Removal of Binary Mixture of Textile Dyes on Prosopis Juliflora Pods – Equilibrium, Kinetics and Thermodynamics studies

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ABSTRACT

Prosopis juliflora pods is a low cost material obtained from semi-arid region, was evaluated as adsorbent for the removal of binary textile dye mixture (Gold HE-R and Green HE-4BD). The effect of pH, concentration of dyes, adsorbent dose and contact time were obtained in batch adsorption technique. The results were analyzed by isotherm models (Freundlich, Langmuir, Redlich-Peterson and Tempkin). The results were in good agreement with Langmuir model and the Redlich-Peterson isotherm models. Langmuir monolayer adsorption quantity was found to be, 50.0 mg g^{-1} and 62.5 mg g^{-1} for Gold HE-R and Green HE-4BD, respectively. Pseudo-first-order, pseudo-second-order, intra particle diffusion and Tempkin kinetic models were used to fit the experimental data, it was well fitted into pseudo second order kinetics. Thermodynamic parameters such ΔH^o, ΔS^o and ΔG^o were calculated, which shows the adsorption process was exothermic, decreasing randomness of solute and negative free energy reveals the feasibility of the reaction. Energy of activation also predicted using Arrhenius equation, which was -16.569 and -20.710 kJ mol^{-1} for GHER and GHE4BD, respectively. FT-IR and SEM analysis were also indicates the adsorption pattern effectively.

INTRODUCTION

Water is essential in an ecosystem, but it has been polluted through rapid industrialization, which cannot be avoidable, due to increasing needs of human population and their consumption, as well as waste generation. Upon several kinds of water pollution, the color in water is not desirable on any means. Especially effluent from the dye manufacturing industry, textile industry, pulp industry and paper industry are highly colored [1]. During the dyeing operation a significant amount of dyes remain unfixed on the fabric and they are directly discharged into the water bodies in South Asian countries [2]. The dye effluents are considered to be highly toxic to the aquatic species and it disturbs the natural equilibrium by reducing photosynthetic activity [3]. Therefore, the treatment of colored effluent from the dyeing industries is necessary. Many chemical and physical methods have been applied to color removal process, among which adsorption is being a successful method for their simplicity and economic aspects.

Activated carbon is being the best adsorbent, but it is costly. Along with this, many other adsorbents were tested for color removal from the water such as, bagasse [4-6], corn stalk [7], peanut hulls [8], natural coagulant [9], palm fruit bunch [10], rattan sawdust [11], orange peel carbon [12], agricultural waste [13, 14] and acid modified clay [15]. In recent years, the interest of research is towards the production of low cost adsorbent. Consequently, a number of low cost and easily available materials, such as biomass, are being studied for the removal of different dyes and heavy metals [16] from aqueous solution at different operating conditions [17]. Also, the complexity increases as competitive adsorption between the dyes on adsorbent, if the dye is binary [18, 19], ternary mixtures. Prosopis juliflora pod (Figure 1) is a fruit of a waste shrub Prosopis juliflora (Velikathan in Tamil). It is widely available in waste land, arid and semi-arid region, as it grows faster even in a dry conditions in semi-arid region. It is used as Feed for live-stocks in rural areas. In this paper we tried to find out the potential of Prosopis juliflora pods, as adsorbent for effective removal of a binary mixture of reactive anionic dyes (Gold HE-R and Green HE-4BD). The adsorption

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studies were carried out using effect of pH, adsorbent dose, initial dye concentration and contact time. The experimental results were fitted and analyzed by four kinetic models, four equilibrium models and by thermodynamic studies.

Figure 1 Sturcture of Prosopis juliflora pods

MATERIAL AND METHODS

Preparation of Binary dye
The reactive dyes Gold HE-R (GHER) [C.I. Reactive Yellow-84, λmax : 405 nm] and Reactive Green HE-4BD (GHE4BD) [C.I. Reactive Green-19, λmax : 630 nm] are received from cotton dyeing industry, Thiruvallur District, Tamil Nadu. It was used as received without further purification. A stock solution of GHER and GHE4BD each 500 mgL^{-1} was prepared then suitably diluted and mixed to the required initial concentration.

Adsorbent preparation
The *Prosopis juliflora pods* (PJP) was collected from waste land in Thiruvallur District, Tamil Nadu. It was washed several times with distilled water and left to dry in sun light, then it was cut into smaller pieces and soaked into Sodium hydroxide solution [20] for five days to remove coloring matters in PJP (which may interact with dye solution under study) and then washed with distilled water, dried in sun light and then in hot air oven at 104±2 ºC. A portion of a dried sample was taken in a china dish, covered with thin aluminium sheet and carbonized. The carbonization was carried out in muffle furnace for one hour at 200 ºC. It was ground well and the portion between 0 and 100 µm sieves was stored in desiccators and used for the adsorption experiments.

Method of Equilibrium Studies
The 50 mL of dye mixtures of concentration between 25–150 mgL^{-1} was shaken at the constant agitation speed (150 rpm) in orbital incubator shaker (Remi Elektrotechnik Limited) with adsorbent dosage between 0.4–2 g L^{-1} were carried out at the temperature (30 ± 1ºC) using batch adsorption technique for a specific period of contact time (300 min) in a orbital shaker, after noting down the initial pH of the solution. The supernatant

liquid was collected by filtering out the solid phase using 0.45µm filter paper and the residual concentration of dye present in supernatant was determined by UV spectrophotometer (Shanghai Mapada Instruments Co. Ltd., Model: UV 1100). The percentage removal of dye was calculated using the following relationship:

$$\% \ Removal \ of \ dye = \frac{C_i - C_e}{C_i} X \ 100 \qquad (1)$$

where, Ci and Ce are the initial and final (equilibrium) concentrations of dye (mg L^{-1}), respectively.

RESULTS AND DISCUSSION

Effect of pH on dye mixture
The pH effect for the adsorption of a dye mixture (10 mg L^{-1}) was studies between the pH of 1-6 on 0.4 g L^{-1} of adsorbent (Figure 2). The adsorption was higher (73.33% for GHER and 80% for GHE4BD) at lower pH and it decreases gradually to 0.1% for GHER and 13% for GHE4BD as the pH of the solution increases. As the dye mixture used were anionic in nature, it may adsorb on the adsorbent at acidic pH since the adsorbent surface was covered by cations (H$^+$) and at alkaline pH the reverse is possible; that is desorption as the amount of cations decreases.
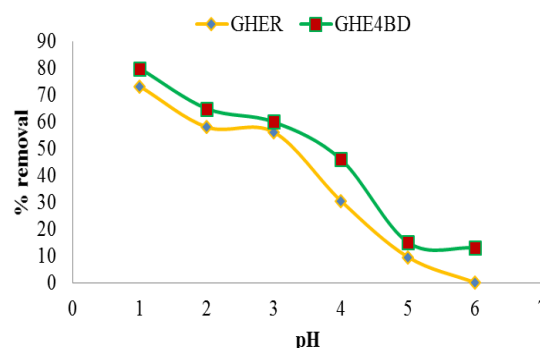

Figure 2. Effect of pH on Equilibrium uptake

Effect of adsorbent dose on binary dye solution
On varying the adsorbent dose at 0.4, 0.8, 1.2, 1.6 and 2 g L^{-1} for 50 mg L^{-1} of dye mixture, the removal of dyes increased to 47.15, 58.54, 68.11, 79.95, 85.65% and 56.02, 71.20, 80.89, 90.05, 93.19% for GHER and GHE4BD, respectively. As the amount of adsorbent increases, the fraction of available area for dye adsorption increases and hence more number of dye molecules freely adsorb on the surface of adsorbent.

Effect of initial dye concentration on PJP
The effect of initial concentration of dye mixture on adsorbent (1.6 g L^{-1}) in terms of quantity adsorbed was studied as shown in Figure 3. When the concentration of

dye mixture increases as 25, 50, 75, 100, 125, 150 mg L^{-1}, the quantity of adsorption increases as 15.33, 24.98, 32.91, 37.17, 42.97, 47.31 mg g^{-1} and 15.38, 28.14, 39.05, 45.63, 52.37, 58.61 for GHER and GHE4BD, respectively. At low concentration, the number of available dye molecule are less; hence the fractional adsorption becomes independent of initial concentration whereas at high concentration the number of dye molecules are high for the fraction of available surface area and hence the adsorption of dye is dependent upon the initial dye concentration.
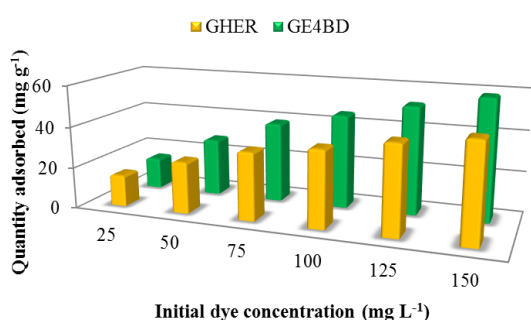

Figure 3. Effect of dye concentration on PJP, between 25-150 mgg-1

Effect of contact time

The effect of contact time on the percentage removal of dye mixture was investigated at 50 mg L^{-1} of initial dye concentration. The initial adsorption is so fast, but it becomes slow when it reached equilibrium. At equilibrium, the pattern of graphs were almost the same for GHER and GHE4BD; the percentage of dye removal were 79.95 and 90.32, respectively. The plots reveal that 50% adsorption takes place within 10 minute and it reaches the maximum percent removal of the dye after about 1 h of mixing. The rate of removal is high in the beginning due to large surface area available for the dyes. Later on the rate of dye uptake is limited, controlled and adsorbed to the interior from the exterior sites of the adsorbent particles (Figure 4).
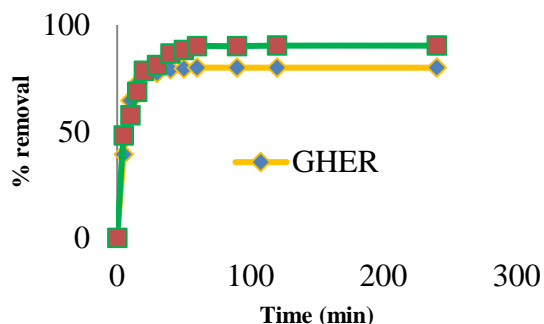

Figure 4. Effect of contact time on equilibrium uptake of 50 mg L^{-1}

Isotherm Models
Freundlich Isotherm model

In order to examine the relationship between the quantity of dye adsorbed (Q_e) and equilibrium dye concentration (C_e), the equilibrium data were analyzed by Freundlich and Langmuir isotherms. The Freundlich adsorption model is the earliest known equation describing the adsorption process [21]. The amount of solute adsorbed, Q_e is related to the equilibrium concentration, C_e of solute in solution by following linear equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

where, K_F is a constant for the system, related to the bonding energy. The fraction value for 1/n is obtained for the adsorption of both GHER and GHE4BD as a mixture, indicates a normal Frendlich isotherm. The values of KF and 1/n are determined from the intercept and slope of the linear regressions of log Q_e vs. log C_e (Figure 5).where, K_F is a constant for the system, related to the bonding energy. The fraction value for 1/n is obtained for the adsorption of both GHER and GHE4BD as a mixture, indicates a normal Frendlich isotherm. The values of KF and 1/n are determined from the intercept and slope of the linear regressions of log Q_e vs. log C_e (Figure 5).

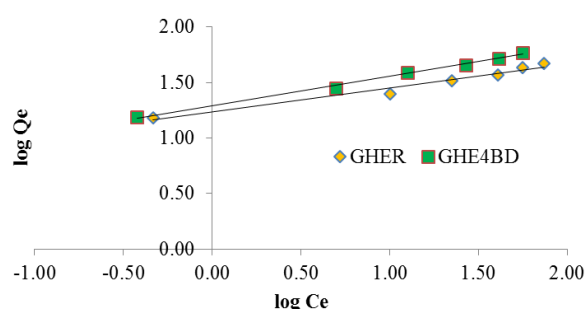**Figure 5.** Freundlich Isotherm model for dye mixture on PJP

Langmuir isotherm model

A monolayer adsorption is well explained by Langmuir [22] theory, can be represented by the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{3}$$

where, Q_m is the monolayer adsorption capacity (mg g^{-1}) and K_L is related to energy of adsorption in L mg^{-1}. Figure 6 shows the linear plot of C_e/Q_e vs. C_e for dye mixture on the adsorbents, the Q_m and K_L values were determined from intercept and slopes of the linear plots (Table 1). The separation factor or equilibrium parameter, R_L, is given by the following equation [23]:

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

where, C_i is the initial dye concentration (mg L^{-1}). The adsorption process is a function of R_L, may be described as $R_L>1$; unfavorable, $0< R_L<1$; favorable, $R_L=1$; linear and $R_L=0$ for irreversibility. The favorability of adsorption process between 25-150 mg L^{-1} is assumed from the calculated R_L values, which lie in between 0 to 1 (Table 2).
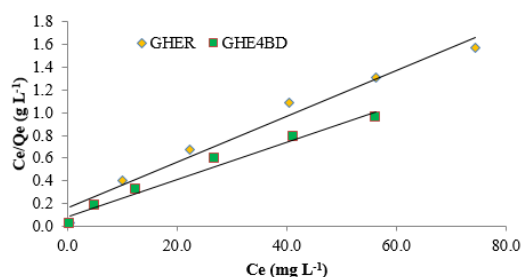

Figure 6. Langmuir isotherm model for dye mixture on PJP

Table 2. R_L values between 25-150mg L^{-1}

Concentration (mg/L)	R_L Values	
	GHER	GHE4BD
25	0.040	0.176955
50	0.020	0.097065
75	0.013	0.066874
100	0.010	0.051008
125	0.008	0.041227
150	0.007	0.034594

Tempkin and Redlich-Peterson isotherm models
Tempkin isotherm contains a factor that explicitly takes place into account adsorbent-adsorbate interactions [24]. Tempkin isotherm has generally been used in the linearized and rearranged form as following:

$$Q_e = \beta \, lnK_T + \beta \ln C_e \tag{5}$$

where, K_T is an equilibrium constant of binding corresponding to the maximum energy of binding (mg L^{-1}) and the β is related to the heat of adsorption. A plot of Q_e vs ln C_e, enables the determination of the isotherm constants K_T and β (Table 1).

Redlich-Peterson(R-P) isotherm can be applied either in homogeneous or heterogeneous system due to the high versatility of the equation [25]. The linearized equation is as follows:

$$log \frac{C_e}{Q_e} = log \, K_R + \beta \, log \, C_e \tag{6}$$

where, β is the desorption constant and K_R is R-P isotherm constant (g L^{-1}). The isotherm constants β, KR and the correlation coefficients, R^2 for the R-P isotherm were found by plot between log (C_e/Q_e) vs log C_e (Figure 7), are listed in Table 1.
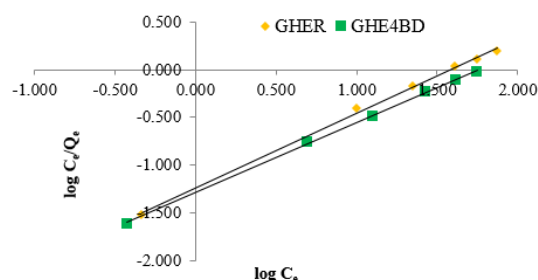

Figure 7. Redlich-Peterson isotherm model for dyes on adsorbent

The obtained results of each model, for the adsorption of GHER and GHE4BD on PJP were presented in Table 1. The value of correlation coefficient, R^2, was used to compare the four isotherm models. As can be seen from the Table 1, R-P model showed a higher correlation coefficient. Therefore the adsorption process follows Freundlich at high concentration and Langmuir at low concentration of dye. Similar results were reported for the adsorption of Orange-G and Methyl Violet dye onto bagasse fly ash [26].

Kinetics of adsorption process
Lagergren pseudo first order kinetic model
The pseudo-first-order kinetic model of Lagergren [27] is more suitable for lower concentration of solute and its linear form is:

$$log(Q_e - Q_t) = log \, Q_e - \frac{k_1}{2.303} \, t \tag{7}$$

where, Q_t (mg g^{-1}) is the amount of adsorbate adsorbed at time t (min); k_1 (min^{-1}) is the rate constant of pseudo-first-order model. The values of k_1 and Q_e for the adsorption of dye onto adsorbent were determined from the plot of log (Q_e-Q_t) vs. time (Table 1).

Pseudo second order kinetic model
Adsorption kinetics was explained by the pseudo-second-order model expressed as following linear equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{8}$$

where, k_2 is the second order rate constant (g mg^{-1} min^{-1}). The values of k_2 for dye mixture on adsorbent were calculated from the slopes of the respective linear plots of t/Q_t vs. t (Figure 8). As can be seen from the Table 1, the values of R^2 are closer to unity for pseudo second order model. Thus, adsorption of GHER and GHE4BD dyes onto adsorbent obey the pseudo second order model [28]. Furthermore, values of Q_e (cal) calculated from pseudo second order model were good agreement with experimental values, Q_e (exp) than those calculated form pseudo first order and Elovich model. Similar results

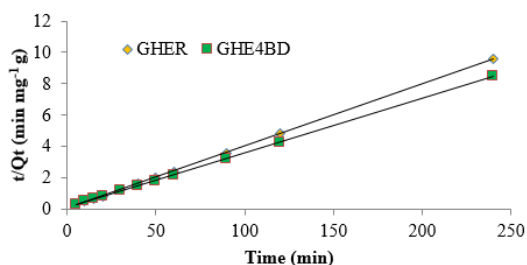were found for the adsorption of MB and GV onto sepiolit [29] and MB onto hazelnut shell [30].

Figure 8. Second order kinetic model for 50 mgL^{-1} dyes on 1.6 g L^{-1} PJP

Elovich and Intra particle diffusion models

Elovich model suggest that the chemisorptions, i.e. a chemical reaction, is probably the mechanism that controls the rate of adsorption. This model can be applied with success in liquid solution and the linear form of the Elovich equation is:

$$Q_t = \frac{1}{\beta}\ln\alpha\beta + \frac{1}{\beta}\ln t \qquad (9)$$

where, α (mg g-1) is the initial sorption rate and β (g mg-1) is the desorption constant. The values of α and β can be calculated from the slope and intercept of the plot of Q_t versus $\ln t$. As can be seen from Table 3, the higher value of 'α' and 'β' for GHER, indicates the higher initial sorption rate, as well as desorption rate, may due to physical adsorption. But, the value of 'α' and 'β' were lower for GHE4BD compared to the GHER, indicates the lower initial sorption rate as well as the desorption rate, which may due to chemical adsorption.

Table 3. Thermodynamic parameters

Dye	ΔH° (kJmol^{-1})	ΔS° (kJmol^{-1})	ΔG°(kJ/mol)				
			298K	303K	308K	313K	318K
GHER	-80.52	252.99	5.128	3.863	2.598	1.333	0.686
GHE4BD	-89.84	277.02	7.288	5.903	4.518	3.133	1.747

The adsorption mechanism for dye removal by adsorption using an adsorbent can be best explained by intra-particle diffusion model. Weber and Morris [31] proposed an equation for intra-particle diffusion of adsorbate on adsorbent is as follows:

$$Q_t = k_{id}\, t^{1/2} + C_i \qquad (10)$$

where, Q_t (mg g^{-1}) is the quantity of dye adsorbed at time t and k_{id} (mg g^{-1}min-1/2) is intra-particle diffusion constant (Table 1). A plot of Q_t versus $t_{1/2}$ gives k_{id}, the slop and C_i, the intercept (Figure 9). Value of C_i gives an idea of the thickness of boundary layer. The C_i value for GHER and GHE4BD is almost equal, indicates the thickness is same, but k_{id} value was higher for GHE4BD

than for GHER, which reveals that the diffusion is higher for GHE4BD than GHER. Also it is evident from the figure, there are two straight lines are obtained, in which first line for surface adsorption and the second line is for the adsorption due to diffusion into the pores.
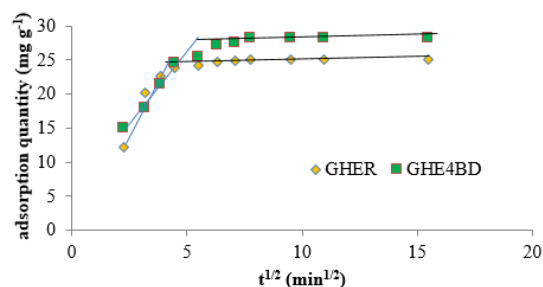

Figure 9. Intra particle diffusion model for mixture of dyes on adsorbent

Effect of Temperature for the Binary mixtures on PJP

The effect of temperature for the adsorption of GHER and GHE4BD as a mixture is studied at 298, 303, 308, 313, 318 and 323K with the help of the following relations:

$$\ln\left(\frac{Q_e m}{C_e}\right) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (11)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (12)$$

where, m is the dose of adsorbent in mg L^{-1}, Ce is the equilibrium concentration in mg L^{-1} and Qe is the amount of adsorption in mg g^{-1} at equilibrium. R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K). Thermodynamic parameters such as ΔH°, ΔS° and ΔG° are change in enthalpy (kJ mol^{-1}), change in entropy (J mol^{-1} K^{-1}) and change in free energy (kJ mol^{-1}) respectively, were determined from the slope (-ΔH°/R) and intercept (ΔS°/R) of the plots of ln (Q_{em}/C_e) vs 1/T (Table 3).

As can be seen from the table, the enthalpy change (ΔH°) and the entropy change (ΔS°) are negative in value for both GHER and GHE4BD indicates the adsorption process is exothermic in nature and the randomness of solute molecule decreases during adsorption. Also, the free energy change is highly negative at lower temperature indicates the feasibility of adsorption, but at higher temperature, the feasibility of the adsorption process becomes unfavorable as the free energy change becomes positive and lower negative for GHER and GHE4BD respectively. The quantity of adsorption decreases from 28.26 to 13.45 mg g^{-1} and 30.02 to 17.75 mg g^{-1} for GHER and GHE4BD respectively, as the temperature increases from 298 to 323K, (Figure 10). This may be explained, as the temperature increases the motion of dye molecules increases and may not be available near the adsorbent; hence adsorption decreases

[32]. Therefore, all the thermodynamic factors such as change in enthalpy ($\Delta H\circ$), change in entropy ($\Delta S\circ$) and change in free energy ($\Delta G\circ$) favors the adsorption of dyes on the adsorbent.
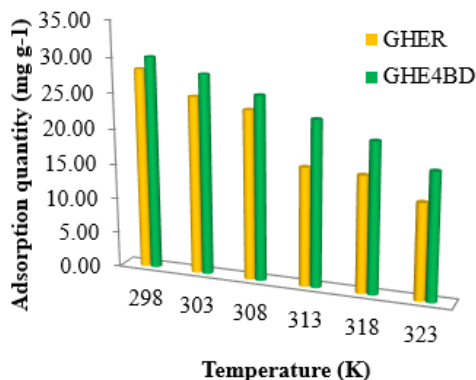

Figure 10. Effect of temperature of dye mixture on equilibrium uptake

The idea of energy barrier is the key strength to describe the reaction nature, which can be determined by linear form of Arrhenius equation. It relates the rate of the reaction and temperature, given as [33]:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{13}$$

where, k, is the rate constant (form pseudo second order kinetics); Ea, is activation energy (kJ mol^{-1}); A, is the Arrhenius factor (g mg^{-1} min^{-1}); R, is the gas constant and T is the temperature (K). The activation energy of the adsorption process was estimated from the slop of the plot ln k vs 1/T . It was found to be -16.569 and -20.710 kJ mol^{-1} for GHER and GHE4BD respectively. Since the activation energy barrier was negative in quantity, the adsorption is favorable.

Therefore, all the results such as, exothermic nature, decreasing randomness of solute, negative free energy of reaction and negative activation energy favors the adsorption process.

FT-IR and SEM micrography
The various functional groups present on the PJP before adsorption and after adsorption of dye mixture were studied by Fourier Transform Infrared Spectroscopy within 400-4000 cm^{-1} range, which are given in Table 4. The peak at 1704 cm^{-1} is characteristic for the presence of C=O (str), which is lowered to 1680 cm^{-1} after the adsorption of dyes, because the dye molecule may have a conjugation with C=O bond. The finger print region of PJP have the peaks at 769 cm^{-1} for C-Cl (str), 1239 cm^{-1} for C-O and or C-N (str), 1432 cm^{-1} for C-H (bend) were shifted to 738 cm-1, 1218 cm-1, 1420 cm^{-1} respectively after dye adsorption. The presence of primary amine were identified before adsorption at 3377 cm^{-1} for N-H (str), 1599 cm^{-1} for N-H (bend) were shifted to 3264 cm^{-1}, 1602

cm^{-1}, respectively after adsorption of dyes (Figure 11). The Scanning Electron Micrography was used to analyze the surface texture of PJP. Figure 12a indicates the presence of porous texture on PJP and 12b shows the different surface texture after adsorption of dye mixture on PJP.
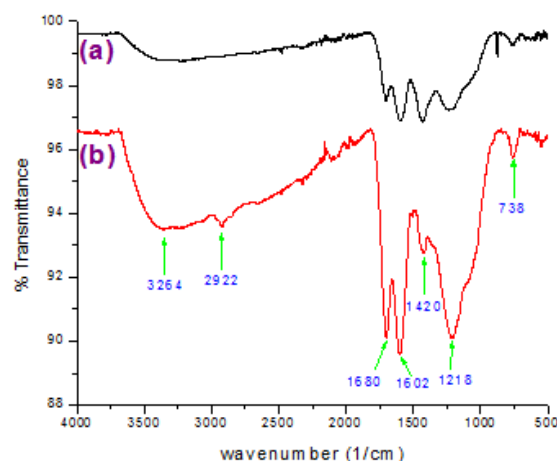

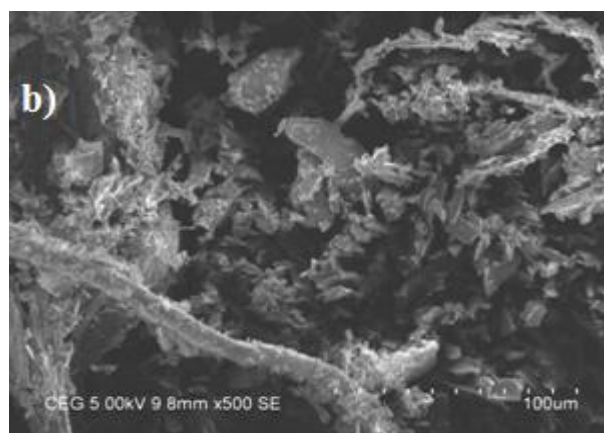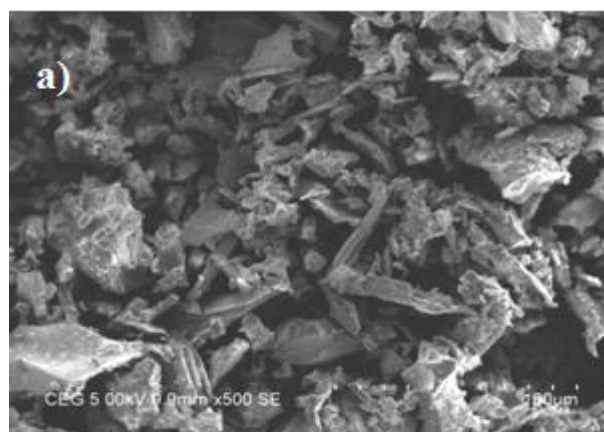**Figure 11.** FT-IR spectra for a) PJP and b) dye loaded PJP

Figure 12. SEM micrography of a) PJP and b) dye adsorbed PJP

Table 4. FT-IR data (cm^{-1})

Functional groups	before	after
N-H (str)	3377	3264
C-H (str)	-	2922
C=O (str)	1704	1680
N-H (bend)	1599	1602
C-H (bend)	1432	1420
C-O, N-H (str)	1239	1218
C-Cl (str)	769	738

CONCLUSION

The potential of Prosopis juliflora pods have been tested for the removal of GHER and GHE4BD as a binary mixture in aqueous solution. The Langmuir monolayer adsorption capacity was found to be 50.00 and 62.50 mg g^{-1} for GHER and GHE4BD, respectively. Adsorption process follows Freundlich at high concentration and Langmuir at low concentration of dye according to Redlich-Peterson isotherm. The pseudo second order kinetics was good agreement with dye mixtures. All thermodynamic factors: change in enthalpy (ΔH^o), change in free energy (ΔG^o), change in entropy (ΔS^o) and activation energy were negative in magnitude, favors the adsorption process at low temperature. As the Prosopis juliflora pods, is easily available low cost adsorbent, which may be useful for local dyeing industries.

Acknowledgements

REFERENCES

1. Hameed, K.S., P. Muthirulan and M.M. Sundaram, 2013. Adsorption of chromotrope dye onto activated carbons obtained from the seeds of various plants: equilibrium and kinetics studies. Arabian Journal of Chemistry.
2. Wasti, A. and M.A. Awan, 2016. Adsorption of textile dye onto modified immobilized activated alumina. Journal of the Association of Arab Universities for Basic and Applied Sciences, 20: 26-31.
3. Malik, A. and U. Taneja, 1994. Utilizing flyash for color removal of dye effluents. American Dyestuff Reporter, 83(10): 20-27.
4. Tsai, W., C. Chang, M. Lin, S. Chien, H. Sun and M. Hsieh, 2001. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl 2 activation. Chemosphere, 45(1): 51-58.
5. Amin, N.K., 2008. Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. Desalination, 223(1-3): 152-161.
6. Noreen, S. and H.N. Bhatti, 2014. Fitting of equilibrium and kinetic data for the removal of Novacron Orange P-2R by sugarcane bagasse. Journal of Industrial and Engineering Chemistry, 20(4): 1684-1692.
7. Fathi, M., A. Asfaram and A. Farhangi, 2015. Removal of Direct Red 23 from aqueous solution using corn stalks: isotherms, kinetics and thermodynamic studies. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 135: 364-372.
8. Nawaz, S., H.N. Bhatti, T.H. Bokhari and S. Sadaf, 2014. Removal of Novacron Golden Yellow dye from aqueous solutions by low-cost agricultural waste: Batch and fixed bed study. Chemistry and Ecology, 30(1): 52-65.
9. Muthuraman, G. and S. Sasikala, 2014. Removal of turbidity from drinking water using natural coagulants. Journal of Industrial and Engineering Chemistry, 20(4): 1727-1731.
10. Nassar, M.M., 1999. Intraparticle diffusion of basic red and basic yellow dyes on palm fruit bunch. Water Science and Technology, 40(7): 133-139.
11. Hameed, B., A. Ahmad and K. Latiff, 2007. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes and Pigments, 75(1): 143-149.
12. Khaled, A., A. El Nemr, A. El-Sikaily and O. Abdelwahab, 2009. Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon. Desalination, 238(1-3): 210-232.
13. Doğan, M., H. Abak and M. Alkan, 2009. Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. Journal of Hazardous Materials, 164(1): 172-181.
14. Ahmad, M.A., N.A.A. Puad and O.S. Bello, 2014. Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. Water Resources and industry, 6: 18-35.
15. Kalipci, E., S. Sahinkaya, M. Dortkol and S. Aras, 2016. Decolorization of Basic Textile Dyes using a Novel Adsorbent Modification Method: Ultrasonic-Acid Modification. International Journal of Environmental Research, 10(1): 31-40.
16. Sasikala S, Muthuraman.G., 2016. Removal of Heavy Metals from Wastewater Using Tribulus terrestris Herbal Plants Powder. Iranica Journal of Energy and Environment 7(1): 39-47.
17. Zhang, F., A. Yediler, X. Liang and A. Kettrup, 2004. Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed CI Reactive Red 120. Dyes and pigments, 60(1): 1-7.
18. Al-Asheh, S., F. Banat, R. Al-Omari and Z. Duvnjak, 2000. Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. Chemosphere, 41(5): 659-665.
19. ŞAHİN, E., 2006. Interpretation of sorption kinetics for mixtures of reactive dyes on wool. Turkish Journal of Chemistry, 29(6): 617-625.
20. Raman, M.K., Muthuraman G, Application of Hyparrhenia hirta - A novel biosorbent for the effective removal of textile dyes. International Journal of ChemTech Research, 7(7): 2860-2866.
21. Freundlich, H., 1906. Over the adsorption in solution. J. Phys. Chem, 57(385): e470.
22. Lanowix, I., 1918. The adsorption of gases on plane surface of glass, mica and platinum. J. Am. chem. soc, 30: 1361.
23. Weber, T.W. and R.K. Chakravorti, 1974. Pore and solid diffusion models for fixed-bed adsorbers. AIChE Journal, 20(2): 228-238.
24. Temkin, M. and V. Pyzhev, 1940. Kinetics of ammonia synthesis on promoted iron catalysts. Acta physiochim. URSS, 12(3): 217-222.
25. Redlich, O. and D.L. Peterson, 1959. A useful adsorption isotherm. Journal of Physical Chemistry, 63(6): 1024-1024.
26. Mall, I.D., V.C. Srivastava and N.K. Agarwal, 2006. Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses. Dyes and pigments, 69(3): 210-223.
27. Largergren, S., 1898. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar, 24(4): 1-39.

28. Ho, Y.-S. and G. McKay, 1999. Pseudo-second order model for sorption processes. Process biochemistry, 34(5): 451-465.
29. Doğan, M., Y. Özdemir and M. Alkan, 2007. Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. Dyes and Pigments, 75(3): 701-713.
30. Sánchez-Martín, J., M. González-Velasco, J. Beltrán-Heredia, J. Gragera-Carvajal and J. Salguero-Fernández, 2010. Novel tannin-based adsorbent in removing cationic dye (Methylene Blue) from aqueous solution. Kinetics and equilibrium studies. Journal of hazardous materials, 174(1): 9-16.
31. Weber, W.J. and J.C. Morris, 1963. Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division, 89(2): 31-60.
32. Raman, M. K. and G. Muthuraman, Decolorization of Red HE-7B by Hyparrhenia hirta-A better carbonization method.
33. Rajamohan, N., M. Rajasimman, R. Rajeshkannan and V. Saravanan, 2014. Equilibrium, kinetic and thermodynamic studies on the removal of Aluminum by modified Eucalyptus camaldulensis barks. Alexandria Engineering Journal, 53(2): 409-415.