



ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(2):670-675

Removal of Erichrome Black T from synthetic wastewater by activated Nilgiri leaves

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ABSTRACT

Adsorption of dye is an alternative technology to remove colour from wastewater. Activated carbon prepared from low cost nilgiri (eucalyptus globulus) leaves has been utilized as an adsorbent for the removal of dye from aqueous solution. In this study the adsorption characteristics of Erichrome Black T dye on to activated nilgiri leaves have been studied. Experiments were conducted at different pH, adsorbent dose, initial concentration of dye and different contact time. The physico-chemical characterization and chemical kinetics were examined for the same dye. The results reveals that activated nilgiri leaves could be employed as low cost alternative to commercial activated carbon in wastewater treatment for dye removal.

Keywords: Adsorption, Activated nilgiri leaves, Erichrome black T, Physico-chemical characterization, Langmuir and Freundlich isotherm.

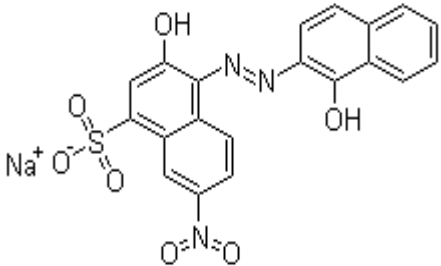
INTRODUCTION

Dyes usually have synthetic origins and complex aromatic molecular structures. They are highly coloured polymers and fewer biodegradables. Dyes are widely used in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharged into environmental water bodies. It not only affects aesthetic merit but also reduces light penetration and photosynthesis [1]. The disposal of coloured wastes into water affects the environment, as they are highly toxic to human and aquatic life.

There are various methods for treating dyes containing wastewater such as coagulation and flocculation, oxidation or ozonation, membrane separation and activated carbon adsorption. The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. Activated carbon (powdered or

granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But, commercially available activated carbon is very expensive [2]. The removal of dyes from effluent using adsorption process provides an alternative treatment, especially if the adsorbent is inexpensive and readily available [3]. A number of non-conventional, low cost plant materials (residues) such as babul Seed [4], the peel of cucumis sativa fruit [5], mango seed shells [6], orange peel and lemon peel [7] are used as adsorbent. The present investigation is an attempt to remove Erichrome Black T (EBT) from synthetic wastewater by adsorption process using a low cost activated carbon prepared from nilgiri leaves as an adsorbent.

Table 1: Characteristics of Erichrome Black T

Structure	
Molecular Formula	C ₂₀ H ₁₂ N ₃ NaO ₇ S
Molecular weight	461.38
λ _{max} , nm	520 nm
CAS number	1787-61-7
CI Number	14645
Water Solubility	50 g / l (20 °C)

EXPERIMENTAL SECTION

Adsorbent preparation

Acid activation method was used for preparation of activated carbon. Leaves of Nilgiri were collected from surrounding area. The leaves were washed with distilled water, dried in sunlight. The material was ground to fine powder, then treated with concentrated sulphuric acid, and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The materials was dried an oven at 105° C for 24 hour. The resulted material was sieved in the size range of 450 - 600 micron mesh ASTM. The adsorbent was dried at 105°C overnight before the adsorption experiments.

Adsorption experiments

In each adsorption experiment, 100 mL of dye solution of known concentration and pH was added to 400 mg of adsorbent in a 250 mL round bottom flask. This was done at room temperature (39±1°C). The mixture were stirred on a rotary orbit shaker (Model No.-REMI-20-RS-24BL Sr. No.-RIS-377) at 180 rpm. The mechanism of adsorption was studied by analyzing adsorption uptakes of the dye from aqueous solution. The samples were withdrawn from shaker every 15 minutes time interval and the adsorbent was separated from the solution by centrifugation at 4000 rpm for 5 minutes. In order to determine residual dye concentration the adsorbances value of the supernatant solution was measured before and after the treatment, at 520 nm with UV spectrophotometer (Systronic, Model no 166). Three main system variables, dye concentration, adsorbent dosage, and pH variation were studied to investigate and check suitability of adsorption mechanism for dye removal by using natural waste nilgiri leave activated carbon (NLAC) as an adsorbent.

RESULTS AND DISCUSSION

The physico-chemical properties of the prepared nilgiri leave activated carbon were determined by standard methods (Table 2).

Table 2: Physico- chemical properties of NLAC

Adsorbent	pH	Moisture Content (%)	Ash Content (%)	Apparent density	Solubility in water (%)	Solubility in HCL (%)	Surface area (m ² /g)
NLAC	7.9	3	80	0.2631	0.72	1.97	178

Effect of initial dye concentration

The experiments were carried out at fixed adsorbent dose (0.4g /100 mL) in the test solution, 39 ± 1 °C room temperature, pH (7.0) and at different initial concentrations of EBT (50, 100,150, 200 and 250 mg/L) for different time intervals (15, 30, 45, 60, 90 and 120 min). The results are shown in Table 3.

Table 3: Effect of initial dye concentration on dye removal using NLAC
(Adsorbent dose = 0.4g / 100 mL, initial pH=7.0, time 120 min)

Initial dye concentration (mg /L)	Percentage of dye removal with time (min)					
	15	30	45	60	90	120
50	16.36	37.27	60.90	76.36	90	90.91
100	21.83	38.02	52.81	75.35	90.14	90.84
150	23.12	44.35	61.25	75.65	88.12	89.37
200	22.27	42.72	57.72	75	89.54	90
250	21.45	42.51	60.32	76.11	88.25	88.66

The results show that some leaves of nilgiri have good potential of dye removal. The equilibrium for dye removal attainment was achieved after 120 min. This may be because sulphuric acid treated leaves of nilgiri have macro and micro pores, resulting in longer contact time between the dye molecules and the adsorbent. In the process of dye adsorption, initially dye molecules have to encounter the boundary layer effect before diffusing from boundary layer film onto adsorbent surface. This is followed by the diffusion of dye into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time [8]. The time profile of dye uptake is a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent.

Table 4: Effect of adsorbent dose on dye removal
(Dye concentration= 100 mg/l, initial pH=7.0, time 120 min)

Adsorbent dose (g/100mL)	Percentage of dye removal with time (min)					
	15	30	45	60	90	120
0.2	18.79	34.22	43.62	48.99	65.77	66.44
0.4	23.94	38.02	52.81	75.35	88.02	90.14
0.6	25.24	52.42	53.39	71.84	89.2	90.29
0.8	26.59	40.42	54.25	75.53	90.42	92.55
1	34.56	51.85	66.66	77.77	92.59	93.82

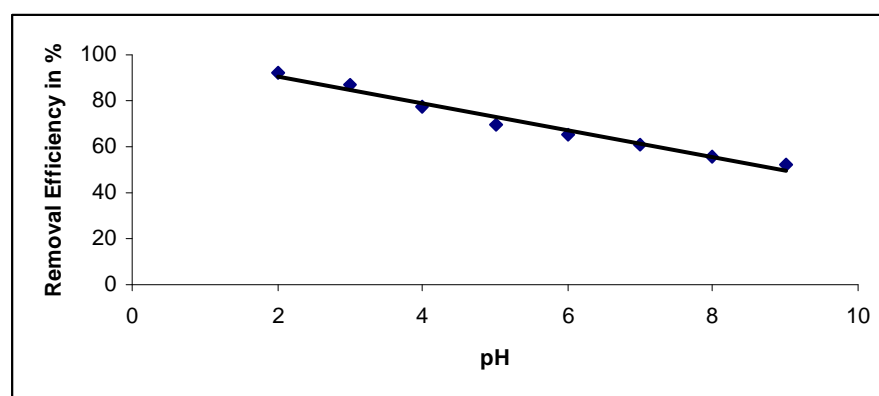
Effect of dose

The adsorption of EBT on NLAC were studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 mL) in the test solution while keeping the initial dye concentration 100 mg/L ($39 \pm 1^\circ\text{C}$) Experiments were carried out at different contact times for 120 mins. The results are tabulated in Table 4. The percent of adsorption increased with increasing adsorbent dose. The increase in the percent removal of dyes with the increase in adsorbent dosage is due to the availability of larger surface area with more active functional groups [9].

Effect of pH

In order to study the effect of pH on EBT by Nilgiri leaves, experiments were carried out at 100 ppm initial dye concentration with 400 mg /100 mL adsorbent mass at room temp ($39 \pm 1^\circ\text{C}$) for 3 hr equilibrium time , The result are shown in Figure 1 . The removal of dye is maximum at lower pH and reduces at high pH.

Figure 1: Effect of pH on dye removal using NLAC.



Adsorption Isotherm

The adsorption data was analysed with the help of the Freundlich and Langmuir isotherms:

The Langmuir isotherm is represented by the following equation

$$(C_e/q_e) = (C_e/Q_0) + (1/Q_0b) \dots\dots\dots (1)$$

Where,

q_e = amount of dye adsorbed at equilibrium (mg/g),

C_e = equilibrium concentration of dye (mg/L),

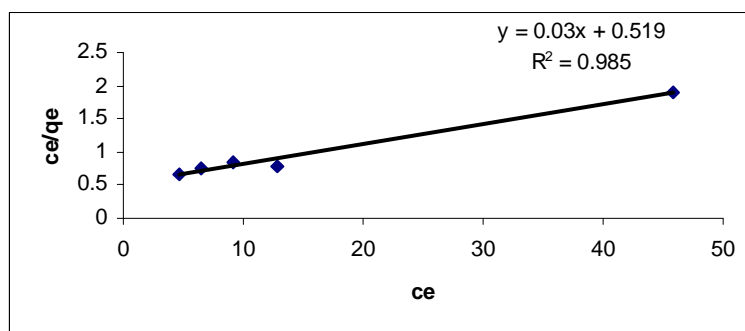
Q_0 = Langmuir Constant related to adsorption capacity (mg/g) and

b = Langmuir Constant related to energy of adsorption capacity (L/mg) [4].

The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms (Figure 2). The values of Q_0 and b were determined from the slope and intercept of the plots (Table 5).

Table 5: Langmuir and Freundlich isotherm of NLAC

Adsorbent	Langmuir isotherm				Freundlich isotherm		
	Q_0	B	Correlation coefficient (r)	R_L	Intercept (k_f)	Slope (1/n)	Correlation coefficient (r)
NLAC	33.333	0.058	0.985	0.108	0.509	0.548	0.938

Fig 2: Langmuir isotherm for the removal of EBT

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L which is given as

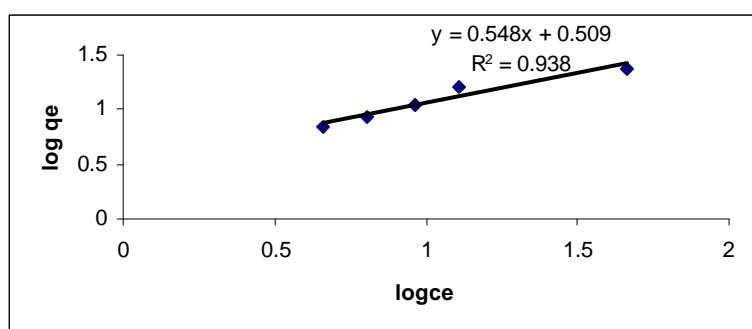
$$R_L = 1 / (1 + bC_o) \dots (1)$$

Where C_o is the initial dye concentration in solution (mg/L). The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be 0.108 suggesting the isotherm to be favorable at the concentrations studied.

Freundlich adsorption isotherm model used to explain the adsorption phenomenon is represented by the equation:

$$\log q_e = (1/n) \log C_e + \log k_f \dots (2)$$

Here q_e is the amount of EBT dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in the solution (mg/L) and k_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of $\log q_e$ versus $\log C_e$ shows that the adsorption of EBT dye follows the Freundlich isotherm (Figure 3).

Fig 3: Freundlich isotherm for the removal of EBT

The values of k_f and n were calculated from the intercept and slope of the plot. The magnitude of the exponent “ n ” gives an indication of the favorability and k_f the capacity of the adsorbent/adsorbate system. The n value was (1.825) was in between 1 and 10 representing beneficial adsorption.

CONCLUSION

The removal of EBT from aqueous wastewater using acid activated nilgiri leaves as an adsorbent

has been investigated under different experimental condition in batch mode. The adsorption of EBT was depending on the adsorbent dose and the EBT concentration in the wastewater. The results show that nilgiri leaves has good adsorption efficiency and adsorption efficiency increase as dose increase. This study also proves that some nilgiri leaves are alternative option for dye removal from dilute industrial effluents.

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