



Adsorption of Dye Olive BGL Using Two Different Samples of Activated Carbon by Static Batch Method

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The removal of dye olive BGL using two different samples of activated carbon by static batch method was studied. Experimental data on optical density of blank solutions of different concentrations ranging from 10-100 mg/L and optical density of solutions after adsorption on activated carbon samples were taken and analyzed. Calibration curves were plotted and the amount of dye adsorbed was calculated. The data was fitted to Langmuir and Freundlich isotherms for two different carbon samples and different concentration values. Constants were calculated from the slope and intercept values of the isotherms. Coefficient of correlation R^2 and standard deviation were also recorded. The data fitted well to the isotherms. Carbon sample C_1 showed higher potential to adsorb the dye olive BGL at lower concentrations of the solution whereas carbon sample C_2 showed better results at higher concentration. Carbon sample C_2 showed better adsorption in acidic pH as compared to in alkaline pH. From the analysis of the data it is shown that activated carbon has good capacity to remove the textile dye from the residue water.

Key Words: Adsorption, Olive BGL, Activated carbon, Textile industry effluent.

INTRODUCTION

The textile industry is using several thousands of quantities of dyes and chemicals in various processes of textile manufacture including dyeing and printing all of which require large quantities of water. Water consumption for dyeing varies from 30-50 L/kg of cloth depending on the type of dye used. An average sized textile mill has a production of about 8000 Kg of fabric per day. It may use as much as *ca.* 1.6 million liters of water 16 % of which may be consumed in dyeing and 8 % in printing. Dyeing section itself contributes to 15-20 % of the total waste water flow¹. Use of synthetic dyes has been seen to have a toxic nature and causes an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. Other harmful chemicals present in the water may be formaldehyde based dye fixing agents, chlorinated stain removers, hydrocarbon based softeners, non biodegradable dyeing chemicals. These organic materials react with many disinfectants especially chlorine and form by products that are often carcinogenic and therefore undesirable. Many of these also show allergic reactions².

The colloidal matter present along with colors and oily scum increases the turbidity, gives the water a bad appearance

and foul smell and prevents the penetration of sunlight necessary for the process of photosynthesis. This in turn interferes with the oxygen transfer mechanism at air water interface which in turn interferes with marine life and self purification process of water. This effluent if allowed to flow in the fields' clogs the pores of the soil resulting in loss of soil productivity. If allowed to flow in drains and rivers it effects the quality of drinking water in hand pumps making it unfit for human consumption³⁻⁶. It is important to remove these pollutants from the waste waters before their final disposal.

The commercial granular activated carbon for adsorption of dyes from aqueous solutions and observed that the adsorption data could be explained by Freundlich isotherms⁷. The adsorption at a given concentration decreased with increase in temperature although the rate of adsorption increased with increase in temperature. Addition of sodium chloride increased the adsorption rate and lengthened the breakthrough time. It was found that direct dyes did not adsorb as readily as other dyes.

Pathe *et al.*⁸ studied the treatment of textile waste water by physiochemical methods. It was pointed out that the major components in dyeing waste waters are dyes, surfactants, starch, chemical aids and suspended solids. Dyes are divided into hydrophilic and hydrophobic compounds. The former are removed effectively by activated carbon and chlorine while

the later are removed by floatation. Starch is removed by flocculation. A treatment scheme was designed using the unit process of floatation, flocculation-settlement, sand filter and activated carbon. Results showed that water from cotton dyeing and processing unit when treated as above could be reused as effectively as river water.

In the present work, experiments were conducted on olive BGL ($C_{19}H_{18}N_4O_5S$) which is an acidic dye used for dyeing wool and silk. It is also called acid black 64 and belongs to 1:2 metal complex dye.

EXPERIMENTAL

Static batch method: Samples of granular activated carbon C_1 and C_2 used were obtained from Brillix Chemical Ltd. Punjab and Industrial Carbon Pvt. Ltd., Gujarat. Surface area of GAC C_1 used in the study was $950 \text{ m}^2/\text{g}$ and that of GAC C_2 was $600 \text{ m}^2/\text{g}$. Bulk density of the two was 500-550 and 600-1000 g/L, respectively. The ash content was 6 % in C_1 and 5 % in C_2 .

A stock solution of the dyes with a concentration of 1000 ppm was prepared and dilutions were made with distilled water to make different concentrations. Optical density of all the solutions was measured on a spectrophotometer (ELICO make, wavelength range 200-900 nm). One gram of activated carbon was placed in each 50 mL solution of 10-100 ppm. The solutions were shaken and kept in a thermostat for 24 h. The samples were then filtered and analyzed spectrophotometrically.

The experimental data for the dyes studied was fitted to Langmuir and Freundlich isotherms. Isotherms represent the relationship between the amount adsorbed and the concentration at a constant temperature. They also provide useful information about the adsorption process and enable determination of useful surface parameters such as surface area, pore size distribution and pore volume of the adsorbant. Each individual type of activated carbon has its own isotherm curve and breaking point characteristics that help to give an estimate of its adsorptive life.

The experimental data was fitted to linear form of Langmuir isotherm for all the pH values of the dye and for the two samples of granulated activated carbon. The data was fitted to the equation of the type:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \frac{1}{C_e} \quad (1)$$

q_e indicates the amount of dye adsorbed per unit weight of adsorbent (mg/g). C_e is the equilibrium concentration of dye in mg/L. Q and b are the Langmuir constants where Q indicates the adsorption capacity in mg/g and b relates to the energy of adsorption (L/mg) in different experimental conditions. These were calculated from the straight line slope and intercept of linear plot between $1/q_e$ and $1/C_e$.

The essential characteristics of Langmuir equation were expressed in terms of a dimensionless separation factor R_L ¹⁰:

$$R_L = \frac{1}{1 + bC_0}$$

R_L values indicate the shape of the isotherm. Value of R_L between 0 and 1 indicate a favorable adsorption¹¹ $R_L > 1$ is

unfavorable. $R_L = 1$ is linear. $0 > R_L < 1$ is favourable. $R_L = 0$ is irreversible.

Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is assumed that once a dye molecule occupies a site no further adsorption can take place at that site and theoretically a saturation value is reached beyond which no further adsorption can take place.

Linear forms of Freundlich isotherms were plotted for all the pH values of the three dyes and for the two samples of granulated activated carbon. The data was fitted to the equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

Freundlich constants K_F and n were calculated from the slope and intercept of $\log q_e$ and $\log C_e$ along with R^2 and SD. K_F (parameter relative to adsorption capacity) and n (process intensity) were calculated. The value of n between 2 and 10 indicates good adsorption¹². Freundlich isotherm is based on heterogeneous surface of adsorbent. The difference in adsorption capacity comes from different molecular structures of dyes and their different molecular weights.

Effect of initial dye concentration: Table-1 and Fig. 1 show the amount q_e of olive BGL adsorbed by C_1 and C_2 samples of granulated activated carbon at various ppm concentrations. It can be seen that q_e on granulated activated carbon C_1 and C_2 was higher at lower ppm concentration as compared to the adsorption at higher ppm concentration with the adsorbent dose being kept constant for all dye. At 10 ppm concentration and initial pH of 6.60 C_1 adsorbed 68 mg/L of the dye olive GBL and C_2 adsorbed 39 mg/L. At 100 ppm concentration the adsorption of the dye was 29.40, 33.7 mg/L on C_1 and C_2 , respectively at the same pH. Thus higher adsorption at lower ppm concentrations was observed.

Effect of pH: Adsorption of olive BGL on granulated activated carbon C_2 was greatly affected by change in pH of the aqueous solution as can be seen in Table-1 and Fig. 1. Amount of dye adsorbed q_e on C_2 in acidic pH is higher at all ppm concentrations as compared to adsorption in a lesser acidic and an alkaline environment. At an acidic pH of 3.32 at 10 ppm concentration C_2 adsorbed 57 mg/L of the dye olive BGL. In an alkaline pH of 9.97 the same C_2 adsorbed only 33.5 mg/L of the dye leaving behind a good number of free adsorption sites on the adsorbent.

TABLE-1
AMOUNT OF DYE OLIVE BGL ADSORBED BY ACTIVATED CARBON SAMPLES C_1 AND C_2 AT DIFFERENT pH VALUES

Dye name	Olive GBL pH			
	C_1	C_2	C_2	C_2
	6.60	6.60	3.32	9.97
C_e (mg/L)	q_e	q_e	q_e	q_e
10	6.800	3.900	5.700	3.350
20	9.800	6.700	9.390	4.800
30	12.930	10.000	12.400	6.200
40	16.910	14.200	16.000	7.330
50	19.590	18.400	20.000	8.950
60	21.690	22.090	23.480	10.100
70	23.930	25.500	28.000	11.200
80	26.600	28.870	32.260	12.500
90	28.600	32.350	34.960	12.900
100	29.400	33.700	36.800	13.300

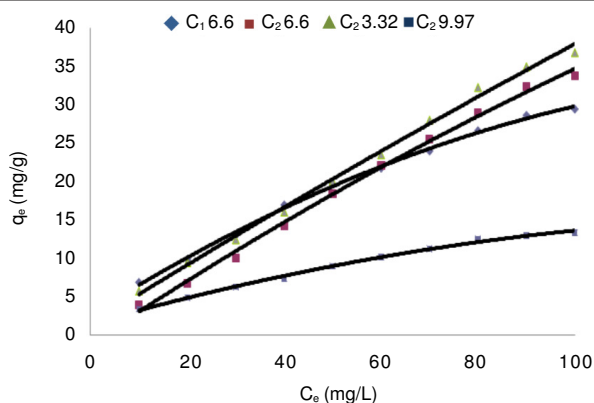


Fig. 1. Adsorption isotherm for dye olive BGL on C₁ and C₂ at different pH values

Table-2 gives the values of Langmuir constants Q and b along with the values of r², R_L and SD for dye olive BGL and at varied pH values and for the two samples of granulated activated carbon, C₁ and C₂. R_L values indicate the shape of the isotherm. Value of R_L between 0 and one indicate a favourable adsorption. Values of constants Q and b also signify good adsorption of the dye on C₁.

Dye name	Olive GBL pH			
	C ₁ 6.60	C ₂ 6.60	C ₂ 3.32	C ₂ 9.97
Q	40.258	175.439	62.035	16.132
b	0.019	0.002	0.010	0.025
r ²	0.958	0.982	0.875	0.967
SD	0.008	0.011	0.008	0.014
R _L	0.008	0.004	0.006	0.004

The linear plots of 1/q_e and 1/C_e for Langmuir isotherm are shown in Fig. 2.

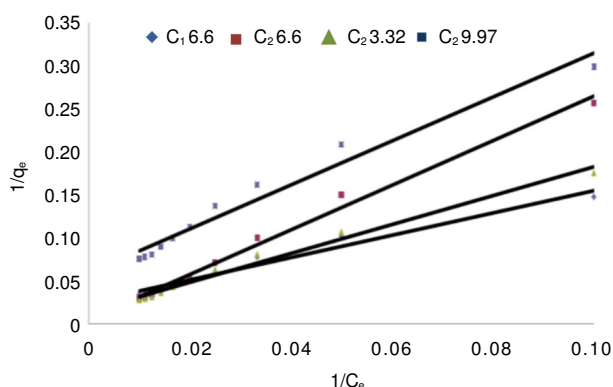


Fig. 2. Langmuir isotherm for dye olive BGL on C₁ and C₂ at different pH values

Table-3 shows the Freundlich constants K_F and n calculated from the slope and intercept of log q_e and log C_e along with R² and SD. K_F (parameter relative to adsorption capacity) and n (process intensity) were calculated. Values of constant K_F indicate higher adsorption capacity on carbon sample C₁ as compared to C₂.

Dye name	Olive GBL pH			
	C ₁ 6.60	C ₂ 6.60	C ₂ 3.32	C ₂ 9.97
K _F	1.383	0.374	0.760	0.758
n	1.490	1.013	1.187	1.592
r ²	0.995	0.996	0.992	0.993
SD	0.016	0.021	0.025	0.107

The linear plots of log q_e and log C_e for Freundlich isotherm are shown in Fig. 3.

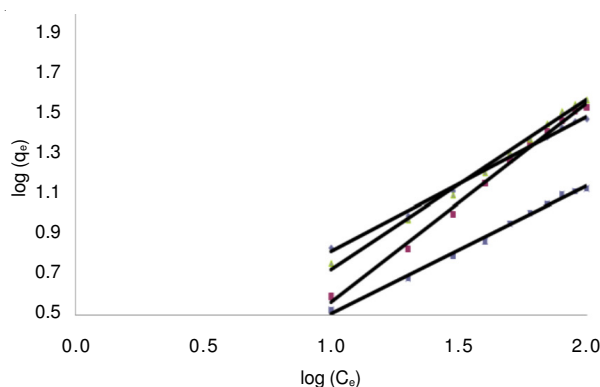


Fig. 3. Freundlich isotherm for dye olive BGL on C₁ and C₂ at different pH values

RESULTS AND DISCUSSION

Granulated activated carbon sample C₁ and C₂ can be effectively used for the removal of dyes from wastewater by adsorption. The present study shows that there is a decrease in percentage removal of dye per gram with increase in ppm concentration of the dye. Change in pH values showed higher adsorption at acidic pH. The dye obeyed Langmuir and Freundlich isotherms. Langmuir isotherm gave a better fit. Carbon sample C₂ showed higher adsorption for the dye at acidic pH and higher ppm concentrations. C₁ fared better than C₂ at lower ppm concentrations.

At acidic pH values the adsorbent tends to form an aqua complex to yield a positively charged surface. The ionic dye releases colored dye anions/cations in solution, which in turn is influenced by the solution pH agents¹³. At acidic pH there is an increase in H⁺ ions in dye solution. The OH⁻ ions on the adsorbent surface tend to be neutralized by protonation which facilitates the diffusion of dye molecules in the vicinity of the adsorbent. The positively charged surface sites on the adsorbent and the solution thus play a significant role in influencing the capacity of the adsorbent towards dye ions due to electrostatic attraction. Having an excess positive charge on their surface activated carbon shows a greater capacity to adsorb the dye when the solution is made acidic. Lower adsorption at alkaline pH may have been due to the presence of OH⁻ ions competing with the dye ions for adsorption sites. As the pH of the system decreases number of negatively charged surface sites increases.

The values of r² indicate that both adsorption models fitted satisfactorily and suggested monolayer adsorption coverage

on the outer surface of the adsorbent. Judging by the value of r^2 Langmuir isotherm gave a better fit. Both samples of activated carbon proved to be reasonably good adsorbents for removing the residual dye olive BGL from waste water.

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