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Removal of textile industrial dyes using Coralwood legume pod as natural adsorbent

Bhanuprakash M.* and Belagali S.L.

Environmental Chemistry Laboratory, Department of Studies in Environmental Science, University of Mysore, Manasagangotri, Mysuru-570 006, Karnataka, India.

Abstract : The dye effluent from textile industry is a major environmental problem which is not only aesthetic to the environment, it affects the perturbation of light to the aquatic environment and death of aquatic organisms and animals. In the present study coral wood legume pod is used as an adsorbent for the removal of textile dye effluent using batch method and parameters like pH, adsorbent dosage, contact time and concentration of dyes were studied. Adsorbent used to be effective, with total removal of all textile dyes of high removal percentage (up to 97 %).After the adsorption study, adsorbent was analysed by Scanning electron microscope and Fourier transforminfrared microscopic spectral studies for the identification of the surface morphology and characteristic functional group analysis. For the adsorption process, adsorption isothermslike Freundlich, Langmuir and Dubinin-radushkevich models were carried out and found that the adsorption process is kinetically favourable.The result concludes that, coral wood legume pod is very good natural bio-adsorbent for the removal of textile dye effluents.
Key words : adsorption, coral wood legume pod, dose, isotherm, SEM, FTIR.

1. Introduction:

Waste water from industry has a challenge to convectional treatment of physico-chemical and biological methods. Waste generated in the textile industry is considered to be most polluting, based on the volume of discharge and effluent composition in the industrial sectors.(Arivoli*et. al*. 2009).Due to utilization of wide variety of chemicals and dyes, textile industries consume intensive water among various industries. Industrial effluents should be recycled and water resources need to be conserved. Reuse, recycle and reduce concept of industry is very important, action to be taken in this direction (Shabudeen 2011). Industry discharge huge volume of waste water on daily basis, organic pollutants ad heavy metals like paper, plastic, food, cosmetic and leather tanning *etc*. Industries use different types of dyes like anionic, cationic and disperse dyes *etc*. (Sarma *et. al*.2003). Most of the dyes are not readily removed by the typical waste water treatment method, because of their complex aromatic structure they are resistant to light, biological and other degradative environments (Joshi *et. al*. 2004). Release of dyes to the water resources even in small amounts can affect the food web and aquatic life. It may lead to alleregic dermatitis and skin irritation. Some of the dyes carcinogenic, mutagenic for humans and aquatic organisms. Removal of colour from textile waste water effluents is a worldwide problem. Many treatment methods for the removal of colours and dyes like ozonisation, coagulation, membrane separation, anaerobic decolourization, oxidation, flocculation and adsorption. Adsorption appears to be the best process among all these methods for treatment of dye stuff effluents(Sonawane *et. al*. 2009). Various adsorbents like Saw dust (Malik 2004), Jute fibre (Senthilkumar *et. al*.2005), Almond husk (Bhanuprakash *et. al*. 2016), Fly ash(Gupta *et. al*.1990), Coconut coir pith (Namasivayam *et. al*.2007), Chewing Tobacco (Geetha *et. al*. 2011), Corn cob and barley husk (Robinson *et. al*.2002), Mango seed shell (Itodo *et. al*.2010), Hair and coal(Mckay *et. al.* 1999), Banana and orange peel (Annadurai *et. al.* 2002), Garlic husk (Geetha *et. al.* 2012), Wood (Poots *et. al.*1978), Palm kernel fibre (Ofomaja 2007), Rice husk (Subir Chowdhury 2017).

1. Materials and Methods:

Processing of the Adsorbent for the study:

Coral wood tree legume pod was collected, washed with water and dried in sunlight followed by hot air oven at 100^o C. Dried adsorbent was broken into small pieces by hand; it was then powdered by the mixer grinder for 10-15 min. and then sieved. Uniform particle size of adsorbent was collected for adsorption. The uniform size particles of adsorbent were treated with 2N HCl and 2N NaOH solutions for half an hour. The adsorbent was washed thoroughly with distilled water.

Textile dye effluent: 50 ml of textile dye effluent from Sunlight textile, Vigneshwara textile, Rang textile and Venkateshwara textile dye were taken in 100 ml beakers.

Batch Experiment:

Adsorption experiments were conducted in batch mode with different textile dye effluents. The variables studied were Adsorbent dose, Concentration, Contact time and pH. The dye solution and adsorbent were observed for adsorption process after keeping the solution aside for adsorption to take place.

2. Results and Discussion:

3.1. Effect of pH

Adsorption of textile dye effluents investigated in different pH media of acidic, neutral and basic by adding adsorbent dose of 0.5gm.Vigneshwara textile dye effluent adsorption takes place in acidic medium during 48 hrs, where the rate of adsorption in neutral and basic medium is very slow.Rang textile dye effluent adsorption takes place in acidic medium during 70hrs, where as the rate of adsorption was very slow in neutral and basic media. Venkateshwara dye effluent adsorption takes place in acidic medium during 96hrs; where as the rate of adsorption was very slow in neutral and basic media.

For all textile dye effluents, adsorption takes place in acidic medium

3.2. Effect of Dose

Five numbers of 50 ml samples of textile effluent dye solutions were taken in four 100ml beakers and 0.5g to-2.0 g dose of adsorbent was added and studied for adsorption. As dose increased,the rate of adsorption increased.

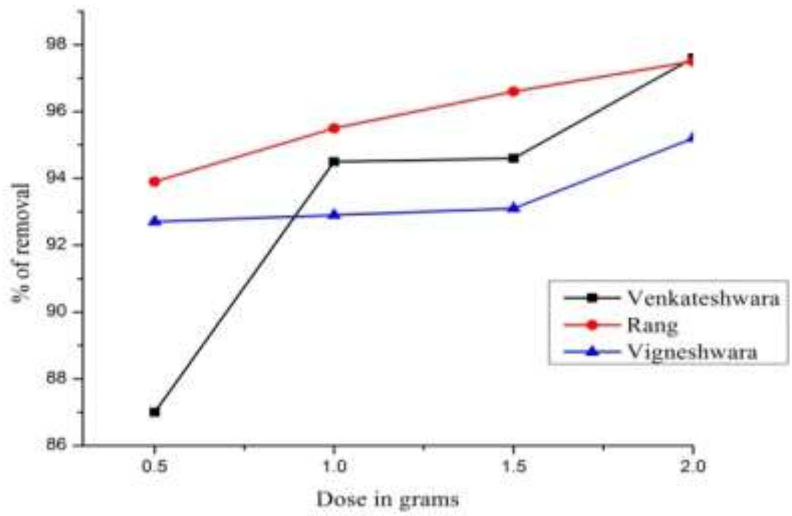

Fig.1 Effect of dose of Coral wood legume pod using textile dyes of Venkateshwara, Rang and Vigneshwara industries

The rate of adsorption in Rang textile dye effluent shows increasein the percentage removal with change in dosage. In venkateshwara textile dye effluent the adsorption rate was very high in the beginning and then it shows adsorption remained constant and once again increases in the rate of adsorption. It shows that, the rate of adsorbption increase was due the complete adheranceof active sites in the adsorbent. In the Vigneshwara textile, the rate of adsorption was slow in the beginning due the interaction of the adsorbent material and the dye molecule

3.3. Effect of Concentration:

Effect of concentrations was studied by taking the 50 ml samples of textile effluent (20%, 40%, 60%, 80% and 100%) solutions in 100 ml beakers and adding 0.5g of adsorbent.

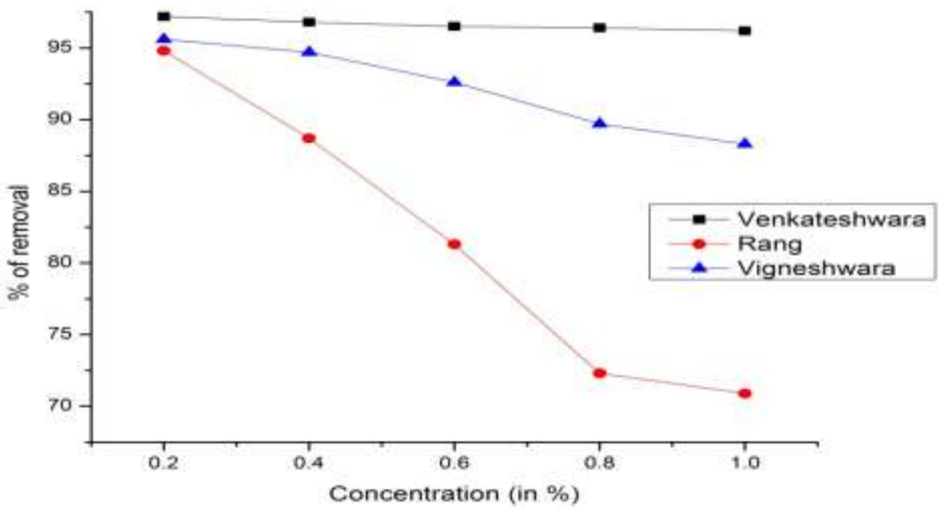

Fig 2. Effect of Concentration of venkateshwara, rang and vigneshwara dyes using coral wood legume pod

In the fig. 2 shows the rate of adsorption decreases while increase in concentration of Venkateshwara, Rang and Vigneshwara textile dye. This is due to the saturation of adhere of dye molecule on the active sites of the adsorbent which leads no more active sites on the surface of the adsorbent , so adsorption process gradually decreases.

3.4. Effect of Contact time:

The investigation of the effect of contact time was carried out with 0.5 g adsorbent dose in 50 ml of 20% dye solutions. The adsorption increased with increase in time. Contact time of all dye solutions was within 10 hrs. The adsorption increased with increase in contact period.

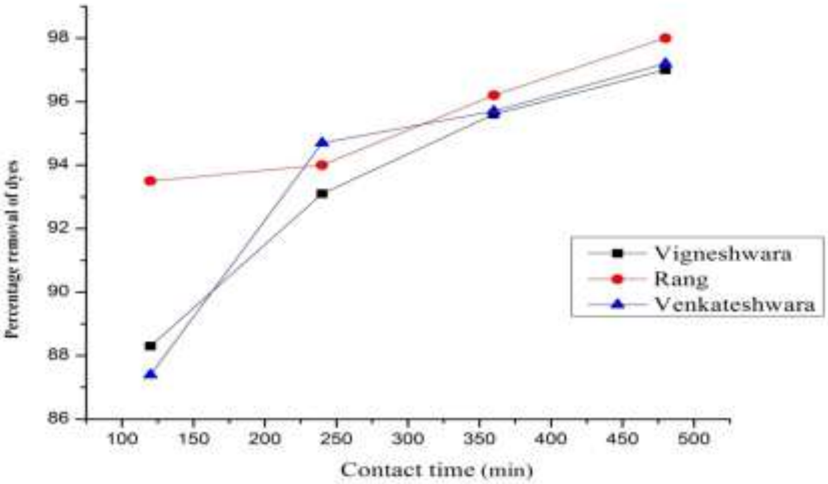

Fig. 3 Effect of contact time for all dyes for coral wood legume pod

Fig. 3 shows the rate of adsorption of Vigneshwara, Rang and Venkateshwara textile dye effluent increased as contact time increased. The time taken for the adsorption depends upon the interaction between the dye molecule and adbsobent to adhere the dye which leads maximum percentage removal efficiency. The Rang textile dye effluent shows maximum percentage removal of dye effluent compared to Vigneshwara and Venkateshwara textile dyes.

3.5. Adsorption isotherms:

Study of adsorption isotherm is essential in order to select an adsorbent for the removal of dyes to determine adsorption potential of an adsorbent. Isotherms of Freundlich and Langmuir were studied for adsorption process(Adamson, 1960).

Freundlich isotherm: $\log q_e = \log K + \left(\frac{1}{n} \log C_e\right)$

Langmuir isotherm: $\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{Q_m\, b}\right) + \left(\frac{C_e}{Q_m}\right)$

where qe is the per unit mass of adsorbent, the amount of dye adsorbed at equilibrium in (mg/g) where K and n are measures of sorption capacity and intensity of adsorption respectively. C_e is the dyes equilibrium concentration in (mg/L) and Langmuir constants of Q_m and b are indicative of sorption capacity (in mg/g) and adsorption of energy respectively from intercept and the slope.

The **Dubinin-Radhuskevich**Isotherm model of was initially formulated for a pore filling mechanism of the adsorption process (Dubinin 1960). Homogenous and heterogeneous nature is generally applied to express the adsorption process.

$$\log q_e = \log q_m - \beta \epsilon^2$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g); q_m is the theoretical isotherm saturation capacity mg/g; β is the Dubinin-Radhuskevich isotherm constant (mol^2/kg^2) and ε is the Dubinin-Radhuskevich isotherm constant.

$$E = \frac{1}{\sqrt{-2\beta}}$$

β can be denoted as isotherm constant mean while the parameter ε can be calculated as

$$\varepsilon = RT\,ln\left(1 + \frac{1}{C_e}\right)$$

where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L).

3.6. Kinetics of the adsorption:

First order kinetics was found to operate for adsorption process, Kannan and Vanmudi (1991) proposed the following equations employed for adsorption data.

$$K = \left(\frac{2.303}{t}\right) log\left(\frac{C_0}{C_t}\right)$$

Here concentration of dyes is expressed at zero time and at time t (min). For all the above dyes, the values of log (C_O/C_t) were found to be linearly correlated with contact time. Langmuir isotherm of essential characteristic can be described in terms of dimensionless constant equilibrium parameter or separation factor (Weber *et.al*. (1974) was defined R_L.

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

Where, b is the Langmuir constant and C_i is the initial concentration of dye (in ppm). The value of the parameter, R_L indicates the nature of the isotherm as given in table 1.

Table 1: Nature of the isotherm and their range

R_L value	Nature of isotherm
$R_L > 1$	**Unfavorable**
$0 < R_L < 1$	**Linear**
$R_L = 1$	**Favorable**
$R_L = 0$	**Irreversible**

The theoretical parameters for isotherm models fitted on experimental data of Vengkateshwara, Rang and Vigneshwara textile dye effluent using biosorbent. The three different adsorption isotherms were studied and their results are tabulated in Tabel 2.

Table 2: Shows the theoretical parameters for isotherm models fitted on experimental data of Vengkateshwara, Rang and Vigneshwara textile dye effluent using biosorbent

Isotherm models	**Parameters**	**Venkateshwara**	**Rang**	**Vigneshwara**
Langmuir	Qo(mg/g) b (L/mg) R^2 R_L	-0.0072 1.9 0.132 0.0012	0.019 0.7 0.602 0.017	0.01 1.52 0.057 0.0090
Freundlich	1/n K (L/g) R^2	1.62 0.5 0.844	0.78 0.22 0.779	0.65 0.3 0.650
Kinetic study of adsorption	K_{ad}	0.023	0.0051	0.0040
D-R isotherm	Qmax(mg/g) E(kJ/mol) R^2	5.2 52 0.942	1.42 280.7 0.851	1.43 181.07 0.911

In the present study, isotherm models of Freundlich and D-R fitted well for the Venkateshwara, Rang and Vigneshwara textile dye effluents. R_L values of all the three dyes are favourable for the adsorption process.

3.7. Scanning Electron Microscopic Images of coral wood legume pod:

The scanning electrone microscope images were taken at 2µm resolution. Fig. 4(a) unadsorbed material shows irregular surface area with voides like structures which are considered as active sites for the adsorption of dyes

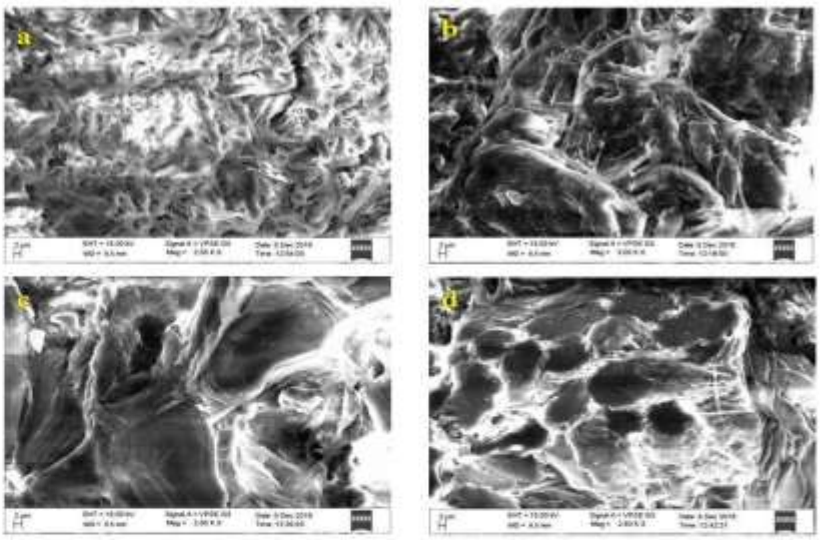

Fig.4 a) Unadsorbed adsorbent, b) Rang textile dye adsorbed adsorbent , c) Venkateshwara textile dye adsorbed adsorbent and d) Vigneshwara textile dye adsorbed adsorbent

Fig. 4 (a) Shows adsorbent before adherence of dye whereas(b),(c) and (d) show adherence of dyes on active sites on the adsorbent material as a formation of layer. (c)Shows the deposition on dyes on the voids of active sites. (d)Shows the adherence of dyes layer by layer on the active site of the adsorbent, which shows the adsorption.

3.8. FT-IR(fourier transform infrared spectroscopy)

Fourier transform infrared spectroscopy instrumental analysis was carried out for the adsorbent textile dyes of Venkateshwara, Vigneshwara and Rang.

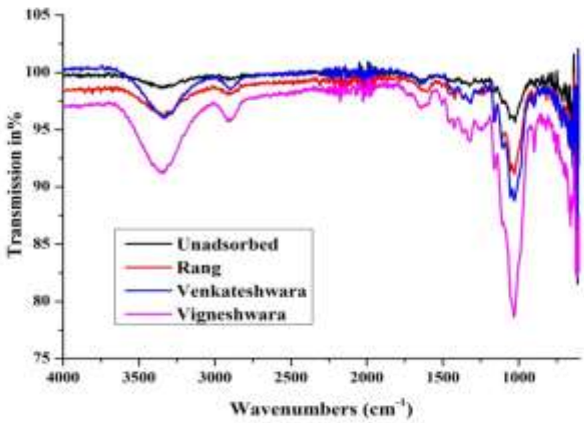

Fig.5 shows the FT-IR spectrum of the adsorbent with adsorbed dye and unadsorbed dye material.

To know the distribution of functional groups before adsorption and after adsorption FTIR spectral analysis were carried out. Fig.5 shows the FT-IR spectrum of the adsorbent with adsorbed dye and unadsorbed dye material. In the spectrum, the changes in the functional groups can be observed. The peak at 3332cm^{-1} is NH stretching frequency which is present in the all the three dyes adsorbed adsorbent but it is not present in the unadsorbed adsorbent. Stretching frequency peaks at 2900 cm^{-1}, 1550 cm^{-1} and 1325 cm^{-1} are from the aromatic C-H, C=C and C-N respectively. These peaks are the chemical constituents of the dye which adhere on the surface of the adsorbent. The remaining peaks are present in the all the adsorbent and is because of the starch and other chemical constituents of the adsorbent comparing from the presence of functional groups in adsorbed dye adsorbent and unadsorbed adsorbent. Presence of the additional functional groups in adsorbed adsorbent can be concluded that, dyes are accumulated on the surface of the adsorbent and adsorption process has taken place.

4. Conclusion:

Coralwood legume pod has been successively utilized as a adsorbent material for removal of textile dyes of Venkateshwara, Rang and Vigneshwara industries using batch adsorption method. Dose, contacttime, pH and concentration were studied. The results show that, isotherms were favourable for the adsorption process and imaging studies confirms the adsorption of the dyes. Coralwood legume pod is a very good adsorbent for the removal of textile dyes of Venkateshwara, Rang and Vigneshwara industries.

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