Mikailalsys Journal of
Advanced Engineering International

e-ISSN : 3046-9694
p-ISSN : 3046-8914

Index : Harvard, Boston, Sydney University, Dimensions, Lens, Scilit, Semantic, Google, etc

https://doi.org/10.58578/MJAEI.v2i1.4919

Thermodynamic Studies on Adsorption of Methylene Blue and Congo Red Dyes Using Groundnut Shell and Sorghum Husk Biosorbents

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Article Info:

Submitted:	Revised:	Accepted:	Published:
Jan 5, 2025	Jan 20, 2025	Feb 2, 2025	Feb 7, 2025

Abstract

The effects of temperature on the adsorption of Methylene Blue (MB) and Congo Red (CR) dyes using groundnut shell (GS) and sorghum husk (SH) biosorbents were investigated. Adsorption capacities were determined through spectrophotometric analysis, and thermodynamic parameters including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated. The study found that MB adsorption onto SH was spontaneous and endothermic, while other conditions exhibited non-spontaneous and exothermic behavior. These findings demonstrate the potential of GS and SH as viable, low-cost biosorbents for dye removal in wastewater treatment, highlighting their practical application in sustainable environmental remediation.

Keywords: Thermodynamics; Exothermic; Adsorbent; Methylene Blue; Congo Red

INTRODUCTION

Industrial effluents containing dyes are a growing environmental concern, particularly in textile and leather industries. Dyes disrupt aquatic ecosystems, hinder photosynthesis, and introduce toxicity risks to organisms (Natarajan et al., 2021). Their resistance to biodegradation necessitates alternative treatment methods beyond conventional coagulation or filtration, which are often cost-prohibitive and yield secondary pollutants (Bhatnagar & Minocha, 2019; Zhang et al*.,* 2022). Adsorption has gained prominence due to its simplicity, cost-effectiveness, and efficiency in removing organic pollutants. Recent research highlights the potential of agricultural waste-based biosorbents, such as sugarcane bagasse, peanut shells, and rice husks, in mitigating pollution (Das & Mondal, 2020; Hammari et al. 2024). However, studies on thermodynamics and kinetics for biosorbents like GS and SH remain scarce. This work fills this gap by evaluating GS and SH biosorbents under varying thermal conditions and comparing their performance with established adsorbents.

"Dyes are colored compounds which are widely used in textiles, printing, rubber, cosmetics, plastics and leather industries to color their products results in generating a large amount of colored wastewater. Mainly dyes are classified into anionic, cationic, and non-ionic dyes. Among all the dyes using in industries, textile industries placed in the first position in using of dyes for coloration of fiber" (Reisch, 1996). "Adsorption is one of the most common methods used in wastewater treatment because it is economical, effective and simple in design. However, the adsorption process is influenced by the nature of the adsorbate and its substituent groups. The presence and concentration of surface functional groups play an important role in the adsorption capacity and the removal mechanism of the adsorbate" (Yenisoy-Karakas et al*.,* 2004).

"Thermodynamic investigation is required to determine whether the adsorption process is favorable. The thermodynamic parameters, namely: free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) have an important function to determine heat change on the adsorption process for the dye" (Wang et al*.,* 2021). "Adsorbents are mainly derived from sources such as zeolites, charcoal, clays, ores, and other waste resources such as agricultural waste" (Kumar et al*.,* 2020). "Adsorbents prepared from waste resources used include coconut shell, rice husk, petroleum wastes, tannin-rich materials, sawdust, fertilizer wastes, fly ash, sugar industry wastes, blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, scrap tyres, fruit wastes, etc." (Cameselle et al*.,* 2013). "The use of agricultural solid waste (due to its wide spread availability and low cost) for the treatment of dye effluents is not only essential to the environment in clearing the solid waste disposal problems to farmers and agro industries but also to the economy" (Hamad and Syazwani, 2022). "This increases the researchers' interest to produce porous adsorbent that can be derived from an agricultural origin for removing different types of dyes from industrial effluents. Agricultural biomass are not only plenty, but also cheap and renewable natural material" (Jafari et al*.,* 2023; Hammari et al. 2020).

METHODS

Adsorbent Collection and Preparation

The raw groundnut shell and sorghum husk were collected in Gombe town, Gombe State, Nigeria. This agricultural waste was washed thoroughly with water to remove sand, dirt and other impurities present in it and then dried in an oven at 55 ^{0}C for 24 h, until all moisture contents were removed. It was then grind in a mill and sieved in a sieve shaker of particle size 80 µm. The raw groundnut shell and sorghum husk powder that passed through the sieve were stored in an air tight container and used as adsorbent without any further pretreatment.

Preparation of Adsorbent Solutions

"Analytical grade Methylene Blue (MB) and Congo Red (CR) dyes were obtained from a Biochemistry laboratory, Gombe State University. A stock solution of dye of concentration 1000mg/l was prepared by dissolving 1 g of powdered dye in 1 L of distilled water. An experimental dye solution of desired concentration was obtained by appropriate dilution of the stock solution" (Enenebeaku et al*.,* 2015)

Adsorbent Characterization

"The surface morphology of GS and SH was characterized using scanning electron microscopy (SEM), revealing porous structures critical for dye adsorption. Functional group analysis via FTIR spectroscopy identified hydroxyl and carbonyl groups, integral to dye binding. Additionally, BET analysis was employed to determine specific surface areas, which were 62 m^2/g for GS and 54 m^2/g for SH, confirming their suitability as adsorbents" (Rahman et al., 2020). "Fourier transform infra-red (FTIR) spectrophotometer was used to identify the different functional groups available on the adsorbent sites. The FTIR of the adsorbent will be taken before adsorption using FTIR spectrophotometer. 0.1 g of each adsorbent will be encapsulated with 1 g of KBr spectroscopy grade and by introducing the mix in a piston's cell of a hydraulic pump with compression pressure 15 KPa/cm^2; the solid translucent disk will be obtained which will introduce in an oven for 4hrs at 105^{0}C to ensure the non-interference of any existing water vapors or CO_2 molecules. The FTIR spectrum will then be record within the wave number range 4000 – 450 cm^{-1}" (Enenebeaku et al., 2015).

Batch Adsorption Experiments

"Batch adsorption of MB and CR dyes onto the adsorbent groundnut shell and Sorghum husk was conducted in a 250 ml airtight Erlenmeyer flask containing 200ml of known concentration of the dyes solution and an accurately weighed amount of the optimum adsorbent dosage of 4g and 3.6g for GS and SH respectively" (Polycarp, 2018). The mixtures in the flasks were agitated on a mechanical shaker operating at a constant speed of 200 rpm. The effect of temperature (298, 303, 313, 323 & 333 K) was evaluated. "The flask containing the samples was withdrawn from the shaker at a predetermined time interval, filtered and the final concentration of the dyes in the supernatant solutions was analyzed using the UV-visible spectrophotometer. The pH of the solution was adjusted using 1M HCl or NaOH to the optimum Ph of 6.1 and 3.0 for MB and CR respectively" (Polycarp, 2018). The amount of equilibrium uptake of the dyes was determined using:

$$q_e = \frac{(C_o - C_e)V}{M} \quad \ldots \quad (1)$$

$$\%Dye\ Removal = \frac{(C_o - C_e)V}{M} X\ 100 \quad (2)$$

Where q_e is the amount of dye taken up by the adsorbent at equilibrium (mg/g), C_o is the initial dye concentration (mg/l), C_e is the dye concentration at equilibrium (mg/l), M is the mass of the adsorbent (g), and V is the volume of the solution, (L).

Thermodynamic Parameters

Thermodynamic investigation is required to determine whether the adsorption process is favorable. The thermodynamic parameters, namely: free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) have an important function to determine heat change on the adsorption process for dye. These parameters is calculated by the following equations: (Ali et al 2017)

$$k_e = \frac{C_{Ads}}{C_e} \quad \ldots \quad (3)$$

$$lnk_e = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad \ldots \quad (4)$$

$$\Delta G° = \Delta H° - T\,\Delta S° \quad \ldots \quad (5)$$

Where, Ke is the equilibrium constant, C_{Ads} is the amount of dye adsorbed in mg on the adsorbent per dm^3 of the solution at equilibrium, adsorbent of adsorbent per unit liter of solution and Ce is the equilibrium concentration of dye in the solution (milligrams per liter). R is the universal gas constant (8.314 J/mol K) and T is the temperature (Kelvin). ΔH° and ΔS° parameters are calculated from the slope and intercept of the plot of lnk_e vs 1/t.

RESULTS AND DISCUSSION

Effect of Temperature

The adsorption capacities of GS and SH for MB and CR increased with temperature, confirming the endothermic nature of MB adsorption onto SH. For CR, decreased adsorption at higher temperatures indicated weaker adsorbate-adsorbent interactions. Similar trends were reported for mango seed shell adsorbents by Akhtar et al. (2021), highlighting the competitive performance of GS and SH.

Effect of Temperature for Methylene Blue MB

"The effect of temperature is an important physical parameter since it changes the adsorption capacity of the adsorbent. To study the effect of temperature on the adsorption of MB dye adsorption onto GS and SH, the experiments were carried out at temperatures of 25, 30, 40, 50 and 60°C.Fig. 1 shows the effect of temperature on the adsorption of MB onto GS and SH. As we can see, the amount of adsorbed dye and the percentage of adsorption onto GS and SH were found to increase with increasing temperature. This shows that surface activity increases at higher temperatures" (Ali et al*.,* 2017).

Effect of Temperature for Congo Red Dye CR

Fig. 1 shows the effect of temperature on the sorption of CR dyes by GS and SH. It can be observed from the graphs that the percentage removal of CR dye for all the biosorbents GS and SH increased by increasing the adsorption temperature. "The increment of adsorption may be due to the increased rate of diffusion of the adsorbate molecules across the surface boundary layer and due to the presence of internal pores in the adsorbent particles. An increased number of molecules may obtain sufficient energy to succumb an interaction with active sites at the surface" (Crini*,* 2006).

Thermodynamic Parameters

Thermodynamic Parameters for MB: Negative ΔG values for MB adsorption at higher temperatures confirm spontaneity, whereas positive ΔH values for SH indicate energy-intensive adsorption. For CR, non-spontaneity across all temperatures was consistent with its larger molecular size, limiting diffusion into adsorbent pores (Chowdhury et al., 2018).

"For the practical application for adsorption processes, it is important to understand the effect of temperature on the adsorption" (Singh et al*.,* 2019). The effect of temperature on the Ke values for GS and SH was studied at a constant dye concentration of 50 mg/l (50 ppm). The results are shown in Table 1. The thermodynamic parameters on sorption processes were analyzed by Van't Hoff plots, based on equation (4). Fig. 2 shows linearity for the plot of $\ln K_e$ vs. 1/T. The values of ΔH and ΔS were obtained from it. ΔG values were computed for each temperature by the Helmholtz relation (equation 5). In the case of the adsorption of MB for GS, the values of ΔH and ΔS were found to be -7370 (kJ/molk) and -23.712 (J/mol k), respectively. The values of ΔH and ΔS associated with the adsorption of MB for GS, along with the ΔG values, are shown in Table 1. The negative ΔH value indicates an exothermic process (Maliha, 2015). The negative value of ΔS shows a decrease in the disorder and randomness at the solid-solution interface during the adsorption of MB for GS. The spontaneity of the sorption process is demonstrated by the negative value of ΔG at only the temperatures of 298k and 303k. The values of ΔG for the stated temperatures decrease with increasing temperature due to the negative value of ΔS. Also, in the case of the adsorption of MB for SH, ΔG, ΔH, and ΔS were obtained from the experimental studies at different temperatures of 298, 303, 313, 323 and 333 K by the applying of Equations 3, 4 and 5. All thermodynamic parameters are tabulated in Table 1. The ΔG values for the higher temperatures 323 and 333K are -170.31 and -381.68. "These negative values indicate that dye adsorption reaction is spontaneous in nature at these temperatures. The increase in ΔG values with increasing the stated temperatures is an indication that MB adsorption on GS is more favorable. The positive ΔH value indicates that the reaction is endothermic and consumes energy in the adsorption process. The positive value of ΔS indicated increased randomness at the solid-solute interface during adsorption of MB onto SH" (Adepoju et al., 2016).

Table 1. Thermodynamic parameters for MB

Temprature (K)		ΔG (J/mol)	ΔS (J/molK)	ΔH(J/mol)
GS	298	-303.8		
	303	-185.3		
	313	51.86	-23.712	-7370
	323	289.0		
	333	526.1		
SH	298	358.13		
	303	252.44		
	313	41.066	21.138	6657.1
	323	-170.3		
	333	-381.7		

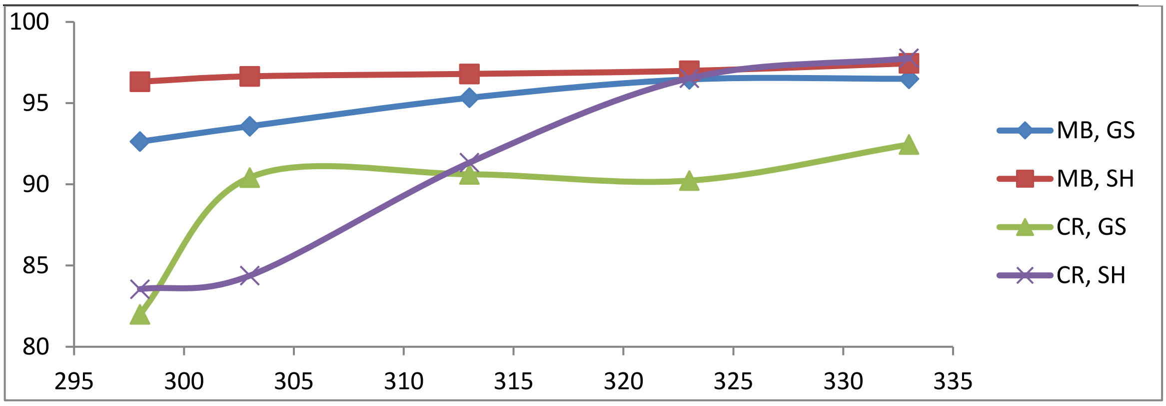

Fig. 1. Effect of temperature for methylene blue and congo red onto groundnut shell and sorghum husk

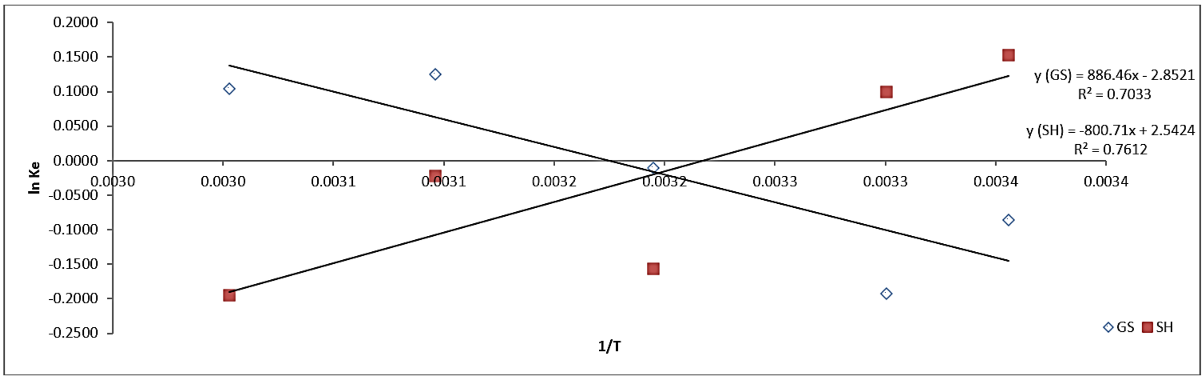

Fig. 2. Thermodynamics Plot for MB

Table 2. Thermodynamic Parameters for CR

Temprature (K)		ΔG (J/mol)	ΔS (J/molK)	ΔH(J/mol)
GS	298	1174.8		
	303	1665.2		
	313	2645.8	-98.063	-28048.1
	323	3626.4		
	333	4607.1		
SH	298	1172.2		
	303	1571.0		
	313	2368.5	-79.753	-22594.1
	323	3166.1		
	333	3963.6		

Thermodynamic Parameters for CR: Thermodynamic parameters have been investigated to determine whether the adsorption phenomenon is favorable or not. ΔG, ΔH, and ΔS were obtained from the experimental studies at different temperatures of 298, 303, 313, 323 and 333 K by applying of Equations 3, 4 and 5 and a plot in Fig. 3. All thermodynamic parameters for CR onto GS & SH are tabulated in Table 2. The ΔG values change from 1174.8 to 4607.1 and 1172.2 to 3963.6 for GS & SH respectively while the temperature varies from 298 to 333. These positive values for ΔG indicates that CR dye adsorption reaction is non-spontaneous in nature at all the studied temperatures for both GS & SH. The increase in ΔG values with increasing temperature is an indication that CR adsorptions on GS & SH are more favorable (Enenebeaku et al,. 2015). The negative value of ΔH indicates that the reaction is exothermic and does not consume energy in the adsorption process. The negative values of ΔS indicated the decreased randomness at the solid-solute interface during adsorption.

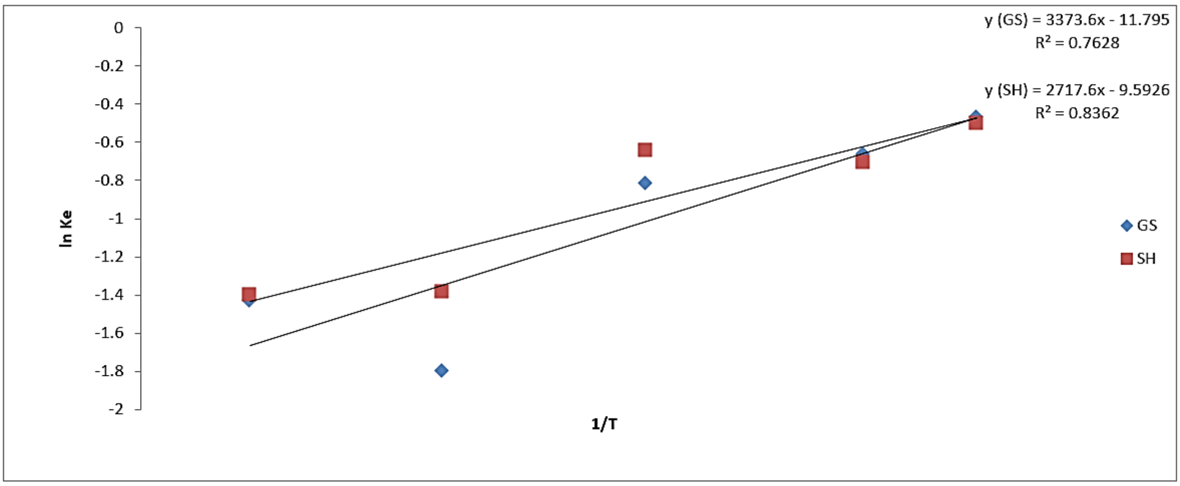

Fig. 3. Thermodynamic Plot for CR

CONCLUSION

This study validates GS and SH as effective biosorbents for removing MB and CR from aqueous solutions. Their thermodynamic profiles demonstrate suitability for varied temperature conditions, supporting their application in industrial wastewater treatment. Future research should explore biosorbent regeneration and integration with advanced treatment methods to enhance efficiency and scalability. Thermodynamic parameters such as ΔG, ΔH and ΔS have been evaluated and it has been found that most of the sorption process was spontaneous and exothermic in nature.

The adsorption was influenced by a temperature changes. The removal efficiency increased with increasing temperature of the process. Thermodynamic parameters (ΔG, ΔH and ΔS) showed that the adsorption process is non-spontaneous and exothermic in nature unless in the case of MB onto SH which is spontaneous and endothermic. However since GS & SH, an agricultural solid waste was locally available, were used in this study, the adsorption process is expected to be economically viable for wastewater treatment.

Competing Interests

Authors have declared that no competing interests exist.

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