

## BIOSORPTION OF CONGO RED BY HYDROGEN PEROXIDE TREATED TENDU WASTE

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### ABSTRACT

Solid wastes from agro-industrial operations can be recycled as non-conventional adsorbents if they are inert and harmless and reduce the cost of wastewater treatment. Tendu leaf *Diospyros melanoxylon* is the second largest forest product in India after timber and is exclusively used in making local cigarette called *Bidi*. Waste leaf cutting remaining after making cigarette was used in present study as a biosorbent for the removal of Congo red dye from aqueous solution. It was treated with hydrogen peroxide to obtain biosorbent with increased adsorption capacity. Batch type experiments were conducted to study the influence of different parameters such as pH, initial dye concentration and dosage of adsorbent on biosorption evaluated. The adsorption occurred very fast initially and attains equilibrium within 60 min at pH= 6.2 and the equilibrium attained faster after hydrogen peroxide modification. Kinetic studies showed that the biosorption of Congo red on tendu waste followed pseudo-second-order rate equation. The data fitted well to Langmuir and Freundlich isotherm models. Comparison was done on the extent of biosorption between untreated and treated forms of the tendu waste. The maximum adsorption capacity for untreated tendu waste was found to be 46.95 mg/g, which was enhanced by 2.8 times after hydrogen peroxide treatment and was found to be 134.4 mg/g. The adsorption process was in conformity with Freundlich and Langmuir isotherms for Congo red adsorption from aqueous solution. The study demonstrated use of milder chemical treatment of tendu waste to obtain a biosorbent with enhanced dye removal capacity.

**Keywords:** Tendu waste, *Diospyros melanoxylon*, Congo red, Biosorption, Chemical modification

### INTRODUCTION

During the past four decades, production of dyes and pigments has been on increase to cater to the needs of not only the textile industries but also of other industries such as paper, plastics, paints, leather, rubber, food, drug and cosmetics. These industries are major consumers of water and therefore cause water pollution. The colored effluents of these industries are harmful to the aquatic life in rivers and lakes due to reduced light penetration and the presence of highly toxic metal complex dyes. Most of the dyes used are stable to photo-degradation, biodegradation and oxidizing agents due to their complex molecular nature (Ramakrishna and Viraraghavan, 1997). It is desirable to remove dyes from colored effluents

for safe discharge in receiving water bodies.

The conventional processes for the color removal from wastewater include biological treatment, coagulation, flocculation, adsorption, oxidation and hyper-filtration that require high capital investment and running cost (Anjaneyulu, 2005). Color removal by adsorption using commercial activated carbon has found widespread use in the treatment of industrial wastewater. However, high cost of commercial activated carbon and its load on non-renewable resources are not affordable for developing countries. Therefore, there is a need to produce activated carbon from cheaper and readily available materials from renewable sources. Crini (2006) recently reviewed use of such non-conventional and low-cost adsorbents for dye removal.

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The search for cost-effective and efficient alternative for commercial carbon has focused on different biosorbents prepared from various types of naturally abundant biomass. Biosorption is a property of inactive and dead biomass to bind different pollutants by passive binding to nonliving microorganisms (bacteria, fungi and algae) and other biomass (such as peat, hull, fruit peel, leave and bark of tree etc.) from even very dilute aqueous solutions (Ma and Tobin, 2003). The process of biosorption is opposite to bioaccumulation by living cells that are metabolically driven. Chemical architecture of cell wall of dead cells is responsible for biosorption. A number of different binding mechanisms to be active in biosorption such as ion exchange, complexation, coordination, chelation, physical adsorption and micro-precipitation have been postulated (Volesky, 2003). Biosorption has many advantages including low cost, the selective removal of pollutants, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and no sludge generation.

Various agricultural products and lingo-cellulosic by-products in literature were investigated for dye removal from aqueous solutions. The recent studies includes dye adsorption onto jute stick (Panda *et al.*, 2009), rice bran (Hashemian *et al.*, 2008), palm kernel fibre (Ofomaja, 2007), peanut hull (Renmin *et al.*, 2005), tree fern (Ho *et al.*, 2005), neem leaf powder (Bhattacharyya and Sharma, 2005) and orange peel (Namasivayam *et al.*, 1996) have been reported. Majority of agricultural wastes and by-products discarded arbitrarily as soil amendment, landfill or burned resulting in resource loss and environmental pollution. Biosorption capacity of such crude biomass is usually low. When chemically modified, these materials presented with enhanced biosorption capacities (Gong *et al.*, 2008). Moreover, cellulosic wastes that are available in bulk and round the year are of interest for search of effective and selective adsorbent. In India, *bidi* rolling industry produces cuttings of tendu (*Diospyros melanoxylon*) leaf as waste, which has no economic value and creates solid waste disposal problem. Therefore, there was a need to valorize this zero-cost tendu waste, available in large quantities round the year through out

India. Several oxidizing agents, including ozone, hydrogen peroxide, hypochlorite, chlorine, chlorine dioxide, and peracetic acid have been used for the chemical treatment of biomass (Chapman, 2003). The goal of this work is to study the adsorption of Congo red (CR) from aqueous solution by tendu biomass after chemical treatment with hydrogen peroxide.

## MATERIALS AND METHODS

### *Preparation of biosorbent*

The waste cuttings of tendu leaf used for making *bidi* (Indian cigarette) 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) was powdered to 0.2 to 0.3 mm mesh size and stored in desiccator until used.

### *Treatment with hydrogen peroxide*

One gram of dried tendu leaf refuse (TLR) was reacted with 250 mL of 1M hydrogen peroxide at room temperature until complete degradation of hydrogen peroxide (where there was no further gas evolution). The sample was washed with distilled water to neutral pH, filtered and dried at 110 °C until constant weight. The material was pulverized and sieved through 80-mesh particle size, stored in the desiccator and used for the study as TLR-H<sub>2</sub>O<sub>2</sub>.

### *Congo red*

Congo red (CR) (CI=22120; chemical formula:  $[\text{C}_{10}\text{H}_5(\text{NH}_2)(\text{SO}_3\text{Na})\text{N}:\text{NC}_6\text{H}_4]_2$ ; FW: 696.7; nature: anionic direct disazo and  $\lambda_{\text{max}}$ : 500 nm) was supplied by Merck, India.

### *Biosorption experiments*

In all batch biosorption experiments, solution volume was 100 mL and the mixture of solution and biosorbent was agitated in 250 rpm. The experiments were conducted at  $27 \pm 1$  °C in a thermostatically controlled water bath. Initial pH of the solutions was adjusted to desired values. The reaction mixture pH was not regulated after the initiation of experiments and final pH

was measured. The samples were withdrawn at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 5,000 rpm for 20 min. All the biosorption experiments were conducted in duplicate and average values used in data analysis. Replicate experiments showed a maximum deviation of 2.5 % in dye uptake measurements.

#### *Effect of pH on biosorption*

The effect of pH on equilibrium capacities of CR biosorption was studied with initial CR concentration of 250 mg/L. Initial pH of solutions was varied from 2 to 10. After pH adjustment to desired pH with 0.1 M HCl or NaOH solutions, 500 mg of adsorbent biomass was added to experiment vessels.

#### *Dye analysis*

The concentration of CR dye was determined by the peak height of UV-Vis spectra at 500 nm using Shimadzu UV-visible double beam spectrophotometer. A linear calibration curve was obtained for concentrations below 100 mg/L of Congo red. The dye uptake was computed from the difference between the initial and final dye concentrations.

#### *Kinetic modeling*

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) have been widely used. It was observed that most of the biosorption systems followed a pseudo-second order kinetic model, 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). Kinetic experiments presented that maximum time required to reach equilibrium was 1 h; therefore, the equilibrium time of 2 hr was chosen for equilibrium experiments.

#### *Isotherm modeling*

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 adsorbent, and for preliminary determination of adsorbent 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 adsorption 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.

$$1/q_e = 1/k_L + 1/bk_L * 1/C_e \quad (2)$$

Where  $C_e$  is the concentration of CR at equilibrium (mg/L),  $q_e$  is the amount of CR 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. Linearized form of Freundlich equation was applied to the sorption equilibria at different adsorbent doses.

$$\log q_e = (1/n) \log C_e + \log k_F \quad (3)$$

Where,  $k_F$  and  $1/n$  are constants, which are considered indicators of adsorption capacity and adsorption intensity. Biosorption isotherm experiments were conducted using different adsorbent dosages (50–1000 mg/L) of TLR, TLR-H<sub>2</sub>O<sub>2</sub> and 100 mL of 50, 75 and 100 mg/L dye solutions at equilibrium time of three hours.

## **RESULTS**

Effect of pH on the removal of Congo red by TLR and TLR-H<sub>2</sub>O<sub>2</sub> is shown in Fig. 1. For 20 mg/L dye concentration, the percent removal increased from 62 to 73, when pH was increased from 2 to 5 and thereafter the percent removal remained almost the same up to pH=10. The adsorption pattern was similar for both TLR and TLR-H<sub>2</sub>O<sub>2</sub>. pH of 6.2 was selected for all further studies

as both TLR and TLR-H2O2 shown identical adsorption. The adsorption of CR dye increased with increasing contact time and became almost constant after 60 min for TLR and after 30 min for TLR-H2O2 as showed in Fig. 2. Sorption process became fast after chemical treatment with hydrogen peroxide.

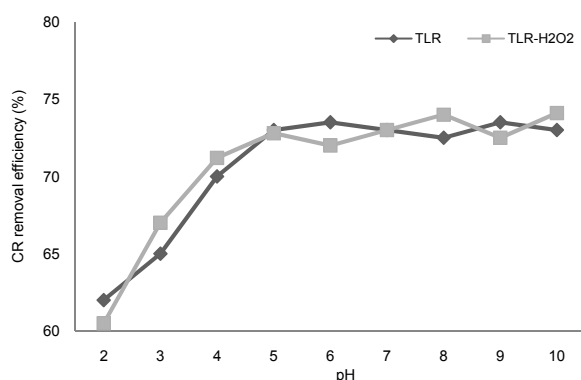


Fig. 1: Effect of pH on the removal of CR dye by TLR and TLR-H2O2 (adsorbent dosage = 2g/L; dye concentration = 20 mg/L)

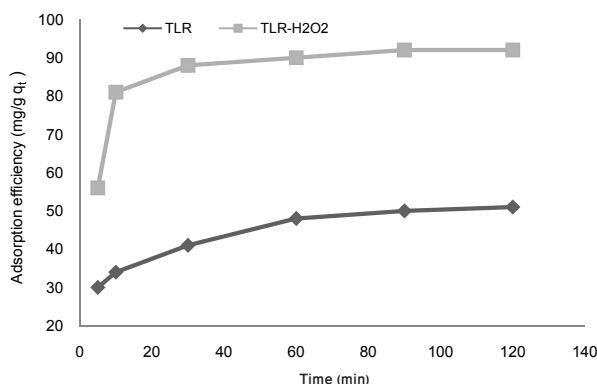


Fig. 2: Effect of contact time on the removal of CR dye by TLR and TLR-H2O2 (adsorbent dosage = 5 g/L; dye concentration = 75 mg/L)

Adsorption of CR dye by TLR and TLR-H2O2 followed pseudo-second order kinetics, with extremely high correlation coefficients ( $R^2 > 0.999$ ) as shown in Fig. 3. The adsorption capacity and affinity of TLR and TLR-H2O2 for CR was determined with two isotherm models, using initial CR concentration of 75 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 ( $R^2$ ) values obtained from the Freundlich and Langmuir isotherms indicate that the adsorption

pattern for CR on TLR and TLR-H2O2 obeyed both Freundlich and Langmuir models.

## DISCUSSION

Biosorption is becoming a promising alternative to replace or supplement the present dye removal processes from dye wastewater. In this study, removal of an anionic disazo direct dye, Congo red, from an aqueous solution by biosorption on tendu waste was investigated. During batch experiments, as the pH of the system increases, the number of negatively charged sites on adsorbent increases and the number of positively charged sites decreases. The adsorption remaining constant over a wide range of pH 5 to 10 is suggestive of chemisorption as more favored mechanism over electrostatic mechanism of adsorption (Namasivayam and Kavitha, 2002). The optimum initial pH for CR dye biosorption in this study was 6.5; similar initial pH was reported for removal of Congo red by fungal biomass (Fu and Viraraghavan, 2002).

The rate of sorption of Congo red on TLR and TLR-H2O2 are shown in Fig. 3. It was observed that the treatment of tendu waste with hydrogen peroxide resulted in reducing the equilibrium time from 60 to 30 minutes. Adsorption was fast on the first 60 minutes; then the rate started to slow down in later stages because initially a large number of vacant surface sites may be difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phase (Ghani *et al.*, 2007). 1g/100 mL was found the optimum adsorbent dose in the experiment. Adsorption followed second order rate kinetics.

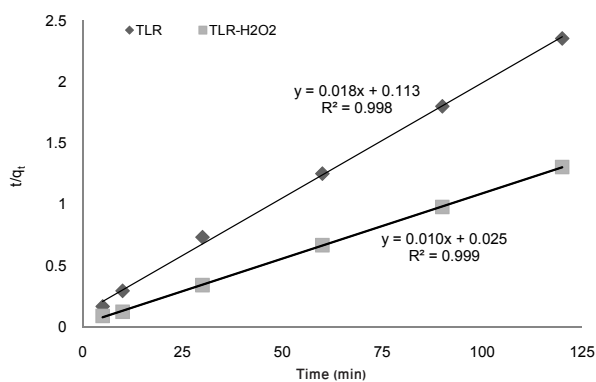


Fig 3: Pseudo-second order kinetics of CR adsorption by TLR and TLR-H2O2



The adsorption data (Table 1) obeyed both Freundlich and Langmuir models exhibiting heterogeneous surface conditions and monolayer adsorption (Lee *et al.*, 1999). The monolayer adsorption capacity of raw biomass (TLR) has been calculated to be 46.96 mg/g for Congo red. Similar values reported for Congo red adsorption by some lingo-cellulosic biomass in native state

are; 35.7 mg/g for jute stick powder (Panda *et al.*, 2009); 34.26 mg/g for sunflower stalk biomass (Shi *et al.*, 1999) and 22.44 mg/g for orange peel powder (Namasivayam *et al.*, 1996). Thus, the tendu waste in its native form showed remarkable adsorption ( $q_{\max}$ ) of Congo red among reported values obtained for various lingo-cellulosic wastes in the literature.

Table 1: Adsorption isotherm parameters for Congo red

Adsorbent	Langmuir parameters			Freundlich parameters		
	KL (mg/g)	Qmax (mg/g)	R-square	Kf	1/n	R-square
TLR	0.005	46.95	0.972	2.193	0.837	0.93
TLR-H2O2	0.002	134.4	0.934	3.192	0.709	0.952

Hydrogen peroxide used for pretreatment of tendu biomass as an oxidizing agent, can produce oxidative delignification and increases the positive valance state of a molecule by removal of one or more electrons from an atom or ion from the adsorbent surface (Chapman, 2003). Comparison of the  $q_{\max}$  values of TLR and TLR-H2O2 (Table 1) shows that there is over 2.8 times enhancement in the adsorption capacity after hydrogen peroxide modification of raw tendu waste. She *et al* (1999) obtained 4.5 times increase in Congo red dye adsorption capacity when sunflower stalk biomass was chemically grafted quaternary ammonium groups. Enhanced Congo red adsorption capacity of 54 mg/g and 154 mg/g for phosphoric acid treated rice straw and water hyacinth biomass respectively after pyrolysis (Rashwan and Girgis, 2004) have been found. The result obtained during present study encourages preferring mild chemical modifications of lingo-cellulosic biomass, to energy intensive methods like pyrolysis to obtain increased biosorption. Tendu waste, which originates from renewable sources available in bulk around the year, makes it attractive and competitive biosorbent for dye removal.

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