Potential of *Polyalthia longifolia* Branches as a Biosorbent to Remove Textile Brilliant Yellow Dye from Aqueous Media

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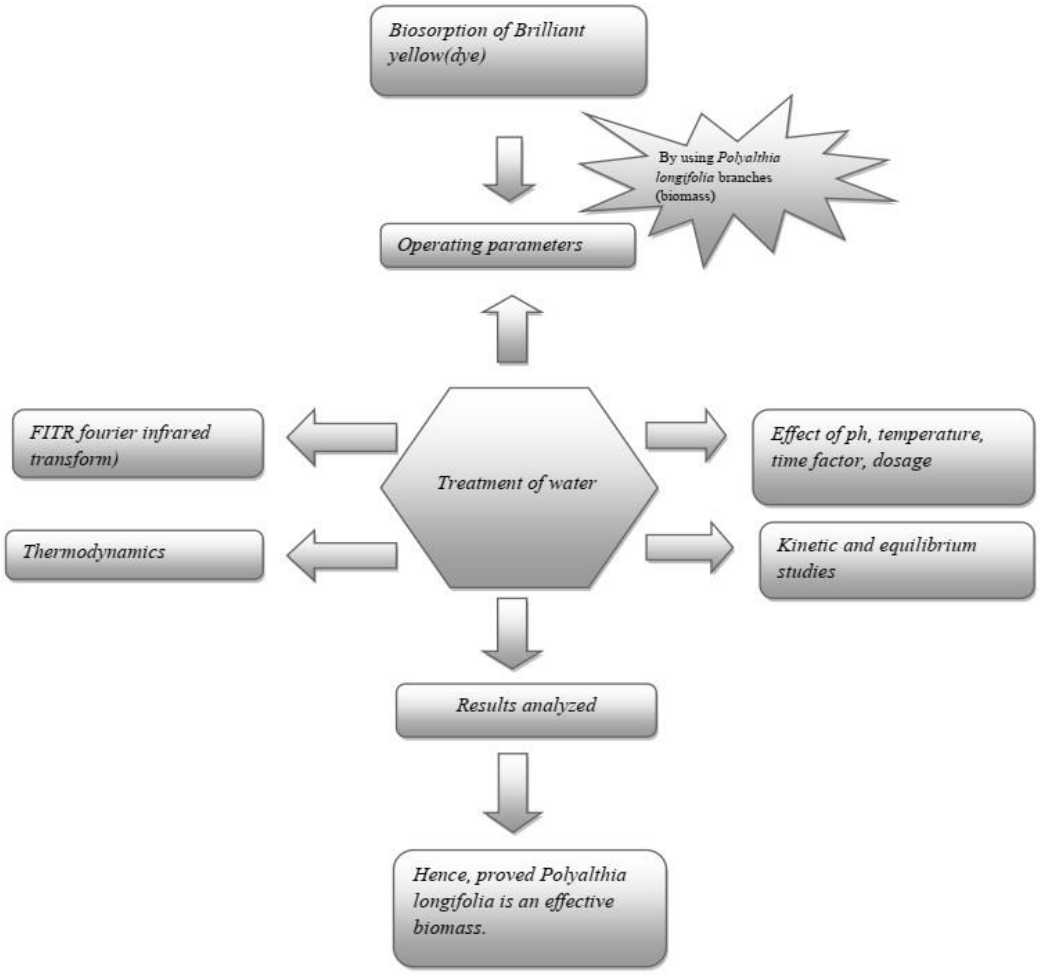
Summary: This study was conducted to analyze the efficacy of *Polyalthia longifolia* branches as an effective biosorbent for elimination of textile dye stuff brilliant yellow. Different operating conditions were tested (adsorbent dose, dye concentration, contact time, pH and temperature) to investigate their relationship with adsorption strength of *Polyalthia longifolia* and subsequently to eliminate toxic color. The absorbent was also characterized by Fourier Transform Infrared (FTIR). Optimum adsorption was observed at pH 6. Model of kinetic explored the adsorption data showing pseudo 2nd order with high correlation coefficient R^2 of 0.996. Langmuir model followed well to equilibrium data relative to Freundlich and Temkin models. Thermodynamic property was also observed, where Gibbs free energy, entropy and enthalpy were analyzed. Through Gibbs free energy it was found that absorbent has endothermic nature. Thermodynamic properties have depicted that adsorption process was natural, endothermic and suitable for treatment of toxic dye.



Key words: *Polyalthialongifolia*, Brilliant yellow, Adsorption, Kinetics studies, Adsorption isotherm

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Introduction

Biosorption is a process designed for elimination of effluents by using adsorbent. Concentration of effluents in the environment is increasing by rapid industrialization such as textile, paper, food and cosmetics and many others [1-3]. The wastewater from such industries contains high levels of heavy metals, chemicals, sludge, organic pollutants and various toxic dyes and their disposal into natural water bodies cause serious threat to environment [1, 4, 5] because wastewater interferes with light penetration in water bodies. Due to presence of sludge, photosynthetic activity stops in the aquatic ecosystem. The bright colored unfixed dyes present in wastewater have low adsorption properties and convert into carcinogenic amines which are highly hazardous in nature. Textile industry produces large amounts of polluted wastewater and consisting huge amount of toxic colorant, suspended Solid, Surfactants, and organic matter with high chemical oxygen demand (COD) and high pH [6,7].

Toxic dyes present in wastewater cause contamination of ground and surface water which in return affect our drinking water quality [8,9]. So, it is necessary to eliminate toxic dyes from industrial wastewater prior to the discharge into natural water channels by using any appropriate technology. Different physiochemical processes are being used for the removal of effluent dyes. The most commonly used physical methods are ozonation, electro-coagulation, photo-catalysis and adsorption [10]. Among these methods, adsorption is a simple and cost-effective technique with high removal efficiency [11-13].While chemical methods include oxidation, reduction, ion-exchange, electrolysis, and catalysis. Generally, dyes are classified into three major categories as cationic, anionic and ionic. Here, we described anionic dye. Brilliant yellow is an anionic azo dye with high water solubility [14-17]. It may cause skin irritation or inflammation of eyes. Molecular weight of brilliant yellow is 624.55g/mol and its color changes from orange to reddish orange at pH 6.5-8.5.

Many adsorbents are being used after modification (Fig 1) for removal of brilliant yellow dye such as sorgum, cardamom leaves, corn cobs, rice husks, plants leave and seed [18-19]. However, *Polyalthia longifolia* (lofty evergreen plant) is a locally available biosorbent with high adsorption potential. Thus, *P. longifolia* branches can be used as biosorbent for the removal of brilliant yellow from waste water. According to report of USGS, there is 2.5% fresh water is available so industrial wastewater should be treated to perverse our natural environment.

Previous studies have focused on chemical treatment of textile wastewater to remove brilliant yellow dye. In chemical treatment different chemicals are being used that cause toxicity of the other ecosystems. Hence, the present study was aimed to bioremediate textile industry wastewater in an environmentally sustainable by using novel *P. longifolia*. The *P. longifolia* branches have proven effective against removal of brilliant yellow dye from aqueous media.

Material and methods

Preparation of biosorbent and standards sample

To prepare modified biomass of *P. longifolia* branches was collected from local area of Lahore, Pakistan. At first, the branches were washed to remove dirt particles and then oven dried. Dried *P. longifolia* branches were ground into powder form, sieved through mesh 60 micron and washed with cold distilled water. Then, soaked in warm distilled H_2O for a day to remove color of biomass. It was also filtered by vacuum distillation. The resulting biomass was dried in the oven at 70℃ temperature. Dry biomass was kept in storing container.

Chemicals used for this study were brilliant yellow (C.I), of molecular weight 624.55 g/mol, HCl (merck 1M, NaOH, merck 40 g/mol). Standard solution of brilliant yellow(dye) of 1000ppm concentration was prepared. Further, dilutions (5 ppm, 10 ppm, 15 ppm, 25 ppm) were prepared from the standard dye solution.

Biosorption experiment

An easily available biosorbent was selected for the adsorption study. *P.longifolia* branches were washed, dried at 70℃ in an oven, grinded to fine powder and sieved to mesh60 microns. Various parameters of adsorption were determined in this technique. Biosorbent of known mass was added to prepared dye solution and allowed to reach equilibrium adsorption. The mixtures were filtered and the dye concentrations in the filtrate was determined by measuring the absorbance of brilliant yellow at 400nm using UV/Vis double beam spectrophotometer (Labomed, UVD-3500) (Table-1). The pH of solution was adjusted by adding).1N

NaOH and HCl and determined by using pH meter (Adwa,130). The effects of adsorbent dosage, contact time, pH of the solution and temperature properties were studied as described by Fan et al. [20]. Range of adsorbent "0.1-0.9g/50ml", contact time (05-45 minutes), pH of the solution (01-10), temperature (15°C) and all these solutions were kept at initial concentration of 25 ppm. The percentage removal was calculated by the following formula.

$$\% \text{ removal} = \frac{C_\circ - C_e}{C_\circ} \times 100$$

where C_o = initial concentration,C_e = concentration at equilibrium. Widely utilization of *P. longifolia* branches as biosorbent is well known due to great absorbance ability, efficiency and low-cost. All experiments were performed with three replicates and to achieve best results experiments were repeated five times for accuracy [21-22].

Table-1: Apparatus used for determination of experimental parameters.

Apparatus	Manufacturer
UV/Vis Double Beam spectrophotometer	**Labomed, UVD-3500**
pH meter	**Adwa,130**
Orbital shaker	**VORTEX-747**
FT-IR	**Agilent technologies**

Result and Discussion

Effect of adsorbent dosages and pH factor on dye adsorption

Initial concentration of dye is considered an important factor that affects adsorption efficiency. So, effect of dose amount on adsorption was studied at initial concentration of dye (25mg/L). It was observed by varying the amount of adsorbent in the range of0.1-0.9. Maximum % removal of brilliant yellow was 95% from an initial concentration of 25 mg/L. In the present study, it was observed that adsorption of dye increased with increased dose of adsorbent [Fig 2(a)]. Effect of pH was studied at an initial adsorbate concentration of 25mg/L. The amount of biosorbent used was 0.4 g. The highest adsorption capacity was observed at13.97mg/g, pH 6 that was chosen as optimum pH.

Equilibrium modeling

Langmuir (1), Freudlich (2), and Temkin (3) were fitted to the equilibrium data (Kumar *et al.*, 2019).

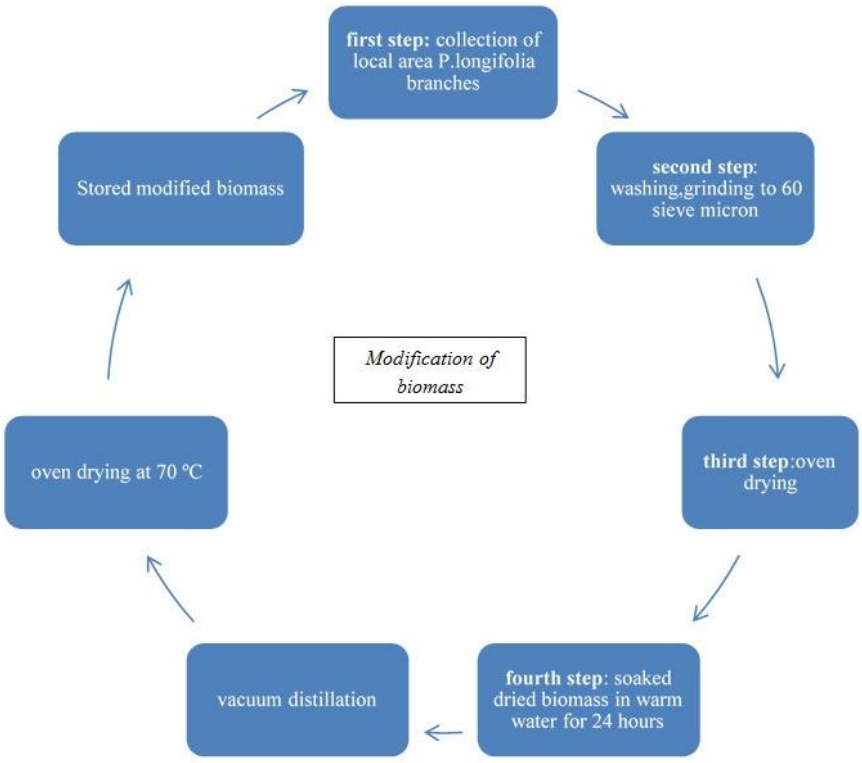


Fig. 1: Schematic diagram for modification biomass.

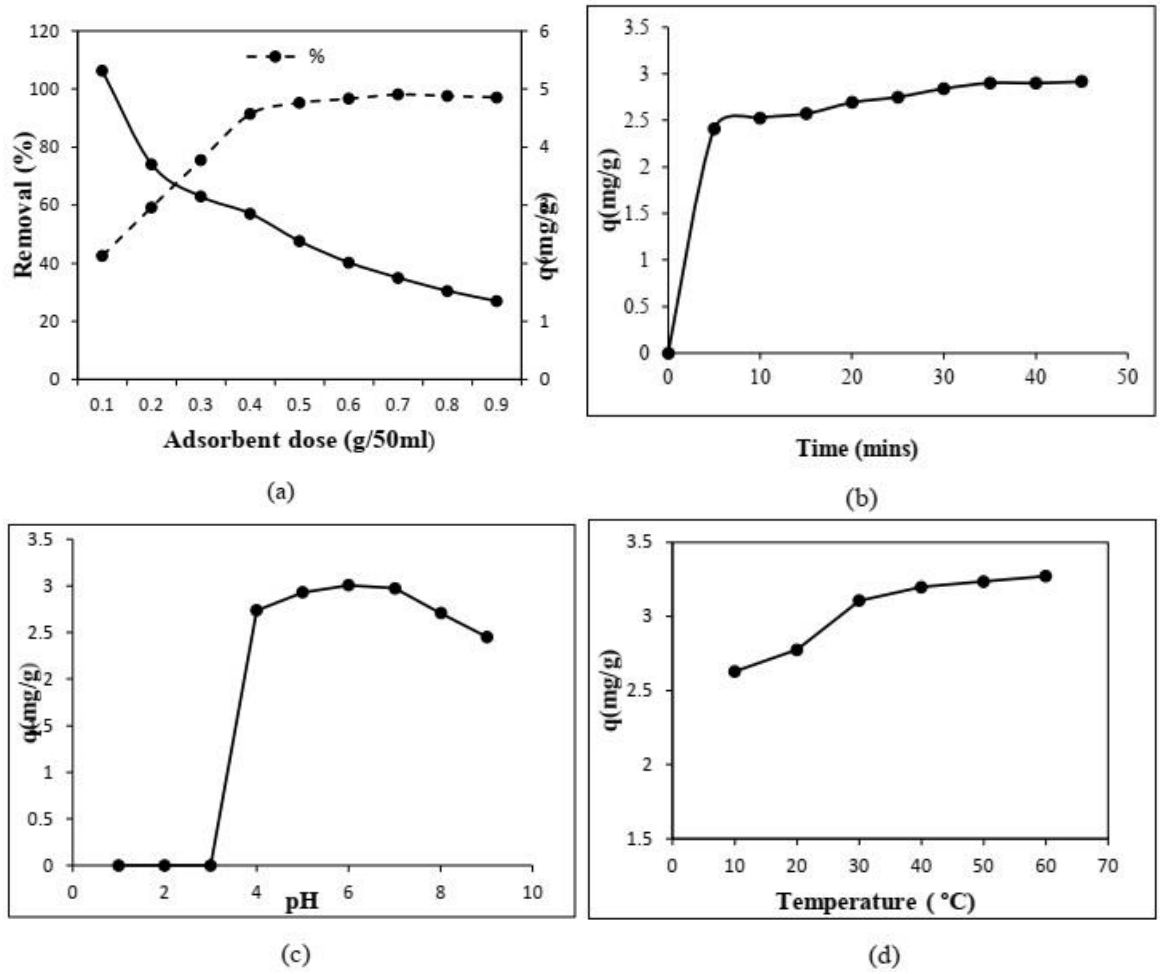


Fig. 2: (a) Effect of adsorbent dosage on adsorption of Brilliant yellow, Initial Concentration of Dye: 25 ppm, Quantity of Adsorbent: 0.1-0.9 g/50mL. (b) Effect of Contact Time on Adsorption of Brilliant yellow, Contact Time: 05-45 minutes, Amount of Adsorbent: 0.4 g. (c) Effect of pH on Adsorption of Brilliant yellow, pH range 0-10. (d) Effect of Temperature on Adsorption of Brilliant yellow, temperature range 10-60. Quantity of Adsorbent 0.4 g, Contact Time 15 mins.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} + \frac{C_e}{b\, q_{max}} \quad (1)$$

$$Log\ q = log\ kf + \frac{1}{n} logC_e \quad (2)$$

$$q_e = B_T.\ \ln K_T.\ C_e \quad (3)$$

Langmuir isotherm model define equilibrium between solid and liquid phases. It explained formation of monolayer absorbate on the outer layer adsorbent. Biosorption process and equilibrium parameters were studied by using adsorption isotherm. Coefficient value R^2 showed that there might be homogenous distribution on the surface of *P. longifolia***.** The adsorption capacity calculated from Langmuir model was 13.97 mg/g.

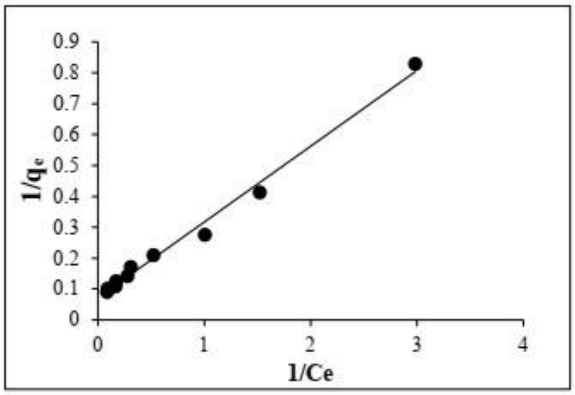
Freundlich model explains adsorption specification for the heterogeneous surface and its parameters were calculated from the Table-2. K_f is a binding constant related adsorption strength and 'n' is adsorption intensity. Table-2 showed that n= 1.743 and the magnitude of K_f = 2.973 mg/g. Table-2 describe different parameters like K_T is the adsorption capacity and B_T is temperature of adsorption. Temperature of adsorption B_T is a vital parameter to describe attractive forces. The value of correlation coefficient was 0.922.

Table-2: Parameters of Langmuir, Freundlich and Temkin models.

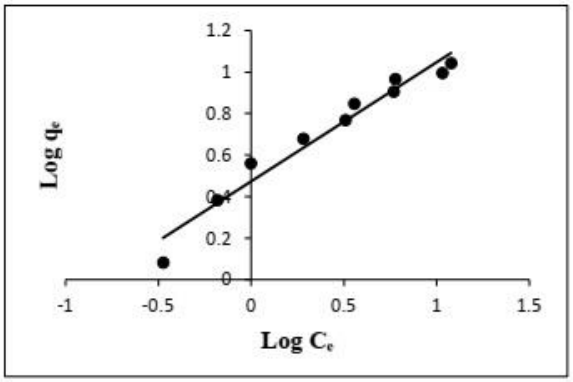
Models		Slope	Intercept	R^2
Langmuir models	q_{max}(mg/g) 13.97 b (dm^3/g) 0.292	0.2452	0.0716	0.9909
Freundlich models	n 1.743 K_f 2.973	0.5737	0.4732	0.9563
Temkin models	K_T 3.494 B_T kJ/mol 2.714	2.714	3.3959	0.922

Table-3: Parameters of kinetic study.

Pseudo first order	Slope	Intercept	qe (exp)	qe (calc)	R^2	k_1	k_2
	-0.1059	-0.2371	2.75	0.789	0.6655	0.1059	-
Pseudo second order	0.321	0.9227	2.75	3.11	0.9962	-	0.112



(a)



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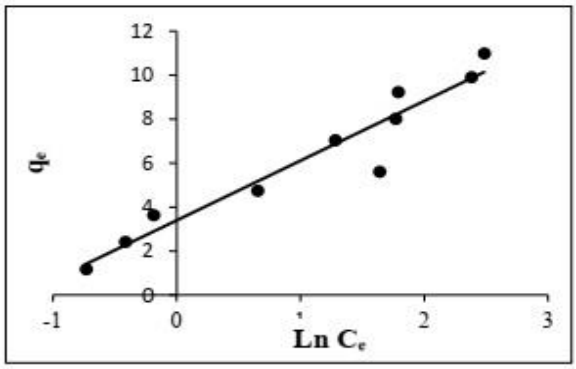


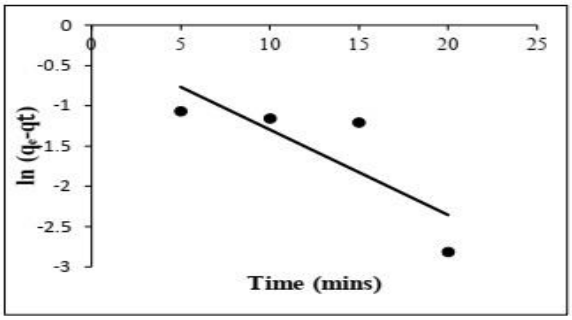
(c)

Fig. 3: Graphical observation of equilibrium models at initial concentration 25 ppm, amount of adsorbent used 0.4 g. (a) linear plot of Langmuir model. (b) Linear plot of freundlich model. (c) Linear observation of temkin model

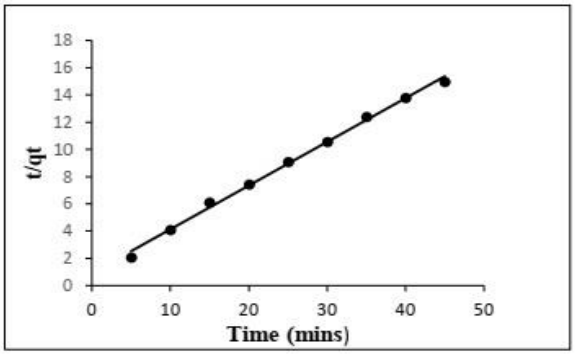
Effect of contact time on the adsorption of brilliant yellow dye

The effect of contact time on dye was observed at an initial dye concentration of 25 mg/L using *P.longifolia* powder as biosorbent. The adsorption capacity of biosorbent increased with increasing contact time in Fig 2(b). Eventually, it gives persistent value where no further effect was observed. In the other words no active sites were available for binding. The adsorption of brilliant yellow was observed in 15-30 minutes. With an initial concentration of 25 mg/L, the contact time was 30 minutes to reach equilibrium.

The kinetics of brilliant yellow biosorption on *P. longifolia* was studied at 25mg/L of initial concentration [Fig 4 (a, b) and Table-3]. The pseudo first order was not well fitted as compared to 2ndorder, with R^2 value of pseudo 1st order as 0.665 and pseudo 2nd order as 0.996. This implies that 2nd order was well fitted to experimental data.



(a)



(b)

Fig. 4: kinetic study observed at initial concentration 25 ppm, time ranges from 5-45. (a) Linear plot of pseudo 1st order. (b) Linear plot of Pseudo 2nd order.

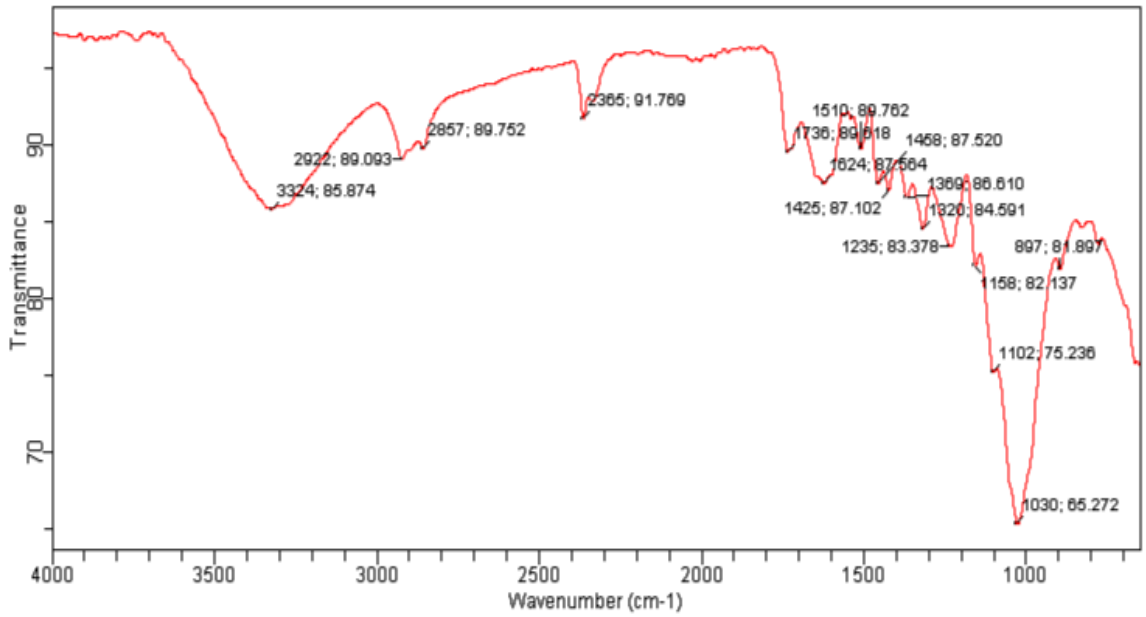


Fig. 5: FTIR of *P.longifolia* branches.

Table-4: Parameters of Thermodynamic.

Temp. K	K_D	ΔG^0KJ/mol	ΔH^0KJ/mol	ΔS^0KJ/mol
283.16	3.014	-2.597	21.78	0.086

Thermodynamic study

Thermodynamic study deals with the heat effect. Temperature plays a vital role in real application of adsorption for waste water treatment. Thermodynamic properties (free energy, enthalpy and entropy) give information about adsorption as presented in Table-4.

Effect of temperature on adsorption of brilliant yellow was observed between 10-60^{0}C with concentration of dye of 25mg/L. Amount of adsorbent used was 0.4g and contact time of 15minutes [Fig 2(d)]. In the present study, it was observed that adsorption sharply increased over the initial temperature, i.e., 10- 60^{0}C. This indicating it was an endothermic process.

Specification of adsorbent by FTIR (Fourier Transform Infrared)

P. longifolia biomass of modified and unmodified dried material was analyzed by FTIR. It is operated for functional groups analysis. Various functional group were found in spectrum (Fig 5). A wide and large peak exhibited at 3324 cm^{-1}. A peak at 2922cm^{-1} indicates (C-H). Spectrum indicating carbonyl group(C=O) was observed at 1736 cm^{-1} and another peak at 1520,1425,1458,1235,1320,1369,1102,1158,1030 and 837 cm^{-1}. Specify disproportionate stretching frequency of carboxylate ion. Therefore, Fourier Transform Infrared study defined *P. longifolia* biomass is highly oxygen containing functional groups. Medium peaks at 2339 and 2365cm^{-1}indicate the presence (C=N) group in the modified biomass. It indicates that modified biomass becomes rich with nitrogen and contain carboxylate ion (O=C-O).

Through Fig.2 (a) it is cleared that adsorption increased with adsorbent doses. After equilibrium established, reduction in % adsorption was observed with further increase in the amount of adsorbent dose.

Another factor that affects adsorption efficiency is pH of adsorbent. The effect of pH is an effective method to control biosorption process and especially the biosorbent capacity. Initially, no adsorption was observed in strong acidic medium at pH ranging from 1-3because structure of dye was destroyed [Fig 2(c)]. Dye removal increased gradually in slightly acidic medium at pH ranging from 4-6. It was revealed that in acidic pH range adsorption potential rise by increasing pH and decreased in alkaline medium [23,24]. Such trend was observed by Wong [25] explaining that forces of attraction means electrostatic forces occur between biomass and dying content.

Equilibrium study describes the link between adsorption and remaining biosorbent in

solution. Frequently used isotherm models are Langmuir, Freudlich, Temkin, Dubinin-Radushkevich, In this study Langmuir, Freudlich and Temkin were fitted to the equilibrium data. Langmuir parameters were calculated and shown in Fig.3. Fig 3(a) explains the slope and intercepts relation for obtaining qmax (mg/g). Great adsorption strength and b (L/mg) constant associated to free energy of adsorption. R^2 coefficient value 0.992 indicated good mathematical fit because R^2 value is near to one which means Langmuir fitted the adsorption of brilliant yellow dye on *P.longifolia*. as reported by Ouahabi [26].

The Freundlich constants 'n' and "k_f" were determined from graph [Fig 3(b)]. Correlation coefficient R^2value i.e., 0.956 is lesser than Langmuir model. The Freundlich linear graph analyzes the equilibrium data. The Temkin isotherm is like Freundlich in scope but adopt a different function to explain the non-lineraity of adsorption [Fig 3(c)]. This includes an element that clearly shows the adsorbent–adsorbate interactions. The model assumes that absorption (heat function) of all the molecules in the layer lower linearly instead of logarithmically with heat coverage [27].

It provides information related to adsorption mechanism, and possible rate controlling steps. There are various kinetics models such as pseudo 1st and 2ndorder, Elovich model. Extensively using method is pseudo 1st and 2nd order. Theoretically explain mechanism of adsorption.

Pseudo 1storder reaction models

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

Pseudo 2ndorder reaction model

$$\frac{t}{q_t} = \frac{1}{K^2 q e^2} + \frac{t}{q_e} \qquad (2)$$

where, 'q_e'means amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g) and 'q_t' is the amount of adsorbate adsorbed at given time 't' (mg/g). k_1 and k_2 are Pseudo 1st and 2nd order rate constants [28]. Kinetic data explained biosorption was standardized with time and observed very fast. Kinetic studies are important for predicting most favorable condition of adsorption processes. First order reaction is adsorption that is associated to number of free active area [Fig 4(a)]. Whereas, second order reaction is associated to square of free active area in adsorbing species [Fig 4(b)]. Similar finding was inspected by Munagapati [29].

Different previous research articles also studied same concept. In their articles, it was also analyzed that remaining vacant free space was hard to occupy because some forces that exist on it. Repulsive forces which occurred on biosorbent molecules. Gulluce [30-31] explained similar concept of kinetic studies.

Thermodynamic properties (free energy, enthalpy and entropy) were examined by using following equation. Semiao [31] reported the same interpretation.

$$\Delta G^0 = -RT\ln K$$

$$\ln k = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Here, "R" = universal gas constant (8.3134 J mol^{-1} k^{-1}), T = temperature (K), and "K" = distribution coefficient, attained from the following equation:

$$K_D = \frac{C_0 - C_e}{C_e}$$

The increase in magnitude ΔG^0 illustrated the endothermic properties. The calculated value of ΔH^0 also supported this same report. ΔS^0 indicated randomness in solid solution interface during adsorption [32]. The K_D values followed perfect to data and obtained from sips parameters (kS and qms) [33]. ΔG, ΔH and ΔS were calculated as shown in Table-4. ΔG negative values indicated that treatment of brilliant yellow on *P. longifolia* branches was natural and positive process [34]. According to Hannachi [24] observation, if negative value formed than removal of pollutant is chemisorption process. Fourier transform infrared method showed that modified *P. longifolia* branches enriched with functional groups and contained nitrogen and carboxylate ion (O=C-O) (Fig 5). Large peak exhibited at 3324 cm^{-1} This peak shows the presence of hydroxyl group (OH) similar result reported by Temesgen [35]. Daneshvar [36] observed same trend and his analysis showed presence of C-H bond in biomass. C-H bond is also a strength of biomass.

Conclusion

In this work, application of *P. longifolia* branches clearly demonstrated that it is a good adsorbent towards water remediation. It is commonly accessible in Pakistan. It helps to eliminate the toxicity from waste water. The results indicated that *P. longifolia* branches are a cost-effective approach. This is an efficient adsorbent for treatment of toxic dye contents Thermodynamic properties examined that adsorption method was a natural, endothermic, and good technique for handling, treatment of

polluted water such as dye wastewater. Equilibrium study was also analyzed. Optimum pH for maximum adsorption was 5-6. Experimental data well fitted to Langmuir isotherm as shown in Table-2 Adsorption potential for brilliant yellow was 13.97 mg/g.

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