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## Removal of Dye from Tannery Effluent using Date Palm (*Phoenix dactylifera* L.) Leaf as Bio-adsorbent

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### ABSTRACT

In this study, the Date palm leaf (DPL) was explored as a low-cost bio-adsorbent for the treatment of dye loaded tannery effluent. The adsorption parameters viz. pH, adsorbent dosage, contact time and initial dye concentration were examined by batch experiment to determine the optimum adsorption condition. Standard NaOH solution was used for the surface modification of raw DPL. The morphological and chemical nature of the prepared adsorbent was studied by microscopic and spectral analysis respectively. The physicochemical parameters of the collected and treated dye effluent samples were investigated to evaluate the adsorption efficiency. Adsorption kinetics and mechanisms were illustrated with respect to various chemical reaction and isotherm models. The test results proved that the operating parameters, like pH (2), adsorbent dosage (3g/L), contact time (6h) and initial dye concentration (350ppm) were found optimum for maximum dye removal (63.23%) at ambient temperature. The value of regression coefficient ( $R^2$ ) was 0.997 and 0.999 for Langmuir and Freundlich isotherm model respectively, denoted the adsorption process. The Freundlich isotherm model best fitted the adsorption mechanism. The sorption kinetics was interpreted by pseudo-second-order reaction, which was thermodynamically exothermic and spontaneous at any temperature. Significant changes were observed in the physicochemical parameters of the dye effluent after treatment and the values were reduced closely to the permissible limit set by Department of Environment (DoE), except the pH. It was concluded that the application of Date palm leaf could be a cost-effective and efficient bio-adsorbent for the removal of dye and other pollutants from hazardous tannery effluents.

Keywords: Bio-adsorbent, dye removal, *Phoenix dactylifera* L., tannery effluent, waste management.

### 1. Introduction

The application of dyes for leather and textile coloration has been one of the most ancient practices to make the products aesthetic and appealing to its users. Despite having extensive industrial applications, the dyes can create toxicological problems in many aspects [1]. Dye containing industrial effluents inhibit sunlight penetration, reduce dissolved oxygen (DO) and photosynthesis rate in aquatic environment, and release a substantial amount of both organic and inorganic pollutants when they mix up with surface water [2, 3]. Moreover, some of these dyestuffs start to decompose in contact of human perspiration and produce toxic substances that cause skin irritation, allergy and other severe sicknesses [4]. As a result, it is imperative to remove coloring agents from industrial wastewaters before discharging them into the environment.

The leather industry is one of the largest users of dyes and pigments after textile, paper and pulp, and paint industry. Approximately, 50-100 types of dyestuffs of different shades and colors are used in the leather industry based on recent fashion trends and hence it discharges a considerable amount of colored effluent into the environment [5]. Among these dyes, Acid red-73 (Brilliant Crocein M/Crocein Scarlet, C. I. 27290) is widely used in the production of bag and other fancy type leathers. This dye is yellowish-red in color, anionic and soluble in water and alcohol. It is also used for the dyeing of other fibrous substrates like wool, paper and anodized aluminum [6, 7]. However, the dye has been listed as a toxic substance due to its adverse

health effect upon inhalation/swallowing [8]. Therefore, the concentration of acid red-73 (AR) dye in tannery effluent should be kept up to the threshold limit.

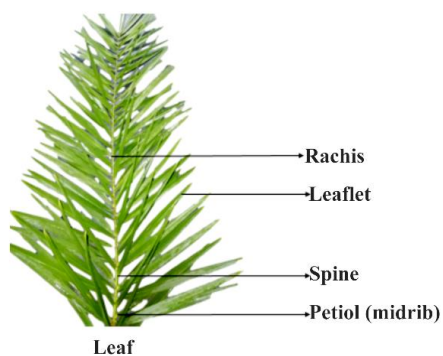
At present, various wastewater treatment methods are available for the removal of toxic matters, colors and other pollutants from industrial effluent such as adsorption, flocculation, coagulation, electrolysis, biodegradation, and photo catalytic degradation [9]. Consequently, dye-loaded effluent require subsequent treatment as most of the dyestuffs are difficult to decompose for their complex structure and xenobiotic nature that increases treatment cost and machine maintenance expenditure [10, 11]. Therefore, the treatment of dye-loaded wastewater with low-cost and efficient treatment agent has become a prioritized subject in advances of wastewater treatment [12]. In recent years, biomass generated from various agricultural and domestic activities is getting interest as adsorbent for its low-cost, easy availability and high adsorption capacity towards dyes and metals [13]. Moreover, the adsorption capacity of biomass can be increased up to some extent by surface modification through chemical and physical methods [14]. However, there is still insufficient literature regarding biomass-based adsorbent for the remediation of dyes from tannery effluent.

In this research, we focused on to find out the suitability and possible recycling of Date palm (*Phoenix dactylifera* L.) leaf, an agro-based biomass as a low-cost bio-adsorbent to treat dye-loaded tannery effluent. In Bangladesh, a significant amount of Date palm leaf

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(Figure 1) is generated per annum as an agro-waste in the northern part of the country that causes serious air pollution upon incineration. Hence, this research will flourish one-step forward to mitigate environmental pollution by utilizing waste Date palm leaf and provide a cost-effective adsorbent to remove dyes from tannery effluent. Besides, the effect of different functional parameters on dye adsorption, adsorption efficiency of the adsorbent, mechanism and adsorbent nature were also studied as the specific objectives of this research.

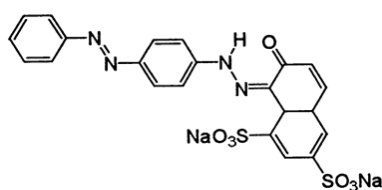


**Fig. 1** Date palm leaf and its different parts

## 2. Materials and methods

### 2.1 Materials

Date palm leaf (DPL) was collected from a local garden of Jashore district, Bangladesh. Analytical grade AR dye, standard sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions were purchased from Inco dyes and chemicals, Spain. The molecular weight of AR dye is 556.5g/mole and its chemical structure is illustrated in Figure 2. Deionized water was used to conduct the experimental works of this research.



**Fig.2** Chemical structure of Acid red-73 dye.

### 2.2 Synthetic sample preparation

Standard stock solution of AR dye (1000mg/L) was prepared by dissolving sufficient amount of dye in 1000ml deionized water using a magnetic stirrer. The stock solution was stirred at a constant speed of 150rpm until complete dissolution of dyestuff. The initial pH of the dye solution (6.5) was measured by a digital pH meter. Finally, it was diluted with deionized water to prepare intermediate standard solution of desired concentration (30-350ppm) for further experiment. Before conducting batch experiments, the pH of the dye solution was adjusted by using 0.1M NaOH/0.1M HCl solution to obtain desired pH (2-8).

### 2.3 Adsorbent preparation

The collected DPL sample was thoroughly washed with tap water to remove dirt and surface adhered contaminants. The washed DPL was cut into small chips with a sharp stainless steel knife and sundried for a week. Dried DPL chips were shredded by a grinder and sieved with a nylon mesh in particle size ranged 600-750 $\mu$ m. DPL powder was soaked overnight into 50% NaOH solution at weight ratio of 1:1 for chemical activation. The treated DPL powder was further washed to remove surplus alkali until a neutral pH (6-7) obtained. Finally, DPL powder was oven-dried at 110°C for 4hours and kept in a desiccators for cooling.

### 2.4 Adsorbent characterization

The prepared adsorbent was subjected to assess its surface pattern and porosity by scanning electron microscopy (SEM) at resolution X1000. Fourier transformed infrared spectroscopy (FT-IR) was conducted at wave number ranged 750-4000 $\text{cm}^{-1}$  to study the nature of existing functional groups in DPL adsorbent and to examine the inset difference in absorption peaks after dye adsorption.

### 2.5 Adsorption experiments

The effect of adsorption parameters viz. pH, adsorbent dosage, contact time, etc. were investigated in batch process. In each experiment, 100 ml dye solution of known concentration (30-350ppm) was treated with a sufficient amount of adsorbent (1.5 - 4.5g/L) in 250 ml Erlenmeyer flask at different pH level (2-8) and different temperature (25-55°C/298-328K). The mixture was agitated at a constant speed of 250rpm in an orbital shaker for predetermined time (6h). Every time, the flask was rested for a few minutes to settle down the adsorbent, the supernatant mixture was filtered by Whatman No. 42 filter paper, and the filtrate was taken for the analysis of residual AR dye concentration by a single beam UV-visible spectrophotometer at wavelength 550nm with respect to a previously prepared calibration curve. The reproducible calibration curve showed a linear relationship between absorbance and AR dye concentration. The following equations were used to calculate the residual concentration of AR dye solution and dye uptake on adsorbent:

$$\text{Amount adsorbed, } q_t = \frac{(C_o - C_t) \times V}{w} \quad (1)$$

$$\% \text{Removal} = \frac{(C_o - C_e) \times 100}{C_o} \quad (2)$$

$$\text{Amount adsorbed, } q_e = \frac{(C_o - C_e) \times V}{w} \quad (3)$$

Where,  $C_o$ = initial concentration of dye solution (mg/L),  $C_t$ = concentration of dye solution (mg/L) at time t,  $C_e$ = concentration of dye solution (mg/L) at equilibrium,  $V$ = volume (L) of the dye solution and  $W$ = mass (g) of the adsorbent.

## 2.6 Wastewater analysis

Dye-loaded effluents were collected from the discharge point of Apex tannery limited, Hemayetpur, Savar in a sealed plastic bottle. The bottle was disinfected by 5% HNO<sub>3</sub> solution to avoid contamination during sample collection. Several physicochemical parameters like pH, dissolved oxygen (DO), chemical oxygen demand (COD), total dissolved solid (TDS), etc. were tested before and after treatment under optimum condition following standard testing methods and calibrated instruments [15].

## 3. Results and discussion

### 3.1 Optimization of adsorption process

#### 3.1.1 Effect of pH (Kindly reconsider this section)

The effect of pH on dye adsorption onto DPL is presented in Figure 3(a). The maximum adsorption capacity (40.2mg/g) was obtained at pH 2. The adsorption capacity was decreasing with the increasing of pH and reached to almost nil at pH 4-5 and again increased to 12.88mg/g with increment of pH up to 8. It indicates that the adsorption of AR dye was effective at lower pH. Wang et al. (2020) [16] also observed the same phenomenon on AR dye adsorption onto rice wine lees. At the strong-acidic condition, the interaction between anionic dye and cationic DPL was enhanced that help AR dye to be easily adsorbed onto the adsorbent [16].

#### 3.1.2 Effect of adsorbent dosage

The effect of adsorbent dosage on dye adsorption is illustrated in the Figure 3(b). The results demonstrated that the removal efficiency increased from 30.44% to 63.23% with increase of dosage from 1.5g/L to 3g/L. Therefore, the optimal dose for DPL adsorbent was 3g/L. Generally, as the increase in adsorbent dosage, the number of activated adsorption sites increases which in turn increases the adsorption efficiency [17]. In the adsorption process, the equilibrium interaction between adsorbate and adsorbent at optimum condition after applying the optimal dose also played significant role [18].

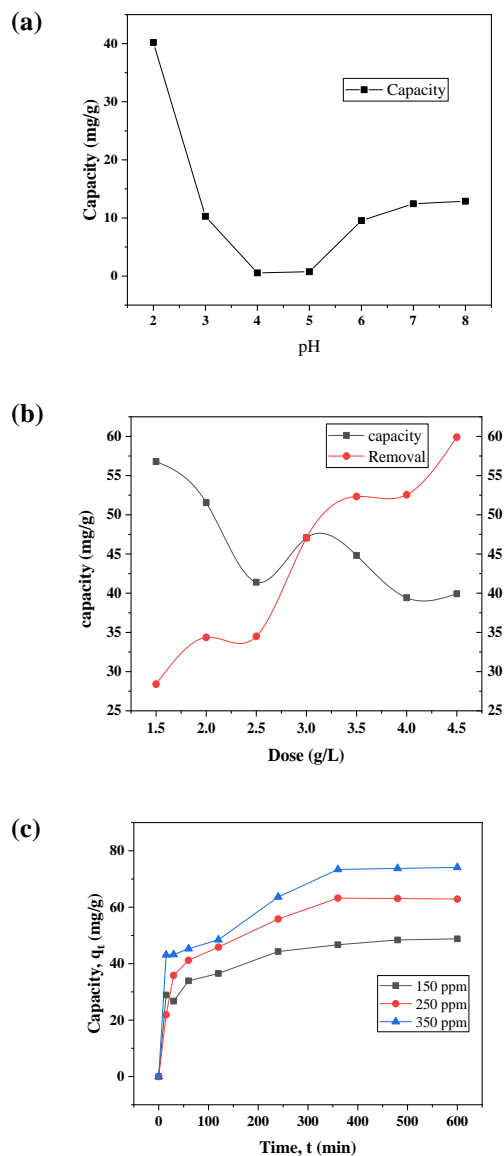
#### 3.1.3 Effect of initial dye concentration

The initial dye concentration is an important variable in adsorption process due to the driving force for mass transfer between adsorbate and adsorbent [20]. The Figure 3(c) illustrated that the dye adsorption capacity was maximum (74.13mg/g) at 350ppm. Moreover, the removal efficiency was increased from 48.80% to 74.23% at increasing the concentration from 150ppm to 350ppm.

#### 3.1.4 Effect of temperature

The adsorption reaction for any specific contaminant can be endothermic if the adsorption is increased with increasing the temperature and be exothermic if the condition is reversed. It was observed

that the adsorption efficiency was decreased with the increment of temperature and the maximum adsorption (75.53mg/g) was obtained at temperature 298 K (25°C) for contact time of 480minutes (Figure 6(a)) which was gradually decreased to 48.23mg/g at temperature 328K (55°C). Therefore, the adsorption process was exothermic.



**Fig.3** Optimum parameters for dye adsorption (a) pH, (b) adsorbent dosage and (c) initial dye concentration.

### 3.2 Adsorption mechanism

Both sorption mechanism and maximum adsorption capacity at equilibrium condition was described by Langmuir and Freundlich isotherm models. The linear form of Langmuir isotherm was expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (4)$$

$$R_L = \frac{1}{1 + C_m b} \quad (5)$$

Here,  $q_e$ = amount of adsorbed dye in per unit mass of adsorbent (mg/g),  $C_e$ = equilibrium dye concentration (mg/l),  $q_m$ = adsorption capacity (mg/g),  $b$ = Langmuir constant (l/mg),  $R_L$ = separation factor.

The value of  $R^2$ , constant ( $b$ ) and ( $R_L$ ) were found 0.997, 0.1167 and 0.0238 for linear Langmuir isotherm model.

The Freundlich isotherm model represents the adsorption of dye molecules on a heterogeneous surface by multilayer adsorption process. The expression of this model is given below:

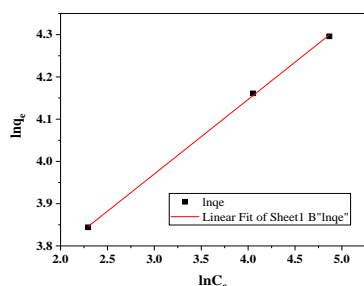
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Here,  $K_F$ = adsorption capacity,  $1/n$ = adsorption intensity.

The graphical representation of  $\ln q_e$  and  $\ln C_e$  showed that the plot was a straight line with an intercept of  $\ln K_F$  and a slope  $1/n$  (Figure 4). The value of correlation coefficient,  $R^2$  was found 0.999 that revealed the heterogeneity of DPL adsorbent surface and multilayer adsorption process. The Freundlich isotherm model best fitted the adsorption mechanism.

**Table 1** Isotherm constants for AR dye adsorption onto DPL.

Langmuir constants		Freundlich constants	
Values		Values	
$q_m$ (mg/g)	77.52	$K_F$	31.218
$b$ (L/mg)	77.52	$n$	5.668
$R^2$	0.997	$R^2$	0.999
$R_L$	0.0238		



**Fig.4** Freundlich isotherm models of dye adsorption.

### 3.3 Adsorption kinetics

To interpret the adsorption of AR dye adsorption onto DPL both pseudo-first-order and pseudo-second-order reaction models were used [19]. In many studies, sorption kinetics was described by pseudo-first-order using Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (7)$$

Pseudo-second-order adsorption kinetics was explained using the following equation:

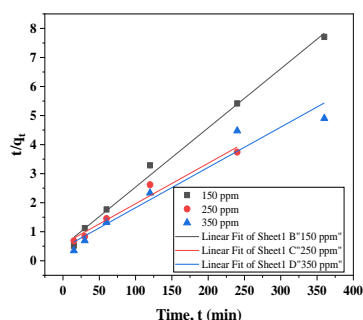
$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (8)$$

Here,  $q_e$ = amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g),  $q_t$ = amount of solute adsorbed at any time (mg/g) and  $k_1$ = adsorption constant for pseudo-first-order reaction and  $k_2$ = adsorption constant for pseudo-second-order reaction. Thus, the experimental data fitted well with the pseudo-second-order kinetic model ( $R^2$  value 0.9971).  $q_e$  and  $k_2$  was established from the slope and intercept of the plot. The parameters related to both kinetic models were showed in Table 2.

**Table 2** Summary of adsorption kinetics.

Kinetic model	Parameter	150	250	350
		ppm	ppm	ppm
Pseudo-first-order	$q_e^*$ (mg/g)	46.7	64.16	73.4
	$K_1$	0.0089	0.0069	20.61
	$R^2$	0.962	0.828	0.915
	$q_e^{**}$ (mg/g)	23.82	39.36	31.12
Pseudo-second-order	$K_2$	0.00082	0.00034	0.00043
	$R^2$	0.994	0.969	0.949
	$q_e^{**}$ (mg/g)	49.26	71.94	72.46

\*E= Experimental, \*\*T= Theoretical.



**Fig.5** Pseudo-second-order kinetic plot for AR dye adsorption onto DPL.

### 3.4 Adsorption thermodynamics

Thermodynamics studies were conducted and the exothermic nature of the reactions was verified. Thermodynamics parameters include  $\Delta G$ ,  $\Delta H$  and change in standard  $\Delta S$  in a system, which are the actual indicator for practical application of the dye by adsorbent. The thermodynamics parameters were determined by the following equations:

$$\Delta G^o = -RT \ln K_d \quad (9)$$

$$\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (10)$$

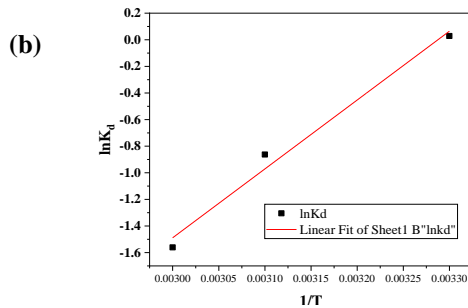
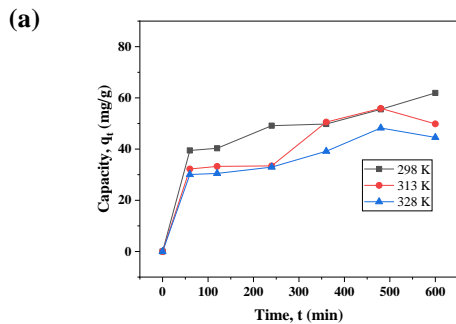
$$\Delta S^o = \frac{\Delta G^o - \Delta H^o}{T} \quad (11)$$

Here,  $\Delta G$  = Gibbs free energy,  $K_d$  = distribution adsorption coefficient constant ( $q_e/C_e$ ),  $\Delta H$  = enthalpy,  $R$ = molar gas constant (8.314J/mol/K),  $T$ = temperature (K),  $\Delta S$ = change in standard entropy of the system.

The findings showed dye adsorption on DPL adsorbent decreased from 75.53 to 48.64mg/g (75 to 52.65%) with the increment of temperature (25-55°C/298-328K). This was attributed to the decreased solubility of the dye at high temperature [20]. Similar increases in the rate of reverse step at increasing temperature were observed for methylene blue adsorption in the research work of Mitrogiannis et al., [21]. The negative values of enthalpy ( $\Delta H < 0$ ) verify the exothermic nature of dye adsorption (Table 2). Value of  $\Delta S$  reflects the decreasing randomness in solid solution interface during adsorption of dye onto adsorbent. The negative value of  $\Delta G$  implies the adsorption was spontaneous at lower temperature.

**Table 3** Thermodynamic parameters of adsorption.

T(K)	$\Delta G$ (KJ/mol)	$\Delta H$ (KJ/mol)	$\Delta S$ (KJ/mol)
298	-0.0708	-43.04	- 0.1414
313	2.245		
328	4.256		



**Fig.6** (a) Adsorption capacity at different temperature and (b) Plots of  $\ln K_d$  versus  $1/T$  for AR dyes adsorption.

### 3.5 Evaluation of physicochemical parameter of tannery effluent

The physicochemical properties of the collected tannery effluents and after treatment effluents were enlisted in Table 4. It was noticed that the COD, TDS and TSS of untreated effluents were beyond the permissible limit of DoE for wastewater discharged into the environment [22]. These values were significantly reduced by COD 61.54%, TDS 94.58%, TSS 97.65%, and the values were closely to the permissible limit after adsorption, except the pH. This depicts the remarkable adsorption potential of DPL as bio-adsorbent towards secondary pollutants.

**Table 4** Characteristics of tannery effluent sample.

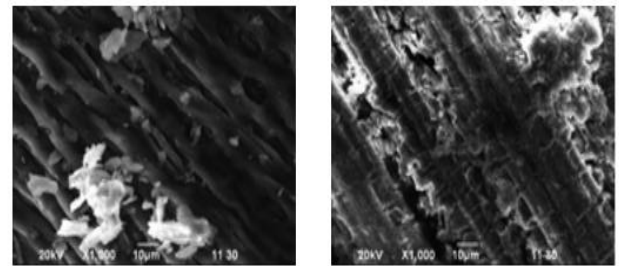
Parameters	Before adsorption	After adsorption	Permissible limit
pH	6.5	2.21	6-9
Color	Deep red	Light red	-
DO	4.62	6.67	4.5-8
COD	992	381	400
TDS	5780	313	2100
TSS	3780.8	893	500
Cl <sup>-</sup>	10.08	1.8	600

\*All the parameters were measured in mg/l except pH and color

### 3.6 Adsorbent nature

#### 3.6.1 Microscopic analysis

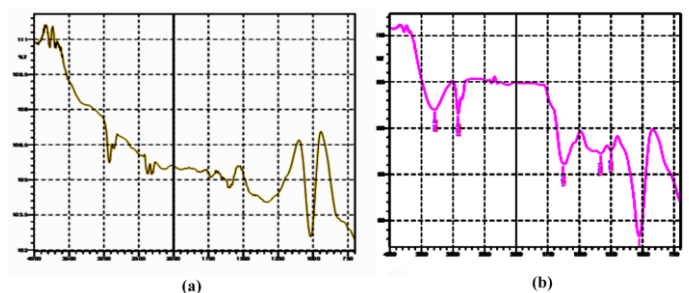
SEM monographs (Figure 7) of DPL evidently displayed that the availability of the availability of pores in the internal surfaces of surface modified DPL. However, the surface porosity and pore structures were less evident and cleared after dye adsorption.



**Fig. 7** SEM analysis of (a) raw adsorbent DPL and (b) after dye adsorption.

#### 3.6.2 FT-IR spectroscopy analyses

The IR spectrum of DPL showed peaks at  $1164.86\text{cm}^{-1}$  and  $1627.92\text{cm}^{-1}$  that represented the existence of C-H stretching and  $>\text{N-H}$  bending. However, the addition of new peaks was found after chemical activation at region  $2920.23$  to  $3286.7\text{cm}^{-1}$  reflected the vibration of -OH stretching. Finally, the presence of the peak at  $1026.13$ ,  $1164.86$ ,  $1246.02$ ,  $1627.92$ ,  $1720.50$ ,  $2920.23$ ,  $3286.70\text{cm}^{-1}$  that confirmed the characteristic peaks of DPL after dye adsorption.



**Fig. 8** FT-IR spectrum (a) raw adsorbent DPL and (b) after dye adsorption.

#### 4. Conclusion

The abundant leaves of *Phoenix dactylifera* L. plant can be used as a cost-effective bio-adsorbent for the treatment of dye-loaded tannery effluents. The optimum adsorption of AR dye was obtained at pH 2, initial dye concentration of 350ppm, adsorbent dosage 3g/L, for contact time 6h at ambient temperature with maximum removal of 63.23%. Consequently, the adsorption was found multilayer and monolayer (based on Freundlich and Langmuir regression data), exothermic and spontaneous at lower temperature. The adsorption kinetics followed pseudo-second-order reaction model. Moreover, the values of physicochemical parameters of the tannery effluents were reduced to the minimal accepted limit upon treatment except the pH. Hence, the effluents after adsorption could be treated further with a little diluted alkali to adjust pH before discharging into the surface water.

#### 5. Acknowledgement

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