal, respectively. The results show that the Temkin model is most applicable to commercial activated charcoal and olive charcoal, but not to pine charcoal. The RL values obtained for the three types of carbon ranged from 0.07 to 0.24, indicating that the adsorption process is favorable. The RL values also suggest that the adsorption isotherm is not irreversible or linear but rather falls in the category of favorable or unfavorable, depending on the specific value of RL. (Junag et al., 1997; Aboushloa & Etorki., 2015). Overall, the Langmuir model was found to be applicable to all three types of carbon, while the Temkin and Freundlich models were most applicable to commercial activated charcoal and olive charcoal. The results suggest that the choice of adsorption model can depend on the specific type of carbon used and the properties of the dye being adsorbed.

3.11 Thermodynamic function of olive coal, commercial activated coal, pine coal.

Table (4) shows the thermodynamic functions of olive charcoal

Temperature	ΔG	ΔS	ΔH
298 K	- 12.6375KJ/mol	142.8124 J/molK	30.657649 KJ/mol
303 K	-12.6254KJ/mol		
313K	-13.0983KJ/mol		
323 K	-14.9518KJ/mol		
333 K	-17.6227KJ/mol		
343K	-18.5731KJ/mol		

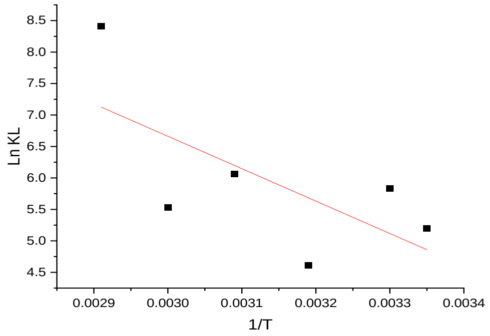

Figure (15) shows the thermodynamic functions of olive charcoal

Table (5) shows the thermodynamic functions of commercial activated coal

Temperature	ΔG	ΔS	ΔH
298 K	-11.3804KJ/mol	17.8261 J/mol.K	63.10450 KJ/mol
303 K	-12.3193KJ/mol		
313K	-11.9837KJ/mol		
323K	-11.0182KJ/mol		
333 K	-12.4056KJ/mol		
343K	-12.8092KJ/mol		

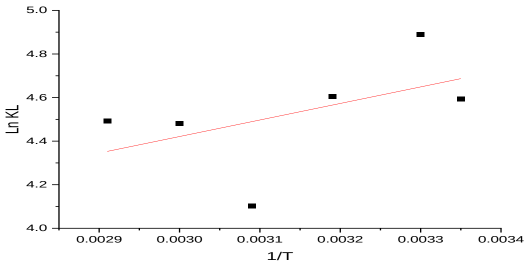

Figure (16) shows the thermodynamic functions of commercial activated coal.

Table (6) shows the thermodynamic functions of pine coal

Temperature	ΔG	ΔS	ΔH
298 K	-12.8719kJ/mol	183.8153 J/mol.K	42.810039 KJ/mol
303 K	-14.6896kJ/mol		
313K	-11.9907kJ/mol		
323K	-16.2900kJ/mol		
333K	-15.3231Jk/mol		
343K	-23.9816kJ/mol		

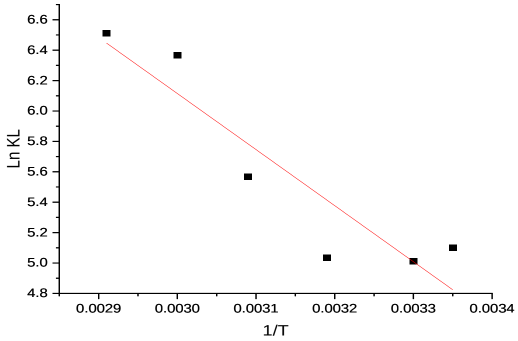

Figure (17) shows the thermodynamic functions of pine coal

The experimental results presented in Tables 4, 5, and 6 for the three types of carbon samples indicate that the adsorption of methylene blue decreases at lower temperatures and increases at higher temperatures. The negative values of ΔG suggest that the adsorption process is spontaneous (Aarfane et al., 2014). while the negative value of ΔS indicates a decrease in randomness at the solid-liquid interface. The positive value of ΔH indicates that the adsorption process is endothermic. The adsorption energy values for pine charcoal and commercial charcoal (> 40 KJ/mol) suggest that the adsorption is chemical in nature, while the adsorption energy value for olive charcoal (< 40 KJ/mol) suggests that the adsorption is physical in nature (Chawki, 2014).

4 Conclusion

Using various types of charcoal, including olive and pine activated charcoal, as well as commercially produced activated charcoal, the adsorption efficiency for removing Methylene Blue from industrial wastewater was evaluated. The results showed that all types of activated charcoal possessed high adsorption capacity for removing Methylene Blue from aqueous solution. This study provides support for the effectiveness of using activated charcoal in treating colored industrial wastewater contaminated with harmful organic substances. The results indicate that sustainable use of plant-based materials as adsorbents may be an effective alternative to relying on traditional activated charcoal. Based on these findings, further research in this field is recommended to enhance our understanding of adsorption processes and develop new, efficient methods for treating dye-contaminated water.

Additionally, industries generating colored industrial wastewater should adopt environmentally friendly practices and implement effective water treatment systems to mitigate pollution effects on the environment and human health. By investing in advanced environmental technology and embracing sustainability principles, a balance between industrial growth and environmental protection can be achieved.

Conflict of Interest: The authors declare that there are no conflicts of interest.

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