

Reduction of Colour in Treated Wastewater from Textile Industry Using Sawdusts as Bio-sorbents

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ABSTRACT: Textile industries use dye such as Rhodamine B, Brilliant Red and Reactive Orange for the fabrics. Thus the colour of the effluent even after the normal treatment is not within the standard to discharge into the environment. A study was conducted to identify suitable bio-sorbents and to optimize the conditions for selected bio-sorbent to reduce the colour of treated waste water (TWW) from a textile industry. Sieved and air dried sawdust from Rubber (*Hevea brasiliensis*), Trincomalee wood (*Berrya cordifolia*), and Breadfruit (*Artocarpus altilllis*) timber were tested with TWW. Rubber sawdust showed a better performance in colour removal than the sawdust from Trincomalee wood and Breadfruit. In order to optimize the conditions with the rubber sawdust, colour removal efficiency of TWW was measured at different pH, sawdust amount, initial dye concentration and different contact times. Sorption data was modelled by Langmuir and Freundlich adsorption isotherms for each dye; Rhodamine B, Brilliant Red, Reactive Orange. Results showed that the best performances of adsorption of dye into Rubber sawdust was obtained at 5 g/L sawdust dosage with 6 minutes contact time up to 0.2 ml of 0.5 M dye concentration under pH 2. Adsorptions of acidic dye (Brilliant Red) and anionic reactive dye (Reactive Orange) followed the Langmuir isotherm. Sorption of cationic dye Rhodamine B was better represented by the Freundlich model. It is recommended to use the sawdust of rubber to remove the colour in wastewater in acidic condition and neutralize the effluent before discharge to the environment.

Keywords: Bio-sorbent, colour, sawdust, textile industry, wastewater

INTRODUCTION

The textile industry consumes a substantial amount of water in manufacturing processes mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition (Chequer *et al.*, 2013). The wastewater includes dilute detergent, dilute spent chemicals, trace contaminants, bleach water, unfixed dye, unfixed ink etc. Other than wash water, make up water in utilities, steam, cooling tower water, chilled water, hot water are also combined to form industrial textile wastewater.

Dyes in textile effluent are of concern to the regulators and community due to the appearance. Most coloured effluent problems arise from dyeing with reactive dyes. Heavy

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metals are associated with the effluents from wool dyeing. With respect to the number and production volumes, azo dyes are the largest group of colourants, constituting 60-70% of all organic dyes produced in the world (Bafana *et al.*, 2011). The success of azo dyes is due to their ease and cost effectiveness for synthesis as compared to natural dyes, and also their great structural diversity, high molar extinction coefficient, and medium- to-high fastness properties in relation to light as well as to wetness (Bafana *et al.*, 2011). One of the most difficult tasks confronted by the wastewater treatment plants of textile industries is the removal of colour of these compounds, mainly because dyes and pigments are designed to resist biodegradation, such that they remain in the environment for a long period of time. Dyes, which represent a large and important group of synthetic chemicals, are also important water pollutants, present in the effluents of the textile industries. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also many azo dyes and their breakdown products are toxic and/or mutagenic.

Some conventional technologies (precipitation, coagulation, flocculation, UV/ozone treatment, electrochemical reduction, biological treatment) may be efficient in the removal of dyes, but their operational costs are very high. Among these methods, adsorption is one of the most economic methods in decolourization of textile effluents because of simple design and operation, availability, non-toxicity, superior removal of pollutants (Suteu *et al.*, 2008). The great advantage of this method is the possibility to use inexpensive and readily available materials with adsorptive and ion exchange properties.

Natural materials that are available in large quantities or certain waste from agricultural operations may have the potential to be used as low cost adsorbents. Large varieties of solid materials have capacity to act as sorbents: synthetic to natural low-cost materials such as activated charcoal, natural zeolites, sphagnum peat, fly ash, ligno-cellulosic materials. Waste materials from industry or agriculture such as sawdust and active or inactive biomass resulted from industrial fermentative technology (food and pharmaceutical industry) are also used as adsorbates. Replacing synthesized compounds, wastewater treatment by sorption onto unconventional natural or biological materials (“green” or “environmental friendly”) have recently become the subject of considerable interest (Suteu *et al.*, 2008).

The sawdust, a low cost locally available material and a solid waste, can be used as bio-sorbent for the removal of contaminant. Sawdust is an abundant by-product composed of fine particles of wood. It is considered as an agricultural waste and a by-product of manufacturing industries. It is readily available in the countryside at zero or negligible price. Sawdust has proven to be a promising effective material for the removal of dyes from wastewaters of many types of pollutants, such as dyes, oil, salts, heavy metals (Baral *et al.*, 2006 and Stankovic *et al.*, 2009).

Effluent from fabric industries are treated using conventional treatment plants. However, the colour of treated wastewater (TWW) has to be reduced to acceptable level. The objective of this study was to identify an appropriate bio-sorbent for colour reduction and optimize the process with the selected bio-sorbent.

METHODOLOGY

Preparation of bio-sorbent

Freely and abundantly available sawdusts in saw mills were considered. Thus saw-dust from rubber (*Hevea brasiliensis*), breadfruit (*Artocarpus altilis*), and Trincomalee wood (*Berrya cordifolia*) were selected for the study. Each sawdust type was air dried and sieved with 1 mm² mesh. Sawdust < 1 mm particle size and moisture content between 15 and 20 (W/W%) were taken for further analysis.

Adsorption study

At the beginning, suitable sawdust was identified. Then, in order to optimize the process, the effect of pH, zero point charge, amount of sawdust, initial concentration of dye, equilibrium time for adsorption were studied for the selected sawdust as illustrated in Figure 1. The water discharged from a conventional treatment plant from a textile industry (Treated wastewater – TWW) was used in this sorption study. The textile dye, *Rhodamine B* was used only to study effect of initial dye concentration. Rhodamine B, Brilliant Red, and Reactive Orange were used for isotherm modelling.

Identification of suitable bio-sorbent material

Suete *et al.*, (2008) have reported that the better colour removal in textile wastewater can be obtained with the saw dust dosage more than 10 gL⁻¹ at pH value 1 - 2 for anionic dyes and 5 -9 for cationic dyes. Therefore, TWW was adjusted to pH 5 and added 10 gL⁻¹ of sawdust of each bio-sorbent; rubber, breadfruit and Trincomalee wood (Figure 1). The mixture was stirred for 10 minutes. Then the suspensions were filtered through filter paper (Whatman 47 mm). Colour of each filtrate and TWW were measured using spectrophotometer (Spectro Direct -Lovibond, UK). Hanna pH meter was used to measure pH.

Effect of pH on adsorption

Preliminary selection test conducted with replication (3 runs) showed that rubber sawdust has comparatively higher sorption capacity than other two types. In order to study the effect of pH on rubber sawdust, the pH of TWW were adjusted from pH 1 to 12 using 1 M NaOH and 1 M H₂SO₄. Then, 250 ml of TWW sample was mixed with 2.5 g of rubber sawdust and stirred for 10 minutes (Figure 1). Suspensions were filtered through Whatman 47 mm white filter paper. Colour of each filtrate was measured.

Zero point of charge

0.01 M NaCl solution was prepared and its initial pH was adjusted from pH 1 to 12 using 1 M NaOH and 1 M H₂SO₄. Then 50 ml of 0.01 M NaCl sample was collected to 250 ml Erlenmeyer flask and 2.5 g of rubber sawdust was added to each solution. Flasks were kept for 48 h and pH was measured using pH meter (Figure 1).

Reduction of colour in treated wastewater

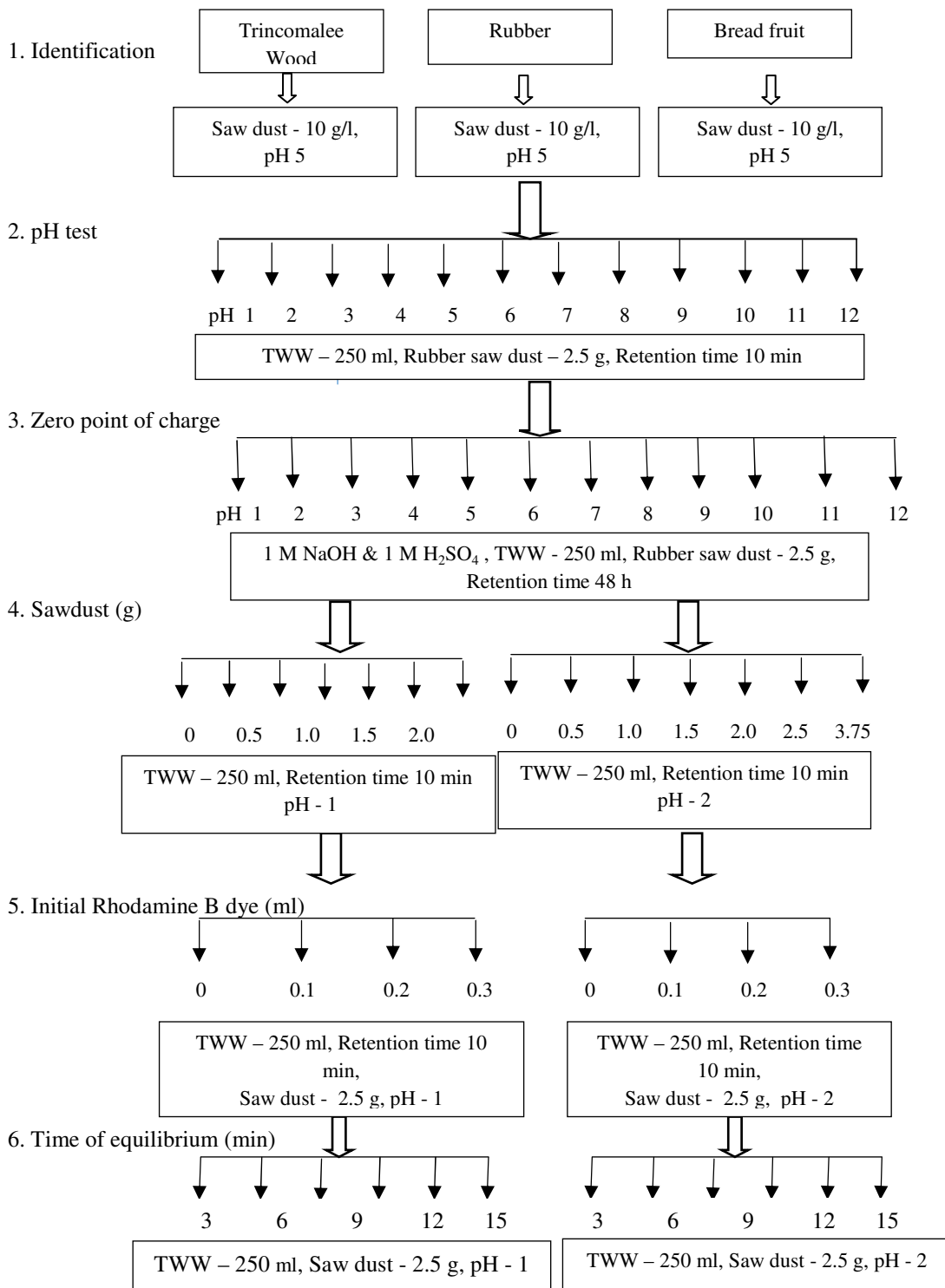


Fig. 1. Flow chart of the sorption experiment

Effect of amount of sawdust on adsorption

From the above test, pH 1 and pH 2 were selected as the most suitable pH for adsorption with rubber sawdust. The pH of TWW(250 ml) was adjusted for both pH 1 and pH 2, separately and 0 (control), 0.50, 1.00, 1.50, 2.00, 2.50, 3.75 g of rubber sawdust was added (Figure 1). The TWW without addition of sawdust but with pH adjustment was used as control for determining the removal efficiency. Then suspensions were filtered through Whatman 47 mm white filter paper. Subsequently colours of each filtrate were measured.

Effect of initial dye concentration on adsorption

Most suitable pH and sawdust amount for adsorption with rubber sawdust were selected. Then, 0 (control), 0.1, 0.2, 0.3 ml of 0.5 M Rhodamine B dye solution were added to pH adjusted TWW sample(250 ml) and stirred for 10 minutes (Figure 1). Suspensions were filtered through Whatman 47 mm white filter paper. Colours of each filtrate were measured.

Effect of contact time on adsorption

The pH of TWW was adjusted to pH 1 and 2 using 1 M H₂SO₄ samples (250 ml) were mixed with 2.5 g of rubber sawdust. Suspensions were collected separately, after 3, 6, 9, 12, 15 and 18 min and filtered through Whatman 47 mm white filter paper (Figure 1). Colours of each filtrate were measured.

Colour removal performance

Colour of the filtrates obtained from the above experiments was measured using Spectrophotometer (Spectro Direct - Lovibond, UK) at 432 nm, 525 nm, and 620 nm wave lengths to represent yellow, red and blue colour, respectively. The colour removal efficiency (R) of the sawdust was evaluated using Equation 1.

$$R (\%) = [(C_0 - C) / C_0] \cdot 100 \quad (\text{Eq. 1})$$

where, C_0 and C are the initial and equilibrium colour values, respectively.

Adsorption isotherm models

Three dyes, Rhodamine B, Brilliant Red, and Reactive Orange were used to model the adsorption. Freundlich and Langmuir isotherms models were fitted using linear Equations 2 and 3 (Suteu *et al.*, 2008).

$$\text{Freundlich isotherm:} \quad \log q = \log K_F + 1/n \log C \quad (\text{Eq. 2})$$

$$\text{Langmuir isotherm:} \quad 1/q = 1/q_0 + 1 / (K_L \cdot q_0) \cdot 1/C \quad (\text{Eq. 3})$$

where, q - amount of dye sorbed (mg of dye per g of sawdust), K_F - parameter related to the adsorption capacity, n - measure of sorption intensity (a favourable sorption corresponds to a value of $1 < n < 10$), K_L - Langmuir constant, and q_0 - maximum value of sorption capacity (corresponding to complete monolayer coverage) and C - equilibrium colour concentration.

The Freundlich constants (K_F and n), and Langmuir constant (q_0 and K_L) were calculated by plotting $\log q$ vs. $\log C$ and $1/q$ vs. $1/C$, respectively (Suteu *et al.*, 2008).

RESULTS AND DISCUSSION

Identification of suitable bio-sorbent material

Initial (C_0), equilibrium (C) values for colour and the removal efficiency ($R\%$) with each sawdust type are shown in Table 1. The values obtained from the spectrometer for each colour, not the concentration are shown in Table 1. This initial test was done at pH 5 as selected from literature (Suteu *et al.*, 2008). Rubber sawdust showed positive and higher colour removal percentages for all three colours; yellow, red and blue compared to Trincomalee wood and Breadfruit. The negative removal percentages from Trincomalee wood and breadfruit may have been due to colour release from the sawdust. Therefore, the rubber sawdust was selected for detail studies.

Table 1. Adsorption performance with various sawdust types at pH 5

Colour	Without sawdust			With sawdust			
	TWW (C_0)	TW(C)	R % (TW)	RB (C)	R % (RB)	BF(C)	R % (BF)
Yellow (436 nm)	2.51	2.93	-16.73	2.41	3.98	3.02	-20.32
Red (525 nm)	2.33	2.31	4.66	2.10	9.88	2.45	-5.15
Blue (620 nm)	1.02	1.00	1.96	0.97	4.90	0.99	2.94

TW – Trincomalee wood, RB - Rubber, BF – Bread Fruit

Effect of pH on adsorption

The effect of initial pH on the bio-sorption was examined and the results are shown in Figure 2. Removal of colour decreased with the increase in pH. Higher removal was observed in lower pH values. Blue colour removal was higher than the red and yellow colour by the rubber sawdust. The negative removal percentages observed in higher pH values may be due to the release of colour from the sorbent which was not tested in this study. Khattri and Singh (2012) reported that the change in pH affects the adsorptive process through dissociation of functional groups of the adsorbate and the adsorbent. This removal percentage at pH 5 is not comparable with the removal performance at the initial study for rubber sawdust since the initial concentration varies in both tests. The effect of initial dye concentration will be discussed in the subsequent section.

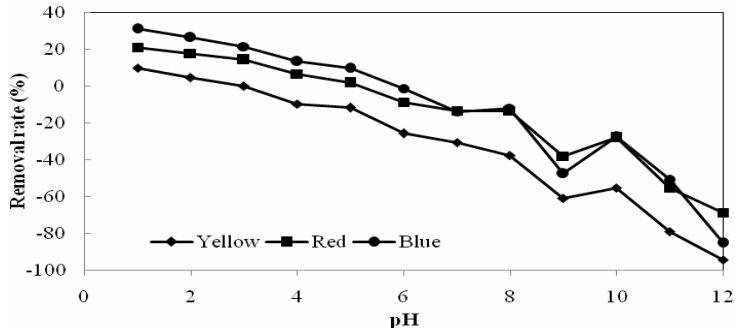


Fig. 2. Adsorption efficiency and pH variation with rubber sawdust

Point of Zero charge was found to be 6.7. Removal efficiency was more favourable in from pH 1 to 3, which was lower than pH of Point of Zero charge as the dyes responsible for yellow, red and blue colour belong to anionic category.

Effect of amount of sawdust on adsorption

Figure 3 shows the percentage of colour removal with different dosage of rubber sawdust at pH 1 and pH 2. The removal rate increased with the increasing sawdust dosage due to the availability of higher number of sorption sites. The saturated level was found as 2.5g dosage in 250 ml TWW in both pH values.

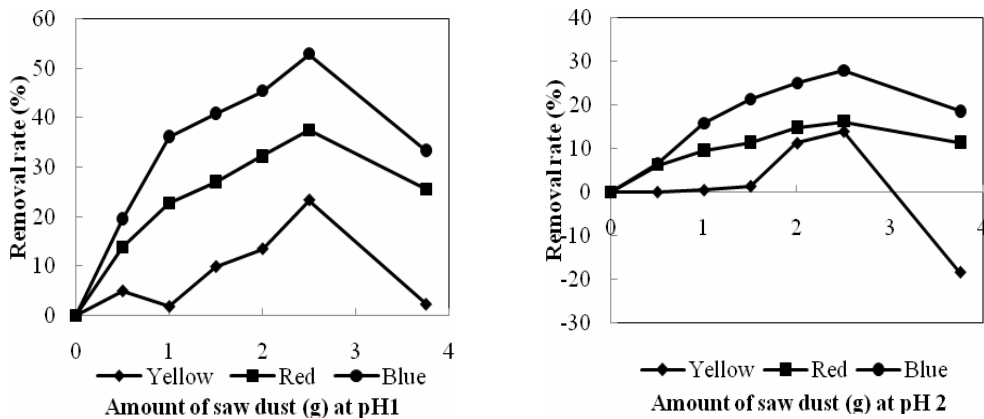


Fig. 3. Dosage of sawdust on adsorption efficiency

Effect of initial dye concentration on adsorption

Adsorption efficiency slightly increased with increased dye concentration for both pH (Figure 4). The performance in pH 1 was better compared to pH 2. Adsorption sites were saturated with certain level of dye, and remained dye molecules added extra colour to the solution. Therefore, gradually the colour increased with increasing dye concentration in TWW.

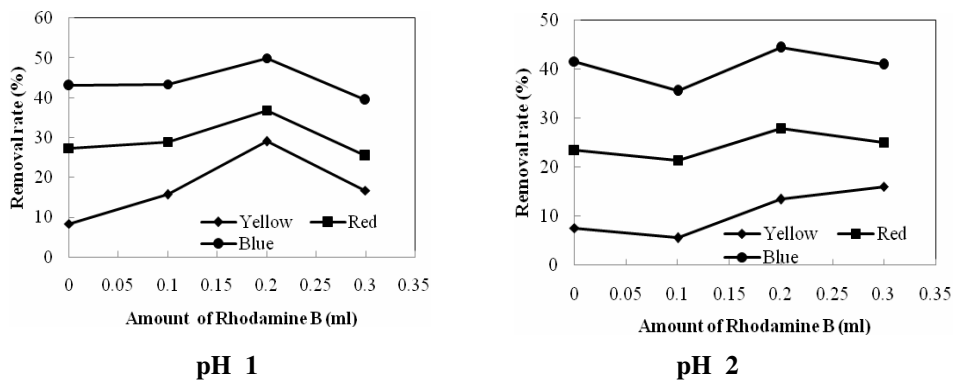


Fig. 4. Removal performance with different initial dye concentration

Effect of contact time on adsorption

Figure 5 shows the removal rates with time at pH2. The removal of dyes were fast at initial stages of contact period and then, amounts of dye absorbed increased slowly near the equilibrium as the adsorption rate decreased with time as all most all the adsorption sites were filled with dye particles at 6 min.

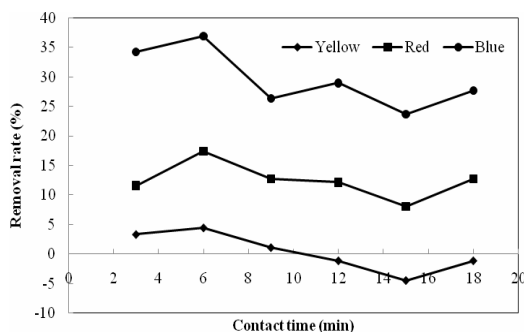


Fig. 5. Removal efficiency with contact time at pH 2

Development of adsorption isotherm

Langmuir and Freundlich isotherms for three dyes, Rhodamine B, Brilliant Red, and Reactive Orange were developed and shown in Figures 6 to 11. The isotherm parameters are shown in Table 2. Adsorption of cationic dye Rhodamine B was better represented by the Freundlich model, indicating a heterogeneous adsorption surface, with sorption sites of different energies and availability. The adsorption of acidic dye, Brilliant Red and anionic reactive dye, Reactive Orange were followed the Langmuir isotherm, indicating the formation of monolayer coverage of dye molecules at the external surface of the sawdust.

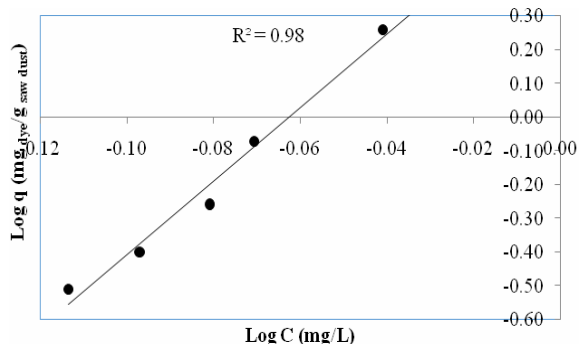


Fig. 6. Freundlich isotherm for Rhodamine B

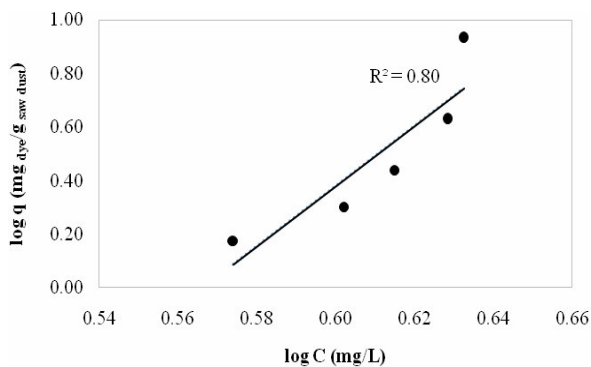


Fig. 7. Freundlich isotherm for Brilliant Red

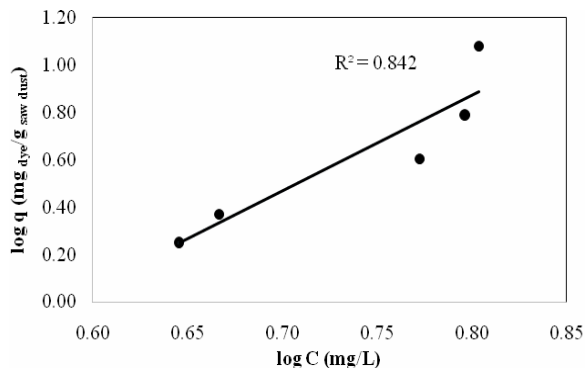


Fig. 8. Freundlich isotherm for Reactive Orange

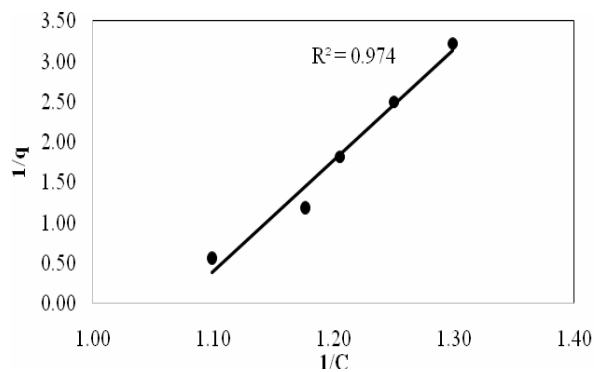


Fig. 9. Langmuir Isotherms for Rhodamine B

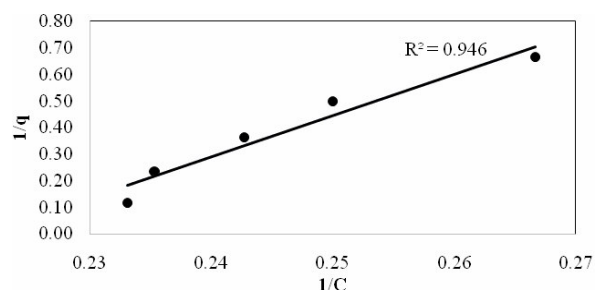


Fig. 10. Langmuir Isotherms for Brilliant Red

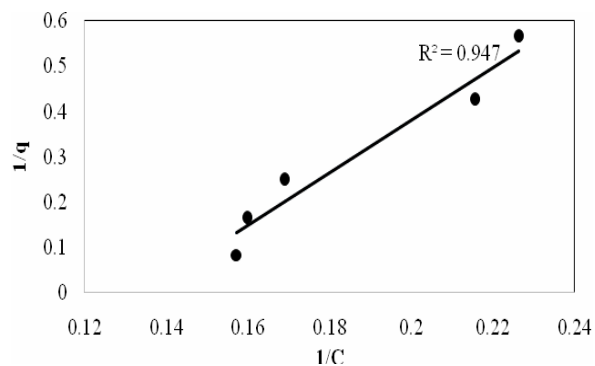


Fig. 11. Langmuir Isotherms for Reactive Orange

Table 2. The isotherms parameters for dyes onto rubber sawdust

Dye	Freundlich Isotherm			Langmuir Isotherm		
	K_F	n	R^2	K_L	n	R^2
Rhodamine B	0.6832	0.0917	0.98	0.0725	0.9338	0.98
Brilliant Red	6.37	0.0889	0.80	0.0644	1.053	0.95
Reactive Orange	2.835	0.2463	0.77	0.1705	0.3878	0.95

CONCLUSION

Rubber (*Hevea brasiliensis*), sawdust performed better compared with other two wood types; Trincomalee wood (*Berrya cordifolia*), breadfruit (*Artocarpus alillis*) for removal of colour in treated wastewater from a textile industry. Best performances of removal of colour into Rubber sawdust was obtained at 5 g/L sawdust dosage with 6 minutes contact time up to 0.2 ml of 0.5 M dye concentration under pH 2. The sorption can be adequately modelled by the Langmuir and Freundlich adsorption isotherms. Brilliant Red and Reactive Orange were followed the Langmuir isotherm while Rhodamine B was better represented by the Freundlich model. It is recommended to remove the colour using rubber sawdust in acidic condition and neutralize the effluent before discharging.

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