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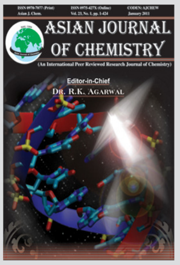

Adsorption of Eosin Bluish on Roots, Stem and Leaves of *Phoenix dactylifera*

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Phoenix dactylifera (Date Palm) was investigated for its ability to perform as a suitable adsorbent for removal of Eosine bluish from aqueous solution. The effect of adsorbent dose, contact time, stirring speed, pH and temperature was investigated using a batch adsorption technique. The results revealed the potential of roots, stem and leaves of *Phoenix dactylifera* (Date Palm) fiber, as a low cost sorbent for Eosine dye examined. Acidic pH (1), low temperature (10 ºC) and low stirring speed (240 rpm) were found to be favourable conditions for the adsorption of eosin dye on all the three adsorbents. Langmuir and Freundlich isotherm equations were applied for the equilibrium data. The comparative study showed that leaves were found to be best adsorbent for removing eosin dye from aqueous solution as compared to roots and stem of *Phoenix dactylifera*.

Key Words: Eosin bluish, Adsorption isotherm, Langmuir constants, Freundlich constants, Pseudo-second order kinetics, *Phoenix dactylifera* (Date Palm).

INTRODUCTION

Over 100,000 commercially available dyes exist and more than 700,000 tones per year are produced annually[1,2]. Through hundred of years, the scale of production and nature of dyes have widely changed and consequently the negative impact of dyes on the environment has increased. Adsorption treatment processes, which lower the concentration of dissolved organic compounds in water effluents are rapidly gaining importance[3,4]. For industrial liquid effluents, colour is the first indication of water pollution. The discharge of coloured waste is not only damaging the aesthetic nature of receiving streams, but is also toxic to aquatic life[5]. As a result of the low biodegradability of dyes, the conventional biological treatment process is not very effective in treating dye waste water[6]. Some of the physio-chemical methods that have been employed to remove dye from wastewater include chemical precipitation, coagulation and oxidation. However these methods are not economical. Adsorption seems to offer the best prospects over the other treatment techniques[5].

Leaves, stem and roots of *Phoenix dactylifera* are good adsorbents for the removal of flourescein[6]. In our laboratories, a series of applications for the utilization of various parts of *Phoenix dactylifera* and other biomasses are undergoing. The objective of this work is to investigate the effect of pH, contact time, stirring speed, adsorbent dose, temperature and initial dye concentration effects on leaves, stem and roots of *Phoenix dactylifera* as bio-sorbent.

EXPERIMENTAL

All chemicals used during experimental work were of analytical grade and were used as such without purification. Eosin bluish (λ_{max} = 515 nm, m.w. 624 g/mol), HCl (Merck, 11.6 M), NaOH (Merck). Double distilled water was used for the preparation of all types of solution and dilution when required.

Preparation of adsorbent: The roots, stem and leaves of *Phoenix dactylifera* (Date Palm) for the experiments were collected, grinded and then particle size between 50-80 mesh were obtained by passing material through standard steel sieves.

Preparation of aqueous dye solution: The dye, Eosin bluish was used without further purification. A stock solution of Eosin bluish was prepared in distilled water by dissolving 1 g of dye in 1000 mL of distilled water. A number of standard solutions were made from the stock solution in the concentration range 5-25 mg/L and a calibration curve was drawn by measuring the absorbance at λ_{max} = 515 nm.

Adsorption experiments: The adsorption studies were carried out at 25 ± 1 ºC. pH of the solution was adjusted with 0.1 N HCl or 0.1N NaOH. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture was filtered through filter paper[7] and dye concentration were determined in the filtrate using (Spectro UV-VIS Double Beam UVD-3500, Labomed. inco) at λ_{max} = 515 nm.

The effect of various parameters on the rate of adsorption process were observed by varying contact time, t (15-90 min), initial concentration of dye C_o (5-25 mg/L), adsorbent amount (0.4-1 g), initial pH of solution (1-5), agitation speed (120-480 rpm) and temperature (10-50 ºC). The solution volume (V) was kept constant (25 mL).

The dye adsorption capacity (% age) at any instant of time was determined by the following equation:

$$\text{Eosin bluish adsorption capacity (\%)} = \frac{C_o - C_e}{C_o} \times 100$$

where, C_o and C_e were the concentration of Eosin bluish at initial condition and at any instant of time respectively. To increase the accuracy of the data, each experiment was repeated 3 times.

RESULTS AND DISCUSSION

Effect of adsorbent size (mesh): Effect of adsorbent size was studied by adsorption of roots, stem and leaves of *Phoenix dactylifera* on Eosin bluish at three different mesh sizes. It was observed that adsorption yield increases with decreasing adsorbent size because small size of adsorbent increases surface area[7] and access to particle size is facilitated when their size is small. Maximum adsorption capacity was seen at 50-80 mesh size for roots, stem and leaves. Roots showed 71 %, stem showed 76 % and leaves showed 73 % adsorption capacity. Results are presented in Table-1 and Fig. 1.

TABLE-1
EFFECT OF VARIOUS PARAMETERS ON % AGE ADSORPTION

Size (mesh)	10-30	30-50	50-80				
Roots (% ads)	40.00	52.00	71.00				
Stem (% ads)	59.00	67.00	76.00				
Leaves (% ads)	44.12	67.00	73.00				
Time(mins)	15	30	45	60	75	90	
Roots (% ads)	52.00	67.00	60.00	50.00	47.00	47.00	
Stem (% ads.)	71.00	77.00	73.00	72.50	72.40	72.10	
Leaves(% ads.)	81.00	82.00	82.50	82.90	84.00	82.00	
Amount of Adsorbent(g)	0.55	0.60	0.65	0.70	0.80	0.90	1.00
Roots (% ads)	62.00	64.00	75.00	62.00	-	-	-
Stem (% ads)	72.00	71.00	70.00	69.00	-	-	-
Leaves (% ads)	73.00	78.00	-	78.00	79.00	81.00	80.00
Initial dye Concentration(ppm)			5	10	15	20	25
Roots(% ads)			68.00	70.00	70.20	71.00	72.00
Stem(% ads)			46.00	66.00	70.00	74.00	75.00
Leaves(% ads)			56.00	70.00	74.00	77.00	79.70

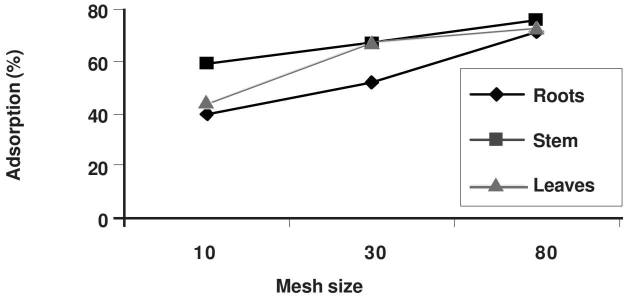

Fig. 1. Effect of adsorbent size on adsorption percentage of eosin [condition adsorbents amount 0.05-0.10 g, pH 3-4, Initial concentration 25 mg/L

Effect of contact time: Effect of contact time was studied by adsorption of roots, stem and leaves of *Phoenix dactylifera* on Eosin bluish in the range 15-90 min. The maximum adsorption (67 %) for roots was observed at 0.5 h, similarly stem showed maximum adsorption (77 %) after 0.5 h while it was (84 %) for leaves after 1.25 h. The results obtained are in agreement with the previous studies[8,9].

Effect of adsorbent dose: Effect of adsorbent dose was studied in the range 0.55 to 1 g. The contact period used for roots, stem and leaves was 30, 30 and 75 min, respectively. The maximum adsorption capacity for roots was at dose 0.65 g (75 %), for stem at 0.55 g (72 %) and for leaves at 0.90 g (81 %). The adsorption capacity increases at low adsorbent amount for roots and stem but for leaves at high adsorbent amount. The decrease in adsorbent dose at constant dye concentration and volume will lead to unsaturation of adsorbent sites through adsorption process[10,11]. Secondly, it may be due to particulate interaction such as aggregation resulting from high adsorbent dose[12]. Such aggregation would lead to a decrease in total surface area of the adsorbent and increase in diffusional path length[13]. Results are presented in Table-1 and Fig-2.

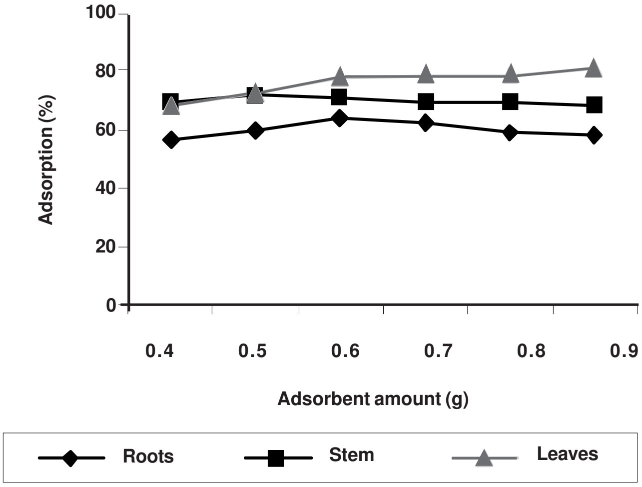

Fig. 2. Effect of adsorbent amount on adsorption percentage of eosin [contact time for roots 30, stem 30, leaves 1.25 h, pH 1, initial concentration 25 mg/L]

Effect of initial dye concentration: Effect of initial dye concentration was studied in the range 5 to 25 mg/L. The maximum adsorption capacity was observed at 25 mg/L. Roots showed 72 %, stem showed 75 % and leaves showed 79.70 % adsorption capacity. Adsorption capacity increases with increase in initial dye concentration due to availability of more active sites. Results are presented in Table-1 and Fig-3.

Effect of stirring speed: Effect of stirring speed was studied from 120 to 480 rpm. The maximum adsorption capacity was observed at 240 rpm. Roots showed 71 %, stem showed 76 % and leaves showed 83 % adsorption capacity. After 240 rpm the adsorption capacity decreased as all binding sites might have been occupied and no binding sites were further available. Results are presented in Table-2 and Fig. 4.

Effect of pH: Effect of pH was studied by adsorption of roots, stem and leaves of *Phoenix dactylifera* on Eosin bluish was observed in the range 1 to 5 (acidic). The contact period

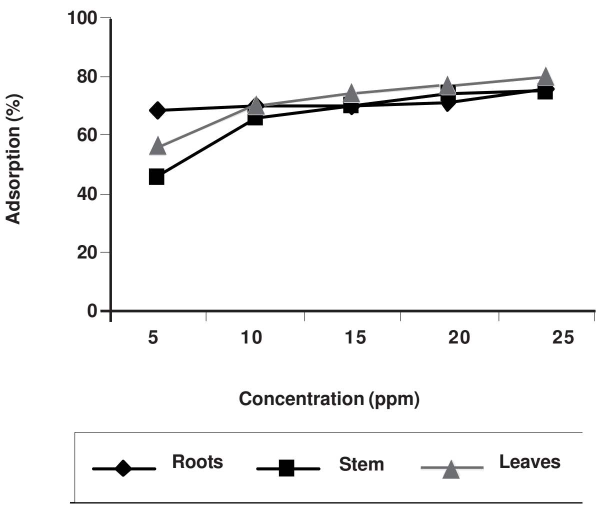

Fig. 3. Effect of initial dye concentration on adsorption percentage of eosin [condition adsorbents amount 0.55 g, contact time for roots 30, adsorbent amount 0.65 g contact time 30 for stem, leaves 0.5 h, 0.9 g amount of adsorbent]

TABLE-2
EFFECT pH, STIRRING SPEED AND TEMPERATURE ON % AGE ADSORPTION

pH	1	2	3	4	5
Roots (% ads)	97.00	77.00	63.00	62.80	62.40
Stem (% ads)	85.84	58.80	52.00	49.00	42.00
Leaves (% ads)	97.00	92.00	84.00	82.00	79.00
Speed(rpm)	120	240	360	480	
Roots (% ads)	68.00	71.00	67.00	56.00	
Stem (% ads)	70.00	76.00	72.80	72.00	
Leaves (% ads)	78.00	83.00	80.00	79.00	
Temperature (°C)	10	20	30	40	50
Roots (% ads)	64.00	63.00	68.00	60.80	60.00
Stem (% ads)	78.00	74.00	71.00	70.00	68.00
Leaves (% ads)	81.00	79.10	79.00	78.00	80.00

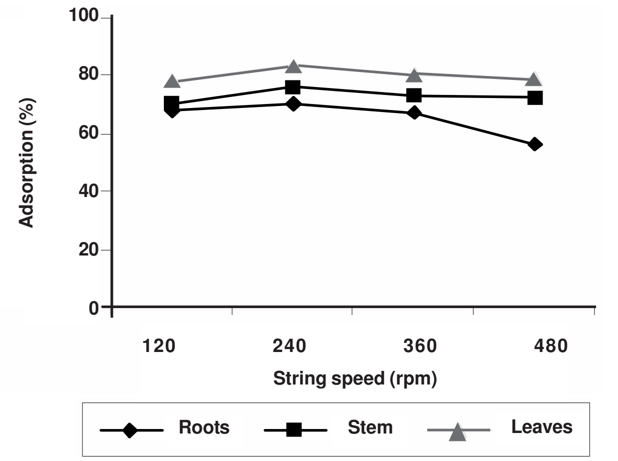

Fig. 4. Effect of stirring speed on adsorption percentage of eosin [condition adsorbents amount 0.55 g, contact time for roots 30, stem contact time 30, amount of adsorbent 0.65 g, leaves 1.25 h amount of adsorbent 0.9 g, concentration 25 mg/L]

used for roots, stem and leaves was 30, 30 and 75 min respectively. The maximum adsorption capacity was observed at pH = 1. For roots and leaves maximum adsorption capacity observed was 97 % and stem showed 85.84 %. Results are presented in Table-2 and Fig. 5.

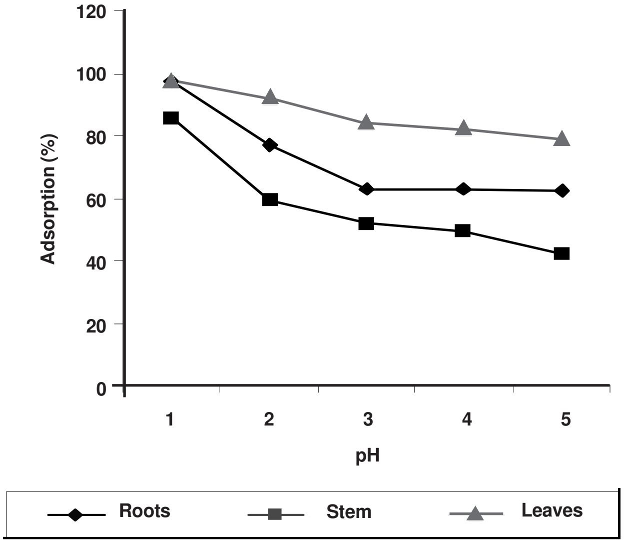

Fig. 5. Effect of pH on adsorption percentage of eosin [condition adsorbents amount 0.55 g, contact time for roots 30, adsorbent amount 0.65 g stem contact time 30, amount of adsorbent0.9 g contact time 75 min leaves, concentration 25mg/L]

Effect of temperature: Effect of temperature was studied by adsorption of roots, stem and leaves of *Phoenix dactylifera* on Eosin bluish was observed in the range 10 to 50 °C. The contact period used for roots, stem and leaves was 30, 30 and 75 min respectively. For roots the maximum adsorption capacity was observed at 30 °C (68 %), stem showed at 10 °C (78 %) and leaves at 10 °C (81 %). The decrease in adsorption capacity with temperature is due to enhancement of the desorption step in the adsorption mechanism indicating that the process is exothermic[14].

It is known that decreasing adsorption capacity with increasing temperature is mainly due to weakening of adsorption forces between the active sites on *Phoenix dactylifera* and anionic dye species and also between adjacent dye molecules on adsorbed phase. For a conventional mechanism of physisorption system, increase in temperature usually increases the rate to approach to equilibrium, but decreases the equilibrium capacity[15].

Adsorption isotherm: Analysis of adsorption isotherm have also been analyzed by two well known adsorption isotherm models. The Langmuir equation is applicable for monolayer adsorption on a surface containing a finite number of identical adsorption sites[16].

$$C_e/q = 1/bQ_{max} + C_e/Q_{max} \qquad (1)$$

where, Q_{max} = adsorption capacity, b = surface energy of adsorption (ratio of adsorption to desorption rate), q = amount of dye adsorbed (C_{ads}), C_e = equilibrium concentration of dye (mq/L). The adsorption plot parameters were calculated by plotting of q/ C_e *versus* q gives a straight line with b = slope/ intercept and Q_{max} = 1/ slope[17,18]. The adsorption capacity q (g/g^{-1}) was calculated by the formula:

$$q = \frac{(C_o - C_e).V}{w.1000} \qquad (2)$$

where, C_o and C_e are the initial and final concentrations of dye in solution (mg/dm^3) respectively, V is the volume of the solution (dm^3) and w is the mass of dry adsorbent used (g)[19,20].

Freundlich expression is an equation based on sorption on a heterogeneous surface. The general Freundlich equation is as follows:

$$q = K_f C_e^{1/n} \tag{3}$$

The linear form of this equation is:

$$\log q = \log K_f + 1/n \log C_e \tag{4}$$

where, q = amount of dye adsorbed, C_e = equilibrium concentration of dye, K_f and n are Freundlich isotherm constants depending on temperature and adsorbent- adsorbate system. A linear plot of loq q verses log C_e gives values of K_f and n, where K_f = antilog (intercept) and n = 1/ slope[17,21].

The coefficient of correlation R^2 indicate that the Langmuir isotherm fitted the adsorption data of roots, stem and leaves of *Phoenix dactylifera* on flourescein better than Freudlich isotherm. Q_{max} is called Langmuir monolayer adsorption capacity, the value is 0.0384 g of dye per gram of roots, 0.14169 g of dye per gram of stem and 0.1623 g of dye per gram of leaves. b is Langmuir isotherm constant is 16.7603 dm^3/g for roots, 38.20 dm^3/g for stem and 44.3574 dm^3/g for leaves. Higher values of Q_{max} and b more effective in terms of capacity of adsorbent[22]. So leaves have maximum adsorption capacity as compared to stem and roots for the removal of Eosin bluish.

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The value of 'n' for roots is 0.8909, stem is 1.06456 and for leaves is 0.491536. The higher value of Q_{max} and lower value of 'n' estimated for leaves indicates the greater tendency to remove Eosin bluish from aqueous solution as compared to stem and roots[9]. The results are presented in Table-3 and Figs. 6-11.

TABLE-3
LANGMUIR, FREUNDLICH AND PSEUDO-SECOND ORDER KINETIC PARAMETERS FOR ADSORPTION OF EOSIN BLUISH ON ROOT, STEM AND LEAVES OF *Phoenix Dactylifera*

	Langmuir adsorption isotherm			Freundlich adsorption isotherm			
Adsorbent	Q_{max} (g /g)	b (dm^3/g)	R^2	K_f	n	R^2	1/n
Root	0.0384	16.7603	0.9989	16.0816	0.8909	0.9482	1.1224
Stem	0.1416	38.20	0.9996	2.4248	1.06456	0.2940	0.93935
Leaves	0.1623	44.3574	0.9844	80.697	0.441536	0.9602	2.2648

Pseudo-second order kinetic model	Roots	Stem	Leaves
q_e(g/g)	0.39394	0.64776	0.46406
k_2 (g/g min)	0.9149	1.448113	5.3235
R^2	0.9586	0.9992	0.9996

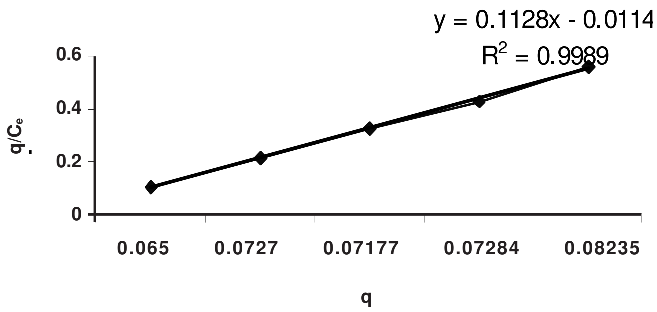

Fig. 6. Langmuir adsorption isotherm for roots

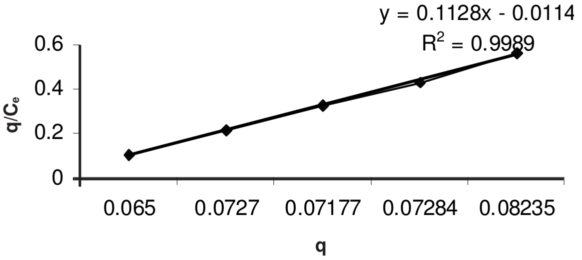

Fig. 6. Langmuir adsorption isotherm for roots

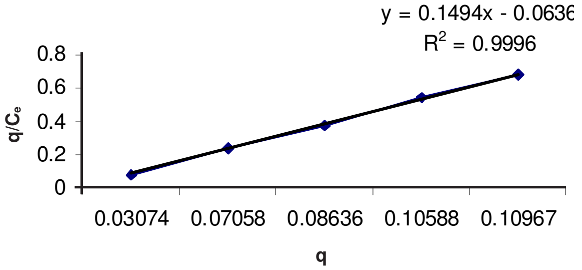

Fig. 7. Langmuir adsorption isotherm for stem

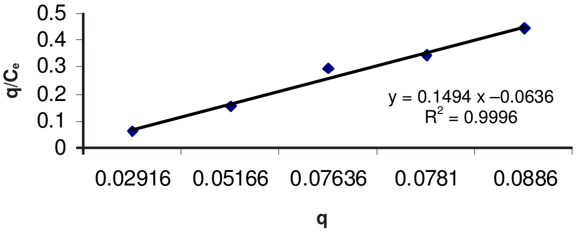

Fig. 8. Langmuir adsorption isotherm for leaves

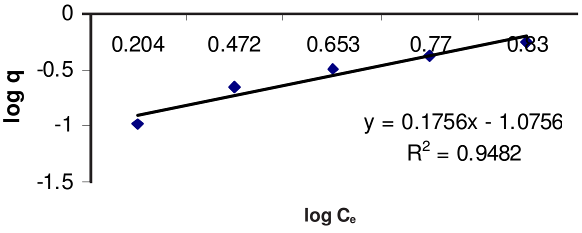

Fig. 9. Freundlich adsorption isotherm for roots

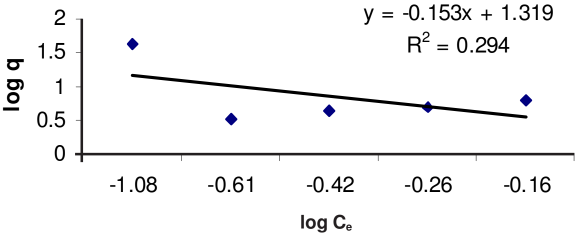

Fig. 10. Freundlich adsorption isotherm stem

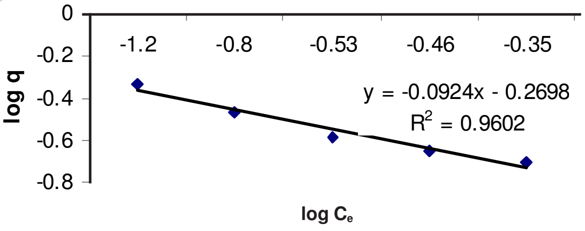

Fig. 11. Freundlich adsorption isotherm for leaves

Kinetic studies: Modeling of kinetic data is fundamental for the industrial application of sorption since it gives information for comparison among different biomaterials under different operational conditions for designing and optimizing operational conditions for pollutant removal from wastewater[23].

Pseudo-second order kinetics was applied to the data. The pseudo-second order chemisorption kinetic equation[24] is expressed as:

$$\frac{d}{dt}qt = k_2(q_e - q_t)^2 \qquad (5)$$

where, q_e and q_t are adsorption capacities at equilibrium and at time, t respectively and k_2 is the rate constant of the pseudo-second order adsorption. For the boundary conditions t = 0 to t = t and qt = 0 to $q_t = q_t$, the integrated form of eqn. 5 becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

The plot of t/q_t *vs* 't' of eqn. 6 gives a linear relationship, from which qe and k_2 can be determined from slope and intercept of the plot respectively. q_e = 1/ slope and k_2 = slope^2/ intercept[17].

Pseudo-first order model cannot describe the adsorption kinetics of the Eosin bluish. Linear regression of the observed values t/q_t on 't' afforded lines with the coefficients of determination better, allowing the estimation of the amount of dye adsorbed at equilibrium and the rate constant. It is clearly found that the sorption of the anionic dye is better described by pseudo-second order reaction. Furthermore the pseudo-second order is based on the assumption that sorption follows a second order mechanism, with chemisorption as the rate limiting step. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites[25]. Results are presented in Table-3 and Figs. 12-14.

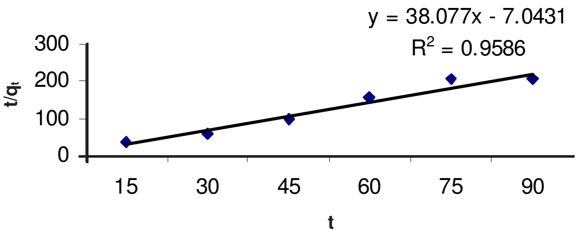

Fig. 12. Pseudo-second order plot for roots

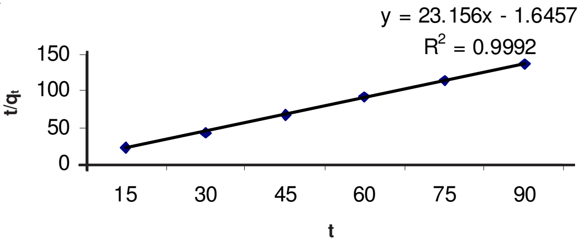

Fig. 13. Pseudo-second order plot for stem

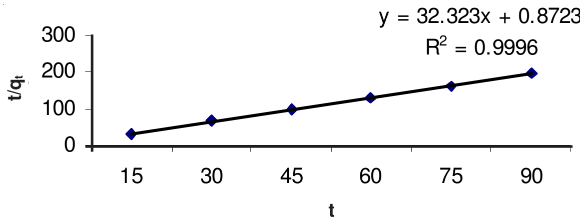

Fig. 14. Pseudo-second order plot for leaves

Conclusion

It is concluded that the absorbents are very cheap and cost effective materials for the removal of eosin dye because roots, stem and leaves of *Phoenix dactylifera* are easily available in Pakistan. Removal of dye is higher at an optimum pH 1. The comparative study showed that leaves were found to be best adsorbent for removing eosin dye from aqueous solution as compared to roots and stem of *Phoenix dactylifera*.

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