RESEARCH ARTICLE
doi: 10.2306/scienceasia1513-1874.2011.37.038

ScienceAsia 37 (2011): **38–42**

Removal of Janus Green dye from aqueous solution by phosphoric acid carbonized agro-industrial waste

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Received 26 Aug 2010
Accepted 1 Feb 2011

ABSTRACT: Meaningful waste use aimed at conservation of resources and lowering the amount of pollution is now inevitable. In the present study, the potential of tendu (*Diospyros melanoxylon*) leaf waste from a local *beedi* (cigarette) industry to remove dye from aqueous solution was studied after its pretreatment with phosphoric acid. The carbon prepared was characterized by analysis of porosity, surface area, scanning electron micrograph, cation exchange capacity, iodine, and methylene blue number. Feasibility of employing this carbon for the removal of Janus Green, a diazine dye, from aqueous solution was investigated. Dye removal was compared simultaneously with commercial carbon. The adsorption was evaluated in a batch process with different concentrations of dye as well as with different adsorbent doses, at a range of pH values, temperature, and contact time. The kinetic parameters were determined and found to follow the Lagergren pseudo first order model. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherms. The Langmuir maximum adsorption capacity was found to be 51 mg/g, which approached the value 57 mg/g obtained for commercial carbon. The changes in standard free energy, standard entropy and standard enthalpy were calculated. The results showed that adsorption of dye onto phosphoric acid treated tendu biomass was spontaneous and found to be physical and exothermic in nature.

KEYWORDS: tendu waste, adsorption, kinetic parameters, isotherm

INTRODUCTION

With dwindling non-renewable fossil materials and mounting pressure on our environment, the progressive use of renewable and recycled materials emerges as an inevitable necessity. Biosorbents prepared from agricultural waste and by-products have been widely studied. The ability of activated carbon, low-cost by-products, and waste material as adsorbents to remove various dyes from aqueous solutions and wastewaters have been investigated[1–4]. While activated carbons produced from non-renewable sources such as coal are used commercially, numerous alternative adsorbents have been proposed[5,6]. In developing countries, procurement and use of commercial activated carbon for water and wastewater treatment is too costly. Indeed, now much emphasis is on the preparation of carbon from locally available materials for ultimate use as adsorbents. Many of the starting materials for these replacement adsorbents are agricultural or industrial by-products and so their reuse as secondary adsorbents contributes to waste minimization, recovery, and reuse. Suitable modification of agricultural by-products could enhance their natural capacity and add value to the waste biomass.

Dyes in industrial wastewater are visible pollutants that are difficult to treat due to their complex molecular nature and synthetic origin. The dyes released into the environment can lead to acute effects on exposed organisms due the toxicity of the dyes. Intense colours of dye effluent have an adverse aesthetic effect while they reduce aquatic diversity by blocking the passage of light through the water. In addition, some dyes or their metabolites are toxic, mutagenic, or carcinogenic[7]. Conventional methods like precipitation, ion exchange, solvent extraction, filtration, electrochemical treatment, and adsorption on activated carbon have significant disadvantages such as high cost, high-energy requirement, production of toxic sludge, or waste that require further disposal. Therefore, these methods do not suit the needs of developing countries. Biosorption using renewable biomass from industrial waste offers a promising potential alternative to conventional methods for dye removal in an economical and eco-friendly manner. Efficient and easily available biosorbents are needed when a search is on for a cheaper alternative to commercial activated carbon.

Tendu leaves (*Diospyros melanoxylon*) are an important non-wood forest product used for hand rolling of *beedis* (local cigarettes). In India, it is not only an extremely important non-wood forest product that serves as a big revenue earner for the government, but is also an important economic resource to the indigenous tribes and local population when they have no other form of employment. About 7.5 million people are engaged as part-time collectors of tendu leaves, and another 3 million process the leaves into beedis. Estimated revenues from tendu leaves are US$ 200 million per year[8]. Around 300 000 tons of tendu leaves are produced annually across India, of which over 20% is waste after hand rolling of beedis[9]. This creates a solid waste disposal problem for the local civic authorities and ultimately tendu leaf refuse finds way into landfills. Textural characteristics of such biomass can be appropriately tailored by selecting a suitable chemical pretreatment to obtain a viable biosorbent. In the present study, tendu waste biomass was subjected to mild chemical treatment with phosphoric acid to obtain an efficient biosorbent for dye removal. Janus Green B, a diazine dye that does not change colour with change in pH, was used as a probe molecule to study dye adsorption. The surface modification using mild chemical treatment that is not energy intensive and less expensive then pyrolysis was used in the present study to enhance the adsorption capacity of the biomass.

MATERIALS AND METHODS

Tendu waste collection

Tendu leaf waste was collected from the dumping sites near beedi industries in the town of Solapur, India. The leaf waste was cut into 4–5 mm pieces, thoroughly washed with distilled water to remove all dirt, and then dried at 80 °C until constant weight. The dried tendu leaf refuse (TLR) was powdered and sieved with an 80-mesh sieve. The product was stored in a desiccator until used.

Pretreatment with phosphoric acid

Dried TLR powder was carbonized with 15% phosphoric acid (PA) in the weight ratio 1:3 (TLR:PA). The carbonization and activation were completed by heating for 12 h in a hot air oven. The resulting mass was washed free of acid with distilled water until a constant pH ($\sim$ 6.5) of the slurry was reached. Then carbon was dried for 4 h at 100 °C in a hot air oven. The dried material was ground and sieved to obtain different sizes. Phosphoric-acid-treated tendu leaf refuse (TLR-PA) was characterized as shown in Table 1.

Table 1 Characteristics of TLR-PA.

Characteristic	Value
Moisture (%)	5.18
Ash (%)	4.50
pH (5% solution)	6.92
Matter soluble in water (%)	0.75
Matter soluble in acid (%)	1.30
Electrical conductivity (mS/cm)	0.36
Bulk density (g/ml)	0.54
BET Surface area (m^2/g)	310
Pore volume (ml/g)	0.17
Cation exchange capacity (meq/g)	1.22
Iodine number (mg/g)	291
Methylene blue number (mg/g)	126

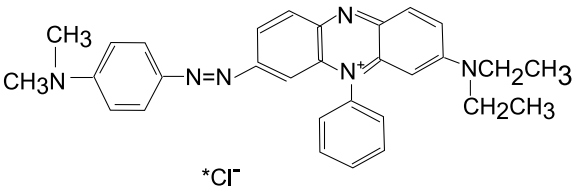

Fig. 1 Chemical structure of Janus Green B.

Chemicals and reagents

Janus Green B dye (Fig. 1) [Synonyms: 3 - diethylamino-7-(4-dimethylaminophenylazo)-5-phenylphenazinium chloride, 3 - (diethylamino) - 7 - ((p - (dimethylamino)phenyl)azo) - 5 - phenylphenazinium chloride, C.I. 11 050, Janus Green V, Diazine Green 5, Union Green B; Molecular formula: $C_{30}H_{31}N_6Cl$ C.I.=11 050, CAS No: 2869-83-2, and λ_{max} = 660 nm] was obtained from Merck. Commercial powdered activated carbon (PAC) was obtained from Merck.

An accurately weighed quantity of the dye was dissolved in distilled water to prepare a stock solution (500 mg/l). Experimental solutions of the desired concentration were obtained by successive dilutions. Calibration curves were constructed for each dilution and pH separately. The range in concentrations of dye prepared from the standard solution was 50–300 mg/l. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.5 N sulphuric acid and sodium hydroxide solutions.

Analytical methods

Physicochemical analysis of TLR and TLR-PA for ash, bulk density, iodine number, cation exchange capacity was determined using standard methods [10, 11].

The Brunauer-Emmeff-Teller surface area and pore volume was determined by nitrogen gas adsorption-desorption at 77 K with a Sorptomatic 1990 (ThermoQuest corporation, Italy). Scanning electron microscopy (SEM) analysis of biosorbents was performed with an Environmental Scanning Electron Microscope (Zeiss EVO-50). Dye concentration was determined using absorbance values at 617 nm (measured before and after treatment) using a Shimadzu UV-Vis spectrophotometer. Experiments were carried out at initial pH values ranging from 4 to 10.

Adsorption studies

Adsorption studies were performed using a batch method in which 100 ml of aqueous dye solutions of varying concentration were placed in 250 ml Erlenmeyer flasks and known amounts of TLR and TLR-PA were added to each flask. The flasks were maintained at 27 °C under constant stirring at 100 rpm. Samples were removed at different time intervals, centrifuged, and analysed for dye concentration. The uptake was calculated from the difference between the initial and final dye concentrations. Data for the adsorption isotherm were obtained by allowing the adsorbents to remain in contact with the dye solution for 24 h. The dye concentrations used were 50–300 mg/l. All experiments were carried out in triplicate with respect to each condition and mean values were used for further calculations. Experiments on the effect of temperature were carried out at the desired temperatures (15, 27, and 40 °C) to determine thermodynamic parameters.

RESULTS AND DISCUSSION

Characterization of the adsorbent

The physico-chemical characteristics of TLR-PA are summarized in Table 1. The scanning electron micrographs with 16 000 × magnification revealed the surface texture and morphology of the biosorbents. Fig. 2a shows uneven surface textures of irregular formats of TLR. It shows original pores of the tendu leaves. A representative scanning electron micrograph of TLR-PA is shown in Fig. 2b. It reveals uniform surface structure after phosphoric acid carbonization with numerous spherical pores of diameter 0.5–1.2 μm. The SEM shown in Fig. 2c is representative of TLR-PA after adsorption of the dye. Micro-crystals of dye are seen adsorbed all over the surface of TLR-PA. Increase in numbers of meso- and micro-pores during carbonization of raw TLR is evident in Fig. 2b.

Effect of pH on adsorption

The experiments carried out at different pH show that there was no significant change in the percentage removal of dye over the entire pH range of 4–12 (data not shown). Biosorption of methylene blue by water hyacinth roots was reported to be unaffected by pH in the range of 5–12 [12]. Removal of Congo Red by cattail root powder was also found to be independent of pH [13]. This indicates there is such a strong interaction between the dye and TLR-PA that neither H^+ nor OH^- ions could influence the adsorption capacity. In other

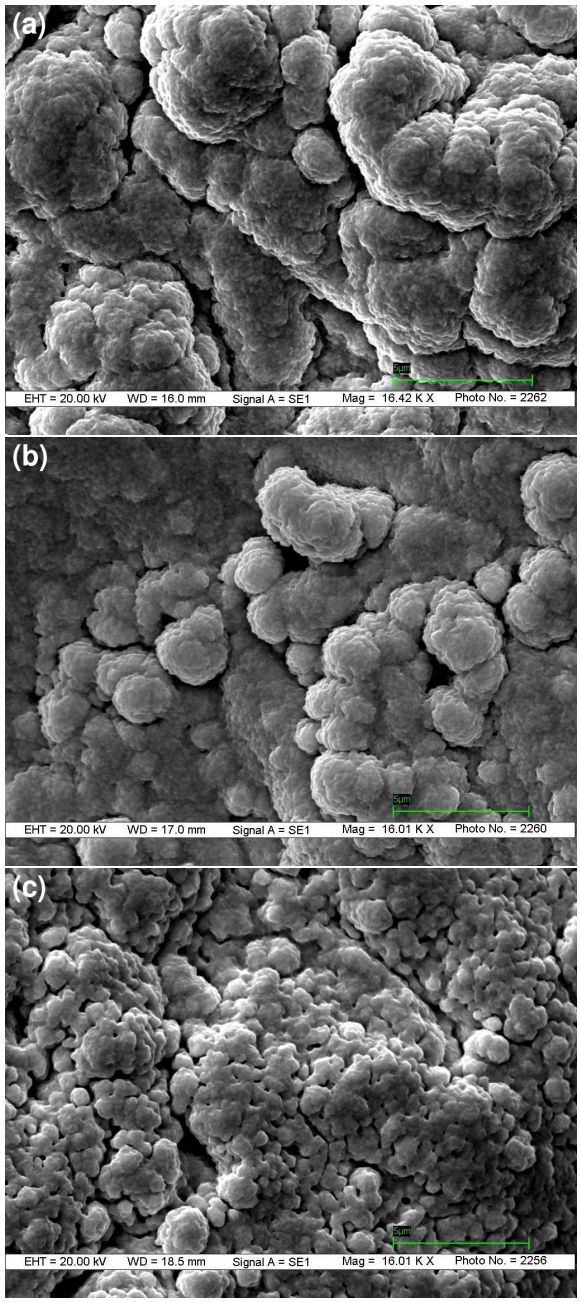

Fig. 2 SEM of (a) TLR (b) TLR-PA (c) TLR-PA after dye adsorption.

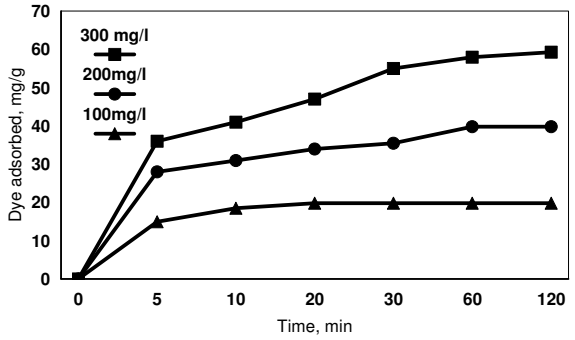

Fig. 3 Effect of initial concentration of dye and contact time on amount of dye adsorbed by TLR-PA.

words, the adsorption of Janus Green dye on TLR-PA does not involve an ion-exchange mechanism.

Effect of initial dye concentration and contact time

To study the effect of different concentrations of dyes on adsorption behaviour, three concentrations (100, 200, and 300 mg/l), were used and the amounts adsorbed were calculated (Fig. 3). Increase in adsorbent dosage increased the percentage removal of dye. This is due to the increase in absorbent surface area of the adsorbent. The dye uptake is rapid and equilibrium was established within 60 min. The course of dye uptake is in agreement with the results of other ionic dye uptake by biomass [14].

Adsorption kinetics

In order to determine the adsorption kinetics of Janus Green dye, the pseudo-first-order and pseudo-second-order kinetics models were tested. The pseudo-first-order kinetic model of Lagergren based on solid capacity is routinely used in the linearized form [15]

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - K_1\, t,$$

where q_t is the amount of adsorbed Janus Green dye onto the adsorbent at time t and K_1 is the rate constant of first-order adsorption. The intercept of the straight-line plots of $\log(q_\mathrm{e} - q_t)$ against $\log t$ should equal q_e. However, if the intercept does not equal q_e, then the reaction is not likely to be first order, irrespective of the magnitude of the correlation coefficient. The pseudo-second-order kinetic mode in its integrated linear form is [6]

$$t/q_t = 1/K_2\, q_\mathrm{e}^2 + 1/q_\mathrm{e} t.$$

If pseudo-second order kinetics is applicable, the plot of t/q_e against t should give a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of the plot. Kinetic parameters obtained after subjecting experimental data to both kinetic models are shown in Table 2. Therefore, the mechanism of adsorption of Janus Green on TLR-PA proceeds through comparatively fast pseudo-first order kinetics on external surface of TLR-PA.

Table 2 Kinetic parameters of Janus Green dye adsorption onto TLR-PA.

Pseudo-first-order model	Pseudo-second order model
$q_\mathrm{e} = 42.66$ (mg/g)	$q_\mathrm{e} = 296.7$ (mg/g)
$K_1 = 0.0424$ (min^{-1})	$K_1 = 0.02 \times 10^{-3}$ (min^{-1})
$r^2 = 0.992$	$r^2 = 0.872$

Table 3 Comparison of adsorption isotherm with commercial carbon (PAC), TLR, and TLR-PA (=T-P).

	Langmuir model				Freundlich model		
	TLR	T-P	PAC		TLR	T-P	PAC
Q (mg/g)	40.3	50.8	56.8	K (l/g)	11.0	10.7	11.2
b (l/mg)	0.318	0.216	0.222	$1/n$	0.361	0.444	0.470
R^2	0.98	0.98	0.992	R^2	0.96	0.96	0.99

Adsorption isotherm

Experimental isotherms are useful for describing adsorption capacity. The Langmuir [16] and Freundlich [17] isotherms are widely used to represent the data of sorption from solution. In order to establish the maximum sorption capacity, the Langmuir equation in following form was applied:

$$\frac{1}{q} = \frac{1}{Q} + \frac{1}{Q\, b\, C_\mathrm{e}},$$

where C_e is the concentration of the dye solution at equilibrium (mg/l), q is the amount of dye adsorbed at equilibrium (mg/g), Q is the maximum sorption capacity of the dye adsorbent system, and b is a constant related to the binding energy of the sorption system. The Freundlich equation in its lineralized form is

$$\log q = (1/n) \log C_\mathrm{e} + \log K,$$

where K and $1/n$ are constants, which are relative indicators of adsorption capacity and adsorption intensity. Values of $1/n$ between 0.1 and 1.0 indicate the favourable adsorption of dye [18]. Both Langmuir and Freundlich isotherm constants obtained experimentally for Janus Green dye on raw TLR, TLR-PA and commercial PAC are presented in Table 3.

For Janus Green dye, adsorption onto both adsorbents conforms to both the Langmuir and Freundlich

Table 4 Thermodynamic parameters for adsorption of Janus Green on TLR-PA.

Temperature (°C)	$\Delta G^{\ominus}$ (kJ/mol)	$\Delta S^{\ominus}$ (kJ/mol K)	$\Delta H^{\ominus}$ (kJ/mol)
15	−3.63	0.638	0.625
27	−3.82	0.638	
40	−4.39	0.639	

models. The Langmuir maximum adsorption capacity of TLR-PA was 51 mg/g which was similar to that of commercial PAC (57 mg/g) for adsorptive removal of Janus Green dye. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent as seen in the scanning electron micrograph (Fig. 3c).

Adsorption thermodynamics

The Gibbs free energy of adsorption $\Delta G^{\ominus}$ was calculated by using Langmuir constants at respective temperatures as described in Ref. 19. Standard enthalpy $H^{\ominus}$ and standard entropy $S^{\ominus}$ of adsorption were calculated using the Van 't Hoff equation[20]. The thermodynamic parameters obtained (Table 4) were from experimental data for TLR-PA with a dye solution (100 mg/l dye) equilibrated for 24 h.

The negative values of $\Delta G^{\ominus}$ at different temperatures indicate the feasibility of the process and the spontaneous nature of the adsorption. The positive $\Delta H^{\ominus}$ reveals the adsorption is endothermic and physical in nature. Furthermore, slightly positive $\Delta S^{\ominus}$ of Janus Green adsorption process indicates an irregular increase of the randomness at the TLR-PA-solution interface during adsorption.

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