

Research Article

Application of Low-Cost Non-Conventional Materials for Effective Decolorization

Lavanya K¹, Deepa M^{1*} and Zakir H²¹Department of Chemical Engineering, Andhra University College of Engineering, India²Department of Chemical Engineering, Rajiv Gandhi Institute of Petroleum Technology, India

*Corresponding author: Deepa M, Department of Chemical Engineering, Andhra University College of Engineering, Visakhapatnam - 530 003, India

Received: January 03, 2018; Accepted: February 05, 2018; Published: February 12, 2018

Abstract

In the present study “groundnut shell powder” was used to adsorb methylene blue dye from its modeled aqueous solution. The parameters affecting the adsorption process like contact time (1-35 minutes), pH (2-10), initial dye concentration (20-100 ppm), temperature (303-333K), adsorbent particle size (0.75-300 μ m) and adsorbent dosage (0.02-0.1g) were studied. The obtained equilibrium data was mathematically modeled using the Langmuir, Freundlich, and Temkin isotherm models. Further, the adsorption kinetics was determined using pseudo-first & second order kinetic models. The important thermodynamic parameters like free energy change (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) are estimated to predict the nature of the adsorption process. Experimental results show that the adsorption is more favored with an increase in contact time, pH, temperature, & adsorbent dosage. It was found that a contact time of just 8 minutes is enough to attain adsorption equilibrium. The Freundlich equation was found to best represent the equilibrium data with a high correlation coefficient ($R^2=0.999$) followed by Langmuir ($R^2=0.993$) & Temkin ($R^2=0.979$) isotherm models. The kinetics of the adsorption was found to be followed by pseudo-second-order model with rate constant $K_{II}=1.76$ g/mg.min. The ΔH and ΔS of adsorption were found to be 6.98 kJ/mol & 0.1kJ/mol. K, respectively. Moreover, the ΔG of the adsorption was found to be negative in all the temperatures and confirms the feasibility and spontaneity of the adsorption process. Thus, the positive value of ΔH confirms that the adsorption is endothermic together with the positive values of ΔS reflect the affinity of the groundnut shell powder for methylene blue uptake. Moreover, it also shows the increased randomness at the solid-liquid interface with some structural changes on the adsorbent. Therefore, the adsorption was found to be spontaneous only at high temperatures subject to the limitation $T\Delta S > \Delta H$.

Keywords: Adsorption; Groundnut shell powder; Methylene blue, Isotherms, Kinetics, Thermodynamics.

Abbreviations

C_o & C_t : Initial Concentration & Concentration of solute in the solution at any Time t, mg/l; C_{eq} : Concentration of Adsorbate in Equilibrium, mg/l; q_t : Dye uptake, mg/g (amount of dye adsorbed per unit weight of adsorbent at equilibrium); W: Weight of adsorbent; V: Volume of solution, ml; d_p : Particle size of the adsorbent, μ m; R^2 : Correlation coefficient; q_{max} : Maximum sorption capacity, mg/g (q_{eq} for a complete monolayer); b: Langmuir isotherm constant, L/mg; K_f : Freundlich isotherm coefficient; m: Measure of adsorption intensity; A_T & B_T : Temkin isotherm constants, L/mg; K_1 : Pseudo-First order rate constant, (min^{-1}); K_{II} : Pseudo-Second order rate constant, (g/mg min); R: Universal gas constant, (8.314 J/mol.K); K_a : Equilibrium constant, L/mol; ΔG & ΔH : Change in Gibb's free energy & enthalpy of adsorption (J/mol); ΔS : Change in entropy (J/mol K)

Introduction

Among all the dyes, azo dyes represent one of the most versatile and largest classes of dyes used in the textile industry and are characterized by having an azo group (comprised of Nitrogen double bonds (N=N)) and associated chromophores [1]. During dyeing process, unfortunately, due to the lower adhesion capacity of dye to

the cellulosic fibers, nearly 50% of the dyes are lost in to the effluents [2,3]. These effluents containing dyes undergo reductive cleavage of N=N linkage and produce toxic amines causing severe health effects on living organisms during metabolism [4]. In particular, the major effect on humans include carcinogenic effects, cause severe mutagenic, and damage to vital organs such as kidneys, brain, central nervous system etc [5]. In light of the adverse effect on health, the dye removal from wastewater has received enormous attention over the

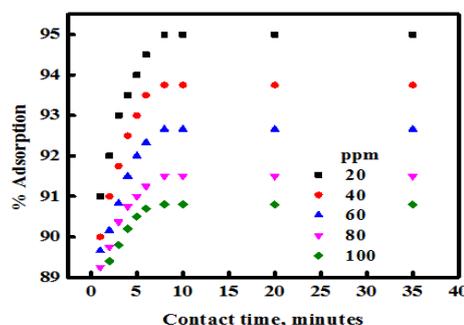


Figure 1: Effect of contact time on % Adsorption.

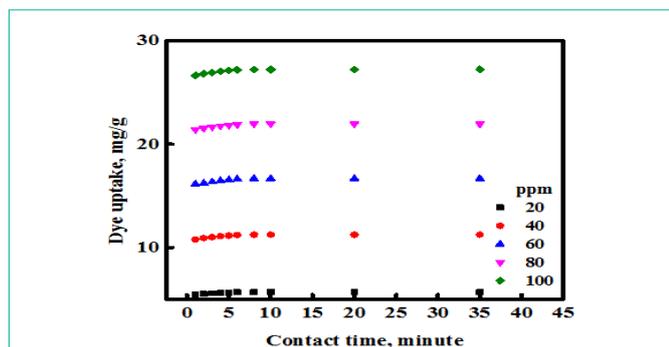


Figure 2: Effect of contact time on Dye uptake.

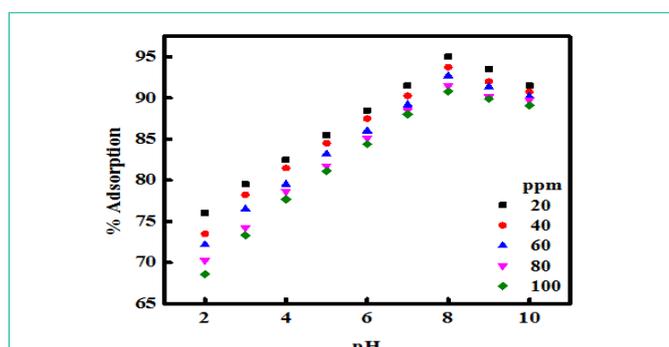


Figure 3: Effect of pH on % Adsorption.

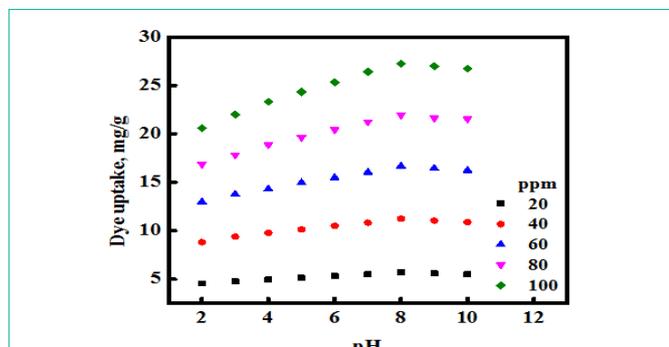


Figure 4: Effect of pH on Dye uptake.

past few decades.

Among the diverse dye removal techniques adsorption is the preferred method due to its suitability in removing the majority of dyes [6]. Activated carbon is the most widely used adsorbent for the removal of textile effluents due to their higher adsorption capacity & greater effectiveness; however, its use is still limited because of its high synthesis cost [7]. Moreover, it is also associated with the problems of limited regeneration and difficulty in separation from the waste water. On the other hand, non-conventional adsorbents come to the rescue of the low-cost wastewater treatment and many researchers have focused on finding non-conventional alternative adsorbents [6,8]. Non-conventional adsorbents are lower in cost due to their origin from industrial & agriculture wastes together they offer a non-hazardous route for waste treatment. In particular, the use of agricultural waste as an adsorbent and catalyst supports

have gained huge attention among the research community due to their abundance. Unlike activated carbons; they do not require complex pretreatment and activation before their application and also regeneration may not be necessary after their use [9]. Moreover, they offer less maintenance and supervision cost in the adsorption process. Nonetheless, use of these low-cost alternative adsorbents for wastewater treatment remains limited due to the one or more associated disadvantages like no proper field trial, insufficient documentation in real wastewater treatment systems and due to insufficient data on the necessity of post-usage regeneration or disposal [10]. The extensive review of the literature was made for these types of adsorbent in removing contaminant [2,4,6-16]. Previously many researchers have assessed the potential of various low-cost adsorbents like banana pith, hardwood, De-Oiled Soya, Indian Rosewood, bagasse pith, neem leaf powder, orange and banana peels, waste coir, barley husk, rice husk, cassava peel, and Mahogany sawdust, etc. especially for the dye removal [17]. However, there are only a few studies using groundnut shell powder as an adsorbent for the removal of methylene blue. Adsorbents which can be easily available, economical and high potential & higher effectiveness are still needed to evaluate their significance in dye adsorption. This led to a search for cheaper substitutes like several agro-industrial residue/wastes which shows adsorption of dyes with varying success [18,19]. Therefore this study will investigate the effectiveness of groundnut shell powder as the new adsorbent in removing methylene blue *via* adsorption.

In the present work groundnut shell powder” was used to adsorb methylene blue dye from its modeled aqueous solution. The parameters affecting the adsorption process like contact time, pH, initial dye concentration, temperature, adsorbent particle size & adsorbent dosage were studied. The equilibrium data were tested using various isotherm models such as Freundlich, Langmuir & Temkin models. Further, pseudo-first order & pseudo-second-order kinetic models were tested for the best fit of experimental data. The important thermodynamic parameters like free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were estimated to predict the nature of the adsorption process.

Materials and Methods

Materials used in this study like methylene blue dye, sodium hydroxide, and hydrochloric acid were purchased from Ranbaxy laboratories India limited and used as received without any further purification. Groundnut shells used in the present study were collected from the local vendor near Andhra University, Visakhapatnam.

Experimental procedure

The groundnut shells were sun-dried for 10 days and then subjected to size reduction in biomass grinder. The obtained powder was screened for different particles sizes ranging from 0- 300 μ m and stored in an airtight container for further use as an adsorbent.

A stock solution of 1000 mg/L was prepared by dissolving 1 g of dye in 1000 ml of distilled water which is later diluted to the required concentration (20-100 mg/l). All the solutions are prepared using double distilled water. Solution pH was adjusted by adding HCl and NaOH, as required. In each experiment, accurately weighed amount of groundnut shell powder is added to 30 ml of dye solution

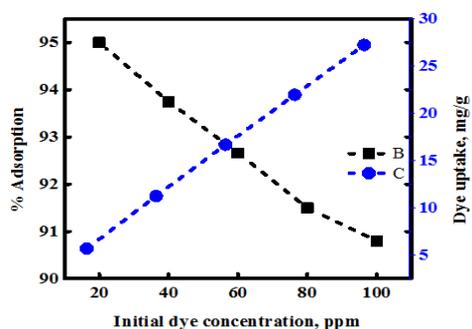


Figure 5: Effect of dye concentration on %Adsorption & dye uptake.

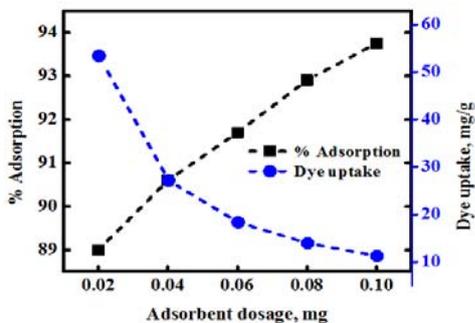


Figure 6: Effect of dosage on % Adsorption and dye uptake.

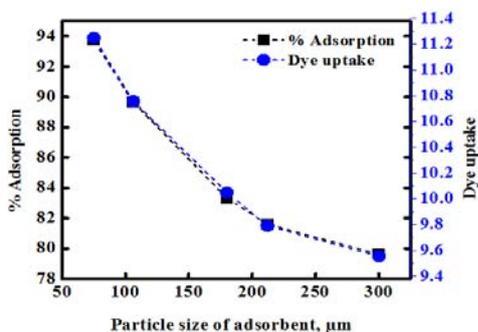


Figure 7: Effect of adsorbent particle size on % Adsorption and Dye uptake.

of desired concentration in a 250 ml conical flask and the mixture is agitated at 200 rpm in an orbital shaker with an incubator. Samples are withdrawn at regular intervals of time and then subjected to centrifugation. After centrifugation, the samples were analyzed for the residual concentrations of methylene blue.

The absorbance values of the solution at the characteristic wavelength ($\lambda_{max} = 665\text{nm}$) was used to determine the concentration of methylene blue. Digital photo colorimeter [NCM-508] was used to analyze the absorbance. Residual concentration of methylene blue in the aqueous solution was determined using the calibration curve plotted between different dye concentrations and their respective absorbance. Equation-1 & 2 are used to calculate the % adsorption & dye uptake respectively [20]. The ranges of adsorption variable studied are represented in (Table 1).

$$\% \text{ Adsorption} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

Table 1: Studied parameters and their ranges.

Parameters	Units	Range	
		From	To
Contact time	minutes	1	35
Solution pH	-	2	10
Initial dye concentration	mg/L	20	100
Particle size of adsorbent	μm	75	300
Adsorbent dosage	g/L	0.02	0.1
Temperature	K	303	333

Table 2: K_R Values at 303 K relating to the initial dye concentrations at pH 8.0.

C_0 , mg/L	K_R
20	0.3144
40	0.1862
60	0.1324
80	0.1027
100	0.083

$$\text{Dye Uptake, } q_t = (C_0 - C_t) \times V / W \quad (2)$$

Results and Discussion

The effect of various process parameters on the adsorption of methylene blue was first analyzed graphically and then attempted to theoretically justify the observations made from the graphical analysis.

Effect of contact time (t)

The time course profiles for the adsorption of methylene blue from its aqueous solution of concentrations ranging from 20 to 100 mg/L is shown in (Figure 1, Figure 2). It was observed that the % adsorption was increased with increase in contact time. The rate of adsorption was fast during the initial contact time of 5 minutes and in between 5 to 8 minutes the rate of adsorption was slow. After 8 minutes of contact time there was no change in % adsorption was observed. This was due to the approach of equilibrium in just 8 minutes of contact time. It is also noteworthy here that with increase in the contact time from 1 to 8 minutes the % Adsorption was increased in case of all the initial dye concentrations. For example, the % adsorption increased from 91 to 95% and dye uptake was increased from 5.46 to 5.7mg/g in case of 20 mg/l initial dye concentration. Therefore, the amount of dye removed and the amount of dye uptake for a particular initial dye concentration at the end of the equilibrium time (8 minutes) are denoted as equilibrium concentration, C_{eq} (mg/L) and equilibrium dye uptake, q_{eq} (mg/g) respectively. For further studies the contact time of 8 minutes was kept constant.

Effect of solution pH

Figure 3,4 shows the effect of initial pH on the % adsorption and dye uptake respectively. It was observed that with increase in pH from 2 to 8 the % adsorption was increased from 76 to 95 and with further increase in pH from 8 to 10, the % adsorption was reduced to 91.5 in the case of 20 mg/l initial dye concentration. So, pH of 8 is considered as optimum. Similarly, with increase in pH from 2 to 8, dye uptake was increased from 4.56 to 5.70 mg/g and with further increase in pH up to 10, dye uptake was reduced to 5.49 mg/g. This

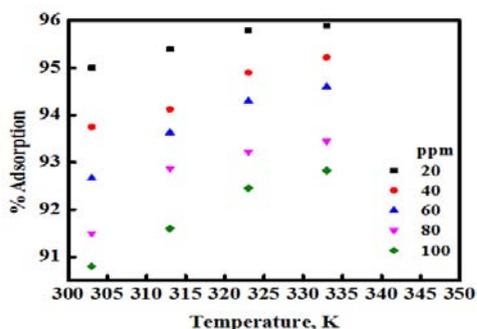


Figure 8: Effect of temperature on % Adsorption.

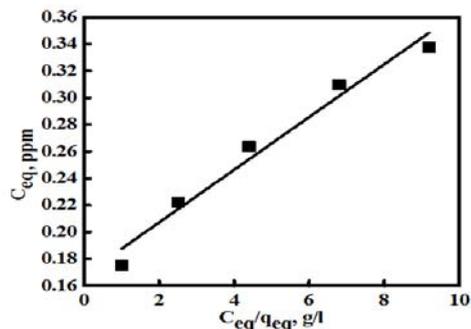


Figure 10(a): Langmuir isotherm.

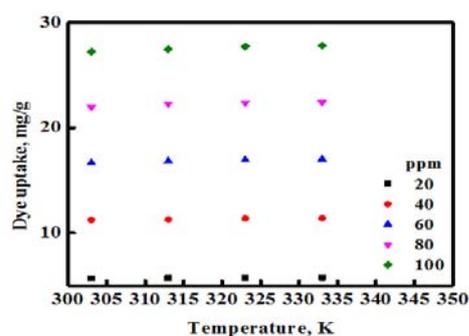


Figure 9: Effect of temperature on Dye uptake.

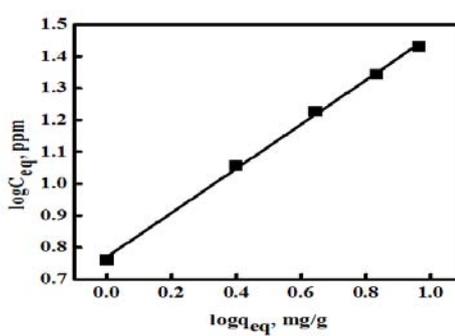


Figure 10(b): Freundlich isotherm.

behavior can be attributed to the fact that at lower pH values both the hydrogen ions as well as methylene blue ions compete together resulting in less adsorption. As the pH is increased the amount of OH⁻ ions will be increased which lead to the electrostatic attraction of the positive methylene blue ions towards the negative ions on the adsorbent, resulting in an increased % adsorption [21,22].

Effect of Initial dye concentration (Ci)

Effect of initial concentration of methylene blue on % adsorption and dye uptake at equilibrium contact time was presented in (Figure 5). It can be observed that with an increase in the initial concentration from 20 to 100 mg/L the equilibrium % adsorption was decreased from 95 to 90.8%. This is due to the fact that at lower initial concentrations, as the dye molecules concentration is low, the complete interaction between the dye molecules with the binding sites of the adsorbent is possible and hence, higher % adsorption is observed [23,24]. As the concentration is increased, the availability of the binding sites of the adsorbent with dye molecules decreases, which in turn, reduces the dye removal capacity of the adsorbent. Similarly, with increase in the initial concentration from 20 to 100 mg/L, the equilibrium dye uptake was increased from 5.7 to 27.24mg/g. similar trends were also reported in other literature [25].

Effect of adsorbent dosage (W)

It is known that increasing the amount of adsorbent favor the removal of dye from its aqueous solution up to a certain limit because of increase in the binding sites. After certain threshold limit of adsorbent dosage, the removal may be decreased or insignificant based on the type of interaction between adsorbate & adsorbent. The common goal of any process is to lower/optimize the requirement of

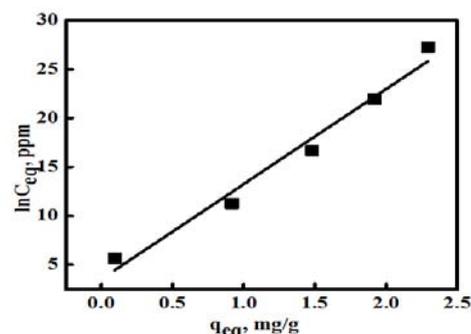


Figure 10(c): Temkin isotherm.

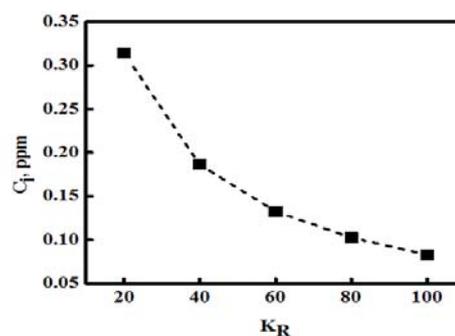


Figure 10(d): Effect of initial concentration on K_R .

raw materials. This can have a huge impact not only on the economics of the process but also minimizes the wastage. The adsorbent dosage was varied from 0.02 to 0.1 g. (highly coveted range) and its effect on

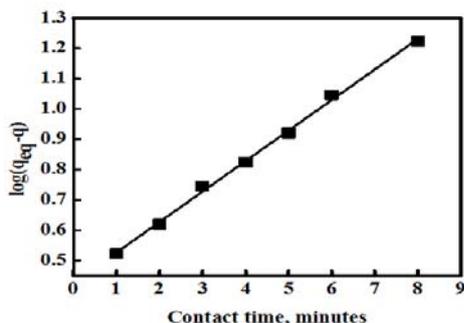


Figure 11(a): Pseudo first order kinetics.

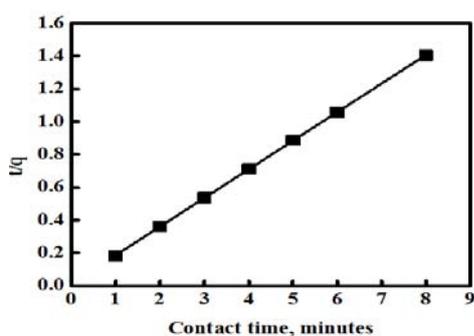


Figure 11(b): Pseudo-second order kinetics.

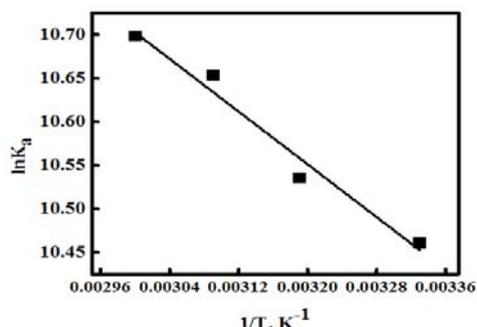


Figure 12: Estimation of thermodynamic parameters.

% adsorption and dye uptake (for $C_i=40$ mg/l) was shown in (Figure 6). It was observed that, with an increase in adsorbent dosage from 0.02 to 0.1 g, the % adsorption was increased from 89 to 93.75%. The increase in % adsorption can be attributed due to an increased surface area and a large number of available binding sites on the adsorbent [25]. Consecutively, dye uptake was decreased from 52.4 to 11.25 mg/g as the adsorbent dosage was increased from 0.02 to 0.1 g, respectively. The decrease in dye uptake was due to the splitting effect of flux (concentration gradient) between sorbate and sorbent and also with an increase in adsorbent concentration results in a decrease in the amount of dye binding onto unit weight of the adsorbent [26]. Similar trends were also reported in equilibrium studies of biosorption of MB using *Paspalum notatum* [27].

Effect of adsorbent particle size (d_p)

Reducing the particle size increases the surface area of the

Table 3: Comparison of constants estimated for different isotherm models.

Freundlich	Langmuir	Temkin
$1/m = 0.712$	$q_{max} = 52.63$	$b_T = 298.8341$
$K_f = 5.559$	$b = 0.10915$	$A_T = 2.1872$
$R^2 = 0.999$	$R^2 = 0.993$	$R^2 = 0.979$

Table 4: Kinetic parameters.

C_r , mg/L	20 ppm	
Parameter	Pseudo-first order	Pseudo-second order
Rate constant	0.227	1.76
q_{calc}	0.371	5.780
q_{expt}	5.70	5.70
R^2	0.996	1.000

Table 5: Thermodynamic parameters.

Sl. No.	Temperature, K	ΔG° , KJ/mol	ΔH° , KJ/mol	ΔS° , J/mol K
1	303	-26.311	6.988	109.9
2	313	-27.41		
3	323	-28.509		
4	333	-29.608		

adsorbent material and increase in surface area is the indicator of good adsorption capacity [26]. To gauge the true potential of the current adsorbent the range of the adsorbent particle sizes considered were: [0-75], [75-180], [180-212] and [212+] μm . Figure 7 shows the effect of adsorbent particle size on % adsorption & dye uptake (for $C_i=20$ mg/L). It was observed that as the adsorbent particle size was increased from [0-75] to [212+] μm , the % adsorption was decreased from 93.75 to 79.62 respectively. This is due to the decrease in the surface area with an increase in the particle size. A similar phenomenon was also observed in case of dye uptake and decreased the dye uptake from 11.23 to 9.53 with an increase in adsorbent particle size from [0-75] to [212+] μm .

Effect of Temperature (T)

Decrease/increase in temperature of the adsorption process will have a huge impact not only on the removal capacity of the adsorbent but also on the overall economics of the process [28]. Figures 8,9 shows the effect of temperature on % adsorption and dye uptake respectively. It was observed that with an increase in temperature from 303 to 333 K in all the case of initial dye concentrations the % adsorption was increased linearly. This indicates that the present adsorption is endothermic in nature. Further, at low initial concentrations, the % adsorption was improved compared to the values at higher concentrations. As the adsorption is endothermic, an increase in temperature results in an increase in adsorption equilibrium constant b , L/mg. This indicated a shift of the adsorption equilibrium to the forward direction. Increase in the temperature is followed by an increase in the diffusivity of dye ion and consequently increases the adsorption rate if diffusion is the rate controlling step [29]. Similarly, the amount of dye uptake was increased from 27.24 to 27.849 mg/g when $C_i=100$ mg/L in between 303-333 K. This increase in binding could be due to the increase in surface activity (interaction) and increased kinetic energy of the dye molecules arising due to the increase in temperature [30].

Adsorption isotherms

An adsorption isotherm is characterized by certain constants whose values express the surface properties & affinity of the adsorbent and can also be used to compare the adsorptive capacity of the adsorbent for various types of dyes [31]. Linearized equations of Langmuir, Freundlich, and Temkin isotherm models were used and their plots are shown in (Figure 10 a,b,c) respectively along with the effect of initial concentration on separation factor (in case of dimensionless Langmuir equation) as shown in (Figure 10d).

Langmuir isotherm: The Langmuir isotherm is the most widely used isotherm & adopted where the solute in liquid solutions binding to solid surfaces. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent [32]. Moreover, it is also based on the monolayer adsorption phenomenon and defines that the rate of adsorption is directly proportional to the concentration (driving force). The convenient & linearized form of Langmuir isotherm equation on taking account for equality in adsorption & desorption at equilibrium along with the fact that the amount of solute ion adsorbed is directly proportional to the fraction of the surface covered ($q_{eq} \propto f$) is given in (Equation 3). The obtained equilibrium data were fitted to the equation 3 and the plot of $[C_{eq}/q_{eq}]$ versus $[C_{eq}]$ is shown in (Figure 10a). The slope $1/q_{max} = 0.019$ and an intercept of $1/b \times q_{max} = 0.125$ obtained from this plot with $R^2 = 0.993$ was used to calculate $q_{max} = 1/0.019 = 52.63$ mg/g & $b = (1/52.63 \times 0.125) = 0.152$ L/mg.

The essential features of the Langmuir isotherm is that it can be expressed in terms of a dimensionless constant called a separation factor or equilibrium parameter K_R as given in equation 4 [33]. The equilibrium parameter is used to predict the shape of the isotherm accordingly: Unfavorable when $K_R > 1$; Linear when $K_R = 1$; Favorable when it is in the range $0 < K_R < 1$; Irreversible when $K_R = 0$. Values of K_R obtained in the present study are given in (Table 2). From (Figure 10d), it can be observed that the adsorption is favorable at low concentrations than at the higher concentration of the solutions.

$$C_{eq}/q_{eq} = 1/(b \times q_{max}) + 1/q_{max} \times C_{eq} \quad (3)$$

$$K_R = 1/(1 + bC_i) \quad (4)$$

Freundlich isotherm: It is defined that the ratio of C_{eq}/q_{eq} is a constant at any given temperature. This empirical isotherm can be used for non-ideal adsorption and is expressed as given in equation 5 [34]:

$$\log(q_{eq}) = (1/m) \times \log(C_{eq}) + \log(K_f) \quad (5)$$

Freundlich isotherm is derived assuming heterogeneity of the surface. K_f and m are indicators of adsorption capacity and adsorption intensity. The value of 'm' should lie in between 1-10 for favorable adsorption. The obtained equilibrium data were fitted to the equation 5 and the plot between $\log[q_{eq}]$ & $\log[C_{eq}]$ is shown in (Figure 10b). The slope ($1/m = 0.712$) & the intercept ($\log K_f = 0.7449$) obtained from this plot was used to obtain the values of adsorption intensity ($m = 1.4$) & adsorption coefficient ($K_f = 7.559$). From the value of adsorption intensity (1.4), it can be concluded that the adsorption is favorable and the Freundlich isotherm was observed to best represent the equilibrium data with a correlation coefficient of $R^2 = 0.99$.

Temkin isotherm: Temkin isotherm assumes that the fall in the

heat of sorption is linear unlike Freundlich equation [35]. The Temkin isotherm has generally been applied in the following form [36]:

$$q_{eq} = RT/B_T \ln[C_{eq}] + RT/B_T \ln[A_T] \quad (6)$$

The obtained equilibrium data were fitted to the Equation-6 and the linear plot with $R^2 = 0.979$ between q_{eq} & $\ln[C_{eq}]$ is shown in Figure-10 (c). The slope ($RT/B_T = 9.6722$) & the intercept ($RT/B_T \ln[A_T] = 3.5524$) obtained from this plot was used to estimate the values of Temkin isotherm constants $A_T = 1.44$ and $B_T = 260.45$.

Therefore the regression values and the correlation coefficients obtained from the Langmuir, Freundlich, and Temkin models are shown in (Table 3). Among the studied isotherm models Freundlich equation was observed to be more suitable followed by Langmuir and Temkin equations.

Adsorption kinetics

The prediction of adsorption rate offers the important information for designing batch adsorption systems and scaling a process to continuous units. Moreover, information on the kinetics of dye uptake is required for selecting the operating conditions for full-scale batch process [37]. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first order, and pseudo-second-order. These models compare the dye uptake values obtained through model & experiment for predicting the fit of experimental data [38]. The rate constants and the correlation coefficients obtained using for both pseudo-first and pseudo-second models are summarized in (Table 4).

Pseudo-first order model: The linearized form of pseudo-first order kinetics for the possible fitting of adsorption data is given by:

$$\log[q_{eq} - q] = [-K_1/2.303] \times t + \log[q_{eq}] \quad (7)$$

In order to obtain the rate constant, $\log[q_{eq} - q]$ versus t was plotted and shown in (Figure 11a). The q_{eq} value obtained from the intercept of this plot was 0.371 mg/g which is not equal to the experimentally observed value of $q_{eq} = 5.70$ mg/g suggesting the insufficiency of Pseudo-first-order model to fit the kinetic data, even though this plot has a high correlation coefficient ($R^2 = 0.996$).

Pseudo-second order model: After unsuccessful fit with pseudo-first order kinetics, the data was tested with a pseudo-second-order model [39]. This model is based on the assumption that the adsorption follows second order chemisorptions [40]. The pseudo-second-order model equation can be expressed as

$$[t/q] = 1/q_{eq} \times [t] + 1/(K_{II} q_{eq}^2) \quad (8)$$

The experimental data were fitted in the Equation-8 and the linear plot of $[t/q]$ versus $[t]$ was obtained as shown in (Figure 11b). The slope and intercept of this plot were used to obtain q_{eq} and K_{II} . It was observed that the calculated equilibrium dye uptake is nearly equal to the experimental q_{eq} , suggesting the suitability of pseudo-second-order model for the present case [41].

Thermodynamic studies

Thermodynamic parameters such as Enthalpy change (ΔH°), Free energy change (ΔG°) and Entropy change (ΔS°) can be estimated using the change in equilibrium constants at various temperatures. To estimate these parameters the van't Hoff equation as given in

Equation-9 was used:

$$\Delta G^\circ = -RT \ln K_a \quad (9)$$

The free energy change indicates the degree of the spontaneity of the adsorption process and the negative value of it reflects the more energetically favorable adsorption [42]. The equilibrium constant may be expressed in terms of enthalpy change of adsorption as a function of temperature as follows [43]:

$$\ln K_a = -(\Delta H^\circ)/RT + (\Delta S^\circ)/R \quad (10)$$

Equation-10 shows clearly that the adsorption process is composed of two contributions, enthalpy change, and entropic change. To estimate the thermodynamic parameters a straight line plot between $1/T$ & $\ln [K_a]$ as shown in (Figure 12) was drawn and the slopes & intercept of the plot was used to calculate the change in enthalpy and entropy of the system. The enthalpy changes (ΔH°) and entropy change (ΔS°) of adsorption were found to be 6.9887 KJ/mol and 109.91 J/mol.K, respectively. The positive value for ΔH° confirms that the adsorption of methylene blue onto the groundnut shell powder was endothermic in nature. The positive values of entropy change reflect the affinity of the groundnut shell powder for methylene blue and increased randomness at the solid-liquid interface with some structural changes in the adsorbent. Further, the values of ΔG° obtained from equation 9 were found to be negative as shown in (Table 5). Negative values of ΔG° show the feasibility and spontaneity of the adsorption process.

Conclusions

The present work helped in identifying a new source of the adsorbent for dye removal. The percentage adsorption of methylene blue was found to increase with contact time and observed a maximum removal of dye (~94%) within 8 minutes of contact time. At an optimum pH value of 8, the % adsorption was found to reach a plateau. The adsorption of methylene blue was found to increase with an increase in adsorbent dosage and consecutively the dye uptake was observed to decrease substantially. With the increase in the particle size of the adsorbent, the decrease in % adsorption was observed. The % adsorption was increased with increase in the temperature indicating the endothermic nature of the adsorption process. A better adjustment of the equilibrium data is observed with the Freundlich model followed by Langmuir and then Temkin. The kinetics of the adsorption was found to best fit with the pseudo-second-order kinetics. The values of free energy, enthalpy, and entropy changes indicate the adsorption was endothermic in nature and found to be spontaneous at high temperatures. The results obtained in this study open the new perspective with relation to the utilization of groundnut shell powder and proposes an avenue to further explore the applicability of groundnut shell powder in the treatment of textile industry effluents.

References

- Sen S, Demirer GN. Anaerobic treatment of real textile wastewater with a fluidized bed reactor. *Water Res.* 2003; 37: 595-601.
- Aksu Z, Çagatay SS, Gönen F. Continuous fixed bed biosorption of reactive dyes by dried *Rhizopus arrhizus*: determination of column capacity. *J Hazard Mater.* 2007; 143: 362-371.
- Bandary B, Hussain Z, Kumar R. Effect of carbon and nitrogen sources on *Escherichia coli* bacteria in removing dyes. *Materials Today.* 2016; 3: 4023-4028.
- Fatima M, Farooq R, Lindström RW, Saeed M. A review on biocatalytic decomposition of azo dyes and electrons recovery. *Journal of Molecular Liquids.* 2017; 246: 275-281.
- Modi M, Sk LA, Hussain Z. *International Journal of Pharmaceutical, Chemical and Biological Sciences.* 2016; 3: 1224-1230.
- Balarak D, Jaafari J, Hassani G, Mahdavi Y, Tyagi I, Agarwal S, et al. The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies. *Colloids and Interface Science Communications.* 2015; 7: 16-19.
- Reddy PM, Verma P, Subrahmanyam CV. *Journal of the Taiwan Institute of Chemical Engineers.* 2015.
- Özer D, Dursun G, Özer A. Methylene blue adsorption from aqueous solution by dehydrated peanut hull. *J Hazard Mater.* 2007; 144: 171-179.
- Malik R, Ramteke DS, Wate SR. Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Manag.* 2007; 27: 1129-1138.
- Yildiz S. Kinetic and Isotherm Analysis of Cu(II) Adsorption onto Almond Shell (*Prunus Dulcis*). *Ecological Chemistry and Engineering S.* 2017; 24: 87-106.
- Kumar S, Gunasekar V, Ponnusami V. Removal of Methylene Blue from Aqueous Effluent Using Fixed Bed of Groundnut Shell Powder. *Journal of Chemistry.* 2013; 2013: 1-5.
- Sun L, Chen D, Wan S, Yu Z. Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids. *Bioresource Technology.* 2015; 198: 300-308.
- Pezoti O, Cazetta AL, Souza IP, Bedin KC, Martins AC, Silva TL, et al. Adsorption studies of methylene blue onto ZnCl₂-activated carbon produced from buri shells (*Mauritia flexuosa* L.). *Journal of Industrial and Engineering Chemistry.* 2014; 20: 4401-4407.
- Islam MA, Benhouria A, Asif M, Hameed BH. Methylene blue adsorption on factory-rejected tea activated carbon prepared by conjunction of hydrothermal carbonization and sodium hydroxide activation processes. *Journal of the Taiwan Institute of Chemical Engineers.* 2015; 52: 57-64.
- Chandra TS, Mudliar SN, Vidyashankar S, Mukherji S, Sarada R, Krishnamurthi K, et al. Defatted algal biomass as a non-conventional low-cost adsorbent: Surface characterization and methylene blue adsorption characteristics. *Bioresource Technology.* 2015; 184: 395-404.
- Reddy PM, Krushnamurthy K, Mahammadunnisa SK, Dayamani A, Subrahmanyam C. Preparation of activated carbons from bio-waste: effect of surface functional groups on methylene blue adsorption. *International Journal of Environmental Science and Technology.* 2015; 12: 1363-1372.
- Srivastava S, Agrawal SB, Mondal MK. A review on progress of heavy metal removal using adsorbents of microbial and plant origin. *Environmental Science and Pollution Research.* 2015; 22: 15386-15415.
- Rafatullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater.* 2010; 177: 70-80.
- Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res.* 2002; 36: 2824-2830.
- Vijayaraghavan K, Padmesh TV, Palanivelu K, Velan M. Biosorption of nickel(II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models. *Journal of Hazardous Materials.* 2006; 133: 304-308.
- Gupta S, Benjamin S. Use of barium chromate in photocatalytic degradation of eosin yellow. *Chemical Science Transactions.* 2015; 4: 851-857.
- Azouaou N, Belmedani M, Mokaddem H, Sadaoui Z. Adsorption of Lead from Aqueous Solution onto Untreated Orange Barks. *Chemical Engineering Transactions.* 2013; 32: 55-60.
- Balraj B, Hussain Z, King P. Experimental study on non sporulating

- Escherichia Coli* bacteria in removing methylene blue. International Journal of Pharma and Bio Sciences. 2016; 7: B629–B637.
24. Ghodbane H, Hamdaoui O. Decolorization of antraquinonic dye, C.I. Acid Blue 25, in aqueous solution by direct UV irradiation, UV/H₂O₂ and UV/Fe(II) processes. Chemical Engineering Journal. 2010; 160: 226-231.
25. Li Y, Du Q, Liu T, Sun J, Wang Y, Wu S, *et al.* Methylene blue adsorption on graphene oxide/calcium alginate composites. Carbohydrate Polymers. 2013; 95: 501-507.
26. Ertugay N, Malkoc E. Adsorption Isotherm, Kinetic, and Thermodynamic Studies for Methylene Blue from Aqueous Solution by Needles of *Pinus Sylvestris* L. Polish Journal of Environmental Studies. 2014; 23: 1995-2006.
27. Kumar KV, Porkodi K. Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*. J Hazard Mater. 2007; 146: 214-226.
28. Deniz F. Adsorption Properties of Low-Cost Biomaterial Derived from *Prunus amygdalus* L. for Dye Removal from Water. The Scientific World Journal. 2013.
29. Çiçek F, Özer D, Özer A, Özer A. Low cost removal of reactive dyes using wheat bran. Journal of Hazardous Materials. 2007; 146: 408-416.
30. Erden E, Kaymaz Y, Pazarlioglu NK. Biosorption kinetics of a direct azo dye Sirius Blue K-CFN by *Trametes versicolor*. Electronic Journal of Biotechnology. 2011; 14: 1-10.
31. Ushakumary ER, Madhu G. Removal of cadmium, chromium, copper, lead and zinc ions by *Alisma plantago aquatica*. Journal of Clean Energy Technologies. 2014; 2: 112-117.
32. Mahmoodi N, Abdi J, Bastani D. Direct dyes removal using modified magnetic ferrite nanoparticle. Journal of Environmental Health Science and Engineering. 2014; 12: 96.
33. Won SW, Kim HJ, Choi SH, Chung BW, Kim KJ, Yun YS. Performance, Kinetics and Equilibrium in Biosorption of Anionic Dye Reactive Black 5 by the Waste Biomass of *Corynebacterium glutamicum* as a Low-Cost Biosorbent. Chemical Engineering Journal. 2006; 121: 37-43.
34. Ho YS, Chiu WT, Wang CC. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. Bioresource Technology. 2005; 96: 1285-1291.
35. El-nafaty U, Sirajuddeen A, Muhammad I. Isotherm Studies on Oil Removal from Produced Water Using Mango Seed Kernel Powder as Sorbent Material. Chemical and Process Engineering Research. 2014; 23: 55-66.
36. Ho YS, Porter JF, McKay G. Equilibrium Isotherm Studies for the Sorption of Divalent Metal Ions onto Peat: Copper, Nickel and Lead Single Component Systems. Water Air and Soil Pollution. 2002; 141: 1-33.
37. Hachi M, Chergui A, Selatnia A, Cabana H. Valorization of the Spent Biomass of *Pleurotus mutilus* Immobilized as Calcium Alginate Biobeads for Methylene Blue Biosorption. Environmental Processes. 2016; 3: 413-430.
38. Kumar YP, King P, Prasad VS. Adsorption of zinc from aqueous solution using marine green algae-*Ulva fasciata* sp. A Chemical Engineering Journal. 2007; 129: 161-166.
39. Kumar KV, Sivanesan S. Pseudo second order kinetic models for safranin onto rice husk: Comparison of linear and non-linear regression analysis. Process Biochemistry. 2006; 41: 1198-1202.
40. Venkatesan G, Rajagopalan V. Adsorption kinetic models for the removal of Cu(II) from aqueous solution by clay liners in landfills. International Journal of Environmental Science and Technology. 2016; 13: 1123-1130.
41. Ghasemi N, Ghasemi M, Khosravi-fard Y. The Sorption of Ni(II) by Grape Shell Ash from Aqueous Solution: Kinetic and Thermodynamic Studies. International Journal of Material Science. 2013; 2013: 1-6.
42. Bueno BY, Torem ML, De Carvalho RJ, Pino GA, De Mesquita LM. Fundamental aspects of biosorption of lead (II) ions onto a *Rhodococcus opacus* strain for environmental applications. Minerals Engineering. 2011; 24: 1619-1624.
43. Uslu G, Tanyol M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature. Journal of Hazardous Materials. 2006; 135: 87-93.