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Effect of Important Selected Parameters on Adsorption Capacity of Brilliant Cresyl Blue Dye onto Novel Adsorbent: *Tamarix Aphylla* Leaves

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Abstract. In the present work, the potential use of *Tamarix aphylla* leaves to remove brilliant cresyl blue dye (BCBD) from aqueous solutions was evaluated. The characterization of *Tamarix aphylla* leaves include solubility in water, IR spectra, surface area and pore size were investigated. The influence of important selected parameters such as: initial pH of BCBD solution, initial concentration of BCBD solution, contact time between *Tamarix aphylla* leaves and BCBD solution and contact temperature between *Tamarix aphylla* leaves and BCBD solution has been studied. The effect of contact temperature on adsorption capacity indicated that, the reaction is endothermic in nature. The maxima values were 491.78, 502.99 and 682.12 mg/g at contact temperatures 20, 35 and 50 °C, respectively.

Keywords: Brilliant cresyl blue, *Tamarix aphylla* and adsorption.

1. Introduction

Synthetic dyes are used extremely in textile, paper and printing industries. The synthetic dyes cause environmental pollution specially water pollution and they also cause a serious health problems depending on the exposure time and concentration of dye. Therefore, removal of dyes from wastewater is of great importance [1].

Dyes are highly visible even if their concentrations as low as 0.005 mg/l. Basic dyes such as BCBD have highly brilliance and colour intensity and highly visible [2].

A different methods may be used to eliminate dyes from aqueous solutions include chemical flocculation, chemical oxidation, ozonation, reverse osmosis, biological and adsorption techniques. Activated carbon could be used as an effective adsorbent. However, the expensiveness and regeneration difficulty of this adsorbent let many workers to search a low cost adsorbents [3]. Among these low adsorbents, agriculture wastes such as coconut shell [4], banana pith [5], *camellia oleifera* shell [6] and rice husk [7] are widely used.

Our attention was focused on *Tamarix aphylla* leaves as a low cost adsorbent to remove BCBD from aqueous solutions. The *Tamarix aphylla* leaves was treated with sulphuric acid, sodium hydroxide and acetone to decrease it's solubility in water.

2. Materials and Methods

2.1. Adsorbent

Tamarix aphylla leaves were obtained locally from Sebha area in the south of Libya, washed many times by hot water than by distilled water to remove any undesirable materials, filtrated and over dried at 80 °C for 3 hours. The dried leaves were treated with sulphuric acid, sodium hydroxide and acetone according to the following procedure:

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1. 25 g of dried *Tamarix aphylla* leaves were added to 150 ml H_2SO_4 (0.2 N) in a conical flask. The mixture was heated at 100 ^oC for 2 hours, filtered, washed by distilled water then dried in an oven at 120 ^oC for 2 hours.

2. The dried *Tamarix aphylla* leaves were placed in a conical flask then 150 ml of sodium hydroxide (0.2 N) was added to contents of the flask. The mixture were heated at 120 ^oC for 2 hours, filtered, washed by distilled water then dried in an oven at 120 ^oC for 2 hours.

3. 10 ml of acetone was added to the previous *Tamarix aphylla* leaves which treated with sodium hydroxide in a conical flask. The mixture was stirred up for 30 minute at room temperature then the acetone was separated from the mixture and the *Tamarix aphylla* leaves were dried at 120 ^oC for 2 hours. The dried *Tamarix aphylla* leaves were sieved and adesirable diameter of 125 μm was obtained.

Some characterization of the treated *Tamarix aphylla* leaves include solubility in water [8], infra red (IR) analysis (FT IR, Nicolet, USA) and determination of surface area and particle diameter (Nova 2200 Quntach Chrome Corporation, USA) were achieved.

2.2. Adsorbate

The BCBD of molecular weight 317.8 g/mol was supplied by BDH, Germany and used as received. The molecular structure of BCBD is illustrated in Figure 1. The stock solution 1000 (mg/l) of BCBD was prepared by dissolving accurately weighted amount of BCBD in distilled water. All working solutions of the desired concentration were prepared by dilution the stock solution with distilled water. The determination of initial concentration of BCBD (C_o) and concentration of BCBD at equilibrium (C_e) were determined using UV-vis spectrotometer (Jenway, Germany) at optimum wavelength 624 nm.

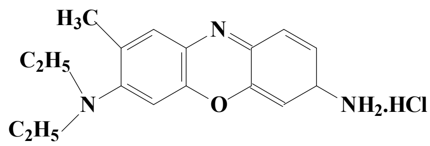


Fig. 1: The molecular weight of BCBD.

2.3. Equilibrium Studies

Equilibrium experiments were carried out by mixing a fixed amount of treated *Tamarix aphylla* leaves with 50 ml of BCBD solution of different initial concentration into a number of 100 ml stoppered flasks. The desirable initial pH was measured by pH meter (Thermo Electron Corporation, USA). The initial pH was regulated using different concentrations of hydrochloric acid or sodium hydroxide (0.01, 0.1 and 1 mol/l for each). Contact time and contact temperature were controlled.

The amount of adsorbed BCBD per gram of treated *Tamarix aphylla* leaves was calculated using the following expression [9]:

$$q_e = \frac{(C_o - C_e)\times V}{W} \quad (1)$$

V (l) is the volume of BCBD solution and W is the weight of treated *Tamarix aphylla* leaves (g).

2.4. Effect of Initial pH

In this study, 50 ml of BCBD solution of 32 mg/l initial concentration and 2 hours contact time at values of initial pH (3-10) was agitated with 0.1 g/l of treated *Tamarix aphylla* leaves in a water bath shaker at 30 ^oC and constant agitation speed of 400 rpm.

2.5. Effect of Contact Time

In this study, 50 ml of BCBD solution of pH 5 and initial concentrations of 28.1 and 32.3 mg/l was agitated with 0.1 g/l of treated *Tamarix aphylla* leaves in a water bath shaker at 30 ^oC. The contact time of agitation was varied from 0 to 150 minute at a constant agitation speed of 400 rpm.

2.6. Effect of Contact Temperature

In this study, 50 ml of BCBD solution at BCBD initial concentration ranged from 44.5 to 799.8 mg/l and 2 hour contact time. The initial pH of 5 was agitated with 0.1 g/l of treated *Tamarix aphylla* leaves in a water bath shaker at three different temperatures 20 ^{o}C, 35 ^{o}C and 50 ^{o}C. The agitation speed was adjusted at 400 rpm.

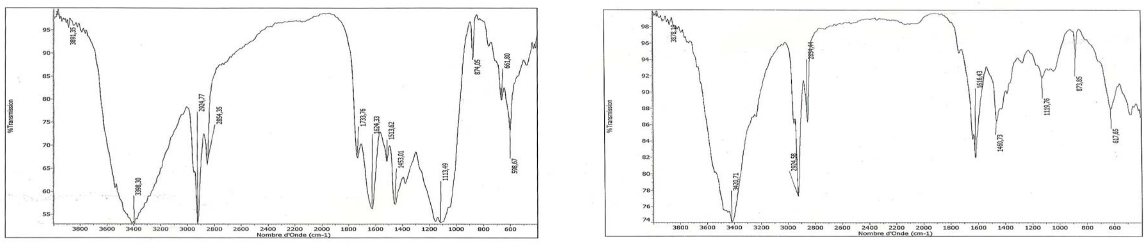
3. Results and Discussion

3.1. Characterization of Adsorbent

The solubility of *Tamarix aphylla* leaves in water before treatment and after treatment with sulfuric acid, sodium hydroxide and acetone were found 43.6 and 2.4 %, respectively. This means that, such treatment is very effective to use *Tamarix aphylla* leaves as adsorbent material in aqueous media.

The IR spectra of the treated *Tamarix aphylla* leaves before and after adsorption of BCBD are presented in Figure 2(a) and 2(b), respectivily. Figure 2(a) shows: stretching O-H groups at 3398.30 cm^{-1} resulted from O-H of cellulose as broad peek, binding O-H group at 1624.33 cm^{-1}, stretching -N-O at 1453.01 cm^{-1}, stretching SO_3^{-2} at 1113.49 cm^{-1}, stretching -N-H groups at 874.05 cm^{-1}, some salts at 661.80 and 598.67 cm^{-1}. Figure 2(b) represents absorb locations for treated *Tamarix aphylla* leaves after adsorption of BCBD. Two new signals were observed at 873.85 cm^{-1} due to stretching -N-H group and at 617.65cm^{-1} due to the binding of -N-O group.

The pore size and surface area of *Tamarix aphylla* leaves are shown in Table 1. The determination was obtained at the following conditions: particles size of treated *Tamarix aphylla* leaves, 0.355 mm; adsorbent dose, 0.03 g/l; BCBD concentration, 20 mg/l and λ max, 624 nm. It is observed from Table 1 that, there is a decrease of the surface area of the treated *Tamarix aphylla* leaves after been exposed to BCBD, where as the pore size did not change. This indicates that, the narrow pores (less than 2 nm) had been blocked.



2a 2b

Fig. 2: IR spectra of the treated *Tamarix aphylla* leaves before adsorption (2 a) and after adsorption of BCBD (2 b).

Table 1: Pore size and surface area of treated *Tamarix aphylla* leaves before and after adsorption of BCBD

Sample	Pore size (nm)	Surface area (m^2/g)
Treated *Tamarix aphylla* leaves	2,30,50,80	1050
Treated *Tamarix aphylla* leaves with BCBD	2,30,50,80	1030

3.2. Effect of Initial pH

The pH of an aqueous solutions of dyes is very important parameter in any adsorption process, particularly on adsorption capacity [10].

Effect of initial pH of BCBD solution on adsorption capacity of treated *Tamarix aphylla* leaves is shown in Table 2. The adsorption capacity was found to increase with increasing initial pH and reached maximum value at initial pH of 5. Low values of adsorption capacity at acid initial pH is probably due to the excess of H^+ ions competing with BCBD cations for active sites of treated *Tamarix aphylla* leaves. At initial pHs (5-7) the adsorption capacity of BCBD onto treated *Tamarix aphylla* leaves was almost constant. For initial pH values higher than 7, it was noticed a decrease in the adsorption capacity. This is mainly due to the solubility of the organic groups present on the surface of treated *Tamarix aphylla* leaves [11].

Table 2: Effect of initial pH

Initial pH	q_e (mg/g)
3	87.6
5	133.01
7	132.89
9	103.80
10	67.86

3.3. Effect of Contact Time

Figure 2 shows the influence of contact time on adsorption capacity of BCBD. The experimental data indicate that, the adsorption capacity of BCBD increased by increasing contact time. This is probably due to the higher contact between the surface of *Tamarix aphylla* leaves and BCBD cations [12]. The system reached equilibrium state after 120 minute. Figure 3 also explained that as the initial concentration of BCBD solution increased the adsorption capacity of BCBD onto *Tamarix aphylla* leaves increased.

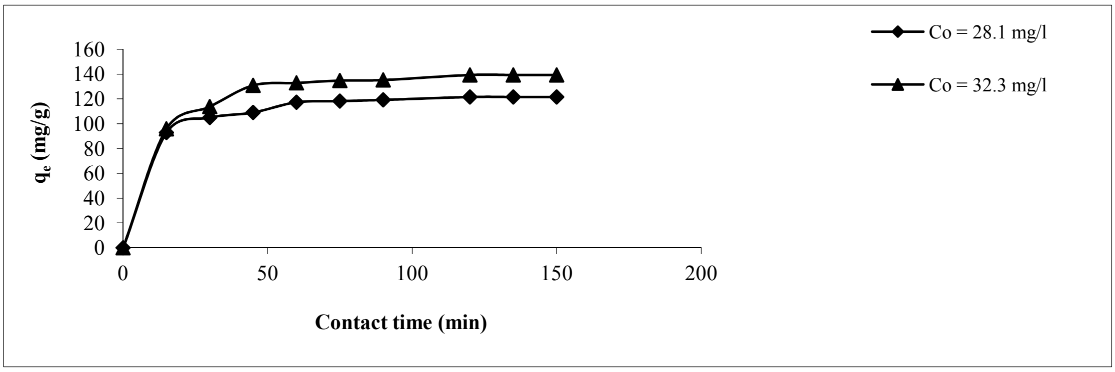


Fig. 3: Effect of contact time on adsorption capacity of cationic BCBD onto *Tamarix aphylla* leaves

3.4. Effect of Contact Temperature

To know an indication about thermodynamic of adsorption, effect of contact temperature on adsorption capacity should be studied. Table 3 shows the effect of contact temperature on adsorption capacity. The adsorption capacity reached maxima values after initial BCBD concentration of 444.11 mg/l. The maxima values were 491.78, 502.99 and 682.12 mg/g. The obtained results indicate that adsorption capacity of BCBD increased by increasing contact temperature. This is probably due to the endothermic behavior between the surface of *Tamarix aphylla* leaves and BCBD cations.

Table 3: Effect of contact temperature

C_o (mg/l)	20 ^oC	35 ^oC	50 ^oC
	q_e (mg/g)		
44.5	134.58	207.12	188.99
88.8	271.49	332.67	293.23
267.1	420.12	469.02	497.59
444.1	491.78	502.99	682.12
622.4	491.72	502.81	682.12
799.5	491.75	503.11	682.12

4. Conclusion

The adsorption of BCBD onto *Tamarix aphylla* leaves was pH dependent and reaches the equilibrium after 120 minutes. The adsorption system was endothermic in nature. The experimental maxima adsorption capacities of BCBD onto *Tamarix aphylla* leaves were 121.5 and 139.24 mg/g at BCBD initial concentration of 28.1 and 32.3, respectively. The optimum conditions found in this study were initial pH of BCBD solution, 5; contact time between the surface of *Tamarix aphylla* leaves and BCBD solution, 120 minutes and contact temperature between the surface of *Tamarix aphylla* leaves and BCBD solution, 50 ^{o}C.

5. References

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