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THE USE OF SAWDUST AS BY PRODUCT ADSORBENT OF ORGANIC POLLUTANT FROM WASTEWATER: ADSORPTION OF MAXILON BLUE DYE

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ABSTRACT

Fugas sawdust *(SD)* (also known a beech wood) was used as an adsorbent for the removal of Maxilon blue dye (GRL) from an aqueous solution. The studies were carried out under various experimental conditions such as particle size, dye concentration, adsorption dose, pH and temperature to assess the potentiality of *Fugas* sawdust *(SD)* for the removal of GRL dye from wastewater. A greater percentage of dye removal was observed with decrease in the initial concentration of dye and increase in amount of adsorbent. The GRL dye adsorption data were fitted to various isotherm models such as Langmuir, Freundlich and Temkin. It was found that Langmuir model fitted well. The optimum pH for the adsorption was 6.7. The adsorption of the maxilon blue dye increased with increasing temperature indicating the endothermic nature of the adsorption process. Thermodynamic parameters such as free energy, enthalpy and entropy change were calculated. This adsorbent was found to be both effective and economically viable.

Key words: *Fugas* sawdust, Maxilon blue GRL, Adsorption isotherm.

INTRODUCTION

Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart colour. The majorities of dyes are complex organic molecules and are required to be resistant to many things such as the action of detergents[1-3]. Synthetic dyes are widely used in many fields of advanced technology, e.g., in various kinds of the paper[1], leather tanning[1], and textile[4].

From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on biodegradation alone[5,6].

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In recent past, considerable attention has been devoted to the study of removal of dyes from wastewater by adsorption using agricultural products and by-products[5]. The sorption of dye onto agricultural by-products is becoming a potential alternative for inorganic/organic removal from aqueous solution. Agricultural by-products are available in large quantities around the world, as wastes. These materials may have potential as sorbents due to their physico-chemical characteristics. Recently, many researchers indicated the effective removal capabilities of various agricultural solid wastes as adsorbents to remove inorganic/organic pollutants including dyes[1].

This study is an attempt to explore the possibility of utilizing green treated sawdust (SD) of waste wood for the removal of hazardous maxilon blue dye (GRL) from aqueous solution by performing batch studies. The effect of factors such as initial pH, particle size, adsorbent dose, initial concentration and temperature was investigated. The equilibrium sorption behavior of the adsorbents has been studied using the adsorption isotherm technique. Experimental data have been fitted to various isotherm equations to determine the best isotherm to correlate the experimental data. Thermodynamics of adsorption process has been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined.

EXPERIMENTAL

Adsorbent

Fugas Sawdust (SD) (also known a beech wood) in Malaysia, was obtained from the mechanical engineering wood shop at the Hilla/Iraq. The raw sawdust was sieved through a 3-2 mm sieve, washed repeatedly with distilled water to remove surface and soluble impurities, and dried at 100°C for 48 h. The dried sawdust was not subjected to further processing or chemical treatment, which might enhance its adsorptive capacity in an attempt to evaluate the GRL adsorption properties of a low-cost unprocessed sawdust, abundantly available in Hilla/Iraq.

Materials and methods

Maxilon blue (GRL) dye was provided by Al-Hilla of textile industries/Iraq. The respective chemical structures are shown in Fig. 1. The chemical product was of analytical grade and used without further purification.

A stock solution of 1000 mg/L was prepared by dissolving 1 g as an appropriate quantity of textile dye (GRL) in 1 L double distilled water. Working solutions of desired concentrations were prepared by successive dilution.

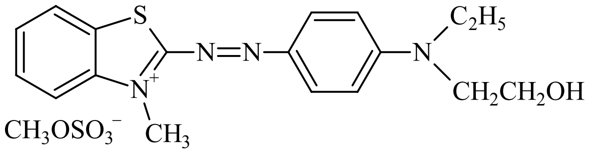

Fig. 1: Chemical structure of Maxilon blue dye GRL

Batch experimental program

Batch experiments were conducted at 30 ± 1°C to examine the effect of important parameters like initial pH, particle size, adsorbent dose, initial concentration and temperature on the adsorptive removal of GRL. For each experimental run, 100 mL of GRL solution of known concentration, pH and a known amount of the adsorbent were taken in a 125 mL stoppered conical flask. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 120 rpm at 25 ± 1°C. Samples were withdrawn at appropriate time intervals. Some SD particles remain suspended and do not settle down easily. Therefore, all the samples were centrifuged (two times) at 3600 rpm for 10 min to settle down suspended particles and then the residual concentration was determined at $\lambda = 609$ nm by using UV/VIS spectrophotometer (UV-1650/Shimadzu/ Japan), which was previously calibrated. Blank experimental runs, with only the adsorbent in 100 mL of double-distilled water, were conducted simultaneously at similar conditions to account for any color leached by the adsorbents and adsorbed by glass containers.

The effect of pH of the initial solution on the equilibrium uptake of GRL dye was analyzed over a pH range from 2 to 10. The pH of the solution was adjusted by either 0.1 M NaOH or 0.1 M HCI solutions. The adsorption studies were also conducted in batch experiments as function of particle size (100-75, 75-50, and less than 50 µm), adsorbent dosage (0.25, 0.5, 0.75 and 1 g/L), dye concentration (5, 10, 20, 30, 50 and 100 mg/L) for maximum adsorption, and the effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 283, 303 and 318 K. The percentage of GRL adsorption by the adsorbent was computed using the equation[7]:

$$E\% = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad \ldots(1)$$

where C_0 and C_e are the initial and equilibrium concentration of GRL ions (mg/L) in the solution. Adsorption capacity (qe) was calculated by using the mass balance equation for the adsorbent[8]:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \qquad \ldots(2)$$

where q_e is the adsorption capacity (mg/g), C_0 is the initial concentration of GRL in solution (mg/L), Ce is the equilibrium concentration of GRL in solution (mg/L), *V* is the volume of GRL ion solution (L) and *W* is the weight of the adsorbent (g).

RESULTS AND DISCUSSION

Characterization of Fugas sawdust

Fugas sawdust mainly consists of lignin, cellulose, hemicellulose and many hydroxyl groups such as tannins. All those components are active ion exchange compounds. Lignin, the third major component of the wood cell wall is built up from the phenylpropane nucleus; an aromatic ring with a three carbon side chain is promptly available to interact with cationic GRL ions[9,10].

FTIR spectra for Fugas sawdust in natural form and loaded with GRL dye are shown in Fig. 2. In case of SD, there is a strong peak at 3445 cm^{-1} representing the –OH stretching of phenol group of cellulose and lignin, and the peak at 2927 cm^{-1} indicates the presence of $-CH_2$ stretching of aliphatic compound. The FTIR spectrum of GRL loaded adsorbent, shown in Fig. 2, indicates that the peaks due to above functional groups are slightly affected in their position and intensity. It indicates that the adsorption of GRL dye on the surface of sawdust is either through complexation or through physical, which might be through weak electrostatic interaction and Van der Waals forces. However, no chemical bonding takes place in this process and thus, the FTIR of the surface moieties remain unchanged.

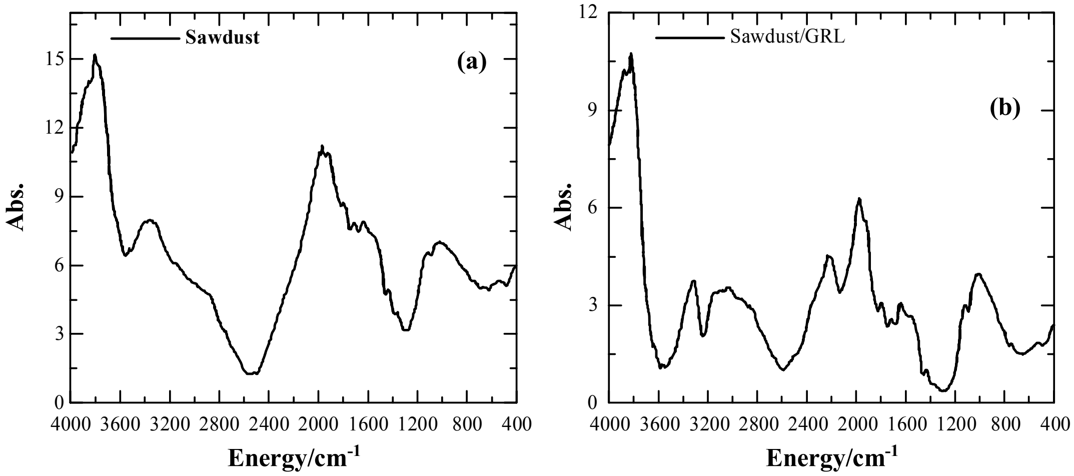

Fig. 2: FT-IR spectra of (a) GRL/sawdust, (b) Sawdust adsorbent

Effect of operational factor on adsorption efficiency

Effect of amount of adsorbent

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally the percentage of dye removal increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for the ability of a dye adsorption to be adsorbed with the smallest amount of adsorbent, so as to recognize the capability of a dye from an economical point of view[11]. Results are shown in Fig. 3.

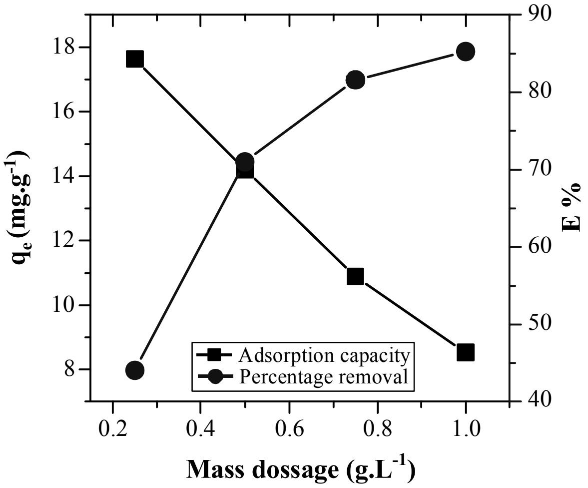

Fig. 3: Effect of adsorbent dose on the adsorption of GRL by SD (T = 303 K, t = 1 h, C_o= 10 mg/L, pH 6.7, particle size less than 100 um)

Effect of particle size

The particle size has an important role to play in the amount of the dye adsorbed. In the present investigation, particle sizes (100-75, 75-50, and less than 50 μm) were used for the adsorption of GRL over SD. The results are shown in Fig. 4. It was obvious from Fig. 4 that with a decrease in the particle size, the amount of the dye adsorbed also increases on SD. The pore structure of the adsorbents affects the adsorption of the dyes in two ways: the size exclusion limits the adsorption of the adsorbates of a given size and shape (sieve effect), and the adsorption capacity may increase with the increase in the specific pore volume. The increase in the adsorption capacity is more significant for the increase in the surface area, through decrease in the particle size. This is mainly due to the increase in the surface area and accessibility of the adsorbent pores for the dye to the increase in mesh size[12].

As known, the adsorption is limited to the external surface area of the adsorbent, and therefore, the decreased particle size reduces the external mass transfer resistance and helps adsorbate to enter into the interior of adsorbent for contacting more active sites during the adsorption process[13,14].

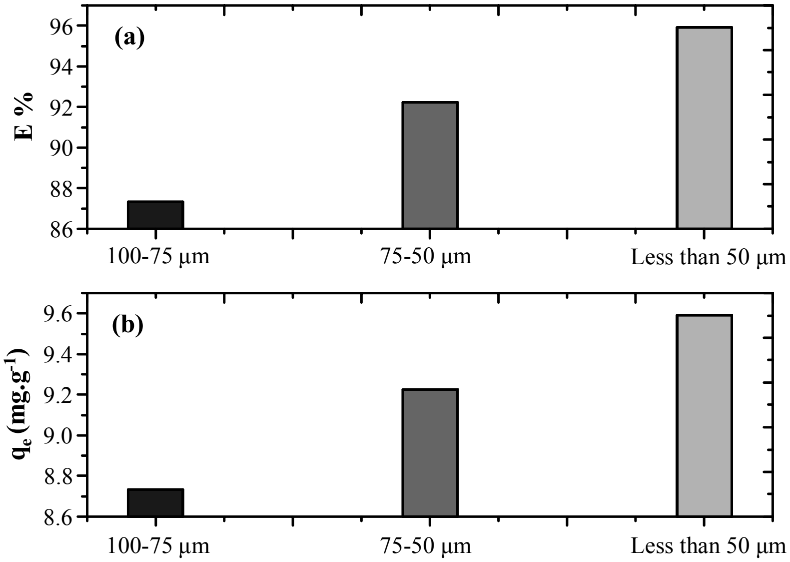

Fig. 4: Effect of particle size on the (a) removal of percentage, (b) adsorption capacity. (T = 303 K, t = 1 h, C_o= 10 mg/L, pH 6.7, mass dosage 0.1 g/100 mL)

Effect of solution pH

Solution pH plays an important role in controlling the surface charge of the adsorbent, the degree of ionization of the adsorbate in the solution as well as dissociation of various functional groups on the active sites of the adsorbent[15,16]. The results are shown in Fig. 5. The adsorption ability of the surface and the type of surface active centres are indicated by the significant factor that is the point of zero charge (pH_{pzc})[17]. The pH at which the surface charge is zero is called the point of zero charge (p_zc) and is typically used to quantify or define the electrokinetic properties of a surface. The value of pH is used to describe p_zc only for systems in which H^+/OH^- are the potential determining ions. Many researchers studied the point of zero charge (p_zc) of various adsorbents prepared from agricultural solid wastes; in order to understand the adsorption mechanism. Due to the presence of functional group such as OH^- group, cationic dye adsorption is favoured at $pH > pH_{pzc}$, whereas, anionic dye adsorption is favoured at $pH < pH_{pzc}$ where the surface becomes positively charged[17].

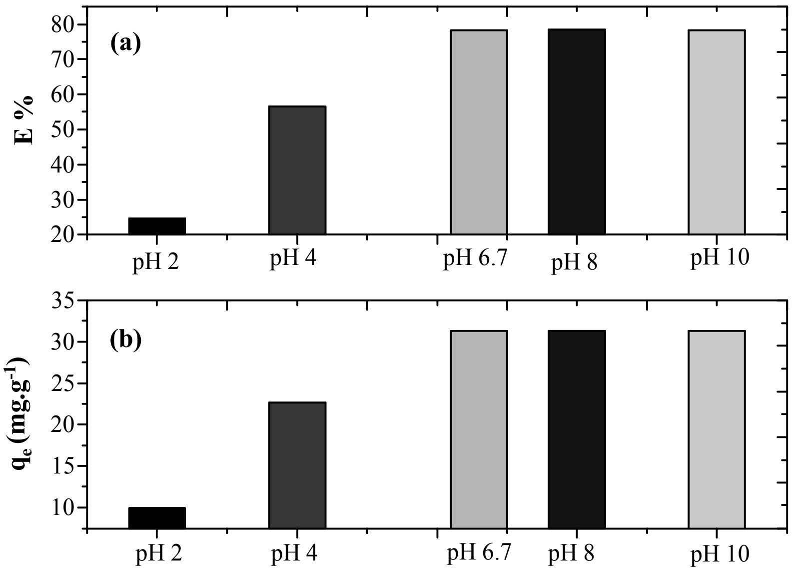

Fig. 5: Effect of pH on (a) removal of percentage, (b) adsorption capacity of GRL on SD adsorbent. (T = 303 K, t = 1 h, C_o= 10 mg/L, pH 6.7, mass dosage 0.1 g/100 mL)

Effect of initial dye concentration

The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface.

The effect of C_0 on the removal of GRL by SD is shown in Fig. 6. It is also evident from the figure that the percentage GRL removal decreased with the increase in C_0, although, GRL adsorbed per unit mass of SD (C_0) increased with the increase in C_0. The q_e increased with the increase in C_0 as the resistance to the uptake of GRL from the solution decreases with the increase in GRL concentration. The rate of adsorption also increases with the increase in C_0 due to increase in the driving force[18].

Applicability of various adsorption isotherm models on dye adsorption

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose[5]. The amount of GRL dye adsorbed (q_e) has been plotted against the equilibrium concentration (C_e) as shown in Fig. 7. The equilibrium adsorption density, q_e increased with the increase in dye concentration.

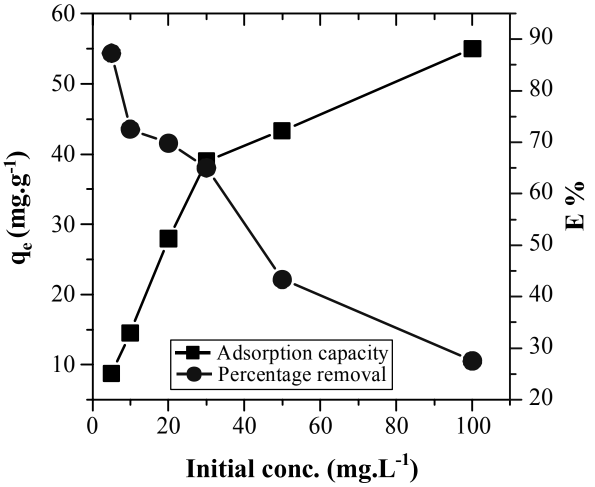

Fig. 6: Effect of initial concentration on adsorption of GRL by SD.
(T = 303 K, t = 1 h, particle size less than 100 um, pH 6.7, mass dosage 0.1 g/100 mL)

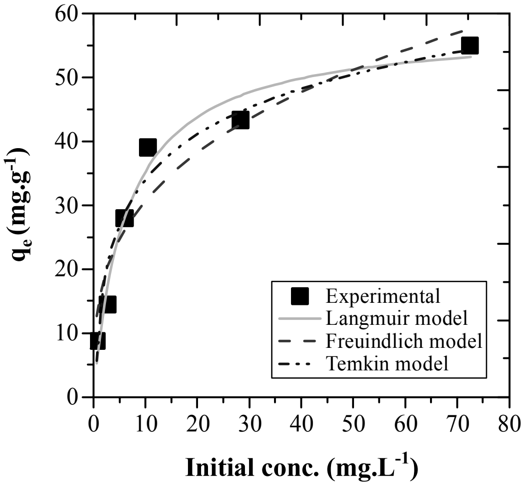

Fig. 7: Equilibrium adsorption isotherm of GRL onto SD adsorbent
(T = 303 K, t = 1 h, particle size less than 100 um, pH 6.7, mass dosage 0.1 g/100 mL)

Several models have been published in the literature to describe the experimental data of adsorption isotherms. In this work, three models (Langmuir, Freundlich, and Temkin) were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

Langmuir adsorption isotherm model to dye adsorption

The Langmuir adsorption isotherm model assumed that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The Langmuir equation is expressed by the following relation[19]:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \qquad \ldots(3)$$

where, q_e is the amount of dye adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), q_m is the maximum adsorption capacity (mg/g) and K_a is the isotherm constants for Langmuir (L mg^{-1}).

The Freundlich isotherm model

The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between adsorbed molecules[20]:

$$q_e = K_f C_e^{1/n} \qquad \ldots(4)$$

Where K_f is the Freundlich isotherm constant, n represents the adsorption intensity, C_e indicates the equilibrium concentration of adsorbate (mg/L), q_e is the amount of dsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g).

The model is applicable to the adsorption on heterogeneous surfaces by a uniform energy distribution and reversible adsorption. The Freundlich equation implies that adsorption energy exponentially decreases on the finishing point of adsorptional centres of an adsorbent[20]. The Freundlich constants are empirical constants depends on many environmental factors. The value of $1/n$ ranges between 0 and 1 indicates the degree of non-linearity between solution concentration and adsorption[21].

The Temkin isotherm model

Temkin equation is the early model proposed to depict adsorption of hydrogen on platinum electrodes within acidic solutions. The derivation of the Temkin isotherm based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic, as implied in the Freundlich equation[22,23]. The model is given by the following equation:

$$q_e = \frac{RT}{b} \log (K_T C_e) \qquad \ldots(5)$$

where Temkin constant (b) is related to the heat of adsorption (kJ/mol), R : Gas constant (8.314 J/mol.K), T : Temperature (K), and K_T : Empirical Tempkin constant related to the equilibrium binding constant is related to the maximum binding energy (L/mg), (L/mol)[24]. The Temkin equation better holds for the prediction of gas phase equilibria. Nevertheless, in case of liquid phase adsorption, particularly of GRL using SD adsorbent, this model fall-short in representing the equilibrium data. The Temkin equation is often not suitable for representation of experimental data of the liquid phase adsorption in complex systems, since the derivation for the Temkin equation is based on simple assumption and the complex phenomenon in liquid phase adsorption are not taken into account[25].

Table 1: Langmuir, Freundlich and Temkin model isotherms parameters for GRL adsorbed on the surface of SD adsorbent

SE	Value	Parameters	Isotherm models
3.877	57.876	q_m (mg.g^{-1})	**Langmuir**
0.0351	0.1555	K_L(L.mg^{-1})	
0.96142		R^2	
2.829	14.7013	K_F	Freundlich
0.0552	0.31909	1/n	
0.90199		R^2	
1.0254	2.73032	B/J.mole^{-1}	Temkin
1.12404	10.2754	K_T	
0.9429		R^2	

q_{max} = Maximum adsorption capacity; K_L = Langmuir constant; K_F, 1/n = Freundlich constants; b, k_T = Temkin constants; R = Universal gas constant 8.314 J.K^{-1}.mol^{-1}.

Effect of temperature and thermodynamic parameters

Effect of temperature is another significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent[26]. If the amount of adsorption increases with increasing temperature, then the adsorption is an endothermic process. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature[1].

In the present study, increase in temperature leads to fast diffusion of dye molecules across the external boundary layer and internal pores of the adsorbent particles due to less resistance offered by viscous forces in the aqueous phase. Also, in some cases, the solubility of the adsorbate molecules is affected, which finally has significant effect on the removal process. The increase in adsorption capacities of adsorbents at high temperature may also be attributed to the pore size enlargement[27].

Thermodynamic parameters such as change in free energy (Δ*G*), enthalpy changes (Δ*H*) and entropy changes (Δ*S*) were determined using the following equations[7,28,29].

$$K_e = \frac{q_e}{C_e} \qquad \ldots(6)$$

where K_e is equilibrium constant, q_e and C_e are the equilibrium concentrations of dye ions on adsorbent (mg/g) and in solution (mg/L), respectively. The change in free energy (Δ*G*) can be calculated from the relation:

$$\Delta G = RT \ln K_e \qquad \ldots(7)$$

where, *T* is the temperature in Kelvin and *R* is the gas constant (8.314 J/molK).

Enthalpy change (Δ*H*) was calculated from the following equation:

$$\ln K_e = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad \ldots(8)$$

Table 2: Thermodynamic functions ΔG, ΔS and, ΔH of GRL adsorbed on the sawdust SD

ΔS ($J.K^{-1}.mol^{-1}$)	ΔH ($kJ.mol^{-1}$)	ΔG ($kJ.mol^{-1}$)	K_e	T/K
108.37657	9.347929	-21.3301	8652.406	**283**
		-22.9317	10464.29	**298**
		-24.5831	12666.67	**313**

Thus, a plot of ln K_e vs 1/*T* should be straight line (Fig. 8). Δ*H* and Δ*S* values were obtained from the slope and intercept of this plot, respectively. The standard free energy change (Δ*G*), standard enthalpy change (Δ*H*), and standard entropy change (Δ*S*), were obtained from the Eqs. (7) and (8) and their values associated with the adsorption of GRL onto Fugas sawdust are listed in Table 2. Negative values of Δ*G* indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of GRL for Fugas sawdust. Positive value of Δ*H* indicates the endothermic nature of the process, while positive value of Δ*S* reflects the affinity of the adsorbents for the GRL and suggests some structural changes in adsorbate and adsorbent[18,30].

Results (Table 2) indicates that the adsorption process was endothermic in nature and the magnitude of adsorption supports the formation of partial chemical processes that are involved during the removal process[31]. The negative value of the Gibbs free energy change (Δ*G*) reveals that the adsorption process was spontaneous in nature[32] and the decreasing value of Δ*G* with increasing temperature shows the spontaneous nature of the adsorption of GRL dye. The entropy change Δ*S* shows positive value, which confirms that the increasing randomness between the solid–solution interfaces during the adsorption process, probably due to the desorption of solvent molecules prior to GRL dye adsorption[33].

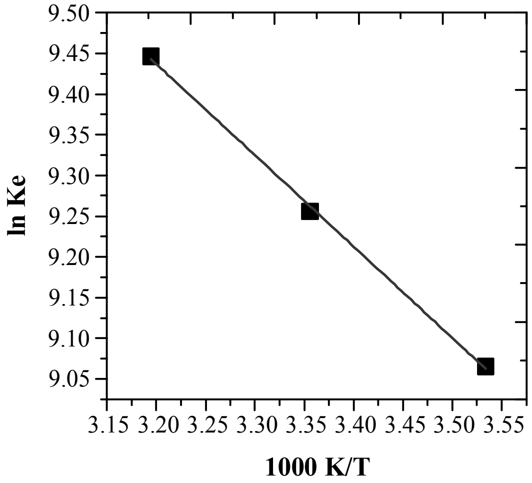

Fig. 8: Van’t Hoff plot for the adsorption of GRL onto SD

CONCLUSION

Thus it is proved that adsorbent Fugas sawdust (SD) can be very effectively employed for the removal of GRL from aqueous solution. The adsorption was found to be strongly dependent on pH, adsorbent dose, particle size, initial GRL concentration and temperature. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 1 h. Equilibrium adsorption data for GRL on SD were well represented by the GRL isotherm model. Adsorption of GRL on SD is favorably influenced by an increase in the temperature of the operation. Thermodynamic parameters were calculated for the removal of dye and their values indicated that the process of removal was spontaneous and endothermic.

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