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Adsorption Studies of Flourescein on Roots, Stem and Leaves of *Phoenix dactylifera*

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The adsorption studies of roots, stem and leaves as adsorbents to remove flourescein dye from its aqueous solution has been carried out as a function of adsorbent dose, contact time, stirring speed, pH and temperature. Acidic pH (3-4), low temperature (10-30 ºC) and low stirring speed (120-240 rpm) were found to be favourable conditions for the adsorption of flourescein dye on all the three adsorbents. The maximum adsorption 100 % at 1 h, 96.7 % at 4 h and 91 % at 2.5 h has been observed for roots, stem and leaves of *Phoenix dactylifera*, respectively. The adsorption equilibrium process has been described well by using Langmuir, Freundlich adsorption isotherms and pseudo-second order kinetics. Present studies showed that roots can be used as low cost adsorbent for the removal of flourescein dye from its aqueous solution as compared to roots and stem.

Key Words: Flourescein, Adsorption isotherm, Langmuir and Freundlich constants, *Phoenix dactylifera*.

INTRODUCTION

Over 100000 commercially available dyes exist and more than 700000 tones dyes are produced annually[1,2]. Due to their water solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that 2 % of dyes that are produced are discharged directly in aqueous effluents[3]. The discharge of dyes into water course is a serious problem threatening the water supply and quality. Increasing concentration of these dyes in water constitute a severe health hazard due to non-degradability, toxicity, accumulation and magnification throughout the food chain. Colour removal from textile effluents has been the subject of great attention in the last few years, not only due to its toxicity but also mainly due to its visibility[4]. Through hundreds 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[5,6] in water effluents, are rapidly gaining importance. Large volumes of wastewater are therefore expected to be generated during the dying and finishing processes which are usually characterized by components high in coloured organic content[7]. It is expected that this generated waste water may contain as much as 10-15 % of the dyes released during the dyeing processes[8]. Majority of these dyes are synthetic in nature and are usually composed of aromatic rings in their structure, which makes them carcinogenic, mutagenic[9], inert and non-biodegradable when discharged into waste streams[10]. Therefore an attempt has been made in this studies to use different parts of *Phoenix dactylifera* which are abundantly available in Pakistan and are low cost for the removal of flourescein dye. The objective of this work is to compare the results shown by root, stem and leaves of *Phoenix dactylifera*. This dye was chosen because of its structures and is commonly present in dyes of the textile industry. The pH, contact time, stirring speed, adsorbent dose, temperature and initial dye concentration effects were studied to investigate the adsorption behaviour of root, stem and leaves of *Phoenix dactylifera*.

EXPERIMENTAL

All chemicals used were of analytical grade and were obtained from E-Merck/BDH/Fluka. All the apparatus used throughout the experimental work had standard quick fit joints and were dried at 110 ºC. The leaves, roots and stem of *Phoenix dactylifera* used in the experiments were obtained from indigenous resources of Pakistan.

Preparation of adsorbent: The roots, stem and leaves of *Phoenix dactylifera* used in the experiments were collected and washed through with distilled water and then with deionized water to remove foreign impurities. They were then dried in oven at 110 ºC until all moisture is evaporated. The dried parts of *Phoenix dactylifera* were ground and different particle size between 50-80 mesh were obtained by passing material through standard steel sieves.

Preparation of standard dye solution: The flourescein dye was used without further purification. A stock solution of dye was prepared in ethanol by dissolving 1 g of dye in 1000 mL of ethanol. 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} = 480 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 0.1 N NaOH. A known amount of adsorbent was added to sample[11] and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered through ordinary filter paper[12] and dye concentration were determined in the filtrate using Spectro UV-vis double beam UVD-3500, Labomed, Inc. at λ_{max} = 480 nm. The effect of various parameters on the rate of adsorption process were observed by varying time, t (30-300 min), initial concentration of dye C_0 (5-25 mg/L), adsorbent amount (0.01-0.15 g), initial pH of solution (1-5), agitation speed (120-480 rpm) and temperature (0-50 ºC). The solution volume (V) was kept constant (15 mL).

The dye adsorption at any instant of time was determined by the following equation:

$$\text{Flourescein adsorption capacity} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C_0 and C_e were the concentration of dye 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 particle size on adsorption experiments were performed with different mesh sizes of *Phoenix dactylifera*. The results are shown in Table-1 and Fig. 1. According to which it was observed that adsorption

TABLE-1
EFFECT OF VARIOUS PARAMETERS ON PERCENTAGE ADSORPTION

Size (mesh)	10-30		30-50		50-80	
Roots (% ads.)	58.92		83.32		92.6	
Stem (% ads.)	51.08		77.12		82.72	
Leaves (% ads.)	44.12		67.00		73.00	
Time (min)	30	60	120	180	240	300
Roots (% ads.)	90.04	100	98.63	98.28	–	–
Stem (% ads.)	94.00	95.3	95.68	95.88	96.7	96.4
Leaves (% ads.)	82.68	82.76	89.24	90.68	90.2	85.12
Amount of adsorbent (g)	0.025	0.05	0.075	0.10	0.125	0.150
Roots (% ads.)	72.52	90.20	91.96	92.60	91.48	79.28
Stem (% ads.)	83.00	85.40	84.80	84.00	–	–
Leaves (% ads.)	76.44	84.00	73.36	61.08	53.44	37.40
Initial dye conc. (ppm)	5	10	15	20	25	
Roots (% ads.)	77.4	85.4	88.6	99.27	99.33	
Stem (% ads.)	96.92	96.44	95.78	95.62	94.76	
Leaves (% ads.)	90.72	93.51	94.12	95.46	94.68	

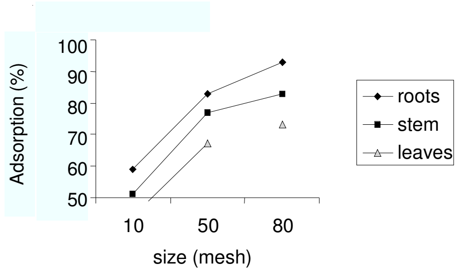

Fig. 1. Effect of adsorbent size on adsorption capacity of fluorescein

yield increases with decreasing adsorbent size because small size of adsorbent increases surface area[12] and access to the particle pore is facilitated when their size is small. The comparative study shows that roots, stem and leaves of *Phoenix dactylifera*, all had maximum adsorption capacity at 50-80 mesh size. Roots show 92.6 %, stem shows 82.72 % and leaves show 73 % adsorption capacity. The comparative study showed that effect of mesh size on the adsorption capacity of dye observed the following order, roots > stem > leaves.

Effect of contact time: Effect of contact time was one of the effective factors in adsorption process. The adsorption capacity of flourescein was studied as a function of time in the range of 30-300 min. The results obtained are presented in Table-1 and Fig. 2. Roots showed maximum adsorption capacity of 100 % (in least time *i.e.*, 1 h), stem showed 96.7 % (in 4 h) and leaves showed 90.68 % (in 2 h). The contact period[11,13] for roots, stem and leaves were observed to be 1, 4 and 2 h, respectively. Comparative study showed that effect of time on adsorption capacity of dye observed the following order, roots > stem > leaves.

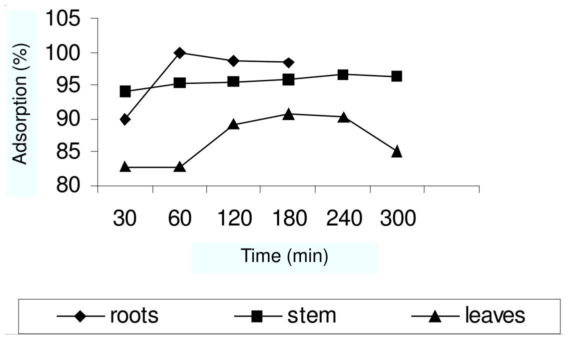

Fig. 2. Effect of contact time on adsorption capacity of fluorescein

Effect of adsorbent dose: The effect of variation in the adsorbent amount on the adsorption process flourescein was studied with different adsorbent amount in the range of 0.01-0.15 g. The contact period used for roots, stem and leaves is 1, 4 and 2 h, respectively. The results obtained are presented in Table-1 and Fig. 3. The adsorption capacity increases at low adsorbent amount of 0.05 g for stem and leaves and for roots at high adsorbent amount of 0.1 g. The decrease in adsorption capacity may be attributed to two reasons first, the increase in adsorbent dose at constant dye concentration and volume may lead to unsaturation of adsorbent sites through adsorption process[14,15] and secondly may be due to particulate interaction such as aggregation resulting from high adsorbent dose[16]. Such aggregation would lead to a decrease in total surface area of the adsorbent and an increase in diffusional path length[14]. Roots

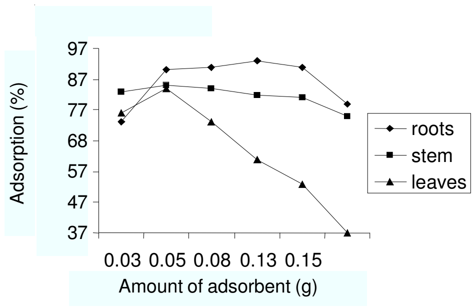

Fig. 3. Effect of adsorbent amount on adsorption capacity of flourescein

show maximum adsorption capacity of 92.60 % (at 0.1 g of adsorbent), stem shows 85.4 % (at 0.05 g of adsorbent) and leaves show 84.00 % (at 0.05 g of adsorbent). Comparative study showed that effect of adsorbent dose on adsorption capacity of dye observed the following order, roots > stem > leaves.

Effect of initial dye concentration: Initial dye concentration was one of the effective factors on adsorption efficiency. The adsorption capacity of flourescein was studied as a function of initial dye concentration in the range of 5-25 mg/L. The contact period used for roots, stem and leaves is 1, 4 and 2 h, respectively. The results obtained have been represented in Table-1 and Fig. 4. In case of roots the adsorption capacity increases with increase in initial dye concentration due to the availability of more active sites while for stem and leaves adsorption capacity increases with increase in initial dye concentration and then starts to decrease due to unavailability of active sites. It further showed a fluctuation in adsorption capacity of dye. The fluctuation may be as a result of desorption occurring along side of adsorption[13]. Roots showed maximum adsorption capacity of 99.33 % (at 25 mg/L), stem showed 96.92 % (at 5 mg/L) and leaves showed 96.46 % (at 20 mg/L). Comparative study showed that effect of adsorbent dose on adsorption capacity of dye observed the following order, roots > stem > leaves.

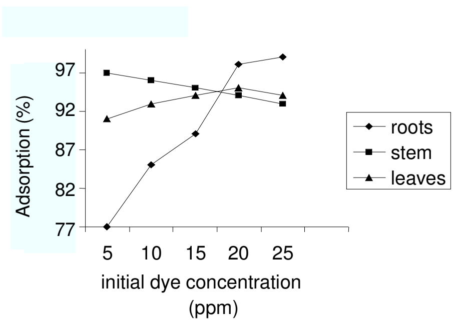

Fig. 4. Effect of initial dye concentration on adsorption capacity of flourescein

Effect of pH: The pH of the aqueous solution was an important parameter that controlled the adsorption process. The adsorption capacity of flourescein was studied as a function of pH in the range of 1-5. The contact period used for roots, stem and leaves is 1, 4 and 2 h, respectively. The results obtained are given in Table-2 and graphically represented in Fig. 5. As the dye is anionic so the adsorption capacity is determined at acidic range. Roots showed maximum adsorption capacity of 94.36 % (at pH = 3), stem showed 86.12 % (at pH = 3) and leaves showed 98.87 % (at pH = 4). The results show a tendency towards greater adsorption for anionic dyes (in the pH range of 3-4). At a pH below 3 the anions in the solution compete with anionic dye and hence decreases adsorption[11].

TABLE-2
EFFECT OF VARIOUS PARAMETERS ON PERCENTAGE ADSORPTION

pH	1	2	3	4	5	
Roots (% ads.)	91.00	92.2	94.36	94.12	93.36	
Stem (% ads.)	82.08	85.00	86.12	85.76	85.36	
Leaves (% ads.)	97.96	98.21	98.39	98.87	98.81	
Speed (rpm)	120	240	360	480		
Roots (% ads.)	90.72	92.36	91.04	89.76		
Stem (% ads.)	92.56	85.32	85.24	83.12		
Leaves (% ads.)	98.00	96.24	92.78	90.80		
Temp. (ºC)	0	10	20	30	40	50
Roots (% ads.)	88.88	89.68	91.8	92.56	92.36	90.12
Stem (% ads.)	87.68	94.92	91.81	90.20	89.00	87.76
Leaves (% ads.)	92.28	92.76	93.72	95.76	95.04	93.48

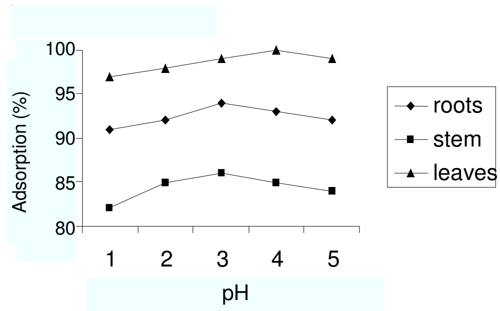

Fig. 5. Effect of pH on adsorption capacity of flourescein

Effect of stirring speed: The effect of variation in the stirring speed on the adsorption process of flourescein was studied at four different stirring speeds in the range (120-240 rpm). The contact period used for roots, stem and leaves is 1, 4 and 2 h, respectively. The results obtained are given in the Table-2 and graphically represented in Fig. 6. For stem (maximum adsorption was 92.56 %) and leaves (maximum adsorption was 98.00 %), the dye was best adsorbed at low stirring speed 120 rpm, after 120 rpm it decreased and no further increase in adsorption was observed. This decrease in adsorption efficiency can be explained as all binding sites might have been occupied and no binding sites were further available. The adsorption of dye by roots (maximum adsorption was 92.36 %) is faster at 240 rpm stirring speed than at lower ones.

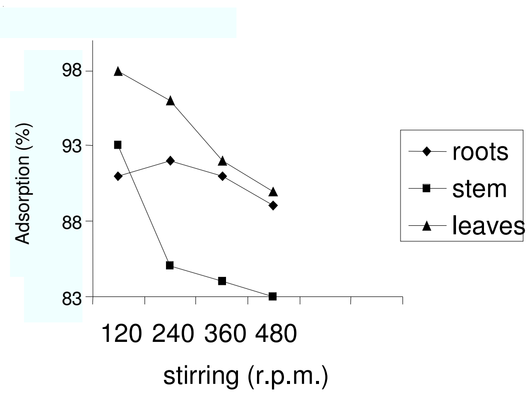

Fig. 6. Effect of stirring speed on adsorption capacity of flourescein

Effect of temperature: Temperature is one of the important factor that effect the adsorption process. The percentage of flourescein adsorption was studied as a function of temperature in the range of 0-50 ºC. The contact period used for roots, stem and leaves is 1, 4 and 2 h, respectively. The results obtained are represented in Table-2 and Fig. 7. For stem, maximum adsorption (94.92 %) was found at 10 ºC while for roots (92.56 %) and leaves (95.76 %), it was found to be maximum at 30 ºC. The decrease in adsorption capacity with temperature is due to the enhancement of the desorption step in the adsorption mechanism indicating that the process is exothermic[17]. 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[10].

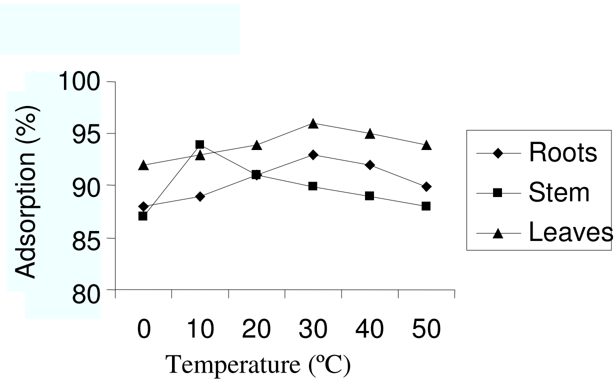

Fig. 7. Effect of temperature on adsorption capacity of flourescein

Adsorption isotherm: Analysis of adsorption data is important in order to develop an equation which accurately represents the results. Experimental data was correlated with Langmuir and Freundlich isotherm models. The Langmuir equation is applicable for monolayer adsorption on a surface containing a finite number of identical adsorption sites[18,19].

The Langmuir model is described by the following linear equation; by using this choice of equation it tends to minimize deviations resulting in best error distribution[20]:

$$\frac{C_e}{q} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \quad (1)$$

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 (mg/L). The adsorption plot parameters were calculated by ploting of q/C_e *verses* q gives a straight line with b = slope/intercept and Q_{max} = 1/slope[21,22].

The adsorption capacity q (g/g^{-1}) was calculated by the formula:

$$q = \frac{(C_0 - C_e) \times V}{w \times 100} \quad (2)$$

where C_0 and C_e are the initial and final concentrations of dye in solution (mg/dm^3), respectively, V = volume of the solution (dm^3) and w = mass of dry adsorbent used (g)[23,24].

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

$$q = K_f C_e^{1/n} \quad (3)$$

The linear form of this equation is:

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

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[21,25]. The coefficient of correlation R^2 indicates that the Freundlich isotherm fitted the adsorption data of roots, stem and leaves of *Phoenix dactylifera* on flourescein better than Langmuir isotherm. The K_f values range of 0.5802-5.6156 obtained in this study is similar to the values reported by adsorption of congo red on bamboo dust, coconut shell, groundnut shell and rice husk[26]. Q_{max} is called Langmuir monolayer adsorption capacity, the value is 2.4254 g/g for roots, 1.6484 g/g for stem and 0.0445 g/g for leaves. Value of b which is Langmuir isotherm constant is 0.2411dm^3/g for roots, 0.6608 dm^3/g for stem and 5.8804 dm^3/g for leaves. Higher values of Q_{max} and b more effective in terms of capacity of adsorbent[27]. Maximum adsorption capacity in case of roots indicates that more active sites of roots are available for dye. The results of Langmuir isotherms are given in Table-3 and graphically represented in Figs. 8-10. The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. The n value for roots is 0.5448, for stem is 0.659 and for leaves is 1.0511. The lower n values and higher Q_{max} values estimated for roots indicates a superior performance for adsorption of flourescein from aqueous solution. However, the roots, stem and leaves are of same mesh size (50-80), thus roots tend to have greater pore volume and better performance. The results of Freundlich isotherms are graphically represented in Table-3 and Figs. 11-13.

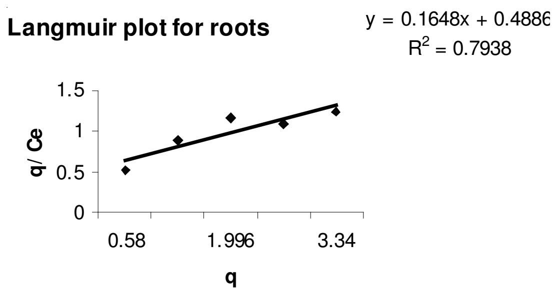

Fig. 8. Langmuir adsorption isotherm for roots of *Phoenix dactylifera*

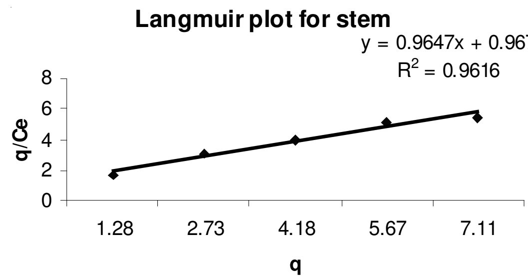

Fig. 9. Langmuir adsorption isotherm for stem of *Phoenix dactylifera*

TABLE-3
LANGMUIR, FREUNDLICH AND PSEUDO SECOND ORDER KINETICS PARAMETERS FOR ADSORPTION OF FLUORESCEIN 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	2.4254	0.241186	0.7938	0.5802	0.54482	0.9342	1.8354
Stem	1.6484	0.66089	0.9616	5.6156	0.659	0.0714	1.5174
Leaves	0.0445	5.8804	0.8929	0.8016	1.0511	0.9342	0.9513
Pseudo-second order kinetic model			Roots		Stem		Leaves
		q_e (g/g)	3.810		7.295		9.142
		k_2 (g/g min)	45.2		182.2		17.377
		R^2	0.9998		0.9998		0.9445

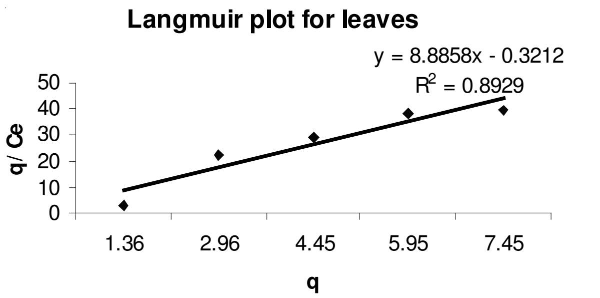

Fig. 10. Langmuir adsorption isotherm for leaves of *Phoenix dactylifera*

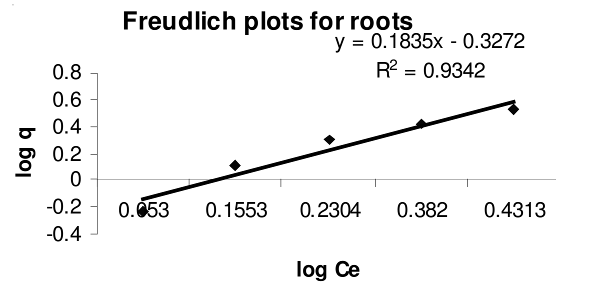

Fig. 11. Freundlich adsorption isotherm for roots of *Phoenix dactylifera*

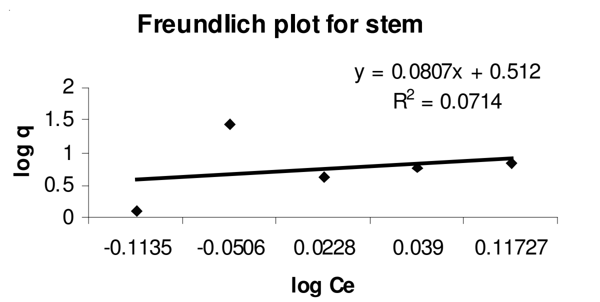

Fig. 12. Freundlich adsorption isotherm for stem of *Phoenix dactylifera*

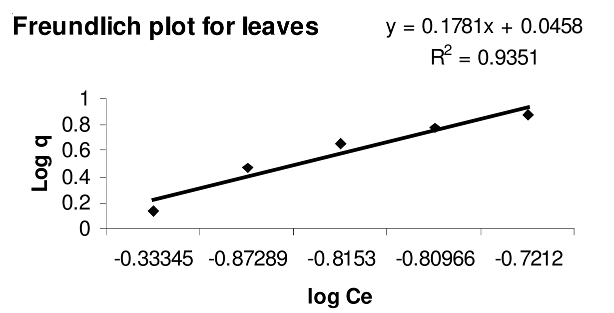

Fig. 13. Freundlich adsorption isotherm for leaves of *Phoenix dactylifera*

Kinetic studies: The experimental data was fitted to pseudo-second order kinetic model. The pseudo-second order chemisorption kinetic equation[28] is expressed as:

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

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

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

The plot of t/qt *versus* t of eqn. 6 gives a linear relationship from which q_e and k_2 can be determined from slope and intercept of the plot, respectively; q_e = 1/slope and k_2 = slope^2/intercept[22]. The corresponding kinetic parameters derived from this model are present in Table-3 and Figs. 14-16. The plots fit linearly to this model indicating that adsorption occurred in at least two steps.

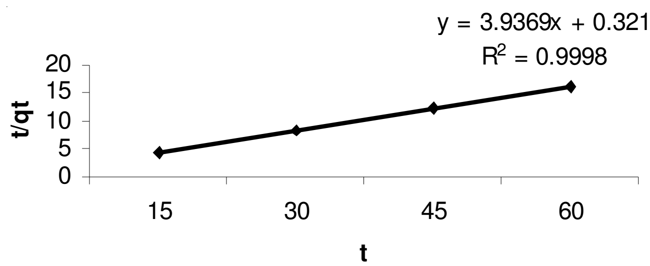

Fig. 14. Pseudo-second order adsorption kinetic of flourescein on roots of *Phoenix dactylifera*

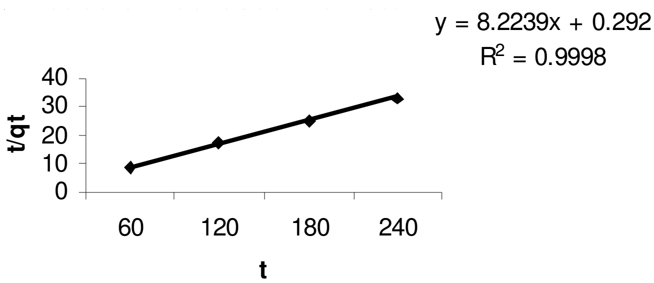

Fig. 15. Pseudo-second order adsorption kinetic of flourescein on stem of *Phoenix dactylifera*

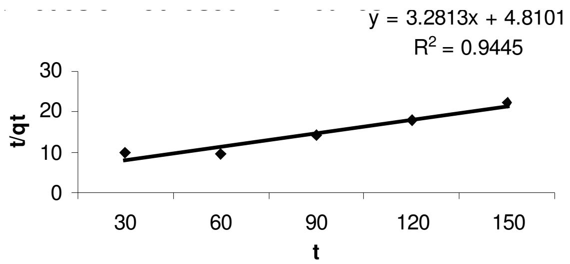

Fig. 16. Pseudo-second order adsorption kinetic of flourescein on leaves of *Phoenix dactylifera*

Conclusion

It is concluded from discussion that the all the three absorbents are cheap and cost effective materials for the removal of flourescein dye because roots, stem and leaves of *Phoenix dactylifera* are easily available in Pakistan. The comparative study showed that roots are best adsorbent for removing fluorescein dye from aqueous solution as compared to stem and leaves.

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