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Adsorption and Recovery of Methylene Blue from Aqueous Solution by NaOH-Treated of Prina

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In the present work, we have investigated the sorption efficiency of base activated prina towards methylene blue removal from their respective aqueous solutions. Base activated prina material was prepared by treatment of olive stones and aqueous solution at room temperature. The resulting material has been thoroughly characterized by FTIR. The sorption study of 0.1 M NaOH base activated prina at the solid-liquid interface was investigated using adsorbent dosage, initial pH, initial dye concentration, temperature and ionic strength. The application of the Langmuir and Freundlich models showed a better fitting of experimental data to the first model. Base activated prina exhibited the highest methylene blue uptake of 12.90 mg/g at natural pH. The methylene blue adsorbed could be desorbed by ultrapure water, ethyl alcohol and hydrochloric acid. In the kinetic of the adsorbent process, the adsorption data followed the second-order kinetic model better than first order kinetic model and particle diffusion models. In addition, the diffusion coefficient values was found in the range from 0.62×10^{-7}-31.79×10^{-7} cm^2/s. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption. The positive value of the enthalpy change (68.122 kJ mol^{-1}) indicated that the adsorption is endothermic process. The results indicate that base activated prina could be fruitfully employed as effective biomaterial and as low-cost sorbents for the removal of methylene blue from effluents.

Key Words: Methylene blue, Biosorbent, Kinetics, Thermodynamic parameters, Desorption.

INTRODUCTION

Dyeing industry wastewater is one of the major environmental problems. Colour is one of the characteristics of an effluent which is easily detected. Most of the dyes are stable to biological degradation. Colour affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action. Some of the dyes are carcinogenic and mutagenic[1]. Today, more than 10,000 chemically different dyes are being manufactured. The world dyestuff and dye intermediates production is estimated to be around 7×10^8 kg/annum[2]. Dyes are used in many industries such as food, paper, carpets, rubbers, plastics, cosmetics and textiles in order to colour their products. As a result, these industries generate a considerable amount of coloured wastewater[3]. Therefore, removal of dyes before disposal of wastewater is necessary. In general, there are five main methods used for the treatment of dye-containing effluent *i.e.*, adsorption, oxidation-ozonation, biological treatment, coagulation-flocculation and membrane processes[4]. Amongst the numerous techniques of dye removal, the adsorption process is one of the effective techniques that have been successfully employed for colour removal from wastewater. Almost all the work related to adsorption techniques for colour removal from industrial effluents was based on studies using activated carbon. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. There is growing interest in using low cost, commercially available materials for the adsorption of dyes. Various low-cost materials have been used for the removal of dyes. Such materials range from industrial waste to agricultural products[5].

This study investigated the possibility of base activated prina (BAP) as a biosorbent for the removal of methylene blue from an aqueous solution. Prina is a vegetable planted extensively in Mediterranean Countries. The system variables was studied include solution pH, base activated prina dose, salt concentration and the initial methylene blue concentration at different temperature. The kinetic models have been obtained using non-linear regressive analysis. The thermodynamic parameters, such as ΔG°, ΔH°, ΔS°, have been calculated.

EXPERIMENTAL

Adsorbent preparation: Prina were provided by Yesilyurt-Mugla. These materials were extracted with hexane into Soxhlet apparatus. In experimental studies, 200 g weight of dry and extract sample was washed many times with hot deionized water and then by deionized cooled water. This sample was dried at 105 ºC for 24 h until no variation in the sample weight observed. After that, the dried sample was grounded and sieved into several size fractions, using standard ASTM sieves. The size of the dried sample used throughout this experiment was 100 µm. The dried material was then suspended in a 0.1 M NaOH aqueous solution and refluxed for 1 h. After cooling, the suspension was filtered and the solid material was washed repeatedly with distilled water and finally dried at 105 ºC overnight and then stored in desiccators.

Adsorbate preparation: The aqueous solution of methylene blue was prepared by dissolving known quantity of $C_{16}H_{18}N_3SCl{\cdot}xH_2O$ (Fluka, 97 %) in double distilled water (Fig. 1). It was further diluted to obtain standard solutions. The pH of the solution was adjusted using either hydrochloric acid (Riedel, 37 %) or NaOH (Merck, 97 %). All the reagents used were of analytical grade.

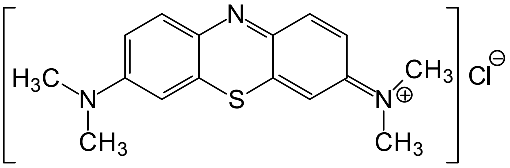


Fig. 1. Structure of methylene blue

Biosorption experiments: The kinetic experiments were carried out using mechanic stirrer (Fig. 2). Methylene blue solution was prepared with ultrapure water (UP-water) and the experiments were carried out by agitating 2.0 L of solution of a constant dye concentration with 20 g of prina at a constant agitation speed (400 rpm), 25 ºC and natural pH. Agitation was made for 1 h. Two millilitres of samples were drawn at suitable time intervals. The samples were then centrifuged for 15 min at 5000 rpm and the left out concentration in the supernatant solution were analyzed using UV-vis spectrophotometer (Shimadzu 1601 UV-vis spectrophotometer) by monitoring the absorbance changes at a wavelength of maximum absorbance (663 nm for methylene blue). Each experiment continued until equilibrium conditions were reached when no further decrease in the dye concentration was measured. Calibration curves were plotted between absorbance and concentration of the dye solution. It was investigated the effects of the following parameters to the removal rate of methylene blue on prina in the experiments.

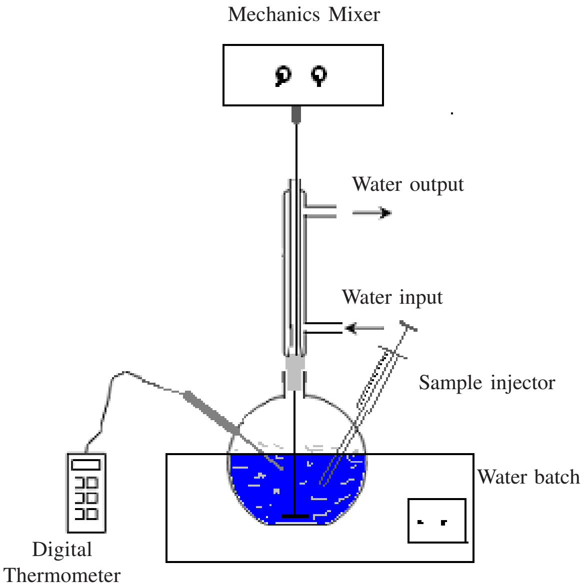


Fig. 2. Reactor of batch process

Effect of stirring speed: The effect of stirring speed on removal rate of methylene blue with base activated prina was investigated at different stirring speeds such as 200, 400 and 600 rpm at the initial dye concentrations of 50 mg L^{-1}, at 25 ºC and natural pH. The best suited mixing speed for adsorption experiments was observed as 400 rpm.

Effect of initial dye concentration: The initial tested concentrations of dyes were 25, 50 and 100 mg L^{-1} for methylene blue at 25 ºC, natural pH and 400 rpm.

Effect of pH: The effect of pH on the rate of colour removal was analyzed in the pH range from 3-11 at 25 ºC, natural solution pH, 400 rpm and constant initial dye concentration. The pH was adjusted using 0.1 N NaOH and 0.1 N HCl solutions by using a WTW 330i pH-meter with a combined pH electrode. pH meter was standardized with NBS buffers before every measurement.

Effect of ionic strength: The effect of ionic strength to removal rate of dyes on base activated prina was investigated at 0.001-0.100 mol L^{-1} KCl salt concentrations at 25 ºC, natural solution pH, 400 rpm and 50 mg L^{-1} initial dye concentration.

Effect of solution temperature: The effect of temperature to the adsorption capacity of base activated prina was carried out at 25, 30 and 35 ºC in a constant temperature bath at natural pH, 400 rpm and 50 mg L^{-1} dye concentration.

Kinetic studies and data evaluation: In the kinetic experiments the amount of dyes adsorbed at any time t, q_t (mg g^{-1}), was calculated using the following mass balance equation by

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{1}$$

where C_0 and C_t = initial and liquid-phase concentrations at any time t of dye solution (mg L^{-1}), respectively; q_t = dye concentration on adsorbent at any time t (mg g^{-1}), V = volume of dye solution (L) and m is the mass of base activated prina sample used (g).

For the kinetic data of the base activated prina, the obtained data for all parameters were analyzed using the Lagergren first-order, pseudo-second-order rate equations and intra particle diffusion models[6].

First-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

Pseudo-second-order models:

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \frac{t}{q_e} \tag{3}$$

Intra particle diffusion models:

$$q_t = k_{dif}\sqrt{t} + C \tag{4}$$

where q_e and q_t are the amount of dye adsorbed per unit weight of the adsorbent (mg g^{-1}) at equilibrium point and time t, respectively. k_1 and k_2 are the rate constant for the first-order and second order kinetics, respectively. The pseudo-second-order constant k_2 can be determined experimentally from the slope and intercept of plot of t/q_t *versus* t. C = intercept and $k_{dif.}$ = intra-particle diffusion rate constant (mg $s^{-1/2}$ g^{-1}). In addition, half-adsorption time ($t_{1/2}$) is an indicator for the adsorption rate. It is calculated from the following equation:

Half-adsorption time ($t_{1/2}$):

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{5}$$

In addition, the diffusion coefficient (D) was calculated by using the following equation and half-adsorption time:

The diffusion coefficient (D):

$$t_{1/2} = \frac{0.030 r_0^2}{D} \tag{6}$$

r_0 = radius of the adsorbent particle in centimetres and the value of D is cm^2 s^{-1}.

Desorption studies: Desorption study was carried out using H_2O, HCl (0.1 M) and ethyl alcohol (12 %) as desorption solutions. These experiments were performed by immersing the base activated prina in 50 mL of desorption solution for 1 h with stirring at 175 rpm. The bulk solute concentration in solution was measured as previously described.

RESULTS AND DISCUSSION

Characterization of prina: The interactions of methylene blue (MB) with the functional groups of base activated prina (BAP) were explained on the basis of the FTIR analyses, so FTIR spectra of methylene blue-base activated prina were compared with that of the raw prina and base activated prina. As shown in Fig. 3, the FTIR spectrum of the raw prina displays a number of absorption peaks, indicating the complex nature of biosorbent. IR spectra of prina after the adsorption of methylene blue denoted that main peaks observed for raw prina are preserved. Nevertheless some perturbations are induced. The transmittance decreases and some peaks change their wavenumbers. The peak around 1734 cm^{-1} (C=O stretching) shifted to higher frequencies (1737 cm^{-1}) in case methylene blue, also the peak[7] around 1632 cm^{-1} (C=O chelate stretching) shifted to 1613 cm^{-1}. The peak around 1263 cm^{-1} (C-O-C stretching) shifted to lower frequencies. This result suggested that carboxyl groups could be the main groups involved in the binding of methylene blue during methylene blue biosorption by base activated prina. However, significant peaks at 3352 and 3332 cm^{-1} (O-H and N-H stretching), 2919 cm^{-1} (-CH stretching) and 1026 cm^{-1} (C-O stretching of alcoholic groups of polysaccharide) are observed[8-10].

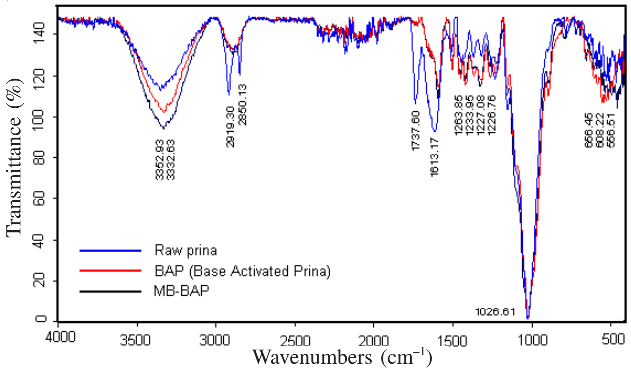


Fig. 3. FTIR spectra belong to raw prina, base activated prina and a methylene blue-base activated prina

Kinetic study

Effect of adsorbents dosage: The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent. The effect of base activated prina dosage on removal of methylene blue is shown in Fig. 4. The increase in adsorption of dyes with adsorbent dosage was due to the availability of more surface area of the base activated prina for adsorption. As adsorbent dosage was increased from 5-20 g L^{-1}, dye removal efficiency increased from 4.71-4.94. In addition, the graphic of pseudo-second-order rate for the adsorption system was shown in Fig. 4(b). Also shown in Fig. 4(b), the correlation between the experimental and theoretical results was good. This implied that the number of adsorption sites (or total surface area) increased in parallel with the increase of adsorbent mass.

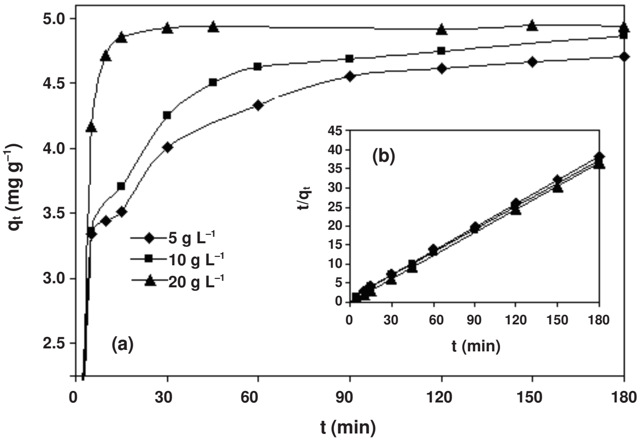


Fig. 4. Effect of adsorbents dosage (a) and pseudo-second-order plots methylene blue onto base activated prina (b) (298 K; natural pH, C_0: 50 mg L^{-1}, ionic strength: 0.0 g L^{-1} and stirring speed: 400 rpm)

Effect of initial concentration: The effect of initial methylene blue concentration on the adsorption rate at the adsorbent amount of 10 g, pH of 6.63 and agitation speed of 400 rpm was investigated (Fig. 5). The amount of dye adsorbed (mg g^{-1}) increased with increase in time and then reached equilibrium at 1 h for all concentration. The amount of methylene blue removal at equilibrium increased from 2.46-9.82 mg g^{-1} with the increase in dye concentration from 25-100 mg/L. From the figure, it is evident that the methylene blue removal decreased with increased initial concentration, although the actual amount of the dye adsorbed per unit mass of adsorbent increased with the increase in initial concentration. In addition, the graphic of pseudo-second-order rate for the adsorption system was shown in Fig. 5(b). The rate of adsorption also increased with increase in initial concentration due to the increase in the mass transfer driving force. Similar results were reported for methylene blue adsorption by pineapple leaf powder[11].

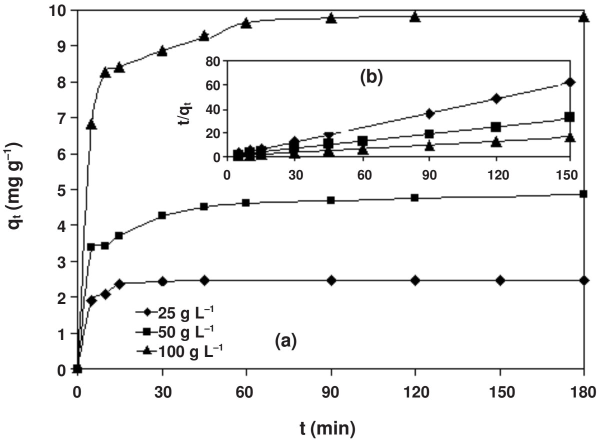


Fig. 5. Effect of initial concentration (a) and pseudo-second-order plots methylene blue onto base activated prina (b) (solid/liquid: 10 g L^{-1}, 298 K, natural pH, ionic strength: 0.0 g L^{-1} and stirring speed: 400 rpm)

Effect of pH on adsorption process: Fig. 6 shows the effect of solution pH on methylene blue adsorption onto base activated prina at various initial solution pH for an initial dye concentration of 50 mg L^{-1} and BAS dose of 10 g L^{-1}. When the value of pH increased from 3-11, the adsorption quantity was increasing from 3.39-4.94 mg g^{-1}. Base activated prina is comprised of various functional groups, such as amine, hydroxyl and carbonyl groups which are affected by the pH of solutions. At pH: 3.0 a considerable high electrostatic repulsion exists between the positively charged surface of the adsorbent, due to the ionization of functional groups of adsorbent and positively charged cationic dye molecules. As the pH of the system increases, the numbers of negatively charged sites are increased. A negatively charged site on the adsorbent does favour the adsorption of cationic dyes due to the electrostatic attraction[12]. Similar results of pH effect were also reported for the adsorption of methylene blue onto neem (*Azadirachta indica*) leaf powder[13].

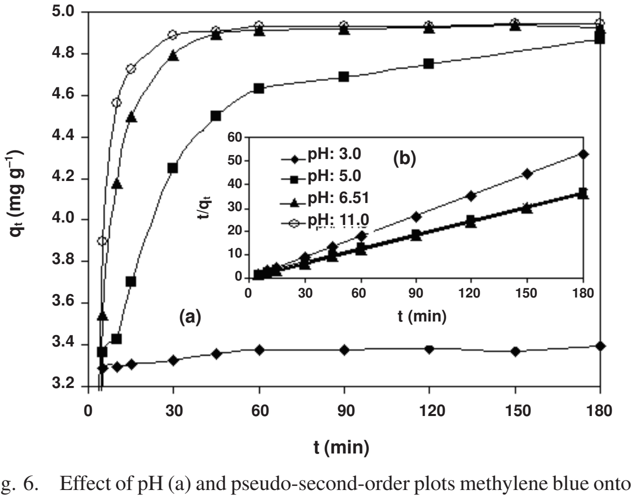


Fig. 6. Effect of pH (a) and pseudo-second-order plots methylene blue onto base activated prina (b) (solid/liquid: 10 g L^{-1}, 298 K, C_0: 50 mg L^{-1}, ionic strength: 0.0 g L^{-1} and stirring speed: 400 rpm)

Effect of temperature: Temperature is an important parameter for the adsorption process. The temperature effect on the sorption of methylene blue on base activated prina is shown in Fig. 7. The results revealed that the sorption capacity increased from 4.86-4.94 mg g^{-1} with the temperature increasing from 298-318 K. Since the sorption increase when temperature rise, therefore this system was endothermic. It was a chemisorption mechanism where an increase in number of molecules acquiring sufficient energy to undergo chemical reaction with functional groups in the base activated prina[14].

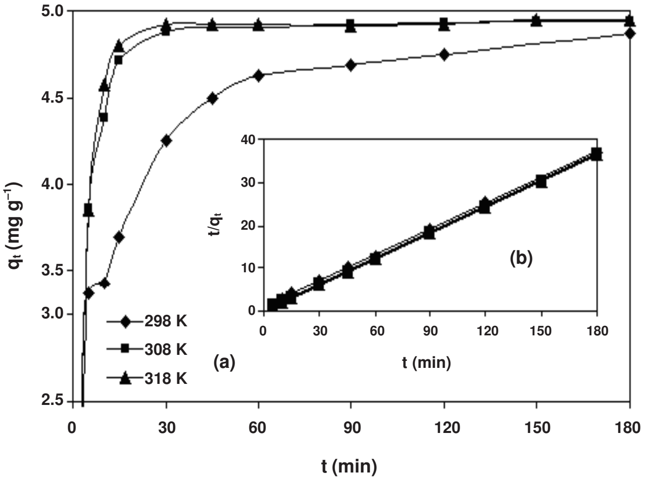


Fig. 7. Effect of temperature (a) and pseudo-second-order plots methylene blue onto base activated prina (b) (solid/liquid: 10 g L^{-1}, natural pH, C_0: 50 mg L^{-1}, ionic strength: 0.0 g L^{-1} and stirring speed: 400 rpm)

Effect of ionic strength: Wastewaters from textile-manufacturing or dye-producing industries contain various types of dissolved and suspended compounds apart from the dyes which can be considered as impurities in the dye removal process. These impurities could be acids, alkalis, salts or metal ions. Cations such as Na^+, K^+, Cu^{2+}, Ca^{2+} and Cr^{3+} are the most common metal ions present in dye bearing wastewater. The presence of ions leads to high ionic strength, which may significantly affect the performance of the biosorption process[2]. The effect of ionic strength on the adsorption rate is shown in Fig. 8. As shown in Fig. 8, the presence of inorganic salt has significantly influenced the adsorption rate of methylene blue. For the adsorption of methylene blue by base activated prina, the adsorption was found to decrease with increasing ionic strength. Since the salt screens the electrostatic interaction of opposite changes of the oxide surface and the dye molecules, the adsorbed amount will decrease with increase of KCl concentration[15].

Desorption studies: In order to probe further into the mechanistic aspects of methylene blue adsorption onto base activated prina, desorption studies were carried out. The methylene blue desorption results are shown in Fig. 9. It was observed that HCl was most efficient among all the desorbents studied while desorption with deionized water and ethyl alcohol was almost negligible.

Adsorption isotherm: In this study, the equilibrium data for methylene blue on base activated prina were modeled with the Langmuir and Freundlich models. The Langmuir equation can be represented as follows:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{2}$$

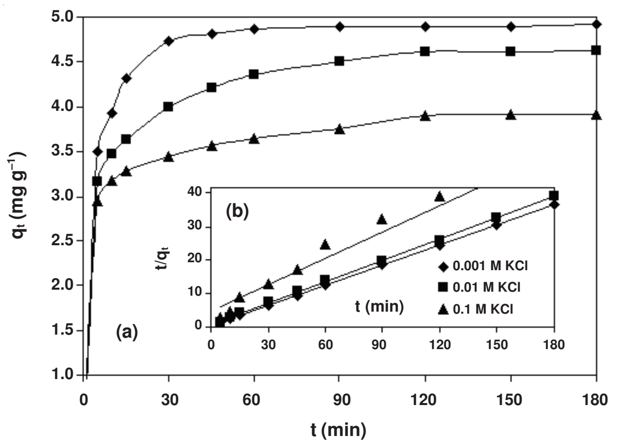


Fig. 8. Effect of ionic strength (a) and pseudo-second-order plots methylene blue onto base activated prina (b) (solid/liquid: 10 g L^{-1}, 298 K, natural pH, C_0: 50 mg L^{-1} and stirring speed: 400 rpm)

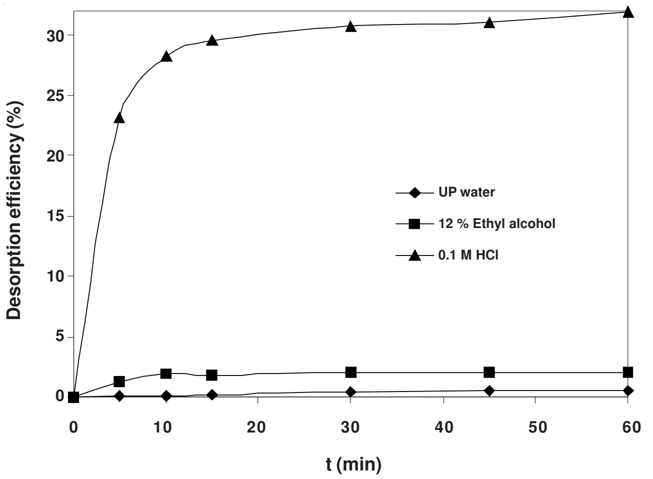


Fig. 9. Methylene blue recovery by different desorbents

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{3}$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of adsorbed methylene blue per unit weight of adsorbent and un-adsorbed methylene blue concentration in solution at equilibrium, respectively, q_m = maximum amount of the methylene blue bound per unit weight of adsorbent to form a complete monolayer on the surface at high C_e and K is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L mg^{-1}). q_m and K were calculated from the slope and intercept of the straight lines of the plot C_e/q_e *versus* C_e.

The Freundlich equation may be written as:

$$q_e = K_F C_e^{1/n} \tag{4}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F = Freundlich constant that shows both the adsorption capacity of an adsorbent and the strength of the relationship between adsorbate and adsorbent. The slope 1/n, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogenity, becoming more heterogeneous as its value gets closer to zero. In general, as K_F increases the adsorption capacity of an adsorbent for a given adsorbate increases. K_F and (1/n) can be determined from the linear plot of ln q_e *versus* ln C_e.

The Langmuir constants q_m and K were determined from the slope and intercept of the plot and are presented in Table-1. It can be seen from the R^2 values, which are a measure of goodness of fit, that the Langmuir shown better fit at 298 K compared to the Freundlich model. The fact that this occurred may be due to homogeneous distribution of active sites onto base activated prina surface.

TABLE-1
CHARACTERISTIC PARAMETERS OF SORPTION PROCESS OF MB ON BAP

Temp. (K)	Langmuir isotherm				Freundlich isotherm
	q_m (mg g^{-1})	K (L mg^{-1})	R^2	R_L	R^2
298	12.90	0.368	0.99	0.172-0.955	0.89

The favourable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by:

$$R_L = \frac{1}{1 + KC_e} \tag{6}$$

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear (R_L:1), favourable ($0 < R_L < 1$) or irreversible (R_L:0). The R_L values were presented in Table-1 which shows the adsorption behaviour of base activated prina. The value of R_L for the adsorption of methylene blue on base activated prina indicates that the adsorption process is favourable because R_L value lies between 0 and 1.

Kinetics analysis: Calculated correlation coefficients, both linear and non-linear, for pseudo-first-order model and pseudo-second-order model by using regression procedure for methylene blue adsorption are shown in Table-2. Since calculated correlation coefficients are closer to unity for pseudo-second-order kinetics model ($R^2 = 0.99$) than the pseudo first-order kinetic model ($R^2 = 0.90$, generally) and intra-particle diffusion models. Intra-particle diffusion process model showed correlation coefficient (R^2) of 0.378-0.988. Therefore, intra-particle diffusion process model is not a good fit for methylene blue adsorption on base activated prina. As a result, the adsorption kinetics could well be approximated more favourably by pseudo-second-order kinetic model for methylene blue. Moreover, $q_{e(calcul)}$ and $q_{e(exp)}$ values for this models are close to each other and the k_2 values are calculated (Table-2).

The D values were calculated from eqn. 6. In these calculations, it has been assumed that the solid phase consists of spherical particles with an average radius between the radii corresponding to upper- and lower-size fractions. The value of r_0 was calculated as 2.5×10^{-3} cm for base activated prina samples. The D values calculated at all parameters are in the range of 0.62×10^{-7}-31.79×10^{-7} cm^2 s^{-1}.

Comparison of adsorption efficiency: Table-3 presented a comparison of several adsorbents employed for methylene blue adsorption. As can be seen from Table-3, the base activated prina biosorbent employed in this work presented higher adsorption capacity when compared with some of the biosorbent reported in the literature.

TABLE-2
FIRST, PSEUDO-SECOND ORDER KINETICS and INTRA-PARTICLE DIFFUSION MODEL PARAMETERS FOR THE ADSORPTION SYSTEMS IN THE STUDY

Parameters	First-order	Pseudo-second-order				Intra-particle diffusion		$t_{1/2}$ (min)
	R^2	$q_{e(calcul)}$ (mg g^{-1})	$q_{e(exp)}$ (mg g^{-1})	k_2 (g/mgmin)	R^2	R^2	$D \times 10^7$ (cm^2 s^{-1})	
Temperature (K)								
298	0.934	4.87	4.95	0.045	0.999	0.845	2.74	4.563
308	0.908	4.94	4.97	0.212	0.999	0.527	13.10	0.954
318	0.544	4.94	4.96	0.267	0.999	0.428	16.49	0.758
Initial concentration (mg L^{-1})								
25	0.913	2.46	2.48	0.367	0.999	0.553	11.29	1.107
50	0.934	4.87	4.95	0.045	0.999	0.845	2.74	4.563
100	0.175	9.82	10	0.036	0.999	0.750	4.42	2.828
Initial pH								
3.00	0.748	3.39	3.39	0.646	0.999	0.877	27.41	0.456
6.51	0.934	4.87	4.95	0.045	0.999	0.845	2.74	4.563
9.00	0.945	4.92	4.98	0.142	0.999	0.585	8.73	1.431
11.00	0.824	4.94	4.96	0.255	0.999	0.484	15.76	0.793
Ionic strength [M]								
0.001	0.844	4.91	4.97	0.107	0.999	0.661	6.56	1.903
0.010	0.954	4.62	4.73	0.049	0.999	0.908	2.82	4.417
0.100	0.934	3.84	3.82	0.013	0.999	0.918	0.62	20.03
Adsorption dosage (g L^{-1})								
5	0.972	4.71	4.84	0.036	0.999	0.907	2.12	5.897
10	0.930	4.87	4.95	0.045	0.999	0.832	2.74	4.563
20	0.325	4.94	4.94	0.514	0.999	0.378	31.79	0.393

TABLE-3
COMPARISON OF ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS FOR METHYLENE BLUE

Adsorbents	$q_{max.}$ (mg g^{-1})	References
Azadirachta indica (neem leaf powder)	8.76	13
Brazil nut shells	7.81	16
Wheat shells	16.56	17
Sawdust	4.89	18
Orange peel	5.87	19
Lemon peel	29.00	20
Raw beech sawdust	9.78	21
Marine seaweed	3.42	22
Base activated prina	12.90	Present study

Thermodynamic study: The activation energy (E_a) of adsorption can be evaluated using the pseudo-second-order rate constants. The linear plot between ln k_2 *versus* 1/T was used to calculate E_a using the Arrhenius equation[23] (Fig. 10a).

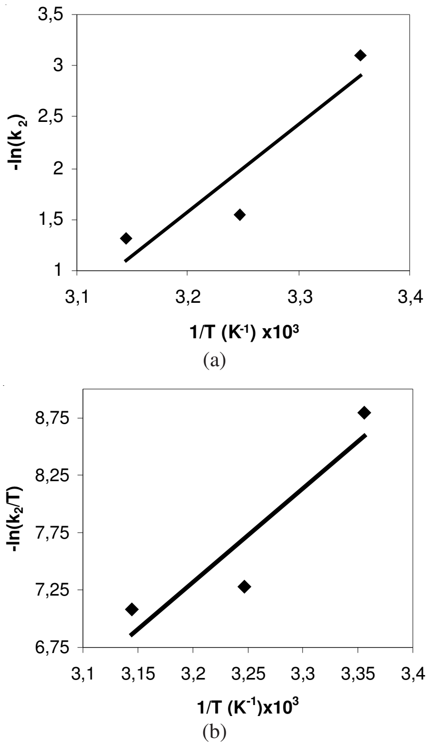
$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \tag{7}$$

The activation energy gives an idea about the type of adsorption, which is mainly a physical or chemical process. The physisorption processes usually have energies in the range of 5-40 kJ mol^{-1}, while higher activation energies (40-800 kJ mol^{-1}) suggest chemisorption[24,25]. The value of activation energy was found (70.68 kJ mol^{-1}).

The thermodynamic experiments were carried out at 298, 308 and 318 using 10 g L^{-1} of base activated prina dosage for 50 mg L^{-1} of dye solutions. The thermodynamic parameters, ΔH° and ΔS°, were obtained from the following Eyring equation[26]:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^o}{R_g} - \frac{\Delta H^o}{R_g T} \tag{8}$$

where k_b and h are Boltzmann's and Planck's constants, respectively. According to eqn. 8, a plot of ln (k/T) *versus* 1/T should be a straight line with a slope $-(\Delta H^o/R_g)$ and intercept $[\ln (k_b/h) + (\Delta S^o/R_g)]$. ΔH° and ΔS° were calculated from slope and intercept of line (Fig. 10b). The thermodynamic parameter, ΔG°, was calculated from the following Gibbs-Helmholtz equation:



(a)

(b)

Fig. 10. (a) Arrhenius plot for the adsorption and (b) plot of ln (k_2/T) *versus* 1/T for adsorption of dye on base activated prina

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (9)$$

where ΔG^o = standard free energy (kJ mol^{-1}). It is found that the values of the free energy ΔG^o, enthalpy (ΔH^o) and entropy (ΔS^o) of activation is 55.67 kJ mol^{-1}, 68.122 kJ mol^{-1} and -40.39 j mol^{-1} K^{-1}, respectively. The positive values of ΔH^o indicate that the adsorption of dyes was endothermic. The negative entropy change (ΔS^o) value (-40.39 j mol^{-1} K^{-1}) corresponds to a decrease in the degree of freedom of the adsorbed species[27].

Conclusion

Base activated prina prepared from olive stone, an agricultural waste, could be used as a potential adsorbent for the removal of methylene blue or cationic dyes from textile wastewater because of adsorption of cationic dyes. Biosorption process followed Langmuir isotherm model. The maximum sorption capacity was found to be 12.90 mg/g at 25 ºC and natural pH. The experimental results indicate that the adsorption process is usually complete when the surface is covered with a monolayer of dye. Desorption and reusability studies indicated that the biosorbent could be regenerated using 0.1 M HCl solution with up to 31.92 % recovery. Kinetic data of adsorption well fitted to pseudo-second order kinetic model. The values of enthalpy change (ΔH^o) were determined to be positive value of 68.122 kJ mol^{-1} for adsorption on base activated prina. In addition, the value of activation energy was found and this value shown that adsorption of methylene blue onto base activated prina was the chemisorptions process. The mechanism was an endothermic process. This tended to involve a chemical adsorption. In addition, because cost analysis for the preparation of base activated prina is not high and as olive stone or prina is found in abundance in Turkey, it can be says that its cost is expected to be economical.

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