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Evaluation of Sorption Capacity of Stem Carbon of *Aerva lanata* (L). For Turquoise Blue Dye Removal from an Aqueous Solution

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ABSTRACT

Researchers are now focusing their efforts on the adsorption of pollutants, including dyes, from wastewater by using adsorbents obtained from plants biomass. Wastewater containing dyes is a major concern to both the environment and human health hence the need to address the problem of taking off the dyes of the wastewater. This paper is aimed at the synthesis of potassium hydroxide activated carbon (PHALC) from *Aerva lanata* (L) stem with high adsorption capacities for turquoise blue (TB) dye. All the necessary factors were investigated in a series of batch studies. Analysis of experimental data revealed that TB dye has a strong affinity for PHALC; the Langmuir isotherm model can account for these findings. The adsorption system follows pseudo-second-order model based on kinetic modeling and the process is endothermic and spontaneous based on thermodynamics.

Keywords: Turquoise blue dye, Potassium hydroxide, *Aerva Lanata* (L), Adsorption.

INTRODUCTION

A healthy environment is a basic human right that wants to be upheld; nevertheless, the trend in the present world is industrialization. In the last few decades, pollution has become a phenomenon that is nearly synonymous with major cities across the globe and developing countries are in the worst position because the resources to manage wastes are scarce. Among them, water pollution has become the most threatening problem to the environment and human health as it negatively affects the functioning of the aquatic environment and directly influences the organisms' well-being. Water is a key resource that is vital for human survival, and the provision of clean water is essential for both home use, farming, and industrial purposes. However, industries like textiles, leather, cosmetics, paint, and food processing release highly polluted wastewater; approximately, 10-15% of dyes get released in effluents[1].

Turquoise blue dye, the popular reactive dyes, is considered a potential threat to water quality when present in wastewater. TB dye is known to cause a noticeable change in the water quality at a concentration as low as 1 mg/L due to its blue color and ability to reduce light penetration and in turn photosynthesis[2]. Hence, it is important to establish some correct treatment processes before discharging such effluents into water sources.

While techniques such as precipitation, coagulation/flocculation, chemical reduction, and oxidation are possible in the removal of dyes, their applicability in industries is hampered by technical and cost constraints[3]. Thus, adsorption is a more efficient process that is versatile, reusable, cost-effective, easily scalable, and non-lethal to other species. As for the main differences between adsorption and absorption processes, it is necessary to note that the latter does not result in the appearance of secondary negative effects.

In this research endeavor, the *Aerva lanata* (L) stem, which is a plant, is used to prepare the activated carbon since it is cheap to obtain. The dye adsorption is enhanced by microwave-assisted potassium hydroxide activation for the process. Microwave heating based on dielectric effect enables energy to be deposited directly to ions or molecules which results in shorter treatment time. Potassium hydroxide is one desiccant that transforms the structure of carbon to make it larger in surface area and reaction points. This makes chemical activation preferable to physical activation since it is done at low temperatures and takes less time[4].

In this research, we were employing microwave radiation in the process for producing activated carbon from the stem of the *Aerva lanata* (L) plant using potassium hydroxide as an activating agent (KOH). The concept of experimental studies can be explained by the process of using activated carbon to remove Tb dye to investigate the efficiency of the prepared carbon. In addition, the study on the adsorption process presents the isotherm, kinetic, and thermodynamic analyses of the process to provide a comprehensive knowledge of the event. Through these multiple analytical methods, it is envisaged to improve the understanding of the process dynamics and performance to create a basis for effective treatment of wastewater.

MATERIALS AND METHODS

Activated carbon Preparation

The stem of *Aerva lanata* (L) was collected from the Trichy area of Tamil Nadu for experimental purposes. To remove any unwanted matter, the stems were cleaned up with distilled water after the collection of the samples. Afterward, they were broken down into smaller sizes and ground into fine powders. The potassium hydroxide solution was prepared in different concentrations of 20%, 40%, and 60% V/V and 20 g of the pulverized stem material was then mixed with 75 mL of the different potassium hydroxide solutions. This mix was then left to stand at room temperature for one day, or 24 hours. Subsequently, microwave (model: MC28A5013AK/TL) heating (850 W) was administered for prescribed intervals of time which varied between 8 and 12 minutes. The residual carbonized samples were then subjected to a series of washings using 0. 5M HCl and then rinsed with hot and cold distilled water. The prepared carbon material was then filtered and dried at 423 K to obtain the prepared carbon material which was termed as potassium hydroxide activated carbon (PHALC)[5].

Preparation of Adsorbate Solution

For the present study, AnalaR grade Turquoise blue dye was carefully used to prepare the dye stock solution. The measured amount of Turquoise blue dye was then dissolved in double distilled water to prepare a stock solution of 1000 milligrams per liter (mg/L). To achieve reliable and repeatable experimental solutions, the guidelines of laboratory practice were strictly followed during the preparation of the experiments. The water used in the preparation was double distilled and this was done because any form of contamination could compromise the results of the experiments. Dilutions of the prepared stock solution yielded the subsequent solutions utilized in the experiment.

Batch Adsorption Experiments

The removal of TB dye from PHALC was examined at three different temperatures (305 K, 315 K, and 325 K) using the batch methodology. This method makes it easier to analyze all operational parameters. With this approach, one variable was gradually changed while the others remained unchanged. There were three dye concentrations used in the adsorption process: As a result, three different doses (20 mg/L, 40 mg/L, and 60 mg/L) were employed. This is how the trials were conducted: One gram of the weighted adsorbent and fifty milliliters of the dye solution were kept in an iodine flask. Subsequently, agitation was conducted in a rotary shaker set at 180 rpm for a predetermined duration. According to Aysha Bukhari *et al.,*[6] the percentage of color removal was calculated using the following formula.

$$\text{Removal (\%)} = C_i\text{-}C_t/C_i\,(100) \quad (1)$$

Where C_t is the adsorbate concentration at equilibrium (mg/L) and C_i is the adsorbate concentration at starting concentration (mg/L).

Adsorption Isotherm

The obtained equilibrium data in the current study are evaluated using a number of isotherm models, as suggested by the literature[7]. In particular, two adsorption models are used: the Freundlich and Langmuir isotherms.

Langmuir Isotherm

This isotherm is based on a number of assumptions, including the following: molecules interact with one another at the supposed site independently of other sites; all adsorption is restricted to monolayer coverage; and all surface sites are assumed to be the same for a specific type of adsorbate. An example linear expression for this equation is as follows:

$$C_e/Q_e = 1/Q_0b + C_e/Q_0 \quad (2)$$

C_e represents the maximum monolayer adsorption capacity or concentration, while milligrams per gram (Q_e) are the amount of solute adsorbed per unit weight of the adsorbent and adsorption equilibrium constant (b). Most users prefer the linear form of this equation because it is easier and versatile. The dimensionless separation factor, R_L, defined as follows:

$$R_L = 1/(1+bC_0) \quad (3)$$

Freundlich isotherm

Applying the Freundlich model to the sorption of both organic and inorganic complexes on various sorbents characterizes the extent of adsorption within a finite range. The expression for this equation is:

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

The amount of adsorbate adsorbed (mg/g) is denoted by q_e and K_f and are n constants that take into account all the factors influencing the adsorption intensity and capacity, respectively.

Kinetic Study

Pseudo-first-order kinetics

The Lagergren pseudo-first-order equation's linearized form is commonly expressed as follows[8,9].

$$\log (q_e\text{-}q_t)=\log q_e - k_1/2.303 \times t \quad (5)$$

The variables q_e and q_t in this equation represent the adsorption capacity at equilibrium and at time t, respectively (in milligrams per gram). K_1 is the pseudo-first-order adsorption process's rate constant. Plotting log q_e-q_t vs. t on graph paper should result in a straight line, from which q_e may be determined from the line's intercept and K_1 from the slope.

Pseudo-second-order kinetics

According to Souhila A. Hamoudi *et al.,* (2018)[10], the Ho equation[11], or pseudo-second-order kinetic model, can be written as follows:

$$t/q_t = 1/ k_2.q_e^2 + 1/q_e\, t \quad (6)$$

$$h = K_2q_e^2 \quad (7)$$

Plotting is then done between t and t/qt. Experimental determination of the theoretical adsorption capacity (q_e) and the second-order rate constant (k^2 in g/(mg min)) can be achieved by analyzing the slope and intercept of these graphs.

Test for kinetics models

The statistical tool mean sum of squared errors (MSSE) can be utilized to determine the most appropriate kinetic model for a given system[12]. The following is the expression for the sum of squared errors:

$$(\text{MSSE})= \sqrt{\sum[(q_e)_{exp}\text{-}(q_e)_{cal}]^2/N} \quad (8)$$

Where N is the total number of data points, $(q_e)_{cal}$ is the calculated q_e, and $(q_e)_{exp}$ is the experimental q_e.

Thermodynamic Study

The viability and spontaneity of adsorption events need to be investigated using thermodynamic analysis. These thermodynamic parameters were examined using equations (9) and (10)[13].

$$\Delta G° = -RTlnK_c \quad (9)$$

$$lnKc = \Delta S°/R - \Delta H°/RT \quad (10)$$

Where ΔS°(J/K/mol) represents entropy, ΔG°(J/K/mol) represents Gibb's free energy, and ΔH°(J/K/mol) represents enthalpy. At a given temperature (K), the apparent equilibrium sorption constant (Kd) is known.

RESULTS AND DISCUSSION

Effect of pH

To investigate the impact of pH on the rate of adsorption, the batch technique involved varying the solution's pH from 2 to 11 while maintaining control over other variables. The experimental results are displayed in the graph denoted by Fig. 1, which shows the pH-dependent percentage of TB dye removal. The highest adsorption capacity to be reached at pH = 2. The strong electrostatic interaction between the positive surface charges of PHALC and the TB dye results in higher adsorption capacity and rate, particularly as contact duration increases[14]. Conversely, the charges on the sorbent's surface may become more negative in an alkaline environment, which could reduce the adsorption capacity. This can be attributed to the anionic nature of TB dye molecules, which may make it difficult for them to penetrate surfaces because of the repulsive forces produced by the charge.

The correlation between pH and the adsorption capacity highlights the importance of pH regulation in the adsorption process, presenting useful information in improving the effectiveness of TB dye elimination with the use of PHALC as the adsorbent material.

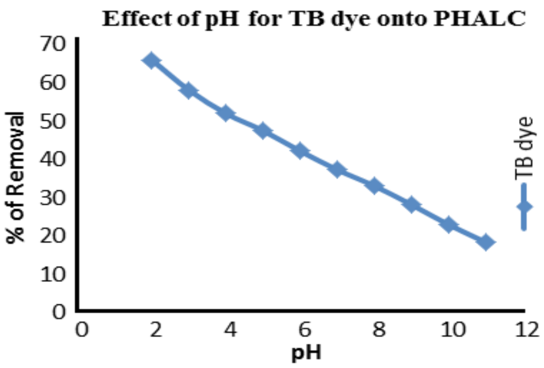

Fig. 1. Effect of pH for TB dye onto PHALC [Ci-40 mg/L; Dose-40 mg]

Effect of Dose

The results, as shown in Fig. 2, show that the amount of TB dye uptake is significantly influenced by the adsorbent dosage. The following were involved in the PHALC-assisted TB dye adsorption experiment: The adsorbent mass was measured in the range of 10 to 100 mg. The removal of dye within the dose range of 10 mg to 100 mg was increased. This makes more adsorption sites available since the larger adsorbent dose increases the surface area available for adsorption to take place. The reason for the decreased elimination rate in this instance was that the adsorption sites became completely occupied as the process went on. However, agglomeration or aggregation of the adsorbent reduced the overall adsorbent surface area, increasing the number of sites that can be removed in a single attempt[15].

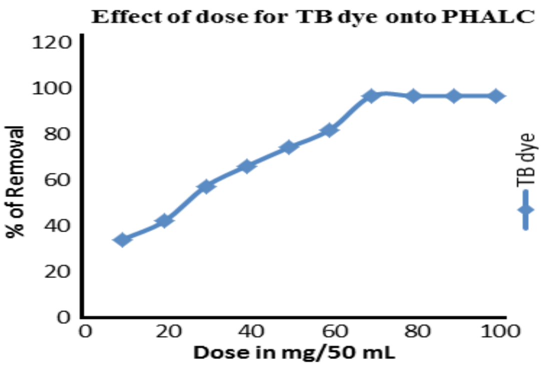

Fig. 2. Effect of dose for TB dye onto PHALC [Ci-40 mg/L; pH-2]

Effect of contact time

Contact time is a crucial measure in adsorption studies and the overall mass transfer process. As the extent of adsorption increased, the adsorbent's capacity to adsorb the dye molecules improved, as Fig. 3 illustrates. The sorption process achieved equilibrium after 80 min and stayed there for an additional 80 to 140 minutes. It is apparent that the adsorption process proceeds very quickly at first and that there are plenty of active sites available for the adsorbate fixation, even before any equilibrium between the adsorbent and the adsorbate is reached. However, as time went on, the amount of available active sites shrank, lowering the material's adsorption capacity and bringing the active sites to saturation, where they may be split into different equilibrium phases[16].

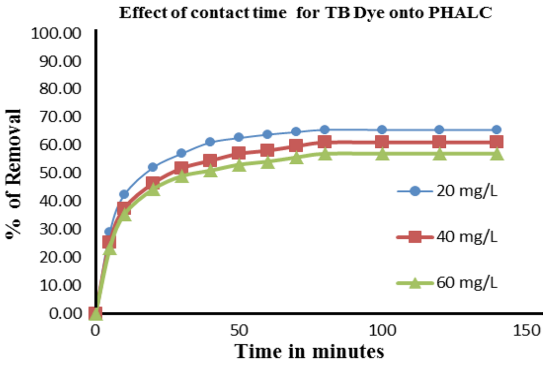

Fig. 3. Effect of contact time for TB Dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2]

Effect of Initial Dye Concentration

Figure 4 illustrates how the degree of PHALC is affected by the initial dye concentration. In the adsorption tests, the dye solution was employed, and the initial concentrations varied between 20 and 60 mg/L. The findings above show that the clearance percentage declined with the original concentration, which is expected given the dye's restricted adsorption sites. Nonetheless, the quantity of dye adsorbed on PHALC rose from 13. 10 to 34. 90 for TB dyes in the 305K, 310K, and 315K temperature range. The higher dye concentration may have provided a stronger driving force for the transfer process, which in turn caused the adsorbent absorption capacity to rise to counterbalance the mass transfer resistance[17].

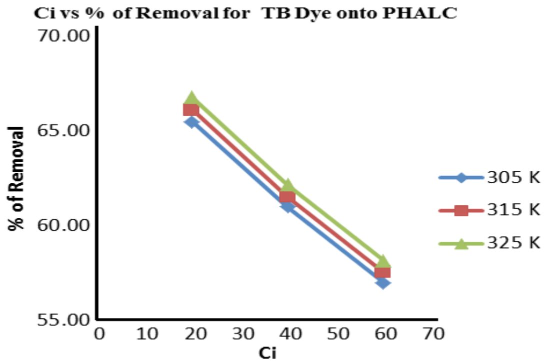

Fig. 4. Ci vs % of Removal for TB Dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2] 3.5 Effect of Temperature

Temperature is also among the most influential parameters that impacts the process of adsorption and its advancement. From 305K to 325K the rate of dye desorption increased drastically as was observed from the changes. Fig. 5 clearly depicts how much extent the experimental temperature influenced the process of adsorption and hence the increase in the extent of surface coverage.

Temperature has an expected effect on the adsorption process and shows an improvement in process efficiency; this may be due to dye molecules entering the micropores more deeply or to the creation of new active sites. Based on temperature variations, our data show that the endothermic nature is the best criterion to explain the adsorption process under steady-state conditions[12]. These results clearly show that temperature affects the adsorption process, making it crucial to consider the temperature factor and search for the best conditions for increasing the adsorption. Such information is essential for adjusting the conditions of the adsorption process and improving its efficiency in practice, particularly in water treatment and the removal of impurities.

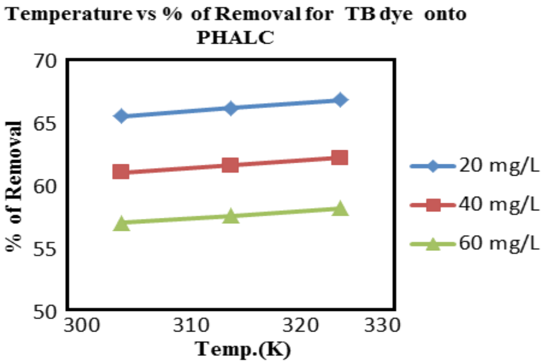

Fig. 5. Temperature vs % of Removal for TB dye onto PHALC

Adsorption Isotherm

In the current work, the results of the TB dye equilibrium on PHALC have been examined using the Langmuir and Freundlich adsorption isotherm equations. As shown in Fig. 6(A) and 6(B), the values of the various isotherm parameters were calculated from the straight line intercept and slope. Based on these findings, the Langmuir model was found to be the best representation of the TB system, followed by the Freundlich model with matching parameters of Q_m = 83.333 and R^2 = 0. K_{f1} = 6. 609 and K_{f2} = 6. 609 are the Langmuir model constants, while K_f = 3 is the Freundlich isotherm model's constant. R^2 = 0 and 3814 as a result. The values found for the Freundlich model are 9989. Based on the Langmuir and Freundlich isotherm models, it is possible to infer from the aforementioned data that monolayer adsorption may be involved in the TB dye's adsorption on PHALC.

These adsorption isotherms are helpful in removing organic contaminants and in comprehending the properties of the adsorbent surface, the adsorption processes, and the adsorption capacity of the adsorbate. The Langmuir and Freundlich isotherm results for the current work are presented in FIG. 6(A) and 6(B) and are summarized in Table 1 Six studies, classified as (B) are reviewed in this paper and are presented in Table 1 below.

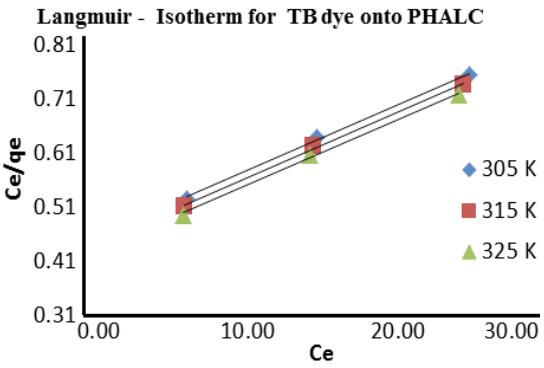

Fig. 6(A). Langmuir-Isotherm for TB dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2]

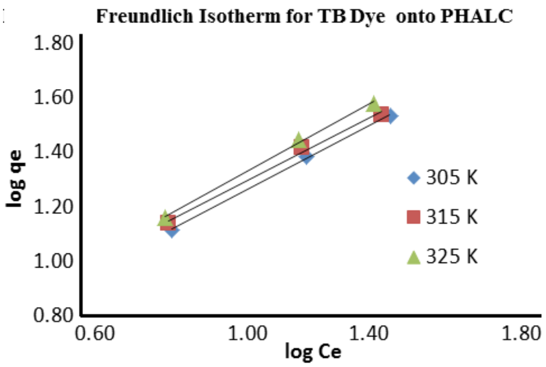

Fig. 6(B). Freundlich Isotherm for TB Dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2]

Table 1: Results of Langmuir & Freundlich isotherm plot for the adsorption of TB dye onto PHALC Ci-40 mg/L; Dose-40 mg; pH-2]

Isotherms	Parameters		TB dye		
			305 K	315 K	325 K
Langmuir	q^0		83.333	82.645	83.333
	b		0.027	0.028	0.029
	R^2		0.9989	0.9979	0.9977
	R_L	Ci			
		20 mg/L	0.6504	0.6416	0.6366
		40 mg/L	0.4819	0.4723	0.4670
		60 mg/L	0.3828	0.3737	0.3687
Freundlich	n		1.3680	1.3872	1.2918
	Kf		3.2151	3.5392	3.3814
	R^2		0.9984	0.9924	0.9962

Adsorption Kinetics

Based on the kinetics analysis, the application of the adsorption process was also investigated. It was shown that pseudo-second-order kinetics, as opposed to pseudo-first-order kinetics, best describes the process's kinetics. The R2 values of 0. 9978 and 0. 9926, respectively, which are displayed in Table 2 and Fig. 7(A & B), clearly demonstrate this. The rate of adsorption and the amount of time required to reach equilibrium are determined using the adsorption kinetics[18]. As demonstrated in Fig. 7(A) and 7(B). To determine the number of attributes for each model, the intercept and slope of the linear regression line of an appropriate curve were used. The computed values in this work are in good agreement with each other, and both theoretical and experimental q_e values were taken into consideration. The instruments listed in Table 2 below were used to record the kinetics and the MSSE values. Because the pseudo-second-order kinetic model has the lowest MSSE value for the adsorption process under discussion, it fits the data the best of the models that were examined, according to the information that was previously supplied.

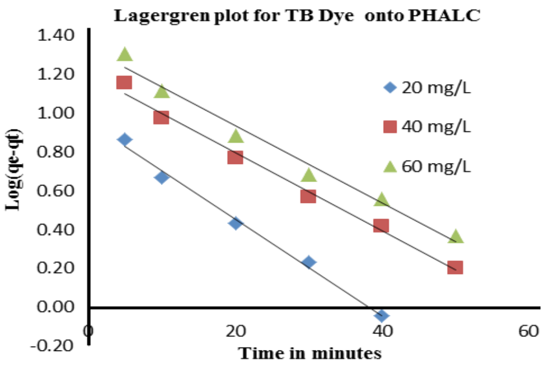

Fig. 7(A). Lagergren plot for TB Dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2]

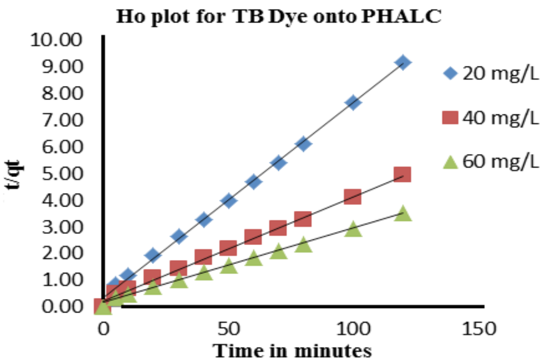

Fig. 7. (B) Ho plot for TB Dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2]

Table 2: Pseudo-first-order and pseudo-second-order models for the adsorption of TB dye onto PHALC.[Ci-40 mg/L; Dose-40 mg; pH-2]

Model/Parameters	TB dye			
Pseudo first order	20 mg/L	40 mg/L	60 mg/L	MSSE
K_1(min^{-1})	0.0553	0.0461	0.0507	
$q_{e(cal)}$ (mg/g)	8.9125	15.8855	21.4783	5.29
$q_{e(exp)}$ (mg/g)	13.10	24.40	34.20	
R^2	0.9920	0.9900	0.979	
Pseudo second order	20 mg/L	40 mg/L	60 mg/L	MSSE
K_2(g mg^{-1}min^{-1})	0.0154	0.0067	0.0046	
$q_{e(cal)}$ (mg/g)	13.6986	25.6410	37.0370	1.05
R^2	0.9970	0.9970	0.9970	

Thermodynamic studies

The results that were obtained from the analysis of this study are displayed in Table 3 and Fig. 8 below. The intercept and slope of a linear plot (lnk vs 1/T) were used to calculate ΔH° and ΔS°.

An endothermic adsorption process is indicated by a value of ΔH° larger than zero, which may result from TB's displacement of water and other molecules during the adsorption process. Additionally, the adsorbent's capacity to promote TB dye contact and the degree of disorder at the adsorbent solution interface are demonstrated by the positive value and magnitude of ΔS°. Furthermore, Wu (2010),[19] postulated negative ΔG° suggests that this reaction will go forward on its own. It indicates that the adsorption process is both feasible and spontaneous. It is therefore clear from the study that the adsorption process is thermodynamically possible and favorable, thus should be very useful in the design of the optimal conditions and actual applications of adsorption in the removal of pollutants.

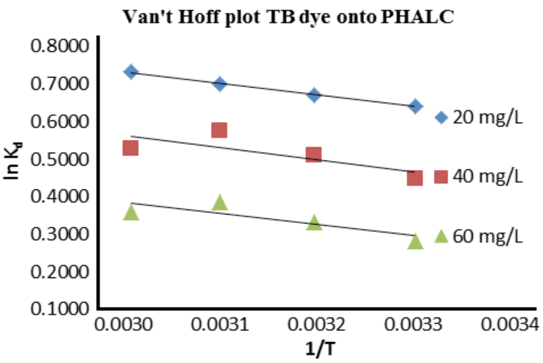

Fig. 8. Van't Hoff plot TB dye onto PHALC [Ci-40 mg/L; Dose-40 mg; pH-2]

CONCLUSION

This study was to examine the adsorption of turquoise blue (TB) dye using potassium hydroxide-activated carbon that was obtained from the stem of *Aerva lanata* (L) (PHALC). The behavior of the adsorbent and adsorbate in the aqueous solution was thoroughly examined by examining the literature that was already available. To investigate the impact of various parameters on the elimination of TB dye, batch procedures were employed.

The amount of time needed to bring the adsorption process to a condition of equilibrium was determined to be 80 min for the TB dye adsorption equilibrium period. Remarkably, the maximum adsorption capacity was obtained at a pH of 2, indicating the importance of solution acidity in removing TB dye. Both the isotherms were able to fit the equilibrium data findings well, suggesting that a monolayer developed on the PHALC surface throughout the adsorption process. This indicates that there is only one layer of TB molecules on the surface of PHALC, increasing the adsorption capacity.

The kinetic study's findings demonstrated how well the TB dye's adsorption on PHALC suited the pseudo-second-order model and supported the idea that surface reactions were the crucial process. The results of the thermodynamic analysis corroborated the notion that the TB dye removal from aqueous solutions was a viable, spontaneous, and endothermic adsorption process in the PHALC system.

Thus, PHALC is a practical and affordable method of removing TB dye from wastewater, according to the study's findings. This material can be a promising option for wastewater treatment because of its inexpensive cost and wide range of pollutant adsorption capacity.

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Conflict of interest

The author declares no conflict of interest

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