

## Utilization of Lignocellulosic Waste from Bidi Industry for Removal of Dye from Aqueous Solution

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**ABSTRACT:** A new, local agro-industrial waste was valorized by chemical treatment and tested for its ability to remove cationic dye from aqueous solution. Tendu (*Diospyros melanoxylon*) leaves refuse, a solid waste from *bidi* industry which caused disposal problem, was studied as a biosorbent. Raw tendu waste (TLR), along with sulfuric acid carbonized tendu waste (TLR-CM) and tendu waste treated with dilute sulfuric acid (TLR-2N) were utilized as sorbent for uptake of crystal violet from aqueous solutions. Adsorption studies were carried out at various dye concentrations and contact times. It followed the pseudo-second-order kinetics and followed the Langmuir adsorption isotherm. Interestingly, milder acid treatment of the tendu waste enhanced biosorption, whereas drastic acid carbonization of tendu waste resulted in reduced adsorption of dye. The maximum adsorption capacities for crystal violet for TLR-2N, TLR and TLR-CM are 67.57, 42.92 and 22.47 mg/g respectively. Commercial activated carbon had maximum adsorption capacity for crystal violet of 151.52 mg/g. Thus a renewable solid waste with mild acid treatment can offer a cost effective alternative to activated carbon.

**Key words:** Biosorption, *Diospyros melanoxylon*, Solid tendu waste, Dye, Crystal violet

### INTRODUCTION

Colored wastewater is a consequence of industrial processes both in the dye manufacturing industries and in the dye-consuming industries. Discharge of dyes in natural water causes severe environmental problems because they are toxic to aquatic life and damage the aesthetic nature of the environment. Moreover, these effluents are difficult to treat by conventional biological and physical-chemical techniques due to the complex aromatic molecular structure of the dyes. Today there are more than 10,000 dye available commercially (Nigam *et al.*, 2000). Two per cent of  $7 \times 10^5$  ton dyes produced per year is discharged directly in aqueous effluent, and 10% are subsequently lost during the textile coloration process (Easton, 1995). The removal of dye from textile effluents is one of the most significant environmental problems. Traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of

synthetic textile dyes because of the chemical stability of these pollutants (Anjaneyulu *et al.*, 2005). The adsorption process has proved itself more versatile and efficient than other methods such as coagulation, chemical oxidation, and froth flotation. Activated Carbons have been the most commonly used adsorbents due to their high adsorption capacity (Robinson *et al.*, 2001). The worldwide demand for activated carbon is increasing. The raw materials used are nonrenewable. Therefore, possible sources should be investigated. However, the relatively high cost of activated carbon restricts its use largely in developing countries. Thus, in these countries, there is a continuing need to identify and develop low cost and efficient adsorbents.

Many novel materials have been tested as adsorbents with a two-fold objective: to replace activated carbon with cheaper alternatives and to utilize various waste products for the purpose. Crini (2006) recently reviewed use of such non-

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conventional low-cost adsorbents for dye removal. Research of the recent past mainly focused on utilizing waste materials as alternatives to activated carbon. Coir pith (Namasivayam *et al.*, 2001), passion fruit and mandarin peels (Pavan *et al.*, 2007), Rice husks (Vasanth Kumar and Sivanesan, 2007), palm kernel fiber (Ofomaja, 2007), and silkworm pupa (Noroozi *et al.*, 2007) are some recent examples of waste materials being tested as biosorbents for color removal. However, as the adsorption capacities of the above adsorbents are not large, new adsorbents are still under development. One such non-conventional waste comes from 'Bidi' industry unique to Indian subcontinent. Bidi a hand-rolled cigarette that consists of a small amount of tobacco flakes rolled in a leaf of tendu (*Diospyros melanoxylon*), a broad-leafed tree native to India. Bidi rolling industry is a home industry in many town and cities across India. It produces large quantities of cuttings of tendu leaf as refuse, which has no economic value and creates a solid waste disposal problem for civic authorities. The objective of this study was to investigate the feasibility of using this zero cost solid waste for the removal of crystal violet as a probe molecule, from aqueous solution by adsorption method. Tendu waste in its native and chemically modified form along with commercial powdered activated carbon, were subjected to adsorption studies under various experimental conditions and the results obtained are discussed in this communication.

## MATERIALS & METHODS

The waste tendu leaf cuttings were collected from the dumping sites near bidi industries in the town of Solapur, India. They were cut in to pieces of about 3 X 4 cm size, washed with tap water to remove soil and dust, rinsed with distilled water and dried in an oven at 80°C to a constant weight. The dried tendu leaf refuse (TLR) were powdered and sieved with an 80-mesh sieve and stored in dessicator until used. Tendu waste was carbonized by treating five parts of TLR with three parts of concentrated sulfuric acid and kept in oven at 120° – 130°C for 4 hours. The carbonized mass was washed free of acid with distilled water and soaked in 1% solution of sodium bicarbonate overnight to remove residual acid. It was further filtered and dried at 110°C till constant weight. The material

was pulverized and sieved through 80-mesh particle size and used for the study as TLR-CM. In order to obtain limited carbonization, one part of tendu waste was treated with five parts of 2N sulfuric acid for 24 hrs. The biomass was washed free of acid as described above, dried, powdered and used as TLR-2N. Powdered Activated Carbon (PAC) used was of reagent grade and obtained from Glaxo (India). Crystal violet (CV) (CI=42555; chemical formula=C<sub>25</sub>H<sub>30</sub>N<sub>3</sub>Cl; FW=407.99; nature=basic violet and  $\lambda_{\text{max}} = 585 \text{ nm}$ ); was supplied by Merck, India.

The adsorption studies were performed by the batch technique to obtain kinetic and equilibrium data. For kinetic study, 100 mL of CV solution of known concentration was added to 100 mg of TLR, TLR-CM, TLR-2N or PAC in a 250 mL round bottom flask at room temperature (27 +/- 1°C), and at agitation speed of 200 rpm. The samples were withdrawn from the shaker at the predetermined time intervals and adsorbent was removed by centrifugation. The CV adsorbed was determined using absorbance values measured before and after treatment, at 585 nm with Shimadzu double beam UV-spectrophotometer. Calibration curves were established prior to the analysis. Calibration range for crystal violet was 1-6 mg/L and dilutions were performed where necessary to bring solutions within the calibration range. During isotherm studies, different mass (50-1000 mg/L) of various sorbents was used. All experiments were carried out in duplicate and mean values are presented. The error obtained was 3.0%.

## RESULTS & DISCUSSION

The study on the effect of pH on the sorption of Crystal violet by TLR, TLR-CM, TLR-2N and PAC could be important in establishing the optimum sorption of dye at the solids/liquid interface and the results are shown in (Fig.1). The effect of initial pH on sorption percentages of dyes was examined over a range of pH values from 2 to 10. When initial pH of the dye solution was increased from 2 to 10, the percentage removal decreased in case of TLR and TLR-CM, whereas the decrease was not steep in case of TLR-2N and PAC. Lower adsorption of crystal violet, an anionic dye, at alkaline pH is probable due to the presence of excess of OH<sup>-</sup> ions competing with

the dye. Various sorption kinetic models have been used to describe the uptake of dyes. The pseudo first-order rate equation by Lagergren (1918) and pseudo second-order kinetic model by Ho and McKay (1999) has been used widely. It was observed that most of the biosorption systems followed a pseudo second-order kinetic model as also reported by Ho and McKay (1999), which can be expressed as:

$$t/q_t = 1/kq_e^2 + 1/q_e \quad (1)$$

Where  $t$  is the contact time (min),  $q_t$  and  $q_e$  are the quantities of sorbate, adsorbed at time  $t$  and at equilibrium (mg/g) and  $k$  is the rate constant (g/mg min). Adsorption of crystal violet by TLR, TLR-CM, TLR-2N and PAC followed pseudo second order kinetics and one of these plots for TLR-2N is shown in (Fig. 2). which agreed with chemisorption as the rate-limiting mechanism through sharing or exchange of electron between sorbent and sorbate (Ho and McKay, 1999).

The rate of sorption of crystal violet TLR, TLR-CM, TLR-2N and PAC are shown in (Fig. 3). It was observed that the treatment with 2N sulfuric acid of TLR resulted in reducing the equilibrium time from 120 to 60 min.

Experimental isotherm are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate sorbent, and for preliminary determination of sorbent dosage requirements. Moreover, the isotherm plays an important role in the predictive modeling procedures for analysis and design of sorption systems. In adsorption process, particular mass of sorbent is added to the solution containing a certain concentration of sorbate. When the sorbent comes in contact with the solution, the sorbate gets accumulated on the surface of the sorbent. In this process, a dynamic equilibrium is established and no significant removal

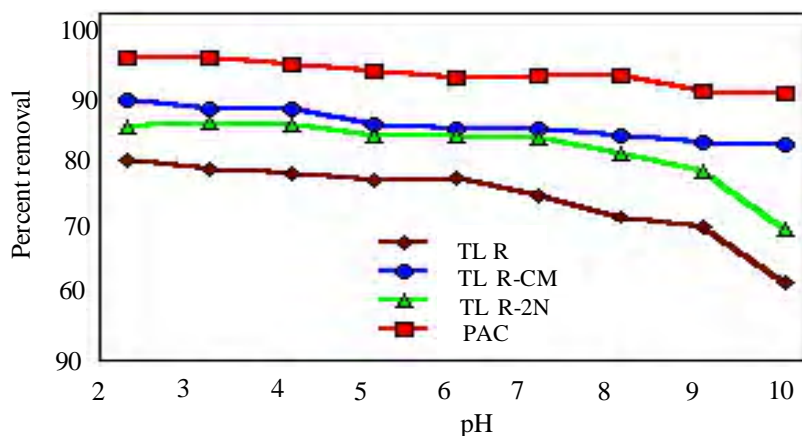


Fig. 1. Effect of pH on the removal of CV

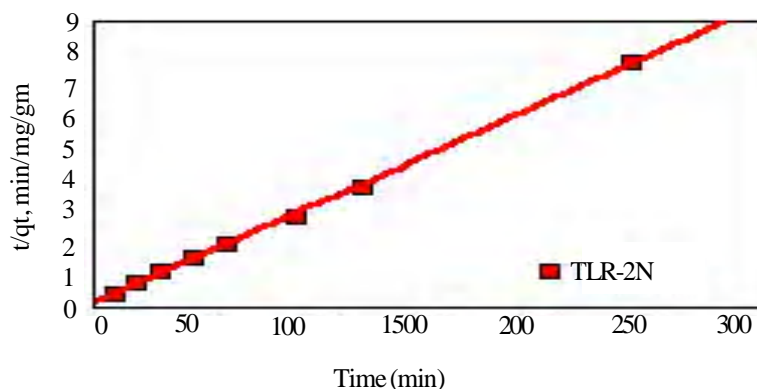


Fig. 2. Pseudo-second order kinetics of CV adsorption by TLR-2N

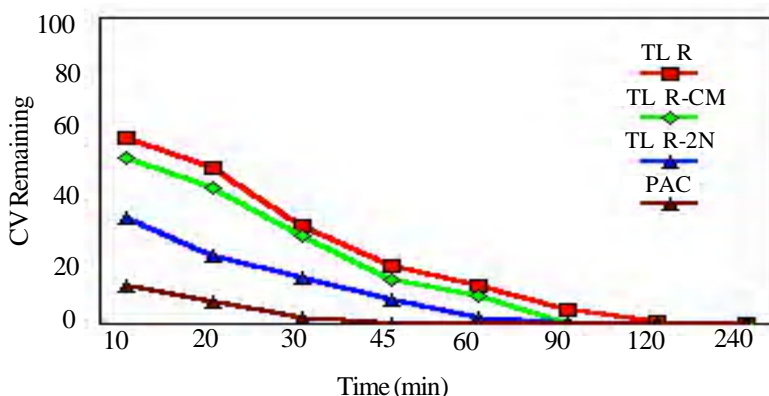


Fig. 3. Rate of sorption of CV on various sorbents

of sorbate is expected further. The Langmuir (1916) and Freundlich (1906) isotherms are most frequently used to represent the data of sorption from solution. In order to establish the maximum sorption capacity, the Langmuir equation of the following linearized form was applied to the sorption equilibria at different adsorbent doses.

$$1/Q_e = 1/K_L + 1/bK_L * 1/C_e \tag{2}$$

Where  $C_e$  is the concentration of CV at equilibrium (mg/L),  $Q_e$  is the amount of CV adsorbed at equilibrium (mg/g),  $K_L$  (mg/L) and  $b$  (mg/g) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption. The constants  $b (=Q_{max})$  and  $K_L$  can be evaluated from the intercept and slope of the linear plot of the experimental data of  $1/Q_e$  versus  $1/C_e$ , respectively. Equilibrium stage at which all potential sites of the sorbent reach the equilibrium,  $Q_e$ , the sorbent is said to be exhausted and the capacity at this point is called maximum sorptive capacity,  $Q_{max}$ .

To assess the capacity of any adsorbents maximum sorptive capacity is the appropriate parameter to be considered. Langmuir model assumes that the sorption energy is constant and independent of surface coverage. Linearized form of Freundlich equation was applied to the sorption equilibria at different adsorbent doses.

$$\log Q_e = (1/n) \log C_e + \log K_F \tag{3}$$

Where,  $K_F$  and  $1/n$  are constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity. The adsorption capacity and affinity of TLR, TLR-CM and PAC for CV was determined with two isotherms models, using initial CV concentration of 150 mg/L. Experimental values obtained for the adsorption capacity experiments were used to calculate the Langmuir and Freundlich parameters and results are shown in (Table 1). The correlation coefficient values obtained from the Freundlich and Langmuir isotherms are also presented. The values indicate that the adsorption

Table 1. Adsorption isotherm parameters for Crystal Violet

Adsorbent	Langmuir			Freundlich		
	$K_L$ (mg/g)	$Q_{max}$ (mg/g)	$R^2$	$K_F$	$1/n$	$R^2$
TLR	0.027	42.29	0.995	2.71	1.802	0.988
TLR-CM	0.029	22.08	0.992	2.25	2.278	0.970
TLR-2N	0.066	67.57	0.977	6.41	1.789	0.977
PAC	0.353	151.52	0.994	33.11	1.866	0.979

pattern for CV on TLR, TLR-CM, TLR-2N and PAC followed Langmuir isotherm more closely than Freundlich isotherm. Experimental isotherms are useful for describing sorption capacity to evaluate the efficacy of a sorbent. Moreover the isotherm is essential in predictive modeling procedure for analysis and design of sorption systems (Venkobachar, 1990).

From above results, CV adsorption capacity of TLR is reduced to nearly half by drastic treatment with sulfuric acid; whereas the same is enhanced by milder treatment of sulfuric acid. Wang *et al.* (2005) have shown that increased sorption of CV occurred with carbon of fly ash with higher un-burnt carbon. In the present study, the maximum sorptive capacity ( $Q_{max}$ ) for CV of 67.57 mg/g was obtained using mild sulfuric acid treated tendu waste. In the literature, the maximum sorptive capacity ( $Q_{max}$ ) for CV reported was 68.03 mg/g for sewage sludge, 61.73 mg/g for coconut husk and 77.52 mg/g for peanut shell carbons (Graham *et al.*, 2001). Commercial powdered activated carbon, during the study exhibited little over double the maximum sorptive capacity obtained for TLR-2N. However, comparing to the low cost of acid treatment, utilization of tendu waste can be viable alternative to the commercial activated carbon.

## CONCLUSION

Present study was carried out to examine the use of tendu waste from local bidi industry as a biosorbent for removal of dye from aqueous solution. The tendu waste biomass was treated by sulfuric acid in strong as well as milder conditions. The sorption of crystal violet as a probe dye was studied and compared with raw tendu waste and commercial powdered activated carbon. Milder treatment with 2N sulfuric acid resulted in a biosorbent with high sorptive capacity. The sorption time was reduced to half as compared with the raw tendu waste. The adsorption followed pseudo-second order kinetics and fitted well with Langmuir isotherm. It exhibited maximum sorption capacity comparable to other biosorbents reported. In developing countries like India, industries cannot afford to use conventional wastewater treatment chemicals like alum, ferric chloride, polymer flocculants and coal-based activated carbon because they are not cost-

effective. Preparation of biosorbent from this zero cost and abundant biomass will eliminate the costly problem of solid waste disposal while at the same time deriving economic benefits from such value-added products.

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