



Adsorption Studies onto Grey BL dye using the leaves of *Trachyspermum ammi* (Ajwain Leaves)

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Abstract : Main objective of the study is to prepare bio mass adsorbent from Ajwain plants (*Trachyspermum ammi*.L) to remove Grey BL dye from aqueous solution by adsorption. To understand the adsorption behaviour of ajwain leaves powder as biomass, studies like effect of biomass, effect of pH, contact time and adsorption isotherms were done effectively by suitable method. The Freundlich isotherm exhibited a better fit for the adsorption data than the Langmuir and Temkin models with maximum multilayer adsorption. The result in this study indicates that ajwain leaves powder is an attractive candidate for removing dyes from waste water.

Keywords : Grey BL dye, *Trachyspermum ammi*.L, biomass, Isotherm, sorption.

1 .Introduction

Colour is an important aspect of human world. We like to wear clothes of all kinds of colours and hues, eat food decorated with colours, even our medicines are colorful¹. Textile industry produces high levels of dye and floating solid materials². It is estimated that 5000 tons of dyeing materials are discharged into the environment every year³. Effects of dye bearing waste water are aesthetic pollution of environment and also carcinogenicity due to their degradation products. Coloured wastes may contain chemicals which exhibit toxic effects towards microbial populations and can be toxic and/or carcinogenic to mammals. In general, dyes are poorly biodegradable⁴. Many techniques like electrochemical coagulation, reverse osmosis, nano filtration, adsorption using activated materials etc., are used for the removal of dye from waste water⁵. Adsorption has been found to be an efficient and economic process for the treatment of dyeing industry effluent. Activated

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carbon is the most popular and widely used dye sorbent but there are certain problems with its use. It is expensive and the higher the quality the greater the cost⁶. Therefore, there is a growing interest in using low cost, easily available biomaterials for the adsorption of dye colours.

Table 1. Effect of sorbent dose on adsorption of Grey BL by TALP

Dosage of sample (g)	Absorbance	% of dye removal
0.1	0.380	79.04
0.3	0.336	81.46
0.5	0.315	82.62
0.7	0.269	85.16
0.9	0.268	85.21
1.1	0.258	85.21
1.3	0.255	85.76
1.5	0.244	85.93
1.7	0.243	86.54
1.9	0.238	86.59

Table 3. Effect of initial pH on adsorption of Grey BL by TALP

pH	Absorbance	% of dye removal
2	0.574	68.33
3	0.419	76.88
4	0.243	86.59
5	0.227	87.47
6	0.211	88.36
7	0.205	88.69
8	0.200	88.96

Table 2. Effect of equilibration period on adsorption of Grey BL by TALP

Time in (min)	Absorbance	% of dye removal
10	0.299	83.50
20	0.283	84.39
30	0.265	85.38
60	0.248	86.32
90	0.245	86.48
120	0.222	87.75
150	0.218	87.97
180	0.218	87.97
210	0.217	88.03
240	0.205	88.69

During last decade, a number of non-conventional, low cost adsorbent such as rice hull ash, sugarcane bagasse, sawdust, pine needle, eucalyptus bark, prawn shell activated carbon, and mango seed kernel powder have been used for the removal of dyes⁷. In this paper, the feasibility of *Trachyspermum ammi*.L leaves powder (TALP) as sorbent has been studied. *Trachyspermum ammi*.L is native of Egypt and is cultivated in Iraq, Iran, Afghanistan, Pakistan, and India. In India, it is cultivated in Madhya Pradesh, Uttar Pradesh, Gujarat, Rajasthan, Maharashtra, Bihar and West Bengal⁸. Grayish brown seeds or fruits of ajwain are considered for medical and nutritional purposes⁹. Leaves pinnate, with a terminal and 7 pairs of lateral leaflets¹⁰. A number of chemical constituents have been reported for the herb. Fiber (11.9%), carbohydrates (24.6%), tannins,

glycosides, moisture (8.9%), protein (17.1%), fat (21.1%), saponins, flavones and other components (7.1%) involving calcium, phosphorous, iron, cobalt, copper, iodine, manganese, thiamine, riboflavin and nicotinic acid are of reported phytochemical constituents of ajwain¹¹⁻¹².

The adsorbate selected was Grey BL ($\lambda_{\text{max}} = 575 \text{ nm}$). These dyes are largely used in textile, rubber, paper and leather industries¹³. Ajwain biomass being low cost adsorbent used without activation to remove pollution causing Grey BL dye from aqueous solution. Disposal of harmful dyes through proper treatment might have a positive result from the view of producing sustainable development.

2. Experimental

Trachyspermum ammi leaves were collected from local fields. It was then dried under sunlight for 5 days and ground to 400 micron for effective adsorption. The TALP (*Trachyspermum ammi* leaves powder) was washed with tap water few times and double distilled water several times to make TALP impurity free. The washed TALP then again dried under sunlight for 2 days, weighed and was stored in an airtight bottles for further use.

2.1 Preparation of stock solution

The dye Grey BL, in commercial purity, was used without purification. An accurately weighed 1 gm of dye was dissolved in 1000 ml of distilled water to prepare stock solution. Experimental solution was obtained by dilutions of stock solution in accurate proportions to different initial concentrations.

2.2 Batch experiment

Batch experiments were conducted for maximum biosorption of dye ions through sorption dose, equilibration period, pH and adsorption isotherm. Experiments were carried out in a rotary shaker at 150 rpm and 27° C using 250 mL shaking flasks containing 100 mL of dye solutions. The initial pH values of the solutions were adjusted with 0.1 M HCl or NaOH using pH meter. Different doses or same doses of biomass depending on the study were added to each flask. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by filtration then centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring adsorbance at maximum wavelengths of dye with a UV-Vis spectrophotometer (UV 2450, Shimadzu corporation, Japan).

3. Results And Discussion

3.1. Effect of sorbent dose

The effects of sorbent dose on the removal ratios of dyes are shown Figure 1. The percentages of dyes sorbed increased as the sorbent dose was increased over the range 0.1-1.9 g/L. The adsorption ratios of dyes increased from 79.04 to 86.59%, Grey BL dye. Above 1.9 g/L of sorbent dose, the adsorption equilibrium of dye was reached and the removal ratios of dye held almost no variety. So, the ajwain leaves biomass of 1.0 g/L was chosen for subsequent experiments.

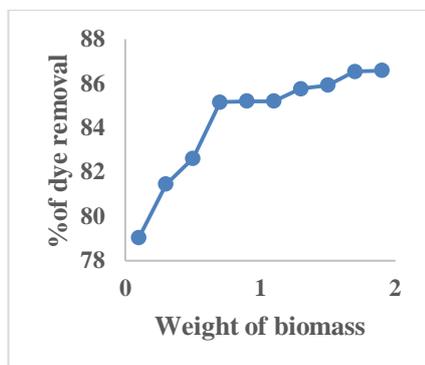


Figure 1. Effect of sorbent dose on adsorption of Grey BL by TALP (dye concentration: 100 mg/L; particle size: 400 μ ; contact time: 4 hrs; pH: 7.0)

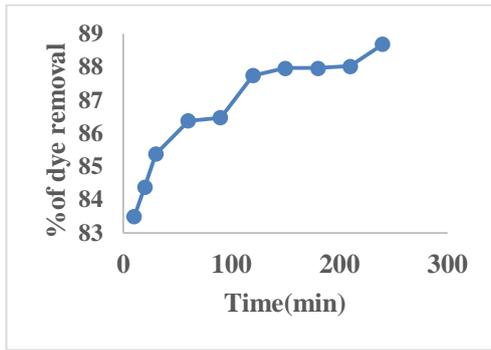


Figure 2. Effect of equilibration period on adsorption of Grey BL by TALP(sorbent dose: 1 g/100 mL; particle size: 400 μ ; contact time: 4hrs; pH: 7.0).

3.2 Effect of Equilibration period

The effect of equilibration period was studied in the range of 10-240 minutes in 100mg/L initial dye concentration with an adsorbent dose of 1 g/100 mL. From Figure 2, it can be observed that the maximum percentage of removal of dye was achieved at 240 minutes after which the removal almost reached a constant. Hence an equilibrium time of 240 minutes were considered for all further studies.

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The pH of an aqueous phase has greater influence on the surface of the adsorbents molecules. The magnitude of electrostatic charges imparted by dye molecules is primarily controlled by the pH of medium. To study the influence of pH on the adsorbent capacity of TALP for dye, experiment were carried out using different initial solution pH values, varying from 2 to 10. The ratio of dye sorbed increased as the initial pH was increased from pH 2 to 8, then the dye removal ratios were not significantly altered beyond pH 8. From the Figure 3, it is observed that in the pH range of 7-8, the pH biomass adsorbs to the extent of 88.96% of the colouring matter. Hence in all the studies an optimum pH of 7.0 is used.

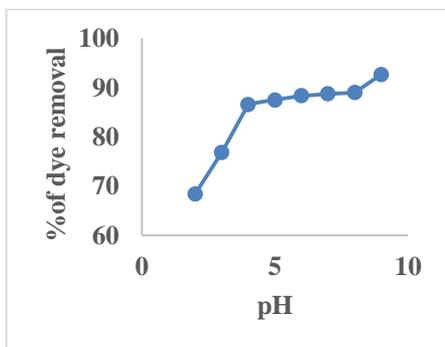


Figure 3. Effect of initial pH on adsorption of Grey BL by TALP(dye concentration: 100 mg/L; sorbent dose: 1 g/L; particle size: 400 μ , contact time: 4 hrs; Temperature 300 K).

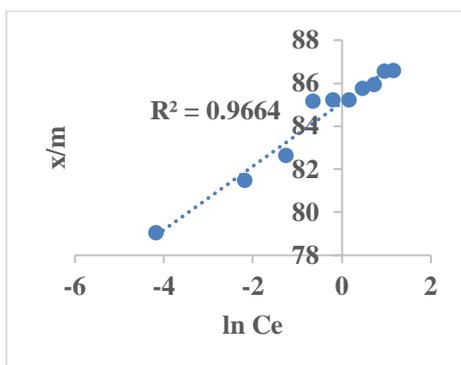


Figure 4. Langmuir plot for the adsorption of Grey BL

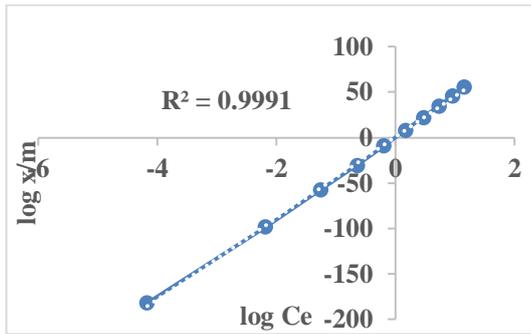


Figure 5. Freundlich plot for the adsorption of Grey BL

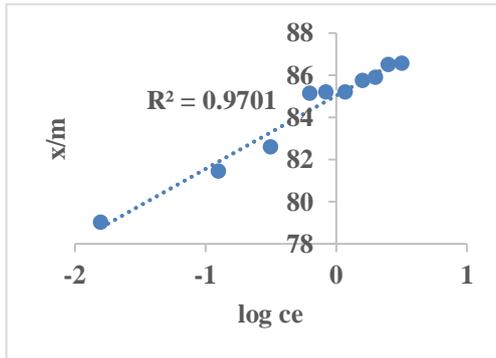


Figure 6. Temkin plot for the adsorption of Grey BL

3.4 Adsorption Isotherm

Adsorption isotherm experiment were conducted by taking adsorbents, ranging from 0.1 to 1.9 g/L in various reagent glass bottles. About 100mg/L dye solution were added to each reagent bottles and shaken for 4 hrs. After equilibration period absorbance of the supernatant clear liquid is determined spectrophotometrically at 575nm. The amount of dye adsorbed was calculated using the graph. Three different isotherm models were used to fit the experimental data the Langmuir, Freundlich and Tempkin models are given in Figure 4,5 and 6.

3.4.1. Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm studies were conducted with experimental data at equilibrium condition. The following Langmuir equation can be used for calculations

$$\frac{x}{m} = \frac{a \cdot b \cdot ce}{1 + b \cdot ce} \quad \text{----- (1)}$$

Where x=amount of dye adsorbed, m=weight of adsorbent used, ce= equilibrium dye concentration, a=constant and b=Langmuir parameter. A plot of x/m vs ln ce is shown in Figure 4. Linear plot was obtained. All the three models explain Correlation-coefficient [R²].

The correlation coefficient R² value for Grey BL dye was obtained as 0.9664.

3.4.2. Freundlich Adsorption Isotherm

Freundlich isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption¹⁴. The modified form of Freundlich equation is given as

$$\text{Log} \left(\frac{x}{m} \right) = \text{log } k + \frac{1}{n} \text{log } ce \text{----- (2)}$$

Where $\left(\frac{x}{m} \right)$ = amount adsorbed per unit mass of adsorbent, ce=equilibrium dye concentration, k=adsorption capacity and $\frac{1}{n}$ sorption intensity.

A plot of $\log\left(\frac{x}{m}\right)$ vs $\log ce$ was shown in Figure 5. The straight line nature of the graph and R^2 value equals to 0.9991 indicates the multilayer formation and fitted with Freundlich adsorption Isotherm. From the straight line we can calculate the slope $\frac{1}{n}$ and intercept $\log k$. The value of k and the value of $\frac{1}{n}$ less than 1 indicate favourable for Freundlich adsorption.

3.4.3. Temkin Isotherm

The equilibrium data was further applied to Temkin isotherm model. The plot of x/m vs $\log ce$ for Grey BL adsorption on TALP is presented in Figure 6. It can be seen from the figure that R^2 value for the adsorption was found to be 0.9701 which is less than the other two models and the model becomes inapplicable.

3.5. SEM of Adsorbent

The biomass were coated with platinum (1) for scanning electron microscopy and micrographs were recorded on FESEM (JEOL JSM-6700 F) instrument equipped with energy dispersive X-ray analysis. The Figure.7 shows the SEM micrographs of TALP sample before adsorption. It shows that all the leaves powder possesses a rough surface morphology with pores of different sizes. These pores are useful for dye adsorption.

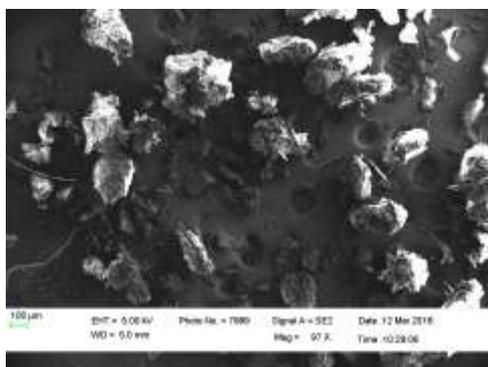


Figure 7. SEM image of TALP before adsorption of Grey BL

Conclusion

The present laboratory study was carried out to assess the adsorption of dye particles by using low cost adsorbent prepared from *Trachysperum ammi* leaves. The selected biomass showed high capacity for adsorption and its cost effective. The experimental data produced perfect fit with Freundlich isotherm. The optimal pH for favourable adsorption of dyes was 7. The leaves were also stable under the atmospheric condition. From the studies it has been confirmed that the bio-adsorbent prepared from the leaves of the *Trachysperum ammi* (ajwain), a low-cost adsorbent could effectively remove Grey BL dye from an aqueous solution.

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