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Biosorption of Methylene Blue from Aqueous Solutions by *Diospyrous melanoxylon* Leaf Waste

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Waste Tendu (Diospyros melanoxylon) leaves from bidi (local cigarette) industry has been used as a raw material to produce activated carbon applying sulfuric acid carbonization method. Batch experiments were conducted to assess the potential for the removal of methylene blue dye from aqueous solution using the activated carbon and compared to raw tendu leaves powder and commercial activated carbon. Equilibrium isotherm and kinetic studies have been done by varying the parameters such initial concentration of dye, adsorbent dose, pH of the dye solution, and varying the contact time between the carbon and the dye. It was found that the methylene blue adsorption on tendu waste-based activated carbon conformed to the Langmuir isotherm. The maximum monolayer adsorption capacities were found to be 219.3, 355.9 and 495.1 mg/g for raw tendu waste, carbonized tendu and commercial carbon, respectively. The kinetic studies were well characterized by a pseudo second order kinetic model. The results of this study indicate that raw tendu waste a renewable bioresource, as such as well as its carbonized form are attractive biosorbent for removing a cationic dye from the dye wastewater.

Keywords: *Biosorption, Diospyros melanoxylon, Tendu waste, dye removal*.

1. Introduction

The discharge of colored wastewater from industries into water bodies upsets aquatic biological activity. Devastation of the ecosystem and incomprehensible loss of endangered species of flora and fauna are of serious concern. Consequently, removal of dyes from wastewater has been one of the significant environmental problems. These dyes are difficult to treat by conventional methods due to complex aromatic molecular structure and non-degradable nature (Anjaneyulu et al. 2005). The processes for the color removal from the dye and textile effluents include biological treatment, flocculation, adsorption, oxidation, hyperfiltration, etc. (Ong et al. 2011). However, the microbiological, photocatalytic and electrochemical decomposition procedures are not efficient, because several dyes are very difficult to be decomposed, and also these procedures are prone to give rise to colorless hazardous species in the water effluents (Forgacs et al. 2004). Of all these processes, the adsorption procedure is the most efficient, because the hazardous species is transferred from the wastewater to a solid phase and also reducing the effluent volume. Among the above treatment methods, adsorption technology would tend to open new opportunities for the treatment of colored wastewaters, especially those containing dyes which are not easily biodegradable. Adsorption of dyes from colored effluents onto the surface of a solid adsorbent has proved more versatile and efficient (Robinson *et al*. 2001).

Activated carbon is the most popular and widely used adsorbent, but there are certain problems with its use since it is expensive and its regeneration is difficult. Most commercial activated carbons are produced from various types of coals; non-renewable material with limited source. In addition, the price of activated carbon has been increasing due to overwhelming demand. Thus, it is reasonable to seek

a new starting material which is cheap, renewable, and has guaranteed steady supply throughout the year. Recently, interest has been focused on the feasibility of using agricultural products and byproducts, industrial byproducts, industrial waste biomass, and natural substances for dye removal from colored wastewaters. Many of such non-conventional and low-cost adsorbents tested for dye removal have been reviewed extensively (Srinivasan, and Viraraghavan 2010; Hubbe et al. 2012). Methylene blue is an important basic dye and widely used in the textile industry. Acute exposure to Methylene blue may cause increased heart rate, shock, vomiting, cyanosis, jaundice, quadriplegia, heinz body formation and tissue necrosis in humans (Vadivelan and Kumar 2005). Many researchers have studied the adsorption of Methylene blue dye using agricultural wastes from biomass of jackfruit leaf (Uddin et al. 2009). Palm karnel fibre (Ofomaja 2007), jute fiber (Senthilkumar et al. 2005), and black cherry shell (Rodríguez Arana and Mazzoco 2010) were studied for removal of methylene blue. Use of low-cost biosorbents for the removal of methylene blue was extensively reviewed (Rafatullah et al 2010). These biosorbents are very cheap solid wastes; hence they can be used once and then further used as fuel.

In present study we used one such non-conventional lingo-cellulosic waste from '*Bidi*' industry unique to India. *Bidi* a hand-rolled cigarette, closely resembling a miniature cigar, consists of a small amount of sun-cured tobacco flakes rolled in a leaf of tendu (*Diospyros melanoxylon*), a broad-leafed tree native to India. Tendu leaf is the second largest forest produce in India after timber and is exclusively used in making Bidi. These trees grow wild in the hilly forest regions of India abundantly and after timber, tendu is the most important forest produce. Annual production of tendu leaves is around 300,000 tones as reported by Gupta and Guleria (1982). Bidi rolling industry produces waste cuttings of tendu leaves as a solid waste creating disposal problem for local civic authorities. Presently, this solid waste finds way into landfills. Recently, tendu leaf is shown to be a rich source of at least nine pentacyclic triterpenes, whose usane skeleton has excellent surface-active properties (Mallavadhani et al. 2001). Therefore, there is a need to valorize this waste biomass which is available in large quantities throughout the country. In present study waste tendu leaves are carbonized using concentrated sulfuric acid to obtain a biosorbent. Removal of methylene blue, a dye often used as a probe molecule to characterize the capacity of a biosorbent, was studied. Widespread use of methylene blue in adsorption studies presents a common base of comparison with published results in the literature (Rafatullah et al. 2010). Tendu waste in its raw and chemically modified form were subjected to adsorption studies along with commercial activated carbon, under various experimental conditions, and the results obtained are presented and discussed in this communication.

2. Materials and methods

Preparation of Adsorbents

The waste tendu leaf cuttings were collected from the dumping sites near bidi industries in the town of Solapur, India. They were cut into 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^{o}C to a constant weight. The dried tendu leaf refuse (TLR) were powdered and sieved with an 80-mesh siever and stored in dessicator until used. Sulfuric acid treated tendu waste carbon, also called chemically modified tendu leaves refuse (TLR-CM), was prepared by treating five parts of TLR with three parts of concentrated sulfuric acid and kept in oven at 120^{o} – 130^{o}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^{o}C till constant weight. The material was pulverized and sieved through 80-mesh particle size and used for the study. The various physico-chemical characteristics of TLR-CM were: apparent density= 0.55 g/ml; ash content= 2.05%; moisture content= 4.13%; cation exchange capacity= 0.44 meq/g; water-soluble matter= 0.75%; acid soluble matter= 3.24% and EC= 0.53 mS/cm. Scanning electron micrographic (SEM) analysis was performed at IIT-Delhi, with an Environmental Scanning Electron Microscope (Model: Zeiss EVO-50, Germany). Powdered Activated Carbon (PAC) used was of reagent grade and obtained from Glaxo (India).

Dye solution preparation

Methylene blue (MB) (CI=52015; chemical formula=C16H18N3SCl; FW=319.86; nature=basic blue and λ_{max}= 660 nm); was supplied by Merck, India. An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare stock solution (500 mg/l). Experimental solutions of the desired concentrations were obtained by successive dilutions. Dye concentration was determined using absorbance values measured before and after treatment, at 660 nm with an ELICO spectrophotometer (Model SL-150). Experiments were carried out at initial pH values ranging from 2 to 10; initial pH was controlled by addition of dilute hydrochloric acid and sodium hydroxide solutions.

Adsorption experiments

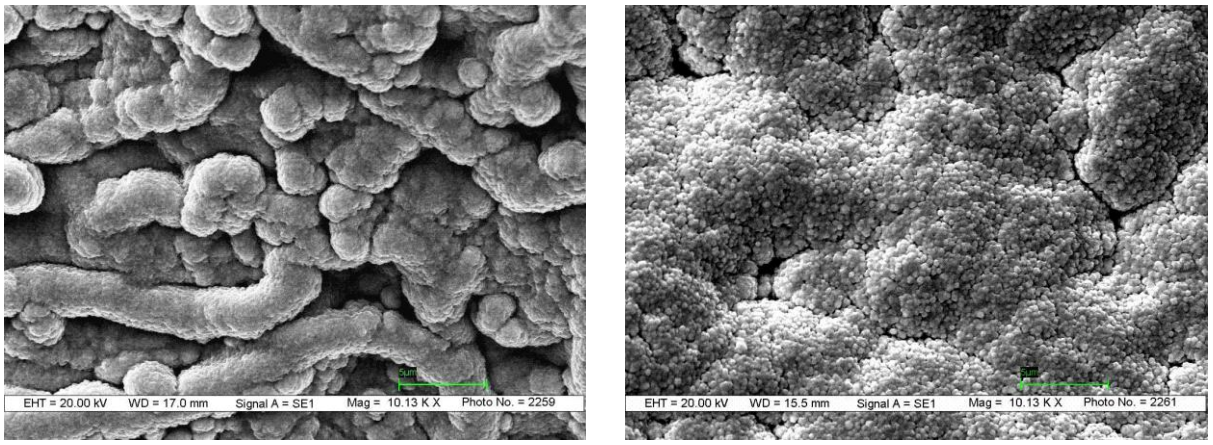
In each adsorption experiment, 100 ml of dye solution of known concentration and pH was added to 100 mg of TLR, TLR-CM or PAC in a 250 ml round bottom flask at the room temperature (27 +/-1^{o}C), and at the agitation speed of 200 rpm. The samples were withdrawn from the shaker at the predetermined time intervals, and adsorbent was separated from the solution by centrifugation at 4000 rpm for 10 min. The absorbance of the supernatant solution was estimated to determine the residual dye concentration. The experiments were performed by varying the amount of adsorbents (0.05–1.00 g/100 ml), concentration of dye solution (50–150 mg/l) and initial pH (2–10) at different time intervals. To

compare the dye removal on the same basis, the pH of all the samples was adjusted to 7.4 before measurement. The experiments were conducted in duplicate and the negative controls (with no adsorbent) were simultaneously carried out to attribute sorption to the adsorbent used only. All experiments were carried out in duplicate and mean values are presented. The error obtained was 3.0 %.

3. Results and Discussion

Scanning electron microscope analyses

Scanning electron micrograph is widely used to study the morphological features and surface characteristics of the adsorbent materials. The surface morphology of TLR and TLR-CM particles were observed by SEM at 10K magnification and are shown in Figure 1a and Figure 1b, respectively. Raw tendu waste has irregular and uneven surface as shown in Figure 1a, while uniform granular surface with increased porosity obtained after sulfuric acid carbonization is shown in Figure 1b. The fine granulation shows a very large surface area that could possibly facilitate the entrapment and subsequent biosorption of MB by the surface functional groups.



1a 1b

Fig. 1. Scanning Electron Micrograph of TLR (1a) and TLR-CM (1b)

Effect of pH

Solution pH is an important monitoring parameter influencing the sorption behavior of adsorbate onto biosorbent surface due to its impact on both the surface binding-sites of the biosorbent and the dye solution chemistry. The study on the effect of pH on the sorption of methylene blue by TLR, TLR-CM and PAC could be important in establishing the optimum sorption of dye at the solids/liquid interface and the results are shown in Figure 2.

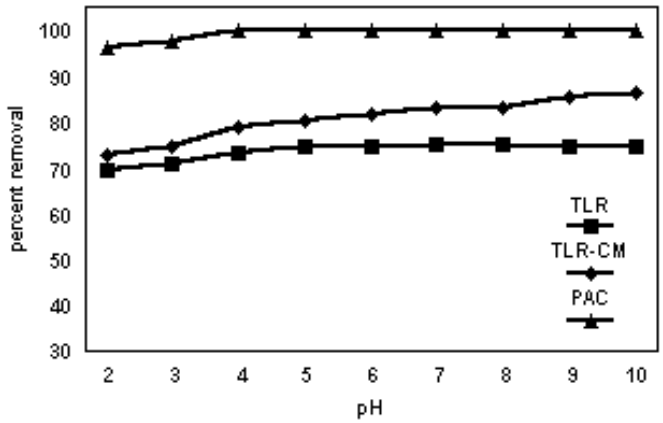


Fig. 2. Effect of pH on removal of MB: adsorbent dose, 100 mg per 100 ml; MB concentration: 50 mg/L, contact time: 180 min.

The effect of initial pH on sorption percentages of dyes was examined over a range of pH values from 2 to 10. The increase in sorption of dye with an increase in pH was not significant except for TLR-CM. For this reason, the pH 7.4 was selected for future experiments. After sorption experiments, it was found that the differences between initial and final pH values of dye solutions were generally less than 0.5 pH unit.

Sorption kinetics

The rate of sorption of MB for TLR, TLR-CM and PAC are shown in Figure 3. It was observed that the carbonization of TLR by sulfuric acid resulted in

reducing the equilibrium time from 90 to 60 minutes. Various sorption kinetic models have been used to describe the uptake of dyes. The pseudo first-order rate equation by Lagergren (1898) and pseudo second-order kinetic model by Ho and McKay (1999) have been used widely.

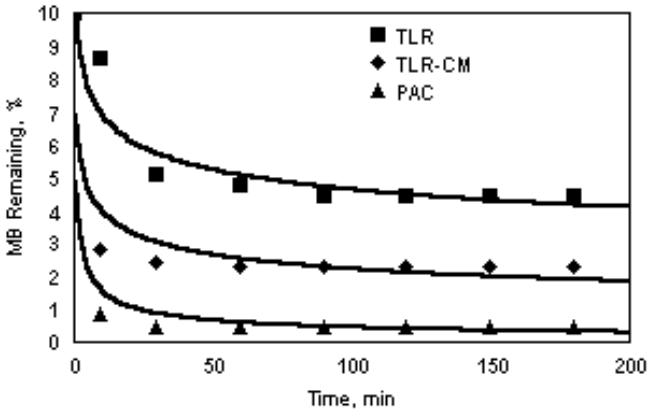


Fig. 3. The rate of sorption of MB by TLR, TLR-CM and PAC: adsorbent dose 2 g/L, MB concentration = 50 mg/L, temp: 27° C, pH = 7.4.

It was observed that most of the biosorption systems followed a pseudo second-order kinetic model as reported by Ho and McKay (1999), which can be expressed as

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

W 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). One of these plots for TLR-CM is shown in Figure 4 indicating that the methylene blue adsorption process followed the pseudo second-order kinetic, which agreed with chemisorption as the rate-limiting mechanism through sharing or exchange of an electron between sorbent and sorbate (Ho and McKay 1999).

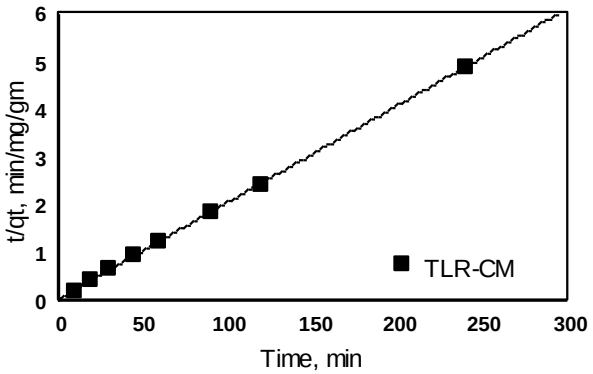


Fig. 4. Test plot for a pseudo second-order model for the removal of methylene blue by TLR-CM: adsorbent dose= 500 mg per 100 ml; initial pH =7.4, temperature= 27° C.

Adsorption Isotherm studies

E Experimental isotherms 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. 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, Langmuir equation of the following linearized form was applied to the sorption equilibriums at different adsorbent doses.

$$1/Q_e = 1/K_L + 1/bK_L * 1/C_e \quad (2)$$

Where C_e is the concentration of MB at equilibrium (mg/l), Qe is the amount of MB adsorbed at equilibrium (mg/g), K_L (mg/l) and b (mg/g) are 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. A linearized form of Freundlich equation was applied to the sorption equilibriums at different adsorbent doses.

$$\log Qe = (1/n) \log Ce + \log KF \quad (3)$$

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 MB were determined with two isotherm models, using the initial MB concentration of 150 mg/l. Experimental values obtained for the adsorption capacity experiments were used to calculate Langmuir and Freundlich parameters and results are shown in Table 1.

The correlation coefficient values obtained from Freundlich and Langmuir isotherms are also

presented. The values indicate that the adsorption pattern for MB on TLR, TLR-CM and PAC followed Langmuir isotherm more closely then Freundlich isotherm. The sulfuric acid carbonization of tendu waste resulted in enhanced sorption capacity from 219.3 mg/g for TLR to 355.9 mg/g for TLR-CM. The sorption capacities of MB for TLR and TLR-CM obtained during present study were compared to some agricultural wastes raw and treated as reported in literature (Table 2).

Table 1. Adsorption isotherm parameters for methylene blue

Adsorbent	Langmuir			Freundlich		
	K_L (mg/g)	Q_{max} (mg/g)	R^2	K_F	*1/n*	R^2
TLR	0.007	219.3	0.987	3.19	0.708	0.952
TLR-CM	0.004	355.9	0.974	2.19	0.837	0.932
PAC	0.065	495.1	0.987	29.51	0.584	0.931

Table 2. Adsorption capacities for some activated carbons derived from agro-industrial wastes. (Biosorbents with Q_{max} values above 200 mg/g included)

Biosorbent	**Adsorption Capacity, mg/g**	**Reference**
Teak wood Bark, Raw	914.59	McKay et al. 1999
Palm karnel fibre	671.78	Ofomaja 2007
Pinewood, Carbonized	556	Tseng et al. 2003
Coconut husk Carbonized	434.78	Tan et al. 2008
Peach stone Carbonized	412	Attia et al. 2008
Tendu leaves, Carbonized	335.9	Present study
Jackfruit leaf powder, Raw	326.32	Uddin et al. 2009
Black cherry stones, Carbonized	321.75	Rodríguez Arana and Mazzoco 2010
Rice husk, Raw	321	McKay et al. 1999
Guava leaves, Raw	295	Ponnusami et al. 2008
Coconut Shell Carbonized	277.9	Kannan and Sundaram 2001
Cotton waste, Raw	277.78	McKay et al. 1999
Banana stalk waste, Raw	243.9	Hameed et al. 2008
Jute Fiber Carbonized	225.6	Senthilkumar et al. 2005
Tendu leaves waste, Raw	219.3	Present study

As evident from above, both TLR and TLR-CM have relatively high uptake capacity for MB. Tendu leaves refuse originates from renewable sources and is waste of an industrial process. Its availability in bulk and in the form that is free of other garbage makes it attractive and competitive biosorbent for dye removal

4. Conclusions

Based on the present investigation, it could be concluded that some simple and low-cost chemical modification on tendu leaf refuse resulted in 52.6 % enhancement in sorption capacity. The uptake of methylene blue was not pH dependent and followed the pseudo second-order kinetic model, which agreed with chemisorption as the rate limiting mechanism. The sorption equilibrium was reached in approximately 90 min in the case of TLR, and 60 min in the case of TLR-CM. Sorption isotherms were better represented by Langmuir model than Freundlich model. Adsorption in this fashion is usually complete, when the surface is covered with a monolayer of methylene blue. The maximum adsorption capacities of methylene blue for the adsorbents used in this study are much higher than those of many potential biosorbents reported. Tendu leaf waste, which is a zero cost biomaterial available in abundance, should be seriously considered for removal of basic dyes from wastewater.

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Mėlynojo metileno biosorbcija iš vandeninių tirpalų naudojant Diospyrous melanoxylon lapų atliekas

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Indinio juodmedžio (*Diospyros melanoxylon*) atliekos, susidarančios *bidi* cigarečių (vietinių cigarečių) gamybos pramonėje, buvo naudojamos kaip žaliava aktyvuotos anglies gamyboje, taikant karbonizacijos sieros rūgštimi metodą. Atliekant eksperimentus, buvo vertinamas gebėjimas iš vandeninių terpių ištraukti metileno mėlynąjį dažą, naudojant aktyvuotą anglį kartu su indinio juodmedžio lapų milteliais ir komercine aktyvuota anglimi. Šio tyrimo rezultatai rodo, kad indinio juodmedžio lapai kaip atsinaujinanti žaliava ir jos karbonizuota forma yra puikus būdas, kaip katijoninius dažus šalinti iš spalvotų nuotekų.