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Removal of Erichrome Black T from Synthetic Wastewater by Cotton Waste

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Abstract: Adsorptions of Erichrome Black T dye in aqueous solution on cotton stem activated carbon have been studied as a function of contact time, concentration and pH. Effect of various experimental parameters has been investigated at 39±1 °C under batch adsorption technique. The result shows that cotton stem activated carbon adsorbs dye to a sufficient extent. The physicochemical characterization and chemical kinetics was also examined for the same dye. The overall result shows that it can be fruitfully used for the removal of dye from wastewaters.

Keywords: Erichrome Black T, Adsorption, Natural waste, Dyes removal, Physicochemical properties.

Introduction

Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetics, and pharmaceutical and food industries because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dyes. Today there are more than 10,000 dyes available commercially, most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and affects the quality of waterbodies[1]. The extensive use of dyes often causes pollution problems in the form of colored wastewater discharged into environmental water bodies. It is not only affects aesthetic merit but also reduces light penetration and photosynthesis[2]. A lot of cases throughout the world are reported about the role of dyes in connection with variety of skin, lung, and other respiratory disorders. The problem can impact several vital activities such as fisheries, livestock and agriculture since the polluted water is no longer suitable for their particular use. There are various methods for treating dyes containing wastewater such as coagulation and flocculation, oxidation or ozonation, membrane separation and activated carbon adsorption. Out of these methods, adsorption is the procedure of choice as it can be used to remove different types of dyes. Activated carbon (powdered or granular) is most widely used adsorbent because it has excellent adsorption efficiency for organic compounds, but its use is usually limited due to its high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. Consequently, a number of low cost and easily available materials such as waste biomass are being studied for the removal of different dyes from aqueous solutions at different operating conditions[3]. Natural wastes from agro based industries are of attention mainly because of their abundance. Production of activated carbon from this source may reduce the cost of wastewater treatment and at the same time open new market for low-cost agricultural by-product. A number of non-conventional, low cost plant materials (residues) such as babul Seed[4], sunflower stalks[5], the peel of cucumis savita fruit[6], tamarind fruit shell[7], orange peel and lemon peel[8] and are used as adsorbent. A number of low cost and easily available materials such as mosambi peel, cotton stem, neem leaves, grass, badam leaves and nilgiri leaves *etc*. can be studied for the removal of different dyes from aqueous solutions at different operating conditions.

The objective of the present study is to determine the optimum conditions for the removal of textile azo dye EBT from aqueous solution by adsorption technique using sulphuric acid treated cotton waste as an adsorbent.

Experimental

The stems of cotton were collected from local field of Jalgaon district in clean plastic bags. These waste materials are washed with distilled water, dried in sunlight, then 60 °C for 24 h in hot air oven. The dried material was subjected for acid treatment (ratio 1:1) and kept at room temperature overnight and stored in a tight lid container for further studies. It is then screened through a mesh sieve with a particle size range of 180-300 µm.

Preparation of activated carbon from adsorbents

Carbon was prepared by treating air-dried prepared adsorbent with concentrated sulphuric acid in a weight ratio of 1:1 for 24 h. The resulting black product was kept in an air-oven maintained at 500 °C for 12 h followed by washing with $NaHCO_3$ and water until free of excess acid; pH become 7.0 and dried at 150±5 °C to obtain sulphuric acid treated cotton stem activated carbon (CSAC). The carbon product obtained was ground well to fine powder and its physical properties were analyzed by usual standard methodologies.

Preparation of dye solution

Stock solution (1000 mg/L) of EBT was prepared by dissolving 1 g of dye in 1000 mL of double distilled water. The stock solutions were diluted with double distilled water to obtain required standard solution. Batch adsorption studies were performed at room temperature.

Experimental methods and measurements

The adsorption experiments were carried out by agitating the carbon with 50, 100, 150 & 200 mg/L dye solution of desired concentration at pH 7.0 and at room temperature in a mechanical shaker (120 rpm). After the defined time intervals, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual dye concentration using a UV-Visible spectrophotometer (Shimadzu UV Visible spectrophotometer, model UV mini 1240) at λ_{max} = 520 nm

Results and Discussion

Characterization of the adsorbent

The physicochemical properties of the prepared activated carbon were determined by standard procedures. Surface area was determined by BET method. The physicochemical properties are listed in Table 1.

Table 1. Characteristic of adsorbent

S.No.	Properties	CSAC
1	pH	7.3
2	Moisture Content, %	7
3	Ash Content	3.2
4	Apperent Density	0.431
5	Solubility in water, %	0.54
6	Solubility in HCl	1.78
7	Surface area, m^2/g	198

Effect of initial dye concentration

The adsorption studies were carried out at fixed adsorbent dose (400 mg/100 mL) in the test solution, at 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 2.

Table 2. Effect of initial dyes concentration on dye removal (absorption dosage 0.5 g 100 m/L pH=7.0)

Time, min	Concentrations, mg/L				
	50	100	150	200	250
	Removal Percentage				
15	30	36.61	13.12	18.63	26.72
30	43.63	51.40	41.25	41.81	44.12
45	56.36	62.67	52.5	59.54	60.32
60	67.27	72.53	60.62	73.63	71.25
90	82.72	83.09	81.87	83.18	83.40
120	82.72	83.09	81.87	83.18	83.40

The initial concentration provides an important driving force to overcome all mass transfer resistance of dye anions between the aqueous and solid phases[2]. In addition, increasing initial dye concentration increases the number of interactions between dye anions and adsorbents, which enhances the adsorption process. Hence a higher initial concentration of EBT will increase the adsorption rate. The equilibrium for dye removal attainment was achieved after 120 min. In dye adsorption process, 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[3].

Effect of adsorbent dose

The adsorption of EBT on CSAC was studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g m/in 100 mL) in the test solution while keeping the initial dye concentration 100 ppm. Experiments were carried out at different contact times for 120 min.

Table 3. Effect of adsorption dose on the dye adsorption

Adsorbent dose, g 50 mL^{-1}	Percentage of dye removal with time, min					
	15	30	45	60	90	120
0.2	18.54	38.41	43.04	49.69	54.96	55.63
0.4	19.01	51.40	62.67	72.53	79.57	80.28
0.6	22.32	40.17	51.78	66.96	85.71	85.71
0.8	29.59	38.77	43.87	71.42	85.71	86.73
1	36.47	47.05	63.52	77.64	90.58	92.94

The percentage removal of dye was found to increase with the increase in does of adsorbent. 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

The effect of pH on adsorption of EBT on CSAC was studied at 100 ppm initial dye concentration with 400 mg /100 mL adsorbent mass at room temperature for 3 h equilibrium time, The results are shown in Figure 1. As the pH value increased from 2 to 9, the efficiency of the dye removal is lessen.

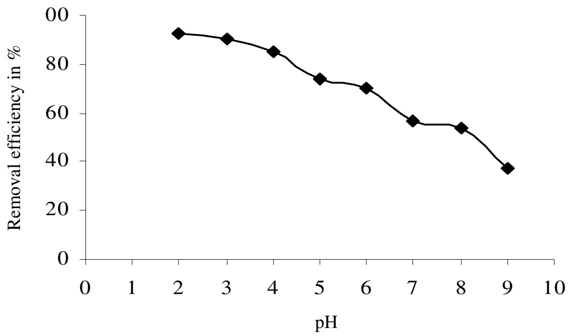

Fig 1- Effect of pH on EBT removal

The pH value of dye solutions plays an important role in the whole adsorption process and particularly in adsorption capacities. In this study, the effect of pH can be explained by considering the surface charge on the adsorbent.

As the pH of the system increases, the number of hydroxide ion increases and will compete with anionic ion of the dye on the adsorption site in the alkaline condition and could reduce the adsorption capacity since the number of positively charged sites decreases. Moreover, there are also no more exchangeable anions on the outer surface of the adsorbent. A negative charged surface site on the adsorbent does not favour the adsorption of dye ions due to electrostatic repulsion and abundance of OH^- ion[10].

Adsorption isotherm

The experimental data are analyzed according to the linear form of the Langmuir and Freundlich isotherms. The Langmuir isotherm is represented by the following equation

$$(Ce/qe) = (1/Qob) + (Ce/Qo) \quad (1)$$

Here Ce is the equilibrium concentration (mg/L), qe is the amount adsorbed at equilibrium (mg /g). Qo and b is Langmuir constants related to the adsorption efficiency and energy of adsorption, respectively [11].

The linear plots of Ce/qe *versus* Ce suggest the applicability of the Langmuir isotherms (Figure 2). The values of Q_o and b are determined from the slope and intercept of the plots and are presented in Table 4.

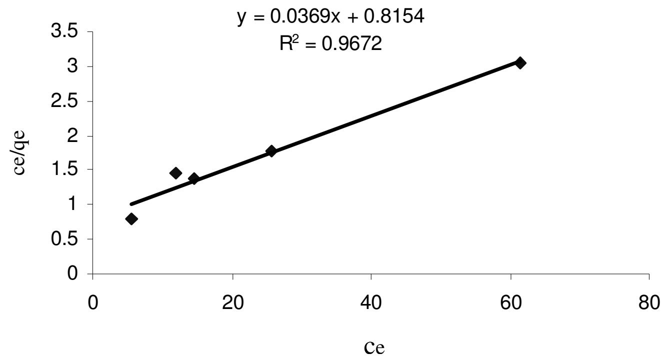

Figure 2. Langmuir isotherm for the removal of EBT by adsorption on CSAC

Table 4. Langmuir and Freundlich parameters of adsorption isotherms

Adsorbents	Langmuir isotherm				Freundlich isotherm		
	Q_0	B	Correlation coefficient (r)	R_L	Intercept (k_f)	Slope (1/n)	Correlation coefficient (r)
Cotton	27.10027	0.043648	0.9672	0.138927	0.4589	0.4759	0.9618

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL that is given in Eq.2.

$$R_L = 1 / (1 + bCo) \qquad (2)$$

The value of RL indicates the type of the isotherm to be either favorable (0 < RL < 1), unfavorable (RL > 1), linear (RL = 1) or irreversible (RL = 0). The value of RL was found to be 0.138927 suggesting the isotherm to be favorable at the concentrations studied[12].

The Freundlich equation is also employed for the adsorption of EBT on the adsorbent. The Freundlich isotherm is represented as

$$\log qe = \log kf + (1/n) \log Ce \qquad (3)$$

Here qe is the amount of EBT dye adsorbed (mg/ g), Ce 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 qe *versus* log ce shows that the adsorption of EBT follows also the Freundlich isotherm (Figure 3).

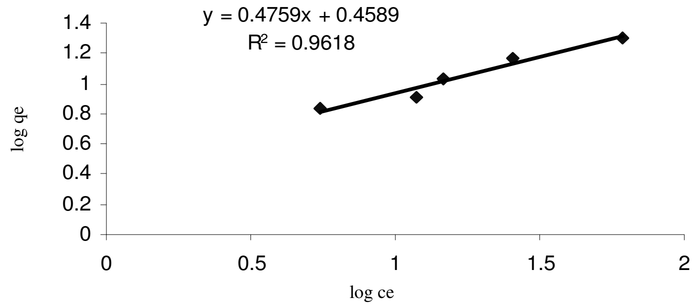

Figure 3. Freundlich isotherm for the removal of EBT by adsorption on CSAC

The values of K_f and n found and given in Table 4, shows the increase of negative charge on the surface that enhances the electrostatic force between the carbon surface and the dye ion, which increases in turn the adsorption of dye. The values clearly show the dominance of adsorption capacity. 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 (2.10128) was in between 1 and 10 representing beneficial adsorption.

Conclusion

CSAC works well as adsorbent for EBT. The adsorption of EBT was depending on the adsorbent dose of CSAC and EBT concentration in the wastewater. CSAC showed more adsorption efficiency and adsorption efficiency increased on increasing adsorbent dose. The adsorption obeyed both Langmuir and Freundlich isotherms. These studies prove that some natural adsorbent such as cotton stem can be an alternative option for dye removal from dilute industrial effluents.

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