Adsorption of Cibacron Blue Dye from Aqueous Solutions onto HCL Treated Waste Biomass

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Abstract : Adsorption of Cibacron blue dye from aqueous solutions onto various biomass materials was studied. Batch experiments were conducted to determine the factors affecting adsorption. Fixed bed column experiments were performed and breakthrough curves were obtained to study practical applicability. Hydrochloric acid treated coir dust, rice husk, saw dust and tea waste are capable of binding appreciable amounts of cibacron blue dye from aqueous solutions. Cibacron dye showed the highest adsorption capacity and affinity in relation to coir dust under all the experimental conditions. Coir dust and granular activated carbon showed similar adsorption capacities. Adsorption capacity was highest at the solution pH range from 2 to 3 for all the adsorbents. The adsorbent to solution ratio, and the adsorbent particle size affect the degree of dye removal. Higher adsorption capacities were observed for smaller adsorbent particles. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. Langmuir constants showed highest dye uptake of 65, 14, 10 and 5 mg/g for coir dust, saw dust, rice husk and tea waste respectively. Kinetic studies revealed that dye uptake was fast with 50% or more of the adsorption occurring within the first 60 to 90 min of contact time. Column operations showed lower adsorption capacities than the batch operation for all the adsorbents except tea. Breakthrough curve results fit the linear Bed Depth Service Time model. The breakthrough time depends on the solution flow rate and initial dye concentration. Amounts of dye adsorbed in the column operations were 31, 9, 12, 8 mg/g for coir dust, rice husk, saw dust and tea waste respectively. 83% of colour removal and 72% of Chemical Oxygen Demand (COD) removal efficiencies were achieved using HCl treated coir dust for the real textile wastewater samples containing a mixture of various dyes.

Key words: Adsorption, Packed bed, Breakthrough curve, Bed Depth Service Time.

1. Introduction

Industrial wastewater generated by the textile, paper, carpet and printing industries contains a high concentration of coloured organic compounds. This effluent is tough to be degraded because of the presence of dyes, which have complex aromatic molecular structures of synthetic origin. The color in dye house effluent from the textile industry is highly visible and affects aesthetics, water transparency and gas solubility in water. Most of the dye compounds are toxic and often carcinogenic. Release of wastewater containing dye compounds into water streams may pose a serious threat to public health and the aquatic community. Due to increased awareness of environmental aspects, many countries, including Sri Lanka, have imposed stringent environmental laws and more attention has been directed towards development of treatment methodologies. The textile industry in Sri Lanka rapidly developed over the last two decades and the effective method of treatment of coloured effluent has become an important issue today.

Removal of colour in textile effluents is achieved by numerous physical and chemical treatment techniques such as coagulation, flocculation, electro-flotation, membrane filtration, precipitation, ion-exchange, ozonization, electrolysis and adsorption [22],[33]. Even though some of these methods are effective, most of them suffer from short comings such as excess usage of chemicals, sludge disposal, expensive operating cost. Among several chemical and physical methods, adsorption is one of the effective techniques that has been successfully employed for colour removal from wastewater.

Activated carbon produced by carbonizing organic materials is the most widely used

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adsorbent. Activated carbon has shown good dye adsorption capacities specially for cationic dyes [39], [18], [14], [12], [38], [25]. However; the high cost of the activation process limits its use in wastewater treatment. Over the last few years a number of investigations has been conducted to test the low cost adsorbents for dye removal from waste water. Among the numerous waste biomass materials available in various parts of the world rice husk, saw dust, coir dust, dry tree leaves, tea or coffee waste and sunflower stalks have been widely experimented for adsorption of dyes [2], [3], [5], [7], [9], [10], [11], [13], [15], [16], [20], [23], [29], [30], [32], [35]. Industrial waste and Mineral waste have also been tested for their dye adsorption properties [1], [4], [8], [14], [19], [24], [28], [36], [38]. Among the low cost adsorbents tested for dye removal approximately 75% of the work has used waste biomass as an adsorbent [6], [26].

Disposal of the biomasses has become an obstacle to sustainable agriculture and the environment in most countries including Sri Lanka. Plant residues, which are mainly carbonaceous has the potential to be converted into adsorbent. This conversion could contribute to a reduction of the volume of waste, whilst producing an adsorbent with a lower cost.

Degree of adsorption and rate of adsorption of dye molecules onto waste biomass depend on the physical and surface properties of adsorbent, dye properties and the operating conditions. Therefore, the effect of adsorbent properties and operating conditions on adsorption depends on the *biomass-dye* system and the knowledge of the same is important for decision making. Most of the previous work on low cost adsorbents is limited to batch experiments. Fixed bed columns are widely used in industry and adsorption isotherms obtained by batch experiments do not give accurate scale-up data in fixed bed systems.

This work investigates the potential of various waste biomass materials available in Sri Lanka as a low cost adsorbent for removal of colour in textile effluents. Adsorption of Cibacron Blue FR dye onto coconut coir dust, saw dust, rice husk and tea waste was investigated. The adsorbents were treated by hydrochloric acid to improve adsorption properties. Batch and fixed bed column studies were conducted to determine the factors affecting the adsorption process and to obtain data for industrial scale designing. The

adsorption characteristics of low cost adsorbents were compared with that of commonly used adsorbent granular activated carbon.

2. Methodology

2.1 Adsorbates

Reactive Blue; namely Cibacron Blue FR dye a commonly used dye in Sri Lanka was used for all the experiments. Synthetic dye solutions were prepared by dissolving dye powder in distilled water to obtain required solution concentrations (50 - 200 mg/l).

2.2 Adsorbent

Coir dust (CD), rice husk (RH) and saw dust (SD) were obtained from a local coir processing plant, a rice mill and a wood mill respectively. Tea waste (TW) was provided by the University of Moratuwa cafeteria. The adsorbent samples were first ground and sieved prior to their use in experiments. The materials were then washed with distilled water and dried. The adsorbents were activated by impregnating them with the activation agent, 0.1 M Hydrochloric acid (HCl), for 15 minutes. Then the samples were washed 2 to 3 times in tap water. Finally, the adsorbents were washed using distilled water and dried in an oven for 10 hours at 100 °C. The fraction between 710 µm to 1mm was used for all the experiments except for the effect of size tests. The dried adsorbents were stored in sealed polythene bags.

Commercial granular activated carbon (GAC) provided by Haycarb Ltd. was used for the experiments for comparison purposes. Densities of the adsorbents were measured using the specific gravity bottle method.

2.3 Experimental Analysis

The dye concentrations in the solutions were determined by measuring the absorbance at maximum wavelength of dyes using a UV visible ERMA PHOTIC 100 spectrophotometer. Absorbance values were recorded at the wavelength of 680 nm for Cibacron Blue FR dye.

2.4 Batch Experiments

The batch adsorption experiments were conducted by adding 0.1g to 1.5 g of adsorbents

into beakers containing 100 ml of 50 mg/l dye solution. The dye solutions were shaken at 100 rpm for 2 hrs to approach equilibrium. Then the contents in the beakers were allowed to settle. The solution was filtered and the colour intensity of the filtrate was measured.

The pH studies were conducted by stirring 100 ml of dye solution with adsorbent over a range of pH values from 2 to 11. Once the optimum pH was identified, the time required to reach equilibrium was measured for each adsorbent. Samples were collected from the top at 10 min intervals and the residual dye concentration analyzed. The experiments were continued until the equilibrium state was achieved.

The effect of the adsorbent particle size on adsorption was determined using particles over a range of 355-2000 μm size.

Equilibrium isotherm experiments were conducted by shaking different quantities of adsorbent varying from 0.1 g to 1.2 g in 100 ml of 50mg/l dye solution each for a time period equal to the equilibrium time for that particular adsorbent. Blank runs, without adsorbent, were conducted simultaneously in similar conditions.

Experiments were conducted at room temperature of $30 \pm 2^\circ\text{C}$. All the tests were repeated to observe repeatability.

2.5 Packed Bed Experiments

Column studies were conducted using a down flow technique in a 3 cm internal diameter glass column. The column was filled with a known weight of adsorbent to the required height (packing factor =0.8). The dye solution containing a known dye concentration adjusted to favourable pH was fed through the packed bed at a constant flow rate. Samples of the effluent leaving the column were collected periodically and analyzed for the dye concentration. Series of experiments were conducted to compare adsorbent types and to determine the effect of initial dye concentration (50-200 mg/l), flow rate (10-50 ml/min) and bed height (5- 20 cm) for coir dust.

2.6 Textile Wastewater Treatment

The packed bed column tests were conducted with the real wastewater containing various dyes, which was collected from a leading textile

mill in Sri Lanka. The wastewater used was bluish black in colour. The adsorbent used was HCl treated coir and a low flow rate of 12 ml/min ($2.83 \times 10^{-3} \text{ m}^3/\text{s}$) was used to yield acceptable treated wastewater. The colour, pH and COD were compared between the untreated wastewater and the treated wastewater.

3. Results and Discussion

The adsorption behavior of the samples were studied by evaluating the colour removal efficiency calculated by equation (1),

$$R_e = \frac{(C_o - C_i)}{C_o} * 100 \quad (1)$$

Where C_o is the initial dye concentration in the aqueous solution, C_i is the solution concentration after adsorption and R_e is the percentage of colour removal. Bulk densities of the adsorbents determined as in section 2.2 and composition as reported in literature are shown in Table 1.

Table 1: Properties of adsorbents (dry basis).

Adsorbent	Solid Density	Cellulose %	Hemi Cellu-	Lignin %	Moisture content %
Coir Dust	0.45	43	<20	45	10-12
Rice Husk	0.73	32.24	21.34	21.44	6.62
Saw Dust	0.66-0.88	40-45	20-35	25-35	7.95
Tea Waste	0.49	4-7		5-6	5.41
GAC	2.1	-	-	-	-

3.1 Effect of Adsorbent Dosage

Figure 1 shows the percentage colour removal as a function of adsorbent dose for the range of adsorbents used.

Figure 1: Effect of adsorbent dosage Co 50 mg/l, pH 2-3, Particle size 710 micron

Results show percentage adsorption increases with the adsorbent dose for all the adsorbents. The number of available adsorption sites increases by increasing the adsorbent dose and therefore, results in the increase of removal efficiency. However, results show that the effect of adsorbent dose on percentage removal decreases at higher doses (>0.8 g/100 ml). Percentage removal of dye was in the order Activated carbon (GAC)> Coir dust (CD)> Rice husk (RH)> Saw dust (SD)> Tea waste. Tea waste shows lowest % removal at low adsorbent doses but increases to a value similar to saw dust at high doses.

Untreated material showed no significant change in colour. This indicates that washing of adsorbents with HCl results in change in surface charge of the adsorbent surface from negative to positive, and thus, will improve their adsorptive properties for anionic species.

3.2 Effect of pH

The pH value of the dye solution plays an important role in the adsorption process and particularly on the adsorption capacity. The removal of dyes as a function of pH is shown in Figure 2.

Figure 2: Effect of pH on % removal of dye adsorbed on various HCl treated adsorbents.

The adsorption of dyes onto all four adsorbents was found to be much higher in the acidic pH range of 2-4 than those in neutral and alkaline conditions. This phenomenon can be explained by the surface charge of the adsorbent and the OH⁻ ions present in the solution. At higher pH anionic dyes compete with OH⁻ ions and hence lower the adsorption. Zeta potential of plant materials is a strong function of pH. At higher pH surface is highly negative and hence attracts less anions. As the pH of the adsorption solution was lowered, the positively charged adsorption

sites increased. This would attract the negatively charged functional groups of dye.

3.3 Effect of Particle Size

The adsorption capacity depends on the surface properties of the adsorbent. Specific surface area available for solute - surface interaction, which is accessible to the solute is the most important parameter.

The decrease in particle size led to an increase in the surface area available for adsorption and hence an increase in the removal capacity. The results showed that for coir dust particles of mean size 2000, 1400, 1000 and 710 μm the percentage of dye removal is 50, 70, 80 and 100 respectively. These results show agreement with the results reported in the literature for fly ash, tea waste, activated carbon and coir pith [7],[27],[39].

3.4 Effect of Contact Time

Effect of contact time on adsorption is shown in Fig. 3. The colour removal efficiency increased with contact time and reaches equilibrium after a certain time. All the adsorbents showed very rapid initial uptake followed by a slower process. This behaviour suggests the occurrence of a rapid external mass transfer followed by a slower internal diffusion process which may be the rate determining step. Coir dust exhibited an equilibrium time of 120 minutes to achieve 100% dye removal. 75 % of colour removal was achieved within 60 mins. Such short times coupled with high removals indicate a high degree of affinity for the dye group. Optimum contact time for rice husk saw dust and for tea waste was found to be 240 minutes. Rice husk removed colour up to 92 % efficiently while saw dust and tea waste exhibited relatively poor removal efficiency of 84 % with the equilibrium time of 240 minutes.

3.5 Adsorption Isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships. Langmuir and Freundlich adsorption isotherm models are widely employed.

For solid-liquid systems, the Langmuir adsorption isotherm is expressed as;

$$\frac{x}{m} = \frac{QbCe}{1 + bCe} \quad (2)$$

Table 2: Linear regression data for Freundlich and Langmuir isotherms on dye removal using various

Adsorbent	Freundlich Isotherm			Langmuir Isotherm		
	n	K	R^2	Q (Mg/G)	B	R^2
Coir Dust	0.85	1.2	0.9879	65.36	0.0151	0.9975
Rice Husk	0.43	1.9	0.9630	10.31	0.0945	0.9855
Saw Dust	0.56	1.0	0.8905	13.93	0.0336	0.9462
Tea Waste	0.30	1.85	0.8618	5.17	0.2479	0.8275
Gac	0.57	5.4	0.7979	45.45	0.0948	0.8516

Figure 3: Kinetic studies for various types of HCl treated adsorbents at 30°C, Co 50 mg/l, pH 2-3, Particle size 710 micron

The linear form of the Langmuir isotherm is given by equation (3),

$$\frac{1}{x/m} = \frac{1}{bQ} \frac{1}{Ce} + \frac{1}{Q} \quad (3)$$

The Freundlich equation is an empirical expression and is expressed as;

$$x/m = K(Ce)^n \quad (4)$$

The linear form of the Freundlich isotherm is given by equation (5),

$$\log x/m = n \log Ce + \log K \quad (5)$$

Where x/m is the amount of solute adsorbed per weight of adsorbent (mg/g) at equilibrium, Ce is the solution dye concentration at equilibrium (ppm), Q is the Langmuir isotherm constants also called monolayer capacity (mg/g) and b is the Langmuir constant, K and n are Freundlich constants related to adsorption capacity and adsorption intensity.

Langmuir and Freundlich isotherm constants for the adsorption of Cibacron Blue (CB) dye onto each of the adsorbents are presented in Table 2. The correlation coefficient (R^2) close to 1 indicates that the adsorption process confirms to both Langmuir and the Freundlich adsorption isotherms. Langmuir isotherm has a slightly

better fitting model than Freundlich thus, indicating to the applicability of monolayer coverage of the dye particle on the surface of adsorbent. The value of n obtained from Freundlich isotherm, for adsorption of most organic compounds by activated carbon is <1 . $0 < n < 1$ indicates the adsorption is favourable. Coir dust shows highest the adsorption capacity (Q) and affinity (n) when compared to the other adsorbents.

3.6 Packed Bed Studies

Packed bed experimental data are essential for industrial-scale adsorber design. The adsorption isotherms obtained by batch experiments do not give accurate scale-up data in fixed bed systems. Therefore practical applicability of low cost adsorbents was also ascertained in column operations.

Figure 4 shows breakthrough curves obtained for the adsorption of Cibacron blue onto four types of adsorbents. The area above the breakthrough curve is a measure of the bed capacity (BC in mg) and is given by the following equation (6). [34].

$$\text{Then, } BC = G \int_0^{\tau} (C_0 - C) dT \quad (6)$$

Figure 4: Breakthrough curves for various types of HCl treated adsorbents at 30°C, Co 50 mg/l, pH 2-3, Particle size 710 micron, Bed height 10 cm, Flow rate 20 ml/min

Where, G is the inlet solution flow rate ml/min, CO and C are the initial concentration of solute in ppm and solute concentration at time T in ppm.

Adsorption capacities in the fixed bed column were calculated using equation (6) and listed in the Table 3. For the comparison of data, the equilibrium capacities obtained from batch experiments are also included in the same table. Adsorption capacities and breakthrough times are in the order coir dust>rice husk>saw dust>tea waste. This order of adsorption capacities are in agreement with the batch adsorption experiments shown in Fig 1.

Table 3: Comparison of bed and batch adsorption capacity

Adsorbent	Packed bed Capacity (mg/g)	Equilibrium batch Capacity (mg/g)
Coir Dust	30.61	65.36
Rice Husk	9.30	10.31
Saw Dust	11.57	13.93
Tea Waste	8.02	5.17

For all the adsorbents except tea waste, the bed capacities are lower than that of the batch system. In batch experiments the mixture was shaken continuously and good interaction between the solid and solute was achieved. In the fixed bed, adsorbent is packed in the column and surface of the solid particles are in contact with each other and therefore results in a less solid-solute interaction. Further, liquid channeling which results in poor solid-metal ion contact and less residence time may therefore occur in the column. Therefore bed adsorption capacities are lower compared to batch operation. Therefore, the batch system may provide better interaction between dyes and adsorbent than in the column system.

Figure 5: Effect of various initial dye concentrations Co , for the system; packed bed height 10 cm, pH 2-3 Flow rate 20 ml/min, Coir dust particle size 710

The effect of initial dye concentration on the breakthrough curve for coir dust is shown in Fig. 5.

The breakthrough time decreases with the initial dye concentration. Therefore, the volume of effluent that a fixed mass of adsorbent can purify decreases with the effluent concentration.

The effect of varying the flow rate was investigated for coir dust and the breakthrough curves are presented in Figure 6. It is evident from this figure that as the flow rate increased, the service time was shortened and hence the volume treated until breakthrough. The breakthrough time for $C/C_0=0.2$ for 10, 20 and 30 ml/min flow rates are 360, 160 and 75 mins respectively. This high reduction in breakthrough time at high flow rates is due to the short residence time of the dye molecules in the column. A similar trend was observed for adsorption of basic dyes onto activated carbon and zeolite by Markovska [17].

Figure 6: Effect of various flow rates at a bed height 10cm, pH 2-3, Co 50 mg/l, HCl treated Coir Dust particle size 710 micron

Figure 7 shows the breakthrough curves of different bed depths at a constant flow rate.

Figure 7: Effect of various bed heights at a flow Rate 20 ml/min, pH 2-3, Co 50 mg/l, HCl treated Coir dust particle size 710 micron

The variation in concentration profile was due to the relatively large adsorption zone. The rate at which the adsorption zone travels through the bed decreases with the depth, suggesting that beds of an increased height may be required for dye adsorption. This phenomenon occurs in the adsorption of dyestuffs because of their large molecular structure, resistance to internal diffusion was much higher than smaller molecules. This resulted in the dye molecules not having enough contact time to diffuse from the surface of the particle to the adsorption sites. However, most research carried out on the adsorption of dyes showed breakthrough curves similar in trend to the profiles reported here [21], [39].

3.7 Bed Depth Service Time (Bdst) Model

The Bed Depth Service Time (BDST) method, based on a model proposed by Bohart and Adams that was later Linearized by Hutchins, (1974) has been reported as offering the simplest approach and most rapid prediction of adsorber performance [27].

This model proposed a relationship between bed depth, Z , and the time taken for breakthrough to occur, and it assumes that the adsorption rate is proportional to both the residual adsorbent capacity and the remaining adsorbate concentration. According to Bohart and Adams, the BDST curves are described by,

$$\ln\left[\frac{C_0}{C_b} - 1\right] = \ln[\exp(KN_0Z/V) - 1] - KC_aT \dots \dots \dots (7)$$

Rearranging by Hutchins;

$$T = \frac{N_0}{C_0V}Z - \frac{1}{KC_0} \ln\left[\frac{C_0}{C_b} - 1\right] \dots \dots \dots (8)$$

Where, T = Service time.
 Z = Depth of adsorbent bed.
 V = Linear flow rate.
 K -- Adsorption rate constant.
 N_0 = Adsorptive capacity.

The BDST equation is easier to use in its simplified form;

$$T = aZ - b \dots \dots \dots (9)$$

Where, $a = \frac{N_0}{C_0V}$
 $b = \frac{1}{KC_0} \ln\left[\frac{C_0}{C_b} - 1\right]$

The bed depth verses service time plots for coir dust at different flow rates and different dye concentrations are shown in Figs. 8 and 9 respectively. The breakthrough point for this study was fixed at 10 % of the feed concentration.

Figure 9 shows BDST plots for the adsorption of Cibacron Blue dye onto coir dust at 10% breakthrough for various inlet dye concentrations. High slope at lower inlet concentrations indicates that bed performs better with a high service time at low flow rates.

Figure 8: BDST plots for various flow rates HCl treated Coir Dust at 30°C, pH 2-3, Particle size 710 micron, Bed height 10 cm, C_0 50 mg/l

Figure 9: BDST plots for various dye concentrations HCl treated Coir Dust at 30°C, pH 2-3, Particle size 710 micron, Bed height 10 cm, Flow rate 20 ml/min

3.8 Real Textile Wastewater Treatment

The colour removal of the real textile wastewater was measured at a wavelength of 560 nm. The comparison of values of absorbance, pH and COD are shown in Table 4. The experiments showed that the column was rapidly saturated at 20 ml/min flow rate. This is due to the competition of several organic matters to be adsorbed. Thus the lower flow rate 12 ml/min was used to treat the real textile wastewater. The results showed that the quality

Table 4: Qualities of wastewater and treated water

Parameter	Waste water	Treated waste water	CEA Standard limit	% Removal
Absorbance (560 nm)	0.18	0.03	-	83.33
pH	9.4	6.9	6.5 - 8.5	-
COD mg/l	790	220	250	72.15

of treated wastewater is within the standard limits of industrial effluents.

Conclusions

Coir dust (CD), rice husk (RH), saw dust (SD) and tea waste (TW), treated with hydrochloric acid are effectively utilized as adsorbents for the removal of cibacron blue dye from textile effluents. Adsorption efficiency depends on the source of the raw material, its preparation methodology and operating conditions. Removal of dye is at highest around solution pH 2 to 3. Coir dust showed highest adsorption capacity and affinity under all the experimental conditions. Percentage removal of dye was in the order $GAC > CD > RH > SD > TW$. However, Langmuir constants, Q , values and column adsorption capacities were in the order $CD > SD > RH > TW$. Adsorption isotherms fit to the Langmuir and Freundlich isotherms. Fixed bed column results show similar trend as batch experiments. However, adsorption capacities are lower compared to batch experiments. The breakthrough through times fits the linear bed depth service time (BDST) model.

These investigations are quite useful in developing an appropriate technology for wastewater treatment. However, the adsorption characteristics largely depend on the type of dye and therefore should be tested for other dye types. The adsorbents under study are suitable for both decolourizing and adsorbing of organic molecules of solution and it could be efficiently and economically applied to clean the wastewater of the textile industry. Regeneration of biomass is not required as the biomasses are available at low or no cost. Used biomass waste can be disposed by incineration.

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