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Sorptive removal of Direct Blue-15 dye from water using *Camellia sinensis* and *Carica papaya* leaves

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Water treatment by an adsorption method is being evolved in recent years. In this work, the effectiveness of removing direct blue 15 dye from aqueous medium by two adsorbents, *viz.*, *Camellia sinensis* (tea) and *Carica papaya* (papaya) leaves was evaluated and compared on a batch scale. Various parameters affecting the biosorption efficiency were optimized and then applied for Langmuir isothermal modeling of equilibrium data. Characterization of *Camellia sinensis* and *Carica papaya* was done by using FT-IR. The results showed that the *Camellia sinensis* waste was more effective and removed 90.9 mg/g of Direct Blue 15 as compared to *Carica papaya* leaves, which removed only 3.98 mg/g of this dye under optimized operational conditions. Hence, *Camellia sinensis* waste was superior to *Carica papaya* leaves for removing Direct Blue 15 dye from waste water.

Keywords: *Camellia sinensis, Carica papaya* leaves, Direct Blue-15 dye, Adsorption, Langmuir isotherm.

INTRODUCTION

Water pollution caused by dyes and other organic pollutants is severely increasing due to rapid flourishing of industrialization and advancement in research, which develops toxic dyeing agents [1]. Waste water coming from leather, printing, dying, textile, cosmetics, food coloring and paper-making industries contains a large amount of such hazardous pollutants [2-4]. They can be accumulated in surface water leading to pollution of drinking water sources. The present research work describes the removal of direct blue 15 dye from water. It is an anionic diazo direct dye. It exists as deep purple to dark blue microcrystalline powder and decomposes in air. It is soluble in water (60 g/l at 85°C) and insoluble in most organic solvents. It is also called direct sky blue A and direct sky blue 5B. Its structural formula is given in Fig. (1) [5].

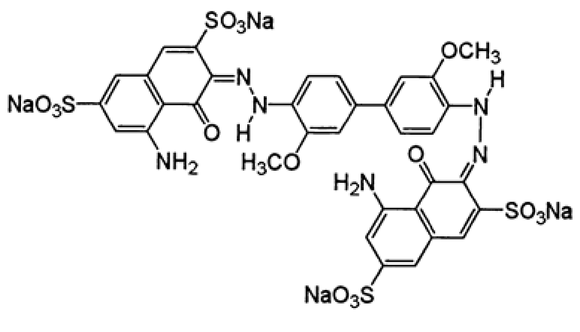

Fig. 1. Direct blue 15 dye

It has strong affinity to cellulose fibers and is thus employed in textile industries. When heated, it emits poisonous fumes of SO_x, NO_x and CO_x which are dangerous to health [6-8].

In dye containing waste water, colloidal matter increases the turbidity of water and gives it bad aroma. It prevents the penetration of sunlight essential for photosynthesis. These effluents clog the pores of soil, decrease soil fertility and prevent penetration to roots [9-11]. Several methods, such as reverse osmosis, chemical oxidation, coagulation, flocculation, sonolysis, ozonation, etc., were used for removing dyes [12]. In last decades, biosorption is becoming popular in water treatment [13]. Increase in search of low-cost biosorbents was more emphasized due to the high cost of activated carbon [14-16]. Several novel biomaterials have been used as adsorbents [17,18]. Numerous adsorbents have been reported for the elimination of direct blue-15 dye from waste water like: activated carbon, palm ash, tea waste, papaya leaves, white rot fungus, coconut, orange peels and *Loofa egyptiaca* [19-25].

In the present research work *Carica papaya* (papaya) leaves and *Camellia sinensis* (tea) waste are used as novel adsorbents for the biosorption of direct blue-15 dye. The leaves and leaf buds of this plant are used for producing tea beverage [26]. *Camellia sinensis* is useful for the treatment of tumors, bladder ailments, lethargy and abscesses [27]. The anti-microbial activity of tea is manifested against the *vibrio cholerae* bacterium which causes cholera [28]. Total cholesterol level can be reduced by consuming green tea. Body fat can also be reduced by green tea, which is supported by randomized control trials [29]. Green tea affects the

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lining of blood vessels. It keeps them relaxed and helps to regulate changes in blood pressure. It prevents the formation of blood clots which are the main cause of heart attacks. The risk of esophageal cancer can be reduced by consuming green tea. It can kill cancer cells without damaging the healthy tissue around them [30-33].

Papaya leaves are large with a diameter of 50-70 cm. The leaf has seven lobes and is palmately lobed [34]. Low platelet counts can be cured by using papaya leaf tea which also helps against clotting. Tea made of papaya leaves acts as a laxative for the treatment of constipation [35].

EXPERIMENTAL

Chemicals used

Direct blue-15 dye (C.I.=24400, mol. wt=992.85 g/mol), HCl and NaOH were purchased from Merck (Germany) and used as such.

Preparation of adsorbents

The *Camellia sinensis* waste was taken from local markets of Lahore, Pakistan. The *Carica papaya* leaves were collected from the gardens of the home institute. Tea waste was placed in acetone for 3 h for removing color and after filtration, was dried in an oven at 110°C for 3-4 h. Papaya leaves were kept in sunlight for 3-4 days to completely remove moisture, followed by oven drying at 110°C. After that the materials were ground. Their FT-IR spectra were recorded and resulting peaks are summarized in Table 1.

Adsorption experiments

They were carried out in batch mode at 25°C. pH was maintained by 0.01 N HCl and 0.01 N NaOH. All factors were studied using a 25 ppm dye solution. After adsorption, dye concentration was checked in the filtrate on a UV-Vis spectrometer at 601 nm. The % removal of dye at any time was determined by the following equation:

$$\% \text{ Removal of dye} = (C_o\text{-}C_e/C_o)\times 100, \quad (1)$$

where C_o and C_e are the concentrations of dye before and after adsorption, respectively. Each experiment was repeated three times for increasing accuracy of the data and average values were used for calculations.

Study of adsorption isotherm

Optimized conditions of all operational parameters were applied on dye solutions with various concentrations (15-90 ppm) for studying the adsorption isotherm. After that the solutions were filtered and dye concentration was checked in the filtrate as described above. Then, applying eq. 2, Langmuir isotherms were plotted for *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL).

$$1/q = 1/bq_mC_e + 1/q_m, \quad (2)$$

The value of ‘q’ is calculated by formula 3:

$$q = (C_o - C_e)V/m, \quad (3)$$

where ‘q’ (mg.g^{-1}) is the amount of dye adsorbed, ‘C_e’ (ppm) is the remaining concentration of dye after adsorption, ‘q_m’ (mg.g^{-1}) and ‘b’ (L.g^{-1}) are Langmuir isotherm parameters which were calculated from the slope and intercept values of the graph of ‘1/q’ *versus* ‘$1/C_e$’. ‘V’(l) is the volume of dye solution, ‘m’ is the mass of adsorbent used. Separation factor ‘R_L’ and ‘ΔG^o’ (thermodynamic parameter) were calculated using equations 4 and 5, respectively:

$$R_L = 1/(1+bC_o), \quad (4)$$

$$\Delta G^o = -RT \ln K, \quad (5)$$

Here ‘C_o’ is 25 ppm and K is the inverse of Langmuir constant ‘b’ [24].

RESULTS AND DISCUSSION

Characterization of adsorbents surface

Characterization of adsorbents surface was done by FT-IR to confirm the presence of functional groups that can be used for bonding with direct blue 15 dye during biosorption. The resulting characteristic vibration frequencies are listed in Table 1. It was found that carboxylic groups are present in the biosorbent samples, as indicated by the –OH group stretching frequencies at 2923.25, 2954.11, 2954.11, 2625.53 and 2923.25 cm^{-1}. Alkane group $–CH_2$ peaks were found at 2725.53, 1458.25, 1457.28 and 721.41 cm^{-1}. Aromatic amine peaks were found at 1304.90 and 1306.83 cm^{-1} [36]. These functional groups can chelate dye molecules.

Table 1. Specific FT-IR absorption frequencies of leaf samples.

Adsorbents	Band frequencies (cm^{-1})
Camellia sinensis	2923.25, 2853.81, 2725.53, 1458.25, 1304.90, 721.41
Carica papaya	2954.11, 2923.25, 2625.53, 1457.28, 1306.83, 721.41

Adsorbent dose effect

The adsorbent dose effect was followed by varying adsorbent dose from 0.1 to 1.0 g. The maximum removal of dye occurred at adsorbent dose of 0.7 g using *Camellia sinensis* and 0.5 g using *Carica papaya*, as shown in Fig. 2. It was found that the adsorption initially increases due to the presence of a large number of adsorption sites on the surface of the adsorbents but when equilibrium is established the adsorption capacity of the biosorbent decreases. The reason is that after establishment of equilibrium, further increase in leaf sample dose leads to increased interference between the active sites, so removal of dye decreases [37-39].

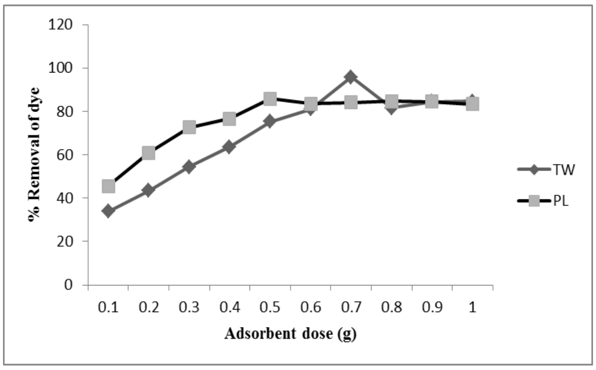

Fig. 2. Effect of adsorbent dose of *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL) on the elimination of direct blue-15 dye from water.

Effect of contact time

The effect of contact time was studied in the range from 5 to 60 min. The results are shown in Fig. 3 which indicates that the maximum removal of dye occurs in 40 and 45 min using *Camellia sinensis* and *Carica papaya* leaves, respectively.

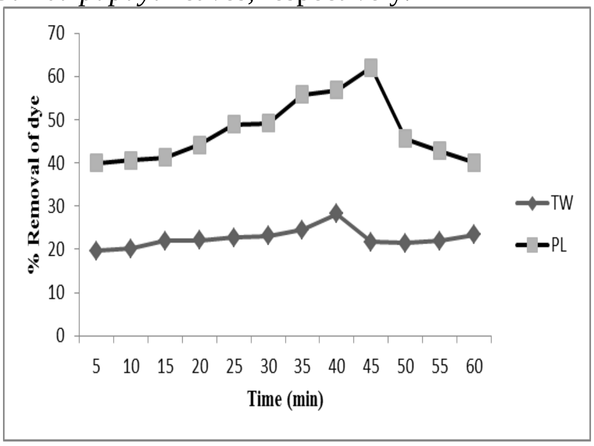

Fig. 3. Effect of contact time of *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL) on the biosorption of direct blue-15 dye from water.

In the beginning, dye adsorption was rapid due to the availability of a large number of vacant binding sites but after the optimum time, decrease in adsorption capacity was observed due to covering of the available binding sites by dye molecules, which repel incoming molecules of dye lowering biosorption.

Effect of initial pH

The effect of initial pH is shown in Fig. 4 which indicates that dye removal is maximal at pH 3.0 using *Camellia sinensis* waste (TW) and at pH 7.0 by *Carica papaya* leaves (PL).

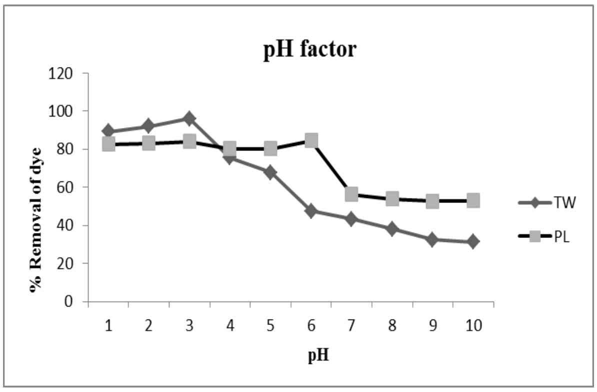

Fig. 4. pH effect on the removal of direct blue 15 dye from water using *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL).

In acidic conditions, leaves surface becomes protonated, which helps in attracting the anionic type dye, thus the removal of dye increases. But in the case of basic conditions, biosorption decreases due to the presence of negative charge on leaves surface, which repels anionic dye species, resulting in poor biosorption [39].

Effect of agitation speed

The effect of agitation speed is graphically presented in Fig. 5.

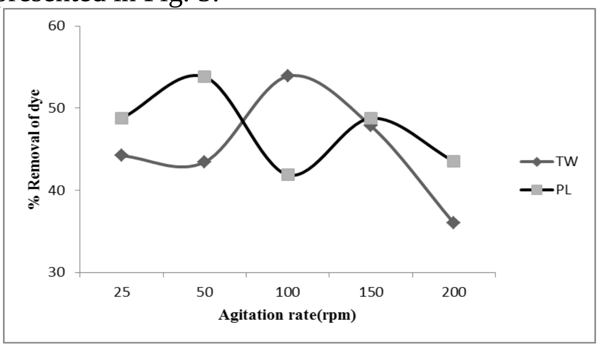

Fig. 5. Influence of agitation rate on the biosorption of direct blue 15 dye from water using *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL).

The maximum removal of dye occurred at 100 and 50 rpm using *Camellia sinensis* waste and *Carica papaya* leaves as adsorbent, respectively. Agitation of dye solution helps for better interaction between leaf waste and dye molecules, so that these molecules penetrate to deeper layers of the adsorbent. When agitation speed surpassed the optimum level, less interaction occurred between dye molecules and adsorbent, so biosorption decreased at higher speed [39].

Effect of temperature

The effect of temperature is shown in Fig. 6. The maximum biosorption of dye occurs at 40 and 30°C using *Camellia sinensis* waste and *Carica papaya* leaves, respectively. It indicates that this process is exothermic, which was further confirmed by isothermal modeling of equilibrium data.

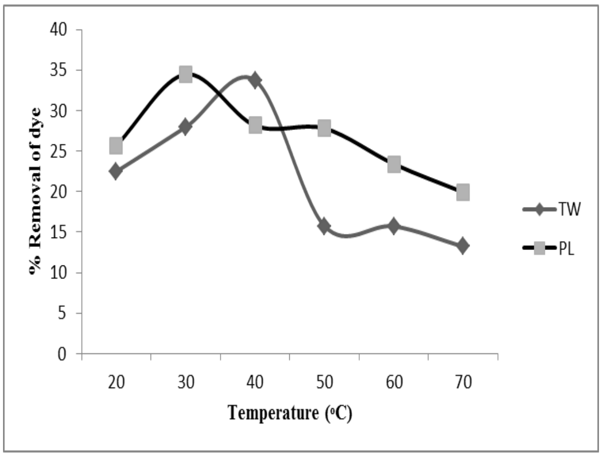

Fig. 6. Temperature effect on direct blue 15 dye adsorption from water by *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL).

Isothermal studies

The Langmuir isotherms for direct blue-15 dye adsorption using *Camellia sinensis* and *Carica papaya* are shown in Fig. 7 and the results are summarized in Table 2.

Maximum removal of dye - q_m' value was 90.9 and 3.98 mg/g for *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL), respectively. The constant '*b*' value for direct blue 15 dye was 2.2 and 1.65 L/g for *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL), respectively. It was

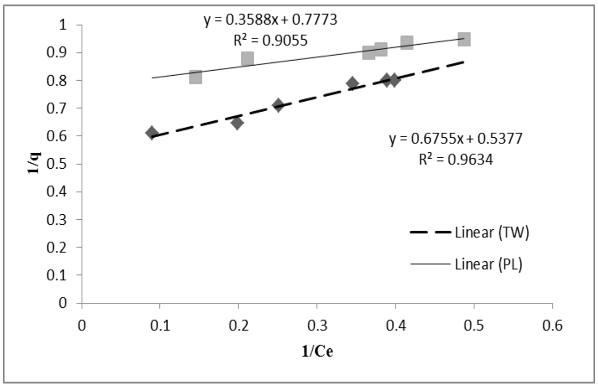

Fig. 7. Langmuir isotherm for direct blue 15 dye adsorption from water using *Camellia sinensis* waste (TW) and *Carica papaya* leaves (PL).

used to calculate ΔG^o and separation factor 'R_L' values. The correlation coefficient 'R^2' values indicated that the Langmuir model was suitable to explain the adsorption of direct blue 15 dye on *Camellia sinensis* waste and *Carica papaya* leaves. This indicates that adsorption sites are arranged in monolayer fashion and homogenously distributed on the biosorbent surface.

ΔG^o value indicated that these processes are exothermic in nature and separation factor 'R_L' value less than unity indicated the favorability of these adsorbents for removing direct blue 15 dye from water on a bulk scale.

CONCLUSIONS

In the present work low-cost adsorbents such as *Camellia sinensis* waste and *Carica papaya* leaves were used for the removal of direct blue 15 dye from water. It was observed that *Camellia sinensis* waste can remove 90.9 mg.g^{-1} of dye, which is 23 times greater than *Carica papaya* leaves' capacity of 3.98 mg.g^{-1}. The process is exothermic in nature and favorable under optimized conditions, as indicated by thermodynamic data. So these adsorbents can be used on a bulk scale for removing direct blue 15 from waste water streams.

Table 2. Results of isothermal studies for adsorption of direct blue 15 dye

Sample	R^2	b (L.g^{-1})	q_m (mg.g^{-1})	ΔG^o (kJ/mol)	R_L
Camellia sinensis waste (TW)	0.963	2.2	90.9	-1.953	0.017
Carica papaya leaves (PL)	0.905	1.65	3.98	-1.238	0.024

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СОРБЦИОННО ОТСТРАНЯВАНЕ НА БАГРИЛОТО ДИРЕКТНО СИНЬО-15 ОТ ВОДА ИЗПОЛЗВАЙКИ ЛИСТА ОТ *Camellia sinensis* И *Carica papaya*

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(Резюме)

Пречистването на води по адсорбционни методи се развива бързо през последните години. В настоящата работа се изследва ефективността на отстраняване на багрилото Директно синьо-15 чрез два адсорбента, а именно листа от *Camellia sinensis* (чай) и *Carica papaya* (папая), като адсорбционната им способност е сравнена по стандартна скала. Оптимизирани са различни параметри, влияещи на биосорбционната екективност и е приложена адсорбционната изотерма за моделиране на равносвесните данни. Охарактеризирането на *Camellia sinensis* и *Carica papaya* е извършено чрез FT-IR. Резултатите показват, че отпадъците от *Camellia sinensis* са по-ефикасни и отстраняват 90.9 mg/g от багрилото в сравнение с листата от *Carica papaya*, които отстраняват само 3.98 mg/g при оптимизирани работни условия. Затова остатъците от *Camellia sinensis* превъзхождат листата от *Carica papaya* при отстраняването на багрилото Директно синьо-15 от отпадъчни води.