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Kinetics and Equilibrium Studies on Biosorption of CBB by Coir Pith

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Abstract: The biosorption of Coomassie Brilliant Blue by acid treated coir-pith has been investigated in batch mode. Effect of time, Initial Concentration of dye and initial adsorbent concentration on biosorption was investigated. The pseudo-first order kinetic model was applied to the adsorption system and high co-relation co-efficient favored Pseudo-second order reaction. Freundlich's and Langmuir's mathematical models were used to describe batch adsorption equilibrium data and the constants were evaluated. The adsorption was found to be favourable in both isotherms. The maximum adsorption capacity was found to be 31.847mg/g. The adsorption capacity for the system was 6.438 and adsorption intensity was 2.8019. The investigation shows that the acid-treated coir pith is better suited for the removal of dyes from the textile industry effluent.

Key words: Biosorption . coco-pith . CBB . Langmuir's . Freundlich's isotherms

INTRODUCTION

The inappropriate disposal of dyes in waste water constitutes an environmental problem and can cause damage to the ecosystem [1]. Water pollution by dyes is one of the major pollution sources in India. Wastewater containing dye cause water pollution by lowering light penetration and photosynthesis and toxicity from heavy metals associated with pigments [2]. Conventional biological processes are relatively inefficient for color removal [3]. In recent years, use of microbial biomass for decolorization of textile industry waste water is promising alternative in which some bacteria and fungi are used to replace present treatment process [4]. Though they are effective in treating waste water they suffer some limitations like production of biomass for large scale process and disposing the biomass after the treatment. Thus using agricultural waste products as a potential biosorbent of dyes is being extensively investigated. A variety of agricultural biosorbent have been investigated like sago waste [5], cassava waste [6], peanut skins [7], banana pith [8], sugarcane waste [9], chaff, apple pomace [10], wheat straw [11], rice husk [12], yellow passion fruit waste [13], coconut husk carbon [14], coir-pith carbon [15] just to mention a few. The chemical modification of sorbent with the help of an acid, base, is done for enhancing biosorption [16]. The kinetic and equilibrium parameters of acid treated coir pith have been investigated in the present study.

MATERIALS AND METHODS

Preparation of adsorbent: The coir pith used in the study was obtained from in and around Salem district, Tamil Nadu, India generated as a waste after coir making. They were washed with de-ionized water thrice and was dipped in one molar solution of acid (HCl) for two days and then washed with double distilled water thrice to remove any residue of acid. The pith was then dried at 55°C for a day in oven and used for biosorption studies.

Preparation of dye solution: 0.1 mg/mL (100 mg/L) solution of Coomassie brilliant blue was prepared and stored in brown reagent bottles in dark place to prevent oxidation of the dye solution. The dye solution was prepared and used freshly, before 24 hours of their preparation . A standard graph of Dye concentration versus optical density at 580 ηm was plotted.

Estimation of optimum time and kinetics: One gram of treated coir pith was added to 100 ml of 100 mg/L of dye solution and shaken at a 30°C. Samples were withdrawn at regular intervals of 15 min and their optical density was measured. The plot of Adsorption Capacity versus Time was plotted and the optimum time was found from the graph. The Adsorption Kinetics was found from the time adsorption data.

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Effect of initial dye concentration and adsorbent concentration: 20, 40, 60, 80, 100 mg/L dye solutions were prepared. 0.2 g of adsorbent was added to 50 ml of solution and shaken for 150 minutes at 30°C. The OD was measured and adsorption capacity was found. For the effect of adsorbent concentration, 0.2, 0.4, 0.6, 0.8, 1.0 g of adsorbent was added to 100 mL of 0.1mg/mL dye solution and shaken for 150 minutes at 30°C. The Absorbance was measured and subsequently the adsorption capacity was determined. From the above measured data, sorption kinetics, Langmuir's isotherm and Freundlich's parameters were evaluated. The dye uptake was calculated using the following mass balance equation

$$q = \frac{V(Ci-Cf)}{S}$$

Where
q = Dye uptake (mg dye/ g sorbent)
V = Volume of Dye solution in contact with sorbent (L)
C_i = Initial Concentration of metal in solution (mg/L)
C_f = Final Concentration of metal in solution (mg/L)
S = Dry weight of the sorbent (g)

Theory and data evaluation

Sorption kinetics: The rate of sorption of a molecule on the adsorbent surface is an important parameter. In batch adsorption system it is necessary to establish time dependence of the process. The Pseudo-second order rate equation developed by Ho *et al.* 1995 was used [17, 18].

$$\frac{dqt}{dt} = K(qe - qt)^2$$

Where k is the equilibrium constant (g/ mg.min), q_t is the amount of dye adsorbed on sorbent at time t (mg/g) and q_e is the equilibrium dye uptake (mg/g). Equation can be rearranged as

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}t$$

A plot of t/q_t Vs t will give a linear plot if the sorption data obeys pseudo-second order kinetics. $h = kq_e^2$ is described as the initial rate constant as t approaches zero.

Adsorption isotherms

Biosorption models: Freundlich, 1906 [19] and Langmuir, 1916 [20] isotherm models were used for interpreting CBB biosorption equilibrium.

Freundlich Isotherm: The Freundlich's equation is given by:

$$q = Kf.Ce^{1/n}$$

Where
q = Dye adsorbed to the adsorbent at equilibrium (mg/g)
C_e = Equilibrium concentration of dye in the solution (mg/mL) in other words C_f
K_f = Empirical constant, indicates the adsorption capacity of the sorbent.
n = Constant indicating the intensity of adsorption.

The equation can be rearranged to linear for as given below.

$$\log q = \log Kf + \frac{1}{n}\log Ce$$

The value of K_f and n are obtained by plotting log q Vs log C_e.

Langmuir isotherm: The Langmuir's equation is given by

$$q = \frac{Q_{max} bC_e}{1 + bC_e}$$

Where
Q = Dye adsorbed to the adsorbent at equilibrium (mg/g)
Q_{max} = Maximum possible amount amount of dye that can be adsorbed per unit dry weight of sorbent.
C_e = Equilibrium concentration of dye in the solution (mg/mL)
b = Empirical constant, indicating the affinity of sorbent towards the sorbate.

This equation can be linearised as:

$$\frac{C_e}{q} = \frac{1}{Q_{max}.b} + \frac{1}{Q_{max}}C_e$$

The adsorption constants Q_{max} and b can be obtained by plotting 1/q as a function of $1/C_e$

RESULTS AND DISCUSSION

The time course profile of sorption of CBB from 100mL 0.1mg/mL solution is shown in Fig. 1 and in Table 1. The Concentration decreased to 0.0102 (89.8% Sorption) and beyond that remained constant with time. From the time adsorption data it was found that the optimum time for adsorption is 150 min to obtain

Table 1: Effect of contact time on sorption process

Time (min)	CONC (mg/L)	Ce (mg/L)	Adsorption capacity
0	0.100000	100.0000	0.0000
15	0.043311	43.3110	5.6680
30	0.035970	35.9701	6.4029
45	0.029363	29.3634	7.0636
60	0.025693	25.6929	7.4307
75	0.021288	21.2884	7.8711
90	0.015049	15.0487	8.4951
105	0.013948	13.9476	8.6052
120	0.012479	12.4794	8.7520
135	0.011011	11.0112	8.8988
150	0.010644	10.6442	8.9355
165	0.010277	10.2771	8.9722
180	0.010277	10.2771	8.9722

Table 2: Effect of adsorbate concentration on adsorption

Conc (mg/L)	Ce (mg/L)	Adsorption capacity (mg/ g)
20	1.1011	9.4494
40	2.9363	18.5318
60	8.8090	25.5954
80	17.6180	31.1909
100	21.2884	39.3557

Table 3: Effect of adsorbent concentration on adsorption

Gm adsorbent (g)	Conc (mg/L)	Adsorption capacity (mg/g)
0.2	46.2473	26.8763
0.4	21.6555	19.5861
0.6	12.8464	14.5255
0.8	6.2397	11.7200
1.0	2.5692	9.7430

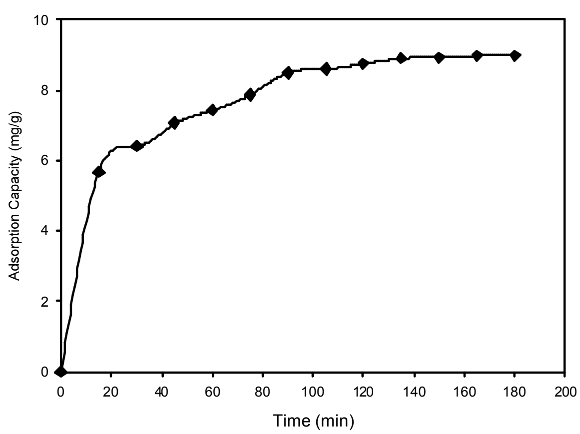

Fig. 1: Effect of time on adsorption

equilibrium and thus the contact time for further experiments were 150 min. The first order kinetics developed by [21] was tried without success. However the sorption of CBB on acid treated coir-pith fitted well to pseudo second order reaction. This is because of the

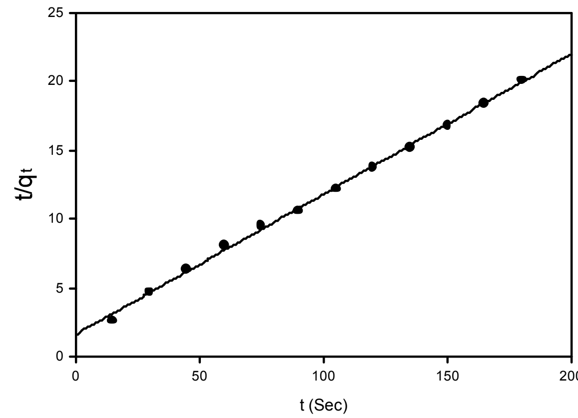

Fig. 2: Pseudo-first order kinetics. Y = 1.5761+ 0.1020X, R = 0.9991

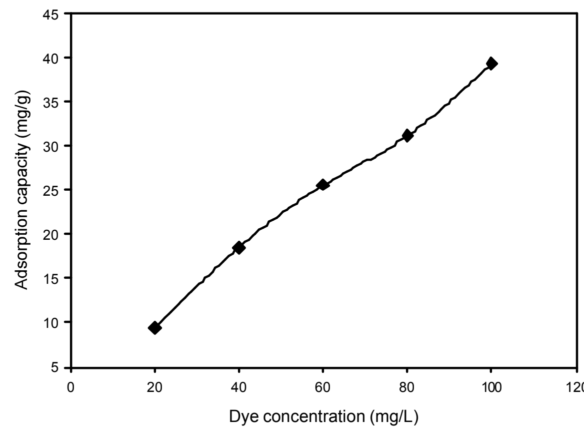

Fig. 3: Effect of initial dye concentration on adsorption

linear relationship between t/q_t Vs t (R=0.9991). The initial rate constant h is 0.63447 mg/g sec.

The data found to be obeying the pseudo-second order kinetics. The plot of pseudo second order reaction is shown in Fig. 2.

The effect of initial dye concentration on adsorption is tabulated in Table 2 and illustrated in Fig. 3. The adsorption capacity was found to be increasing with adsorbate concentration. The plot on effect of initial dye concentration on biosorption shows the sorption increases with the initial concentration of the dye. The plot is likely to be linear. The plot of adsorption capacity Vs adsorbent concentration shows that the adsorption capacity reduces with the increase in adsorbent concentration.

The effect of amount of sorbent on adsorption is given Table 3 and in Fig. 4. The Freundlich's plot and Langmuir plot shown in Fig. 5 and 6 respectively. The regression coefficients are 0.9828 and 0.9080 respectively.

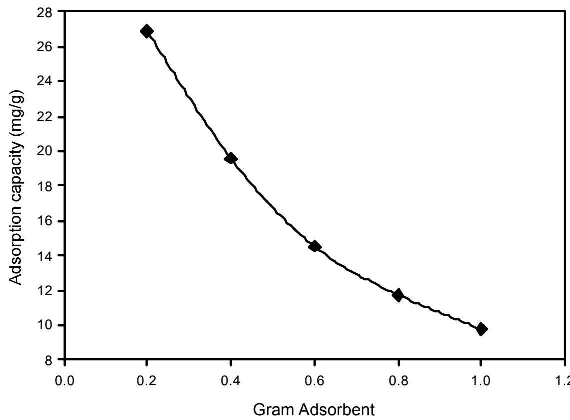

Fig.4: Effect of adsorbent concentration on adsorption capacity

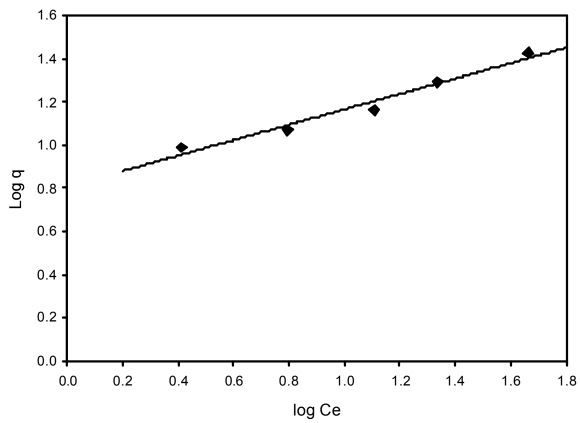

Fig. 5: Freundlich plot. Y = 0.8088+0.3569X, R = 0.9828

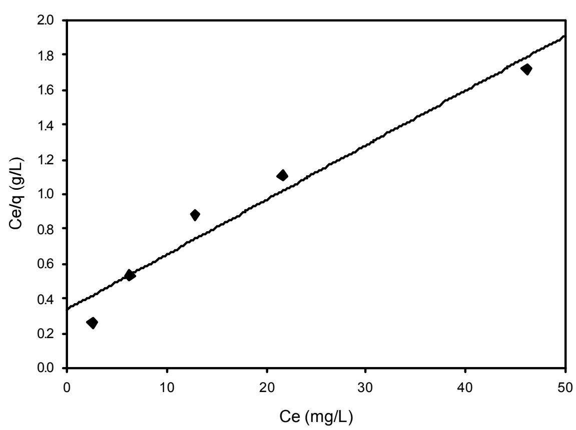

Fig. 6: Langmuir plot. Y = 0.3385+0.0314X, R = 0.9771

The Freundlich's isotherm best fitted the data with n = 2.8019 and K_f = 6.438. According to Kadirvelu and Namasivayam (2000) [15] n values between 1 and 10 represents beneficial adsorption and thus the adsorption of Dye on acid treated coir-pith is also beneficial.

From the Langmuir plot, q_{max} = 31.847 mg/g. and b = 0.0926 L/mg (0.295 L/mg). The essential characteristics of the Langmuir isotherm can be expressed as dimension-less constant separation factor or equilibrium parameter given by R_L.

$$R_L = \frac{1}{1+K_LC_o}$$

Where K_L is Langmuir's Equilibrium Constant which is related to the affinity of binding sites and K_L=Q_{max}b [22]. C_o is the initial dye concentration.

According to McKay *et al*. [23], R_L between 0 and 1 indicates favourable adsorption. In the current experiment R_L is found to be 0.0034 and again the adsorption is found to be favourable.

CONCLUSION

The adsorption of CBB on coir pith undergoes pseudo-second order kinetics. The maximum dye adsorption is about 0.21 mg/g of acid treated coco-pith. Evaluation by both Langmuir and Freundlich's isotherm has been found to undergo favourable adsorption. So the acid treated Coir-Pith can be used as a potential source for adsorption of textile dyes. The coir-pith thus can be used to play a vital role in the effluent treatment of Dyeing industries. Developing this adsorption data to textile dyes may help for the survival of many textile industries in India and in many other countries which suffer from water pollution due to dyes.

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