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# Biosorption of Direct red 81 dye from aqueous solution on prepared sonchus fruit plant, as a low cost biosorbent: Thermodynamic and Kinetic study

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## Abstract

The biosorption of reactive azo dyes (Direct red 81) found in textile wastewaters by activated carbon prepared from sonchus fruit plant has been investigated. Batch experiments were carried out for the biosorption of dyes molecules onto biosorbent at different temperature. The biosorption kinetics was found to follow pseudo- second order kinetic model with high degree of correlation coefficient ($R^2$>0.99). The equilibrium isotherms of biosorption and kinetics were studied. The biosorption equilibrium data were analyzed by using Langmuir and freundlich isotherm models and the results have shown that biosorption behavior of this dye could be follow to Langmuir isotherm model. Various parameters such as contact time, initial dyes concentrations, temperature, stirring speed and does of biosorbent were taken into account, and promising results were obtained. Furthermore, it was also found that the sonchus fruit plant can using as a low cost material for azo dye biosorbtion.

**Keywords**: Biosorption, Isotherm, Kinetic, Azo dye, Thermodynamic.

## 1. Introduction

Now a day, more than 700,000 tones and 10,000 different types of dyes and pigments are produced annually across the world and are extensively used in many industries such as leather, textile, paper, pulp, plastics and foods [1-3]. The treatment of dye-contaminated wastewater is one of the most serious environmental problems. Among the chemical classes of dyes, azo dyes are more versatile and account to more than half of the annual dye production. And also, azo dyes are considered more carcinogenic to humans [4]. The presence of dyes in watercourses is both aesthetically unacceptable and possibly toxic inasmuch that a genotoxic effect on organisms tends to be associated with contamination. As a result, the appropriate biotreatment of textile effluents is very important nowadays [5–7]. Dye-based effluents are usually treated by coagulation, precipitation, membrane filtration, oxidation, adsorption, and photodegradation processes [8-11]. Among the chemical and physical treatment processes, adsorption is considered to be superior to other techniques. This is attributed to its easy availability, simplicity of design, ease of operation, biodegradability, insensitivity to toxic substances and ability to treat dyes in more concentrated forms [12, 13]. Adsorbents from

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agriculture by-products are particularly advantageous due to their low cost and high availability as starting materials. Many other materials, for example, clays [14], cane waste [15], wood [16], cellulosic materials [17], fish scales [18] and mineral carbon [19] have been tested as adsorbent on remediation of contaminated water. The most commonly used material for this purpose is activated carbon. The high adsorption capacity of activated carbon is due to its high surface area and porous grain structure [20]. However, activated carbon is expensive. Also its re-use is somewhat limited by the material loss that occurs during the recovery process.Therefore, the present article reports the feasibility of activated carbon prepared from sonchus fruit plant, as a low cost biosorbent for the removal of Direct red 81 from aqueous solutions.

## 2. Materials and methods

### *2.1. Preparation of adsorbent*

Sonchus fruit plant was washed several times with distilled water and dried in an oven at 120 ºC for 3 h. The raw materials were subject to chemical activation. The activation was carried out using diluted H3PO4 (28 %) solution for 24 h. After decantation the samples were dried in an oven at 150 ºC for 24 h, it was carbonized in a muffle furnace at 500 ºC for 1 h and then sieved to an average particle size.

### *2.2. Chemical*

Direct red 81 was purchased from Merck Chemicals and its chemical structure is illustrated in Fig. 1. Stock solution of 1000 ppm of dye was prepared by dissolving an accurately weighed quantity of dye, in deionised water. Experimental solutions of desired concentration were prepared by diluting this stock solution with deionised water.

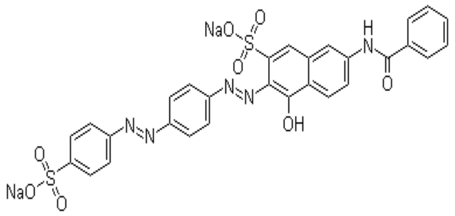

**Figure 1**. Molecular structure of direct red 81.

### *2.3. Biosorption experiments*

In order to calculate the concentration from each experiment a calibration curve of Direct red 81 was first prepared by using the standard dye solution with known concentrations. Different concentrations were prepared and absorbance values was recorded at Λmax = 508nm. The batch adsorption studies were performed by adding a fixed amount of adsorbent into a number of 250 mL stoppered Erlenmeyer flasks containing of fixed initial concentration of dye solution. The solutions were agitated. Effect of different parameters such as contact time, agitation speed, temperature, dye concentration and biosorbent dosage were studied. Concentrations were measured using a double beam UV–Vis spectrophotometer (Perkin Elmer lambda 25) at the wavelength of maximum absorbance.

## 3. Results and discussion

### *3.1. Effect of initial dye concentration and contact time*

The initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. The effect of initial concentrations of Direct red 81 on biosorption by prepared sonchus fruit plant was investigated in the range of 25-85 mg $L^{-1}$ of the initial dye concentration. The results show that an increase in the dye concentration had caused a decrease in the percentage of dye removal (figure 2). This is due to the saturation of the sorption sites on the adsorbents as the concentration of the dye increased.

At the beginning adsorption rate was rapid but higher in the beginning due to the large surface are available of biosorbent. When the adsorption of the exterior surface reached saturation, the dye ions exerted onto the pores of the adsorbent particles and were adsorbed by the interior surface of the particles [21-23].

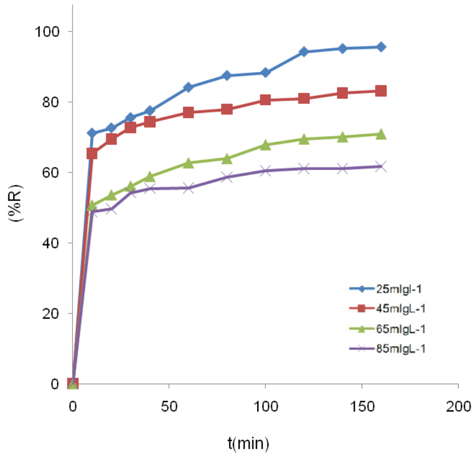

**Figure 2**. Effect of initial concentrations on the removal of Direct red 81 dye onto activated carbon (sonchus fruit plant).

### *3.2. Effect of dose of adsorbent*

The removal efficiency of Direct red 81 dye was studied by varying the biosorbent dose between 0.1 g and 1.5 g at a dye concentration of 25 mg $L^{-1}$. The results show, the amount of dyes biosorption increased with increase in the biosorbent dosage. This was due to the fact that as the dosage of adsorbent was increased, there was less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the biosorbent and increase in availability of surface active sites resulting from the increased dose and conglomeration of the biosorbent [24].

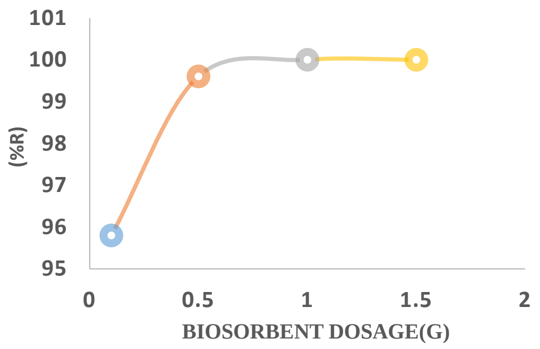

**Figure 3**. Effect of biosorbent dosage on the removal of Direct red 81 dye onto activated carbon (sonchus fruit plant).

### 3.4. Effect of agitation speed

400, 500, 700 and 900 rpm agitation speeds were used in conjunction with initial dye concentration of 25 and 45 $mgL^{-1}$. Adsorbent dose, temperature and contact time were kept constant. Figure 4 shows that the removal of Direct red 81 increase by increasing of agitation speed from 400 to 900 rpm. Increase in the adsorption with increasing of agitation speed can be attributed to increasing number of collision between biosorbent site and dye molecules.

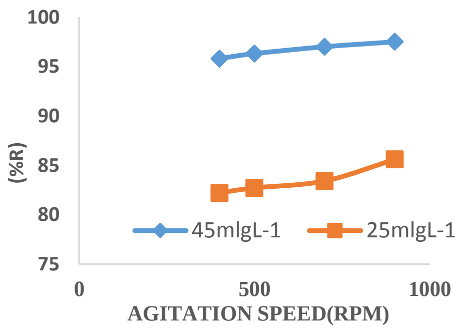

**Figure 4**. Effect of agitation speed on the removal of direct red 81 dye onto activated carbon (sonchus fruit plant).

### *3.5. Kinetic studies*

In order to study the biosorption rates of reactive dye by biosorbent, the pseudo first-order and pseudo second-order rates models were investigated. The Lagregren equation describes pseudo first-order model [25], gives:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Where $q_e$ and $q_t$ are the amount of dye adsorbed (mg $g^{-1}$) at equilibrium and at time t respectively, $k_1$ is the rate constant of pseudo first-order adsorption process ($min^{-1}$). After integration of Equation 6 for the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\log(q_e - q_t) = \log q_e - k_1 t$$

By plotting of log ($q_e - q_t$) versus t first-order rate constant $k_1$ and equilibrium adsorption density $q_e$ were calculated from slope and intercept of plot (Figure 5). The pseudo second-order model, gives:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)$$

Where $k_2$ is the equilibrium rate constant for pseudo second order adsorption
(g $mg^{-1}.min^{-1}$). After integration of Equation 8 and applying boundary conditions $t = 0$ to t and $q_t = 0$ to q, gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

$$h_i = k_2 q_e^2$$

Where $h_i$ is the initial dye adsorption (mg $g^{-1}.min^{-1}$). The slope and intercept of plot of ($t/q_t$ versus t) were used to calculate the pseudo second-order rate constant $k_2$ and $q_e$. The results are shown in Figure 6 and Table 1.

The correlation coefficients of all examined data were found very high for pseudo second-order equation. It showed a good compliance with the pseudo second-order equation. These results determined that the experimental data for the adsorption kinetics of reactive dye on biosorbent were fitted by the pseudo second-order kinetic model. Similar phenomenon was observed for the adsorption of basic dyes onto pomegranate peel, cotton and apricot stone [26].

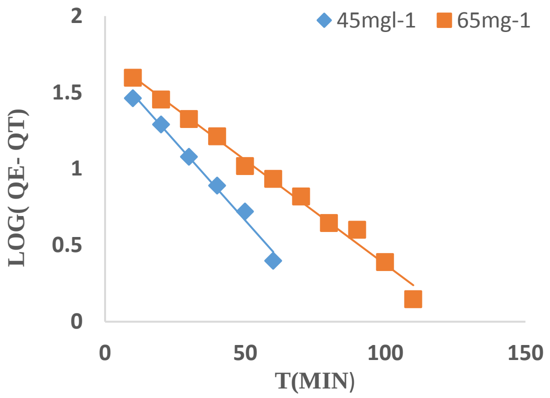

**Figure 5**. Plot of log ($q_e$ - $q_t$) versus t for biosorption of Direct red 81 by using the pseudo First-order kinetic model

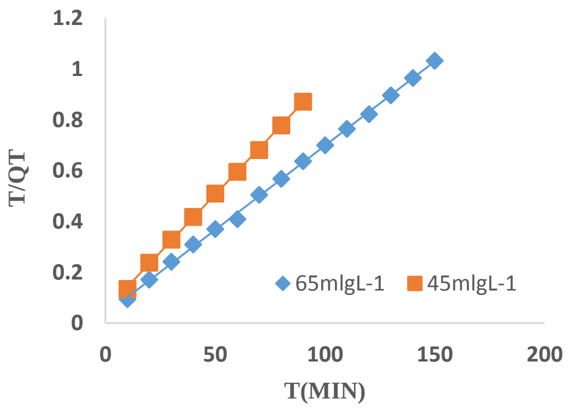

**Figure 6**. Plot of 1/$q_e$ versus t for biosorption of direct red 81 by using the pseudo Second-order kinetic model.

**Table 1**. Kinetic parameters calculated by using pseudo first-order and pseudo second-order rates models for biosorption of Direct red 81.

| Concentration (mgL$^{-1}$) | pseudo first-order | | pseudo second-order | |
|---|---|---|---|---|
| | k$_1$(min$^{-1}$) | R$^2$ | k$_2$(g mg$^{-1}$min$^{-1}$) | R$^2$ |
| 45 | 0.0477 | 0.9899 | 0.00157 | 0.9991 |
| 65 | 0.0313 | 0.990 | 0.0011 | 0.9998 |

### *3.6. Biosorption isotherm*

Langmuir and Freundlich biosorption isotherm equilibrium models (in linearised form) were used for the analysis of biosorption of Direct red 81.

### *3.7. Langmuir isotherm*

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

Where $C_e$ and $q_e$ are equilibrium concentration and equilibrium adsorption capacity, $q_m$ is the maximum adsorption capacity reflected a complete monolayer (mg gr$^{-1}$); $K_L$ is adsorption equilibrium constant (L mg$^{-1}$) that is related to the apparent energy of biosorption.

A plot $C_e/q_e$ versus $C_e$ indicate a straight line of slope 1/$q_m$ and an intercept of 1/($K_L q_m$). The Langmuir isotherm parameters and correlation coefficient are presented in Figure 7 and Table 2. The isotherm of activated carbon was found to be linear over the whole concentration range studies and the correlation coefficients was extremely high as shown in Table 2. The values of $q_m$ increase with temperature increase from 25 to 55°C.

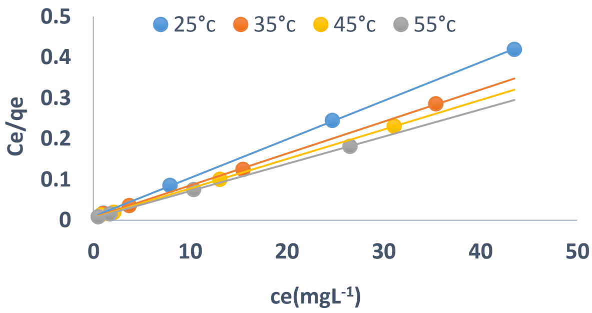

**Figure 7**. Langmuir plot for Direct red 81 biosorption at different temperature

### *3.7. Freundlich isotherm*

The Freundlich isotherm model is the earliest known relationship that describing the biosorption process. This isotherm is an empirical equation can be employed to describe heterogeneous systems and is expressed as follow:

$$q_e = K_F \, C_e^{\frac{1}{n_F}}$$

Where, $K_F$ is the Freundlich constant (L g$^{-1}$) related to the bonding energy. $K_F$ can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/$n_F$ is the heterogeneity factor and nF is a measure of the deviation from linearity of adsorption. Equation 2 can be linearized in the logarithmic form Equation 3 and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n_F}\log C_e$$

The plot of log ($q_e$) versus log ($C_e$) was employed to generate the intercept value of $K_F$ and the slope of $1/n_F$ (Table 2).

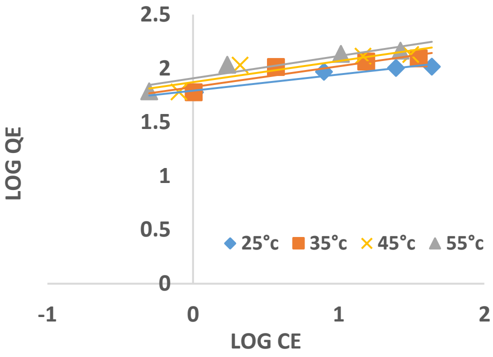

**Figure 8**. Freundlich plot for Direct red 81 biosorption at different temperature

**Table 2**. Comparison of the Langmuir and Freundlich isotherm parameter for biosorption of Direct red 81 at different temperature

| Temperature (K) | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|
| | $K_F$ | $1/n_F$ | $R^2$ | $K_L$ | $q_m$ | $R^2$ |
| 298 | 62.19 | 0.149 | 0.945 | 1.02755 | 105.263 | 0.999 |
| 308 | 67.55 | 0.200 | 0.859 | 1.13045 | 128.25 | 0.996 |
| 318 | 74.80 | 0.198 | 0.805 | 1.2000 | 138.89 | 0.998 |
| 328 | 80.80 | 0.208 | 0.904 | 0.311370 | 149.254 | 0.999 |

### *3.8. Calculation of activation energy*

The activation energy (Ea) for the biosorption of Direct red 81 onto biosorbent prepared from sonchus fruit plant was calculated from the rate constants k2 and by using the Arrhenius equation.

$$\ln k = \ln A - \frac{E_a}{RT}$$

Where, Ea, R and A refer to the Arrhenius activation energy, the universal gas constants and the Arrhenuis factor respectively. The plot of Arrhenuis (ln k *versus* 1/T) for the biosorption of Direct red 81 onto biosorbent (sonchus fruit plant) is shown in Figure 9. The activation energy was obtained 47.7kJ mol$^{-1}$.

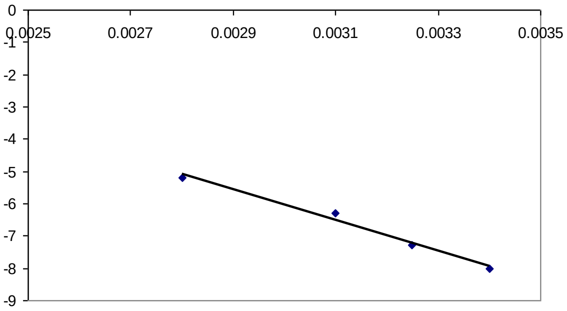

**Figure 9**. Arrhenuis plot for the biosorption of Direct red 81 onto biosorbent (sonchus fruit plant)

### *3.9. Thermodynamic study*

Thermodynamic parameters were calculated to confirm the biosorption nature of this study. The equlibrium constants, free Gibbs energy change and enthalpy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the biosorption. Therefore, the thermodynamic constants can be obtained from the following equations:

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

Where, DGº is the free Gibbs energy change (kJ mol$^{-1}$), R is the universal gas constant (8.314 J-1 mol K$^{-1}$), K the thermodynamic equilibrium constant and T is the absolute temperature (K). The values of K may be calculated from the relation ln qe/Ce *versus* qe at different temperatures and extrapolating zero [27, 28].

The thermodynamic parameters are listed in Table 3. The negative DGº values confirm the spontaneous nature and feasibility of the biosorption process. The values of enthalpy change (DHº), may be determined from Van't Hoff equation:

$$\ln K = \frac{-\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}$$

ΔHº can be obtained form the slope of Van't Hoff plot of ln K *versus* 1/T. The data are presented in Table 3. The posetive value of ΔH further confirm the endothermic nature of the biosorption process.

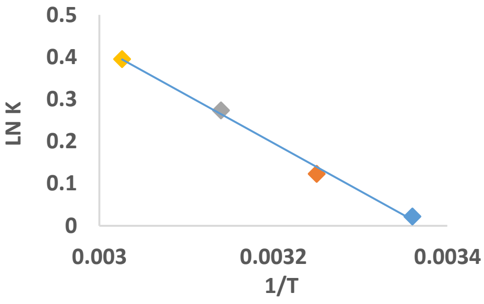

**Figure 10**. Van't Hoff plot for the biosorption of direct red 81 onto biosorbent (sonchus fruit plant)

**Table 3**. Calculated thermodynamic parameters for the biosorption of Direct red 81 onto biosorbent (sonchus fruit plant)

| T(K) | ΔGº | ΔHº |
|---|---|---|
| 298 | -0.053 | 9.504 |
| 308 | -0.314 | |
| 318 | -0.721 | |
| 328 | -1.076 | |

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