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Dolichos lablab Peel Powder: A Novel and Economical Adsorbent for Removal of Aniline Blue from Aqueous Solution

N. PANDIARAJ[1] and K. ANANTHAKUMAR[2,*]

[1]Post Graduate Studies & Research Department of Chemistry, Raja Doraisingam Government Arts College, Sivagangai-630 561, India
[2]Department of Chemistry, Kamarajar Government Arts College, Surandai -627 859, India

*Corresponding author: E-mail: rakeshraahul@gmail.com

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The current study focused on the removal of aniline blue from aqueous solution using *Dolichos lablab* peel powder. The effect of initial concentration, contact time, dose of adsorbent, temperature and pH on the removal of aniline blue by adsorption on *Dolichos lablab* peel powder has been studied. The percentage removal of dye on adsorbent was found to be decrease with increase in initial concentration of dye. The percentage removal of dye increases with increase in contact time, while the exponentially increases with increase in dose of adsorbent. This was due to the availability of active sites. The percentage removal of dye increases with increase in temperature. By using this data the thermodynamic parameters such as ΔH°, ΔG° and ΔS° were calculated. The negative value of ΔG° shows the adsorption is favourable and spontaneous. The high positive values of ΔH° confirm the endothermic nature of adsorption process. Langmuir and Freundlich adsorption models were tested.

Keywords: ***Dolichos lablab*** **peel powder, Aniline blue, Thermodynamic parameters, Adsorption models.**

INTRODUCTION

In textile industries, treatment of effluents is one of the most important economic problems. Due to high toxicity of dyes it is harmful to some organisms and it disturbs the ecosystem Dyes are highly toxic to some organisms and hence it affect the ecosystem. Some of the conventional waste treatment methods such as flocculation, electro flotation, precipitation, solvent extraction, photo degradation and reverse osmosis are used for the removal of dyes [1-5] from the adsorbent. But these methods are unsuccessful some time for the removal of dyes due to high operational cost and sludge disposal problems *etc.*, [6,7]. When compared to this, adsorption technique is most efficient and economic process to remove dyes and pigments from the adsorbent and also it controls the biochemical oxygen demand.

Generally conversion of adsorption of dyes and pigments into granulated activated carbon or powdered activated carbon is a common method but the technology used for producing a good quality activated carbon requires high cost and the disposal of used activated carbon is a tedious one. Hence it is necessary to use biological material as a adsorbent especially a waste from agriculture and other is promoted because it is a cost effective one and easier to dispose. The various bio sorbents are sunflower stalks [8], seaweeds [9], orange peel [10], palm kernel seed coat [11] and guava leaf powder [12] were used for removal of heavy metals and dyes.

Aniline blue which is dark blue in colour and is an organic dye used in wide variety industrial applications because it is water soluble and it causes harmful effect to humans like eye burn, causes irritation in skin and some effect in respiratory track. It is used for dying cotton, silk paper, bamboo, weed, leather, *etc.* The molecular formula for aniline blue is $C_{32}H_{25}N_3O_9S_3Na_2$. It is also phototoxic and photo allergic. The molecular weight of aniline blue is 737.7 g/mol; λ_{max} = 586 nm. The structure of aniline blue dye was given in Fig. 1. The dye was supplied by S.D. Fine Chemicals, Mumbai, India.

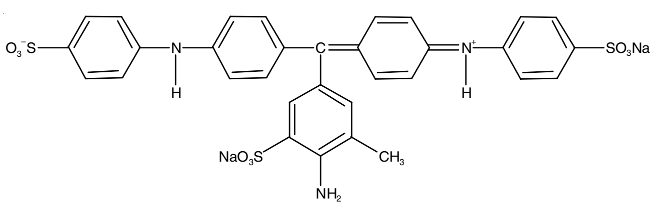


Fig. 1. Structure of Aniline blue dye

EXPERIMENTAL

Preparation of biosorbent: The *Dolichos lablab* peels were collected from kitchen waste and it is washed continuously with distilled water to remove dust and other insoluble impurities present in it. *Dolichos lablab* peel were cut into smaller size and then it is dried in sunshade and then in air oven at 333 K for several hours till it becomes crisp. Then the *Dolichos lablab* peel crisp was crushed by using an crusher or grinder to obtain it in a powder form. The powder was collected in accurate size by using a 200 mesh sieve and it was preserved using a clean air tight glass bottle.

Preparation of dye solution: Accurately 1000 mg of the aniline blue dye was separately weighed and made up to 1000 mL in a standard measuring flask to get a dye solution of 1000 ppm. These were kept as the stock solutions. Whenever needed, the dye solutions for the kinetic experiments were suitably diluted from the diluted stock solutions of dye containing 500 ppm using double distilled water.

General procedure for adsorption studies: The stock solution (500 ppm) was diluted with distilled water to get the required initial concentration of [aniline blue]. Next 50 mL of the dye solution was taken in each 250 mL leak proof corning reagent bottles. Then required amount of adsorbent (0.1 g) of fixed particle size was be weighed and then transferred into each bottles. The bottles were placed in a mechanical shaker and shaken vigorously for a period of contact time *i.e.*, 15 min and then taken out. After shaking for a certain period, the flask was kept separately for the adsorbent to settle out and the sample taken out from the flask was filtered through Whatman No. 41 filter paper. After filtration the filtrates were collected in clean dry conical flasks. The optical density of each solution be measured using systronic spectrophotometer (model no: 106) at 586 nm (wave length of maximum absorption for this particular dye). By using the spectrometer the optical density of dye solution before and after adsorption is obtained. A plot of optical density *versus* concentration results a straight line for this particular dye. The corresponding relative concentration can be obtained from the standard curve. Generally in all adsorption type experiments, the extent of adsorption of dye is calculated in terms of the percentage adsorption of dye and amount adsorbent (mg g^{-1}) using the following requirements.

$$\text{Adsorption } (\%) = \frac{(C_i - C_e)}{C_i} \times 100$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_e)}{m}$$

where C_i and C_e are the initial and final equilibrium concentration (mg L^{-1}) of dye, respectively and m is the mass of adsorbent, *Dolichos lablab* peel powder (g L^{-1}).

RESULTS AND DISCUSSION

The present work deals with the removal of aniline blue by adsorption technique using low cost adsorbent like *Dolichos lablab* peel powder.

Effect of initial concentration of dye: The concentration of dye was varied from 10 to 50 ppm for the same amount of adsorbent dosage 2 g/L and 15 min contact time. The graph is plotted between initial concentration *versus* percentage removal (Fig. 2). The result showed that the percentage removal increases with decrease in initial concentration of dye and this was due to the saturation of the adsorption sites on the surface of the adsorbent [13]. The higher uptake of aniline blue dye at low concentration may be attributed to the availability of more active centers on the surface of the adsorbent for lesser number of adsorbate species. Aniline blue adsorption curves are single, smooth and continuous suggesting the possible monolayer coverage of dye molecules on the surface of the adsorbent.

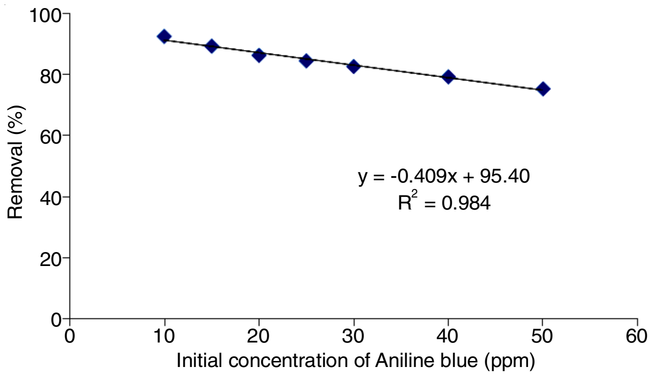


Fig. 2. Effect of initial concentration of dye on the removal of aniline blue by *Dolichos lablab* peel powder

Effect of adsorbent dose: The effect of varying the adsorbent dose for a constant dye concentration (10 and 20 ppm) is shown in Fig. 3. It was observed that increasing the adsorbent dose, increased the percentage of dye removal from aqueous solution. It is apparent that by increasing the dose of the adsorbent, the number of sorption sites available for sorbent – dye ion interaction is increased, thereby resulting in the increased percentage removal from solution [14].

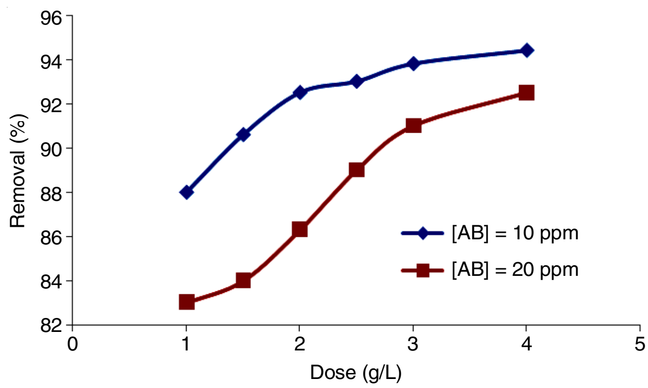


Fig. 3. Effect of adsorbent dosage on the removal of aniline blue by *Dolichos lablab* peel powder

Effect of agitation time: The uptake of aniline blue from water by *Dolichos lablab* peel powder increases when the agitation time was varied from 5 to 60 min and attains equilibrium in 60 min at 30 °C. The increase in percentage adsorption of aniline blue with increase in agitation time may be attributed to the increased intra particle diffusion occurring at long shaking time [15]. The data obtained are graphically represented in Fig. 4.

Effect of pH: The effect of pH for the removal of dye was carried out at different pH values such as 2, 4, 5, 6, 7, 8 and 10. The pH *versus* percentage removal was plotted (Fig. 5). The result indicated that at low pH the percentage removal of

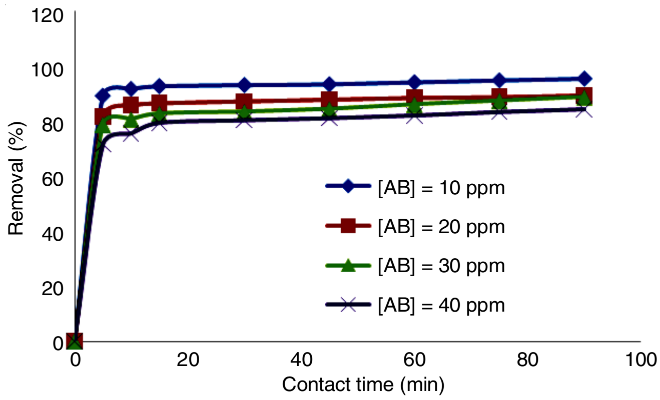


Fig. 4. Effect of contact time on the removal of aniline blue by *Dolichos lablab* peel powder

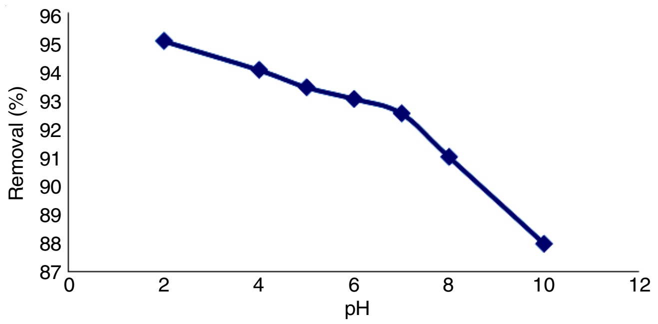


Fig. 5. Effect of pH on the removal of aniline blue by *Dolichos lablab* peel powder

dye was high and at high pH the removal of dye was low. In acedic medium, the number of H^+ ions would be large and they are likely to neutralize some of the anionic functional groups present on the surface of *Dolichos lablab* peel powder [13].

Effect of temperature: The effect of temperature on the removal of aniline blue indicates that the percentage removal of dye increases with increase in temperature (Fig. 6). The adsorption process is endothermic in nature [16].

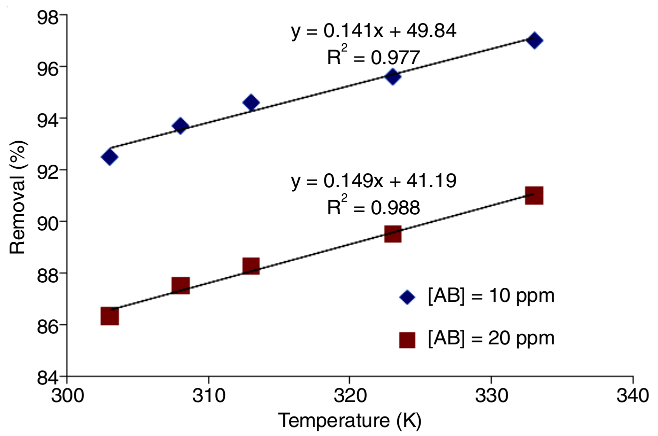


Fig. 6. Effect of temperature on the removal of aniline blue by *Dolichos lablab* peel powder

Thermodynamic parameters are calculated from the variations of the thermodynamic distribution co-efficient (K_c) with change in temperature. The value of K_c for the aniline blue adsorption is determined by plotting log K_c *vs.* 1/T and extrapolating to zero. The standard free energy change (ΔG°) for the interaction of the *Dolichos lablab* peel powder with aniline blue has been calculated using ΔG° = - RT ln K_c. From the variation of log K_c with inverse of temperature (Fig. 7) the standard enthalpy (ΔH°) and entropy change (ΔS°) were computed using the equation ln K_c = ΔS°/R – ΔH°/RT.

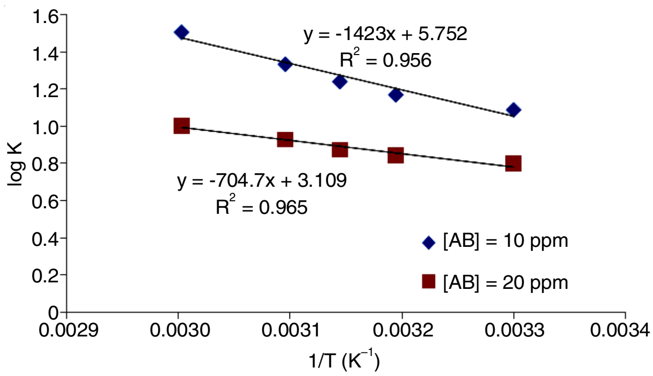


Fig. 7. Vant Hoff plot for removal of aniline blue by *Dolichos lablab* peel powder

The negative value of ΔG° indicates the adsorption is favourable and spontaneous. The high positive values of ΔH° confirm the endothermic nature of adsorption process. The positive values of ΔS° indicate the increased disorder and randomness at the solid solution interface of Aniline blue with the adsorbent. The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface.

Modeling of adsorption: The modeling of adsorption has been of importance and significance in the water and waste water treatment by the adsorption technique as they provide an approximate estimation of the adsorption capacities of the adsorbent for aniline blue. The data obtained for the adsorption of aniline blue on *Dolichos lablab* peel powder at optimum experimental conditions are modeled with Freundlich isotherm, log x/m = log k + 1/n log C_e and Langmuir isotherm C_e/q_e = C_e/Q_o + $1/Q_0b$. When the pertaining parameters for each isotherm were plotted, linear plots were observed (Figs. 8 and 9). The linearity indicates the applicability of the two isotherms for the adsorption of aniline blue on the *Dolichos lablab* peel powder.

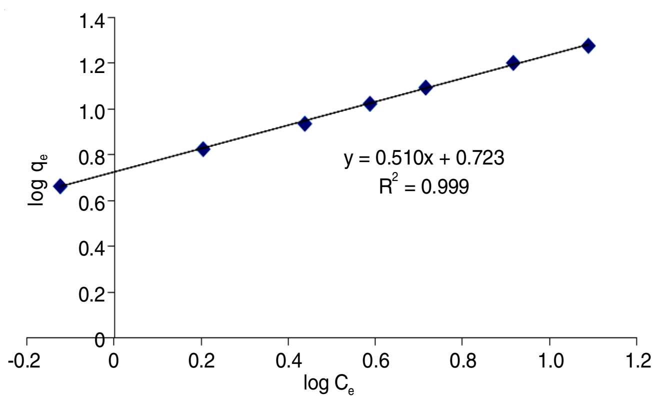


Fig. 8. Freundlich adsorption isotherm for removal of aniline blue by *Dolichos lablab* peel powder

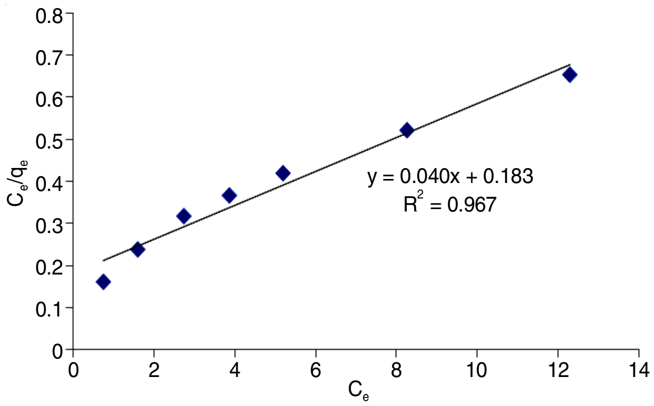


Fig. 9. Langmuir adsorption isotherm for removal of aniline blue by *Dolichos lablab* peel powder

The correlation coefficients of each isotherm were calculated for the adsorption of aniline blue (Freundlich r = 0. 990; Langmuir, r = 0.967). The curve fitting indicated that the Langmuir equation well explained the observed data. Various useful parameters like adsorption capacities of the *Dolichos lablab* peel powder, separation factor, *etc.,* obtained from various models are collected in Table-1. Value of R_L, separation factor obtained for the adsorption of aniline blue is found to be 0.172 indicating a favourable adsorption [17].

TABLE-1
VARIOUS PARAMETERS OBTAINED FROM ADSORPTION ISOTHERM MODELS

Langmuir				Freundlich		
Q_o	B	R_L	R	K	1/n	r
24.865	0.220	0.172	0.998	5.296	0.510	0.999

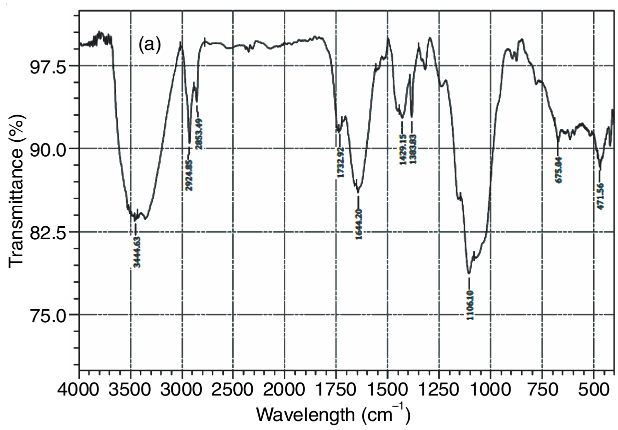
Characterization of *Dolichos lablab* peel powder

FTIR analysis: The FTIR spectra of *Dolichos lablab* peel powder (Fig. 10) revealed that there were various functional groups detected on the surface of *Dolichos lablab* peel powder sample before and after adsorption. There were some peaks that were shifted, disappeared and new peaks were also detected which indicates that no chemical bond is formed between adsorbent and adsorbate molecules after adsorption. Three significant bands decrease of the functional groups on the adsorbent were detected. These three significant bands in the spectrum indicated the possible involvement of that functional group on the surface of *Dolichos lablab* peel powder in aniline blue adsorption process.

SEM: Figs. 11a and 11b show the SEM micrographs of *Dolichos lablab* peel powder before and after dye adsorption. SEM images show that *Dolichos lablab* peel powder possesses a rough surface morphology with some pores. The surface morphology of aniline blue loaded adsorbent shows that the surface of fly ash is covered with dye molecules.

Conclusion

From this study, the *Dolichos lablab* peel powder could be effectively employed as an adsorbent for the removal of aniline blue from aqueous solution. The percentage removal of dye on adsorbent was found to decrease with increase in initial concentration of dye. The percentage removal of dye



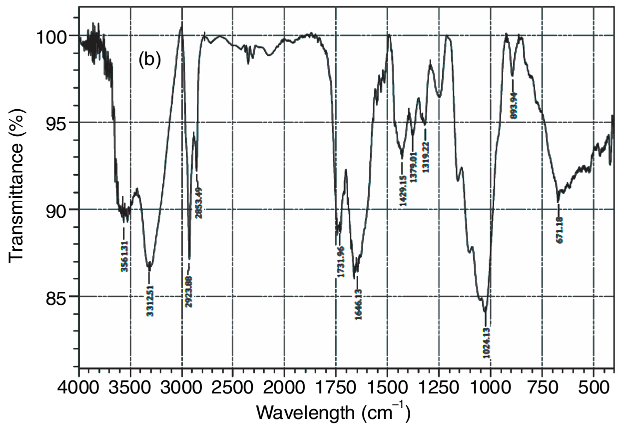


Fig. 10. FTIR spectra of (a) *Dolichos lablab* peel powder (b) aniline blue adsorbed *Dolichos lablab* peel powder

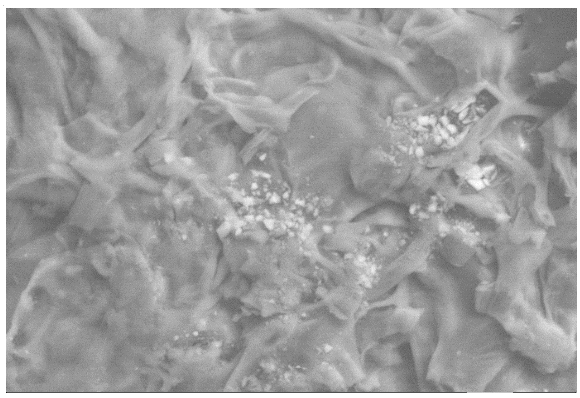


Fig. 11a. SEM image for *Dolichos lablab* peel powder before aniline blue adsorption

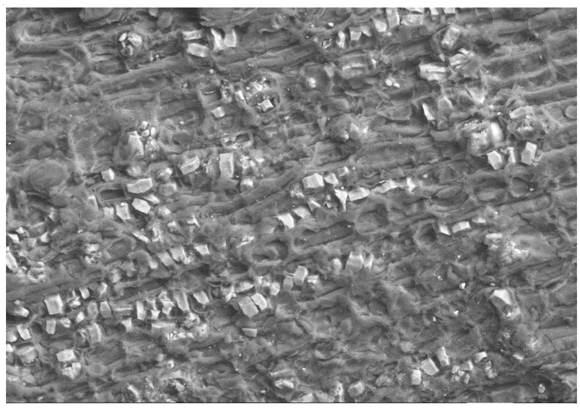


Fig. 11b. SEM image for *Dolichos lablab* peel powder after Aniline blue adsorption

was found to increase with increase in contact time. The percentage removal of dye exponentially increases with increase in dose of adsorbent. This was due to the availability of active sites. The percentage removal of dye was found to decrease with increase in temperature. From this data the thermodynamic parameters such as ΔH°, ΔG° and ΔS° were calculated. Langmuir and Freundlich adsorption models were tested.

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