Adsorption of Terasil Blue on Prosopis Farcta: Performance and Modelling Study

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Abstract. Natural materials which are readily available in large amounts in nature may be used as low cost additives. The purpose of this research is to inspect the possibility of the naturally available material; Prosopis Farcta (PF) plant; to improve dyes from textile wastewater. Prosopis Farcta and activated carbon were used as adsorbents in order to make a comparison to remove terasil blue dyes (TB). Batch tests investigated the adsorption isotherm of TB at room temperature and various parameters such as the adsorbent dose, contact time and initial dye concentration. The experimental results showed that the maximum removal efficiency of PF was found to be 85% at a fixed 200 rpm mixing speed, pH value 8, mixing time 90 minutes and the dose of adsorbent 0.5g. The maximum removal efficiency of AC was found to be 96% at a fixed 200 rpm mixing speed, pH value 8, mixing time 90 minutes and the dose of adsorbent 0.5g. The above removal efficiencies were obtained at temperature 24±1 °C and initial TB dye concentration 15 mg/l. Langmuir and Freundlich isotherm models were assigned to analyse the test data. Findings revealed that Langmuir adsorption isotherm was best model for TB adsorption onto AC and PF with energy of adsorption (Qo) 2.495 mg/g and 1.652 mg/g, the maximum adsorption capacity (b) 7.08 l/mg and 0.307 l/mg at coefficient of determination 0.9958 and 0.9718 respectively.

1. Introduction
Getting a potable water is a human rightful. Despite, recently, more than 1100 million people survive lacking of getting a potable water, exclusively in growing countries. Solving to this universal difficulty is directed to create easy, efficient, cheap and simple to use technical knowledge, which are capable of decreasing physical, chemical and biological water pollution [1]. One of the most essential industries in the last few decennials is the textile industry. It is explained that more than two-third of the dyes world yield is resulted from textiles processes. It was measured that 10 – 20 % of dye was done during the dyeing process and liberated as wastewater [2]. The chemicals used in textile industry are very different in the structure. The non-biodegradability of textile wastewater is because of the large quantity of additives that used to fix the colours [3]. Many chemical, physical, and biological processes have been used such as image oxidation and ad-sorption processes; to remove the chemical dyes used in the dyeing process. At all times, the adsorption process is used to collect chemical dyes on a solid matrix before the biological and chemical treatments [4]. Recently, adsorption has been considerably investigated by investigators globally as an effective and cheap sustainable technology for dye removal from textile wastewater [5-10]. A large selection of cheap substances, especially wastes from manufacturing and agricultural processes such as orange husk, banana shell, apple leaves, wheat straw, pine leaves, etc. has been discovered for their reduction of dyes from aqueous solutions [8, 10, and 11]. Choosing of adsorbent type is an important point in the development of the absorption process. Several materials can be used to remove industrial dyes. One of the materials used as an adsorbent is activated carbon powder although it has a high price but it is the most effective material used to remove organic com-pounds due to its high ability for absorption [12]. Therefore, it would be correct to use alternative and low cost
materials such as agricultural to remove dyes and all solid waste. [13 & 14]. This research used natural available plant called Prosopis Farcta (PF) as a natural adsorbent for dye adsorption in textile wastewater treatment. Prosopis farcta is a small, prickling flower, 0.3 m to 0.8 m tall and is found in Algeria, Egypt, Tunisia, Iran, Iraq and Kazakhstan [15 & 16]. This natural plant is also success-fully habituated to aridity and hot and presents a high level of salty soil [17]. Prosopis Farcta reproduces from seeds and basal buds on the rhizomes found at or just under the soil level. It restarts germination after a very short inactivity period in the winter and spring, and re-grows during the summer through the autumn [16]. The aim of this study is to investigate the susceptibility of the locally available material, PF plant without chemically treated, to improve the quality of wastewater discharged from textile industry. Activated carbon was used as adsorbent in order to make a comparison and to test the PF efficiency for terasil blue (TB) dye removal; studying the ability of adsorbents to adsorb dye using batch system; studying the behaviour of the equilibrium isotherm for the TB dye adsorption onto PF plant and activated carbon; studying the effect of flow, initial concentration of TB dye and bed depth on the dynamic behaviour of the continuous adsorption process in fixed and fluidized bed absorbers and finally prediction of breakthrough curves through the use of experimental data.

2. Materials

2.1. Preparation of adsorbate – Terasil Blue (TB) Dye

Terasil blue dye is one of the main dyes which are used in Kut Textile Factory, Wasit Governorate. This dye is utilized for the dyeing of the polyester fabric in knitting department. High concentrations of TB dye are discharged with the effluent wastewater. Representative concentrations of the dye were prepared to be used as adsorbate in the experiments of the present study. A standard solution of 30 mg/l of TB was prepared for adjustment process. From the stock, different concentrations (5, 10, 15, 20 and 25 mg/l) of TB were prepared by diluting with water [18]. These concentrations of solution will be used for batch and continuous experiments sequentially. Table 1 shows the dye components of TB [19]. A calibration curve of TB concentrations versus absorbency was constructed as shown in Fig. 1.

| Element | C  | O   | Na  | S   | Cl  | Br  |
|---------|----|-----|-----|-----|-----|-----|
| Weight %| 37.45 | 35.52 | 9.89 | 8.52 | 3.72 | 4.9 |
| Atomic %| 50.29 | 35.81 | 6.94 | 4.29 | 1.69 | 0.99 |

Table 1. The components of TB dye.

![Figure 1. Calibration curve of TB dye at 663.5 nm](image_url)
2.2. Activated Carbon
Activated carbon AC (German origin) was used as adsorbent in the experiments.

2.3. Prosopis Farcta
The Prosopis Farcta (PF) is a common plant germinating in wide range area. The fruits were gathered, dehydrated under the impact of sun rays. The PF was crushed and lastly screening them using (150 - 300) μm sieve. The plant can be shown in Fig 2 and the physical properties of both activated carbon (AC) and Prosopis Farcta (PF) are shown in Table 2.

![Prosopis Farcta plant (leaves and fruits)](image)

Table 2. Physical properties of PF & AC.

| Specification                    | Prosopis Farcta (PF) | Activated Carbon (AC) |
|----------------------------------|-----------------------|------------------------|
| Color                            | 37.45                 | 35.52                  |
| Odor                             | odour                | odourless              |
| Solubility                       | insoluble in water    | insoluble in water     |
| Specific surface area (m²/g)     | 5                     | 732                    |
| Bed porosity                     | 0.725                 | 0.42                   |
| Bulk density (g/cm³)             | 1.5                   | 2.25                   |
| Real density (g/cm³)             | 0.0005                | 0.55                   |
| Pore volume (cm³/g)              | 16.5                  | 3                      |

2.4. Point of Zero Charge
Accordingly the samples about (0.25g) of PF were adding to conical flasks that contain 60 ml distilled water plus 40ml of (0.1 mol/l NaCl solution, then shaked for 24 hours. Initial pH values (2,3,4,5,6,7,8,9,10,11,12) were adjusted using NaCl or HCl. After 24 hours, the final pH is measured and the difference between the initial pH values and the final pH values were obtained as shown in Fig (3). The best pH value is found from the interception point of zero with the curve that obtained by a plot of (ΔpH v.s pH initial) [20]. From the Fig. 3, the optimum value of pH for PF is (7.9) so it is chosen roughly 8 for all experiments.
Batch Experiments
Batch experiments were designed to study the isotherm & TB efficiency removal onto the PF adsorbents, using synthetic aqueous solution. Impacts of many variables on the degree of adsorption operation are detected by changing PF dose, contact period and TB dosage. Batch studies were used to define the optimum circumstances for treatment process. These experiments are applied to certify the action of the reactive adsorbate and the adsorption isotherm. The tests were applied using double beam UV/visible spectrophotometer. A UV spectrophotometer of double beam was utilized for calculating the results of TB concentration before and after adsorption at 633 nm wavelength. Different masses (0.1, 0.2, 0.3, 0.4 and 0.5) grams of natural PF were used. Series of 250ml flasks are used and each flask is loaded with 100ml of stock solution which have primary concentration of TB dye of (5, 10, 15, 20 and 25 mg/l). A known weight of adsorbents mentioned previously was equilibrated with 100ml of stock solution into different flasks. The flasks were agitated at a constant speed 200 rpm [19], permitting adequate equilibrium period. It was supposed that the adapted agitation speed enables all the surface area to be in touch with TB ions during of the examinations. A constant size 20 ml of the aqueous solution was taken from each flask. The taken sample was filtrated by using suitable filter paper for remove any suspended solids particles of PF. The amount of TB adsorbed per unit mass is calculated from equation 1.

\[ qe = (Ci - Ce) \times \frac{V}{W} \]  

Where qe (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t, Ci is the liquid phase concentration (mg/l) of TB dye at the initial condition, Ce is the liquid phase concentration (mg/l) of TB dye at the equilibrium condition, V is the volume of solution (l), W is the mass of adsorbent (g). The percent of TB removal was calculated using the following equation 2.

\[ R\% = \left( \frac{(Ci - Ce)}{Ci} \right) \times 100 \]  

2.6. TB adsorption experiments in packed-bed columns using PF
Dynamic adsorption tests are done in a glass tube with 25mm cm of internal diameter and 150 mm of length. Five different feed TB concentrations (5, 10, 15, 20, and 25 mg/l) and feed flow rate 40 mL/min are adopted to find TB breakthrough curves. Three different ports at heights 5, 10, and 15cm are used to take effluent samples at regular periods. The data were analysed and compared using Thomas model.
3. Results and Discussion

3.1. Effect of adsorbent dose and contact time
One of the significant parameter to the adsorption performance is the adsorbent dose. To investigate the effect of adsorbent dose on TB dye adsorption onto two adsorbents AC and PF surfaces, series of experiments were carried out at room temperature with initial TB dye concentrations (5, 10, 15, 20 and 25 mg/l), constant pH=8, constant agitation speed=200 rpm, various contact time (20, 40, 60, 80, and 100 min). Figs 4 and 5 show the effect of adsorbent dosage on the TB removal efficiency. The reduction efficiency increased with increasing PF dosage (0.1g to 0.5g) at initial TB concentration (15 mg/l). It may be because that the more adsorbents particles more AC and PF for crash with TB to increase the TB removal efficiency. The removal efficiency about 96% using AC, while under the same condition the removal obtained when using 0.5 of PF was 85% at 90 min.

![Figure 4. Removal efficiency of TB adsorption by AC as function of contact time and adsorbent dose (Ci=15 mg/l, pH=8)](image1)

![Figure 5. Removal efficiency of TB adsorption by PF as function of contact time and adsorbent dose (Ci=15 mg/l, pH=8)](image2)

3.2. Estimation of the adsorption isotherm constants
Tables 3 & 4 show experimental equilibrium data of TB dye adsorption on the AC and PF respectively. Figs 6 & 7 show that the adsorption obeyed the Langmuir mode, the linear plot of (Ce/qe) vs the Ce.
The constants $b$ (energy of adsorption) and $Q_o$ (maximum adsorption capacity) are resulted from the gradient and $y$-intercept of the line. All constants are listed in Table 5 while Figs 8 & 9 showed Freundlich model.

**Table 3.** Experimental equilibrium data of TB adsorption on AC as adsorbent (pH=8, adsorbent mass =0.5g, S=200 rpm, time 90 min).

| $C_i$ (mg/l) | $C_e$ (mg/l) | $q_e$ (mg/g) |
|-------------|-------------|-------------|
| 5           | 0.18        | 1.205       |
| 10          | 1.98        | 2.005       |
| 15          | 3.5         | 2.875       |
| 20          | 10.5        | 2.375       |
| 25          | 15          | 2.5         |

**Table 4.** Experimental equilibrium data of TB adsorption on PF as adsorbent (pH=8, adsorbent mass =0.5g, S=200 rpm, time 90 min).

| $C_i$ (mg/l) | $C_e$ (mg/l) | $q_e$ (mg/g) |
|-------------|-------------|-------------|
| 5           | 2           | 0.75        |
| 10          | 6           | 1.0         |
| 15          | 10          | 1.25        |
| 20          | 15          | 1.25        |
| 25          | 19          | 1.5         |

**Figure 6.** Langmuir isotherm for adsorption of TB on AC (pH=8, mass=0.4g, S=200 rpm, time=90 min)
Figure 7. Langmuir isotherm for adsorption of TB on PF (pH=8, mass=0.4g, S=200 rpm, time=90 min)

Figure 8. Freundlich isotherm for adsorption of TB on AC (pH=8, mass=0.4g, S=200 rpm, time=90 min)
Figure 9. Freundlich isotherm for adsorption of TB on PF (pH=8, mass=0.4g, S=200 rpm, time=90 min)

Table 5. Adsorption isotherm constants for TB adsorption onto AC and PF.

| Adsorbent | Langmuir constants | Freundlich constants |
|-----------|---------------------|----------------------|
|           | Qi (mg/g) | b (l/mg) | R² | Kf (mg/g) | 1/n | R² |
| AC        | 2.495     | 7.08     | 0.9958 | 1.761 | 0.1684 | 0.7649 |
| PF        | 1.652     | 0.307    | 0.9718 | 0.608 | 0.2924 | 0.9653 |

Experimental data may provide different isotherm shapes such as: linear, favourable, strongly favourable, irreversible and unfavourable [21] as shown in Fig. 10.

Figs 11 & 12 show the shapes of the isotherm obtained from experimental data for both AC and PF respectively, the isotherms can be considered as favourable.

Figure 10. Isotherm shapes [21]
3.3. Continuous Flow Experiments (Column test – Thomas model)

Thomas model [22] can be explained by the following equation (3):

\[
\frac{C_t}{C_i} = \frac{1}{1 + \exp\left(\frac{Q}{K_{Th} q_{Th} M} - K_{Th} C_i t\right)}
\]

(3)

where \(K_{Th}\) is the Thomas rate constant (ml/min.mg), \(q_{Th}\) is the equilibrium sorbent uptake per gram of adsorbent (mg/g), \(M\) is the mass of adsorbent (gram), \(C_i\) is the inlet sorbent dose (mg/l), \(C_t\) is the outlet sorbent dose (mg/l), \(Q\) is the discharge (ml/min), and \(t\) is the sampling period (minutes).

The kinetic coefficient \(K_{Th}\) and adsorption quantity of column \(q_{Th}\) can be calculated from the drawing \(\ln\left(\frac{C_t}{C_i} - 1\right)\) versus to time \(t\) at a known discharge.

The regression of the Thomas model with the investigational TB adsorption information also displays better interrelationships in furthermore of the situations. Tables 6 & 7 as shown in furthermore runs as
the inlet dosage increased the value of \( q_{th} \) increased. This was done because the governing factor for adsorption is the dosage difference between the dye on the adsorbent and the dye in the solution. Thus the high force driving due to the higher TB concentration resulted in better column removal rate. With increasing discharge the value of \( q_{th} \) decreased but the value of \( K_{th} \) increased this is the similar finding got by [23]. As the bed depth increased, the value of \( q_{th} \) increased while the value of \( K_{th} \) decreased. Fig. 13 shows the linearized Thomas model for adsorption of 15 mg/l TB by AC with 40 ml/min flow rate at different bed depths. While Fig. 14 shows the linearized Thomas model for adsorption of 15 mg/l TB by PF with 40 ml/min flow rate at different bed depths.

### Table 6. AC predicted Thomas model parameters.

| Initial Concentration (mg/l) | Bed depth (cm) | Flow Rate (l/min) | \( K_{th} \) (l/mg.min) | \( Q_{th} \) (mg/g) | \( R^2 \) |
|-----------------------------|----------------|--------------------|-------------------------|-------------------|----------|
| 5                           | 5              | 40                 | 0.00188                 | 1.350             |          |
| 10                          | 5              | 40                 | 0.00094                 | 2.700             |          |
| 15                          | 5              | 40                 | 0.00063                 | 4.028             | 0.9592   |
| 20                          | 5              | 40                 | 0.00047                 | 5.400             |          |
| 25                          | 5              | 40                 | 0.00038                 | 6.678             |          |

### Table 7. PF predicted Thomas model parameters.

| Initial Concentration (mg/l) | Bed depth (cm) | Flow Rate (l/min) | \( K_{th} \) (l/mg.min) | \( Q_{th} \) (mg/g) | \( R^2 \) |
|-----------------------------|----------------|--------------------|-------------------------|-------------------|----------|
| 5                           | 5              | 40                 | 0.00082                 | 1.854             |          |
| 10                          | 5              | 40                 | 0.00041                 | 3.710             |          |
| 15                          | 5              | 40                 | 0.00027                 | 5.633             | 0.9334   |
| 20                          | 5              | 40                 | 0.0002                 | 7.605             |          |
| 25                          | 5              | 40                 | 0.000165                | 9.218             |          |
4. Conclusions
In this study, low-cost and naturally available adsorbent (Prosopis Farcta) was studied for the removal of terasil blue dye from synthetic textile wastewater. The results obtained from series of batch and column experiments, application of adsorption isotherms were analysed so as to calculate the effectiveness and behaviour of (Prosopis Farcta) and compared it the efficiency of well-known absorbent activated carbon (AC) in removing of terasil blue dye from wastewater. The equilibrium isotherms for TB adsorption onto PF is favourable type according to the results obtained by [21]. It is formed that Langmuir model shows the perfect suitable for the experimental data with very high coefficients of determination for PF. From the Thomas model with the experimental TB adsorption data it was found that the value of qth increased when the influent concentration and bed depth in-creased, while the value of Kth decreased when the depth increased. As a results all the findings of batch and continuous experiments show that the possibility of using naturally and locally available plant (Prosopis Farcta) as
an absorbent for terasil blue dye adsorption from textile wastewater. For farther study the heavy metals adsorption using PF could be well studied, also evaluation could be done for the removal efficiency of PF for real textile wastewater that contained a mixed of dyes.

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6. References
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