

Removal of basic dye from aqueous solution using tree fern as a biosorbent

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Abstract

A batch sorption system using tree fern as biosorbent was investigated to remove Basic Red 13 from aqueous solutions. The system variables studied include sorbent particle size and temperature and results revealed the potential of tree fern, an agriculture product, as a low-cost sorbent. The Langmuir isotherm was found to represent the measured sorption data well. The dye sorption capacity of tree fern increased as the sorbent particle size decreased. Maximum saturated monolayer sorption capacity of tree fern for Basic Red 13 was 408 mg/g. Various thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated indicating that this system was a spontaneous and endothermic process.

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1. Introduction

The removal of dye from textile effluents is one of the most significant environmental problems. Dyes are used widely in modern industrial society. Since they have a synthetic origin and complex aromatic molecular structures which make them inert and difficult to biodegrade when discharged into waste streams, people always overlook their undesirable nature. Some are harmful to aquatic life in rivers where they are discharged. The occupational exposure of workers in the textile industries is linked to a higher bladder cancer risk [1]. The use of hair colouring products and breast cancer have also been linked [2]. Consequently, methods to remove dye species from wastewaters have been the subject of several research papers.

The most widely used industrial sorbent is activated carbon. However, it is an expensive material unless regeneration becomes relatively easy but is unlikely to be cost-effective. Various agricultural products and by-products have been investigated to remove dyes from aqueous solutions. These include cotton waste, rice husk, bark [3], sugar industry mud

[4], palm-fruit bunch [5,6], Jack fruit peel [7], wood [8], orange peel [9], sugar cane dust [10], peat [11] and pith [12]. The obvious advantage of this method is the lower costs involved. Hence, there is a need to search for more economical and effective sorbents.

Tree fern is naturally and commercially available in Taiwan. This variety of tree fern is generally marketed for horticultural purposes because of its character of sorbability to retain water and manure for plants. Tree fern is generally dark brown in colour and is a complex material containing lignin and cellulose as major constituents [13]. Chemical sorption can occur via the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers as chemical bonding [14] and ion exchange [15]. Tree fern, an agricultural by-product, has been currently investigated to remove heavy metals from aqueous solutions [16,17].

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies give the capacity of the sorbent and describe the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed

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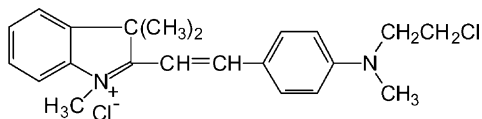
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temperature at equilibrium. The major interest of this study was to investigate sorption of basic dye, Basic Red 13, from aqueous solution using tree fern. The system variables studied include sorbent particle size and temperature.

2. Materials and methods

This study was focused in investigating sorption of basic dye using tree fern. The raw tree fern was dried in an oven at 100 °C for 24 h. The sorbent was screened to obtain four different ranges of geometrical sizes: 38–45 μm, 61–74 μm, 74–88 μm and 104–124 μm. The solutions of dye were prepared in distilled water using C.I. Basic Red 13. All working solutions were prepared by diluting the stock solution with distilled water.

The sorbate (C.I. Basic Red 13) used in the experiments and their structure is listed below. The maximum adsorption wavelength in the visible light range is 524 nm.



Batch sorption experiments were conducted at a constant temperature on a rotary shaker at 100 rpm using 250 ml capped conical flasks. In all sets of experiments, 0.25 g of tree fern was thoroughly mixed into 250 ml of dye solution with initial pH value of 5. After shaking the flasks for 24 h, the tree fern was separated by filtration through a membrane filter (0.25 μm). The filtrate was analysed for the concentration of dye.

2.1. Temperature effect

Batch sorption experiments were carried out at the desired temperature (10, 20, 30 and 40 °C) using particle size of 74–88 μm and each used a range of initial dye concentrations from 0.25 to 1.8 mmol/dm³.

2.2. Particle size effect

Batch sorption experiments were performed at a constant temperature (30 °C). Each used four different tests at particle sizes ranged 38–45 μm, 61–74 μm, 74–88 μm and 104–124 μm and a range of initial dye concentrations from 0.25 to 1.8 mmol/dm³.

3. Results and discussion

Basic forms of Langmuir sorption isotherm [18] have reasonable agreement with a large number of experimental isotherms including those have different interfaces between the two phases [3,4,16,17]. Therefore, the Langmuir sorption isotherm is most widely used for the sorption of a solute

from a liquid solution assuming the sorption takes place at specific homogeneous sites within the sorbent. Furthermore, it also assumes that once a dye occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. If the fraction of covered surface is ϕ , the rate per unit of surface is:

$$r_a = k_a C(1 - \phi) \quad (1)$$

The desorption from the surface is proportional to the amount of surface covered:

$$r_d = k_d \phi \quad (2)$$

where k_a and k_d are the rate constants, r_a the sorption rate, r_d the desorption rate, C the concentration in the solution and ϕ the fraction of the surface covered.

The two rates are equal at equilibrium and we find that:

$$\phi = \frac{k_a C_e}{k_d + k_a C_e} \quad (3)$$

and

$$K_a = \frac{k_a}{k_d} \quad (4)$$

Since q_e is proportional to ϕ :

$$\phi = \frac{q_e}{q_m} \quad (5)$$

The saturated monolayer sorption capacity, q_m , can be obtained. When ϕ approaches 1, then $q_e = q_m$.

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (6)$$

The above equation can be rearranged to the following:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \quad (7)$$

where C_e is the equilibrium concentration (mmol/dm³), q_e the amount of dye sorbed (mmol/g), q_m is q_e for a complete monolayer (mmol/g), K_a the sorption equilibrium constant (dm³/mmol). A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

The structure of tree fern is cellulose-based and the surface of cellulose in contact with water is negatively charged [16]. Basic Red 13 will ionise to give the coloured cationic dye base and this will undergo attraction on approaching the anionic tree fern structure. On this basis, it is expected that a basic dye will have a strong sorption affinity for tree fern.

3.1. Particle size effect

Isotherm experiments were carried out and the data analysed using the linear form of the Langmuir equation to determine the effect of particle sizes on the dye removal capacity

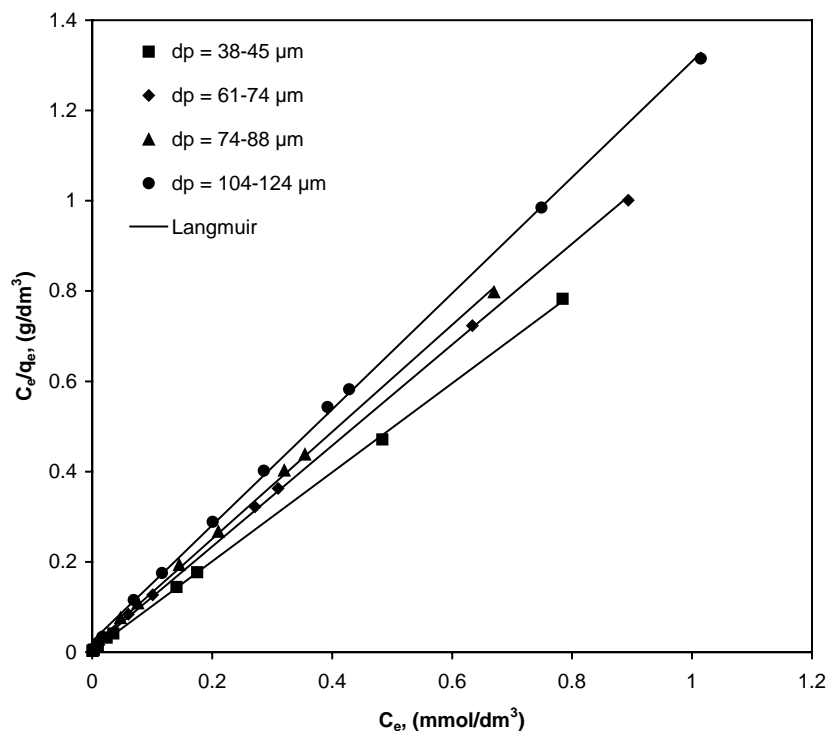


Fig. 1. Langmuir isotherms for the sorption of Basic Red 13 by using tree fern at various particle sizes.

of the various dye/tree fern systems. Isotherms were determined for four tree fern particle size ranges from 38–45 μm to 104–124 μm with constant contact time of 24 h. Fig. 1 showed these isotherms were found to be linear in the concentration range studied and the coefficients of determination, r^2 , were fairly high (Table 1). These values of r^2 indicated the dye/tree fern sorption data strongly followed the Langmuir model of sorption. The isotherm constants, q_m and K_a were presented in Table 1. The monolayer saturation capacities, q_m , increased from 0.778 to 1.01 mmol/g as the tree fern particle sizes decreased ranging from 104–124 μm to 38–45 μm . Therefore, with a given mass of tree fern, smaller particle size would increase surface area availability hence the number of sites increased. Furthermore, the effect was probably due to the inability of the large dye molecule to penetrate all the internal pore structure of the tree fern particles. Values of the monolayer equilibrium capacity of other sorbents from the literature are given in Table 2 for comparison. The square of mean diameter of the tree fern,

Table 1
Langmuir isotherm constants for the Basic Red 13 at various tree fern particle sizes

d_p (μm)	r^2	q_m (mmol/g)	K_a (dm^3/mmol)
38–45	1.000	1.01	256
61–74	1.000	0.894	109
74–88	0.999	0.844	82.8
104–124	0.999	0.778	53.4

d_p^2 , the Langmuir sorption constant, K_a , and the monolayer coverage, q_m , from Table 1 can be used to derive a mathematical relationship. The relationship having a coefficient of determination as high as 0.995 are:

$$q_m = \frac{d_p^2}{1.34d_p^2 - 818} \quad (8)$$

Table 2
Comparison of monolayer equilibrium capacity for basic dye with other agriculture sorbents

q_m (mg/g)	Sorbents	Sorbates	Reference
1120	Bark	Safranine	[3]
915	Bark	Methylene Blue	[3]
875	Cotton waste	Safranine	[3]
838	Rice husk	Safranine	[3]
519	Sugar-industry-mud	Basic Red 22	[4]
320	Palm-fruit bunch	Basic Yellow	[5]
312	Rice husk	Methylene Blue	[3]
278	Cotton waste	Methylene Blue	[3]
253	Peat	Basic Blue 69	[11]
242	Palm-fruit bunch	Basic Red 18	[6]
166	Jack fruit peel	Malachite Green	[7]
71.9	Wood	Basic Blue 69	[8]
22.4	Orange peel	Congo Red	[9]
14.4	Peat	Acid Blue 25	[11]
4.88	Sugar cane dust	Malachite Green	[10]
4.26	Sugar cane dust	Rhodamine B	[10]
3.23	Orange peel	Rhodamine B	[9]
1.33	Orange peel	Procion Orange	[9]
408	Tree fern	Basic Red 13	This study

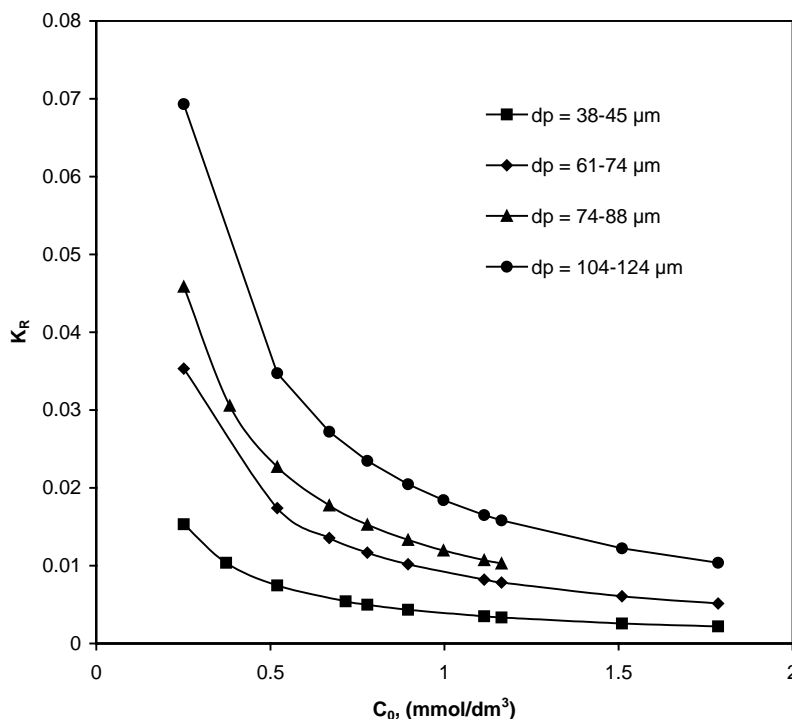


Fig. 2. Values of the separation factor, K_R , for the sorption of Basic Red 13 by using tree fern at various particle sizes.

$$K_a = \frac{6.97 \times 10^4}{(d_p^2)^{0.762}} \quad (9)$$

The effect of isotherm shape can be used to predict whether a sorption system is 'favourable' or 'unfavourable' both in fixed-bed systems [19] as well as in batch processes [20]. According to Hall et al. [21], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0} \quad (10)$$

where K_R is a dimensionless separation factor, C_0 the initial concentration (mmol/dm³) and K_a the Langmuir constant (dm³/mmol). The parameter K_R indicates the shape of the isotherm accordingly:

Values of K_R	Type of isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The values of K_R for Basic Red 13 at different particle sizes are shown in Fig. 2. The K_R values indicated that sorption was more favourable for the higher initial dye concentrations than the lower ones. However, the sorption process became more favourable with decreasing particle size of tree

fern. Nevertheless, referring to Fig. 2, it was obvious that tree fern would be an effective sorbent for removing dye from solution.

3.2. Temperature effect

The temperature effect on the sorption of Basic Red 13 on tree fern is shown in Fig. 3. The results revealed that the sorption capacity increased from 0.702 to 0.900 mmol/g with the temperature increasing from 283 to 313 K. Since the sorption increased when temperature rose, therefore this system was endothermic. It was a chemisorption mechanism where an increase in number of molecules acquiring sufficient energy to undergo chemical reaction with lignins and hemicelluloses in the tree fern. A conventional mechanism, physisorption systems, where the increase of temperature usually increases the rate of approach to equilibrium, but decreases the equilibrium capacity. In addition, the creation of some new active sites for additional sorption on the surface of the sorbent also was endothermic [22].

3.3. Thermodynamic parameters

Based on fundamental thermodynamics concept, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions

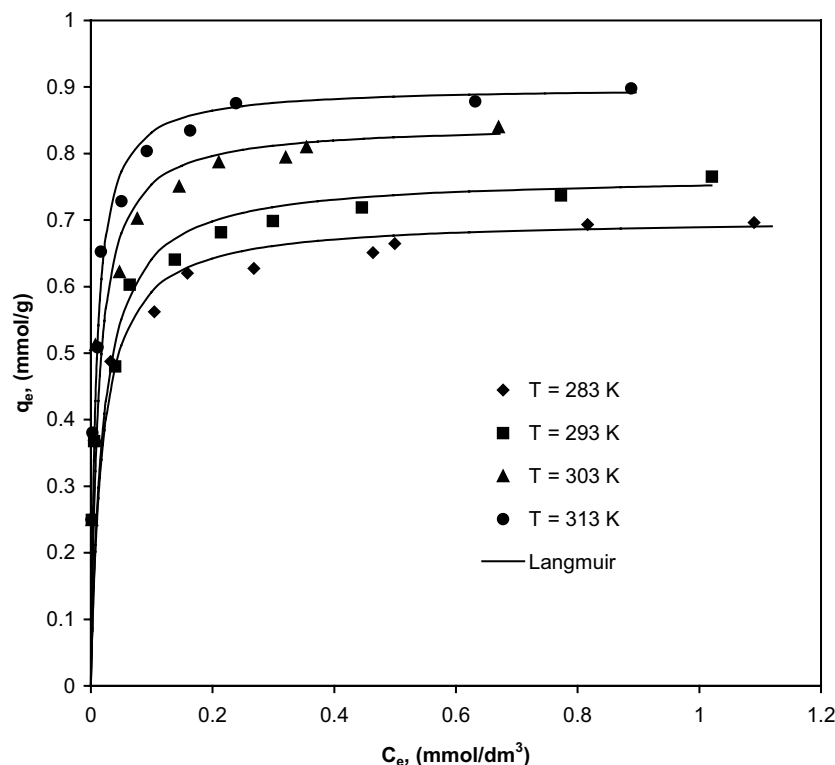


Fig. 3. Langmuir isotherms for the sorption of Basic Red 13 by using tree fern at various temperatures.

occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant, K_a , is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \quad (11)$$

where ΔG° is the standard free energy change (J); R the universal gas constant, 8.314 J/K mol and T the absolute temperature (K).

The Gibbs free energy change, ΔG° , can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

A plot of ΔG° versus T was linear. Enthalpy change, ΔH° , and entropy change, ΔS° , were determined from the slope and intercept of the plots. The values for the sorption equilibrium constant, K_a , decreased with increasing temperature. The thermodynamic parameters Gibbs free energy change, ΔG° , for the sorption processes are shown in Table 3. The

negative values of ΔG° confirmed the feasibility of the process and the spontaneous nature of sorption with a high preference of Basic Red 13 dye on tree fern. The value of ΔH° was positive (21.7 kJ/mol), indicating that the sorption reaction was endothermic. The positive value of ΔS° (0.109 J/mol K) reflected the affinity of the tree fern for the dye and suggested some structural changes in dye and tree fern [23]. In addition, positive value of ΔS° also showed the increase of randomness at the solid/liquid interface during the sorption of dye on tree fern.

4. Conclusion

It is evident that tree fern, a commercially available natural material, is a good sorbent for Basic Red 13 and it can be suggested for the removal of basic dye from wastewater. Both the increase of the temperature and decrease of the tree fern particle size resulted in a higher dye loading per unit weight of the sorbent. Values of the separation factor, K_R , indicated the dye/tree fern system was a favourable sorption. The results gained from this study were extremely well described by the theoretical Langmuir isotherm. The equilibrium monolayer sorption capacity of tree fern for Basic Red 13 was 1.01 mmol/g when the temperature was 30 °C and the tree fern particle size range was 38–45 μm . The thermodynamics of the system pointed out the system was spontaneous and endothermic.

Table 3
Langmuir isotherm constants for the Basic Red 13 at various temperatures

T (K)	r^2	q_m (mmol/g)	K_a (dm ³ /mmol)	ΔG° (kJ/mol)
283	0.999	0.702	53.9	-9.38
293	0.999	0.766	51.2	-9.59
303	0.999	0.844	82.8	-11.1
313	1.000	0.900	122	-12.5

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