Adsorption of yellow dye: Acid yellow RR from its aqueous solution using two different samples of activated carbon by static batch method

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ABSTRACT

Removal of dye Acid Yellow RR, 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 to 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 q_e adsorbed was calculated. The data was fitted to Polynomial, Langmuir and Freundlich isotherms for two different carbon samples and different concentration and pH values. Constants were calculated from the slope and intercept values of the isotherms. Coefficient of correlation R^2 and Standard Deviation SD were also noted. The data fitted well to the isotherms. Carbon sample C_1 showed higher potential to adsorb the yellow dye. Adsorption was higher at lower concentrations of the solution. 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 C_2 sample has a good capacity to remove the textile dye from the residue water although sample C_1 was still better.

Keywords: Adsorption; Acid Yellow RR; Activated Carbon; Textile Industry Effluent

1. INTRODUCTION

Color is the main attraction of any fabric. As far back as in 3500 B.C. natural dyes extracted from vegetables, fruits, flowers, certain insects and fish were being used to dye fabric. With the discovery of synthetic dyes by W H Perkins in 1856 use of synthetic dyes gave way to natural dyes that gave a limited and dull range of colors that had lower fastness to light and washing [1]. More than 3600 individual textile dyes are being manufactured by the industry today. Large quantities of water are required in the industry for textile processing, dyeing and printing. The daily water consumption of an average sized textile mill having a production of about 8000 Kg of fabric per day is about 1.6 million liters. Dyeing section contributes to 15% - 20% of the total waste water flow [2]. The entire waste water may contain elements like sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all of which collectively make the effluent highly toxic [3] Other harmful chemicals present in the water may be formaldehyde based dye fixing agents, chlorinated stain removers, hydro carbon based softeners and non bio degradable dyeing chemicals. All these organic materials are of great concern in water treatment because they react with many disinfectants to form by products (DBP'S) that are often carcinogenic and therefore undesirable. Many of these show allergic reactions. The colloidal matter present along with colors and oily scum increases the turbidity, gives the water a bad appearance, and prevents photosynthesis [4]. Depletion of dissolved Oxygen in water adversely effects marine life. In addition when this effluent is allowed to flow in the fields it 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 consumption. Such polluted water can also be a breeding ground for bacteria and viruses.

Geetha A., Siva Kumar P., Sujatha M., Palanisamy P.N. and Somasundaram T. [5] studied the adsorption of dye Acid Blue from an aqueous solution onto activated areca nut shell carbon using batch adsorption method. Adsorption kinetics, equilibrium and thermodynamics were investigated as a function of initial dye concentration, temperature and pH. Kinetic studies indicated that the adsorption followed Elovich model. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The adsorption capacity of ANSC was found to be increasing with increase in temperature. Based on regression

coefficient, the equilibrium data found fitted well to Freundlich model. Thermodynamics parameters such as ΔG^0, ΔH^0, ΔS^0 for adsorption were evaluated. The thermo dynamics of Acid Blue-ANSC system indicated endothermic nature of the process. It is found that the areca nut shell activated carbon is effective for the removal of Acid Blue from aqueous solution.

The adsorption capacity of riverbed sand, saw dust, vermiculite and soil for Cr(III) ions from tannery effluent has been investigated in detail by Sumathi K.M.S. and Mahimairaja S. [6] in order to evaluate their possible application as filter material in reed bed treatment system. The adsorption isotherm was determined alongwith the effect of contact time, initial Cr concentration and pH on the efficiency of Cr removal. It was concluded that the maximum adsorption of Cr (>90 percent) was achieved by vermiculite and soil within 24 hours. The equilibrium isotherm data for vermiculite was found to follow Freundlich and Langmuir equations and a separation factor was used to judge the favorable adsorption. Vermiculite exhibited a higher adsorption capacity followed by sand, sawdust and soil .The Cr retention capacity of adsorbents in different pH was calculated on the basis of the distribution coefficient (Kd) and the highest Kd value was achieved by vermiculite (61.1) at pH 5.0.

V.K. Rattan, Abhiti Purai, Harminder Singh, and Mahboobeh Manoochehri [7] studied the ability of Cow dung ash without any pretreatment to remove color from textile dyes N Blue RGB, Green B, and Eosin YWS from aqueous solution. Cow dung ash an eco friendly and low cost adsorbent was prepared by burning cow dung cakes in muffle furnace at 500˚C. The adsorption was achieved under different pH and adosrbate concentration. The data was fitted to simple polynomial and the isotherms similar to Langmuir and Freundlich isotherms.

2. MATERIALS AND METHOD

2.1. Adsorbate Preparation

Samples of Granular Activated Carbon C_1 and C_2 used were obtained from Brillex Chemical Ltd. Punjab and Industrial Carbon Pvt. Ltd., Gujarat. Surface area of GAC C_1 used in the study was 950 m^2/g and that of GAC C_2 was 600 m^2/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 dye with a concentration of 1000ppm 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 to 100 ppm. The solutions were shaken and kept in a thermostat for 24 hrs. The samples were then filtered and analyzed spectrophotometrically.

2.2. Adsorption Dynamics

The experimental data for the dye studied was fitted to simple Polynomial, 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 adsorpion 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 the following polynomial equation:

$$q_e = A + B_1 C_0 + B_2 C_0^2 \qquad (2)$$

q_e shows the amount of dye adsorbed per unit weight of adsorbent (mg/L), where C_0 is the initial concentration of the dye. A, B_1, B_2 represent the constants. The experimental data was also fitted to Linear forms of Langmuir isotherm of the type:

$$1/q_e = 1/Q + 1/bQ\, 1/C_e \qquad (2)$$

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:

$$R_L = 1/(1 + bC_0)$$

R_L values indicate the shape of the isotherm. Value of RL between 0 and one indicate a favorable adsorption [8]. $R_L > 1$ is unfavorable. $R_L = 1$ is linear. $0 > R_L < 1$ is favorable. $R_L = 0$ 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 yellow dye and for the two samples of GAC. The data was fitted to the equation:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

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 [9]. K_F (parameter relative to adsorption capacity) and n (process intensity) were calculated. The value of n between 2 and 10 indicates good adsorption. 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.

3. RESULTS AND DISCUSSION

3.1. Effect of Initial Dye Concentration

Table 1; **Figure 1** show the amount q_e of dye Acid Yellow RR adsorbed by C_1 and C_2 samples of granulated activated carbon at various pH values and various ppm concentrations. It can be seen that q_e on GAC 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. At lower ppm concentration a substantial amount of dye got adsorbed leaving behind a good number of free adsorption sites on the adsorbent. At higher ppm concentrations the adsorbent was used to its greater capacity and lesser number of active sites remained available on GAC surface for further adsorption to take place.

Table 1. Amount of dye Acid Yellow RR adsorbed by activated carbon samples C_1 and C_2 at various pH values.

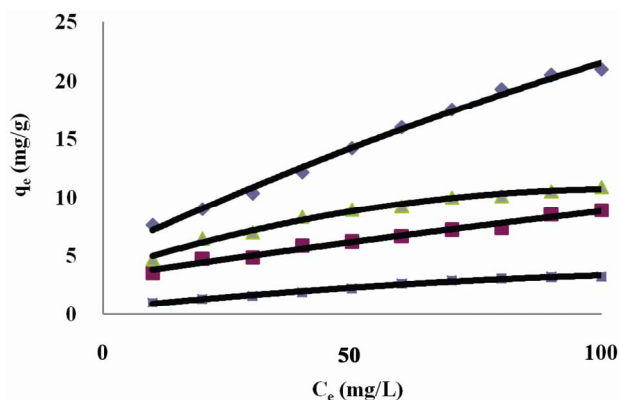| Dye Name	Acid Yellow RR			
	pH			
	C_1 7.06	C_2 7.06	C_2 3.55	C_2 10
C_e (mg/L)	q_e	q_e	q_e	q_e
10	7.600	3.500	4.700	1.000
20	9.000	4.760	6.450	1.290
30	10.330	4.870	6.980	1.580
40	12.170	5.850	8.300	1.880
50	14.240	6.150	8.910	2.210
60	16.030	6.650	9.180	2.610
70	17.550	7.150	9.980	2.880
80	19.290	7.320	10.100	3.070
90	20.490	8.150	10.500	3.180
100	21.000	8.870	10.900	3.220

Figure 1. Amount of dye Acid Yellow RR adsorbed by activated carbonsamples C_1 and C_2 at various pH values. ◆C_1 7.06 ■ C_2 7.06 ▲C_2 3.55 ▪ C_2 10.

3.2. Effect of pH

Adsorption of dye Acid Yellow RR on GAC C_2 was greatly affected by change in pH of the aqueous solution as can be seen in **Figure 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 10 ppm concentration C_2 adsorbed 47% of Acid Yellow RR at acidic pH. At alkaline pH the adsorption was only 1% at the same ppm concentration. However carbon sample C_1 showed better adsorption as compared to carbon sample C_2. At 10 ppm concentration at initial pH value 76% of Acid Yellow RR was adsorbed as against 35% on C_2 in the same pH environment.

C_1 as compared to C_2 shows higher adsorption at initial pH. It also shows better adsorption than C_2 did in acidic environment.

The linear plots of $1/q_e$ and $1/C_e$ for Langmuir isotherm are shown in **Figure 2**. **Table 2** gives the values of Langmuir constants (calculated from the slope and intercept) Q and b along with the values of r^2, R_L and SD for the dye at varied pH values and for the two samples of GAC, C_1 and C_2. R_L values indicate the shape of the isotherm. Value of R_L between 0 and one indicate a favorable adsorption Values of Q signify good adsorption of the dye on C_1 and C_2 samples of carbon. It particularly indicates a better adsorption at acidic pH on C_2.
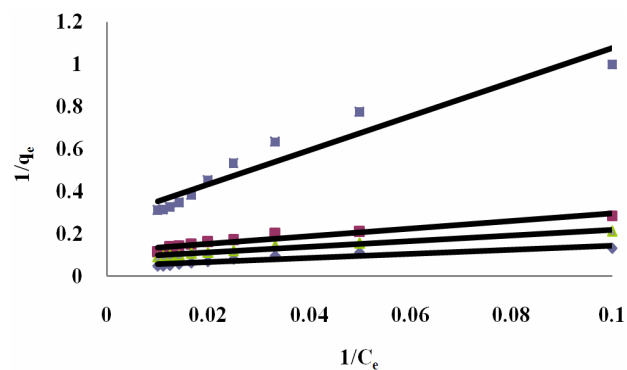

Figure 2. Langmuir Isotherm for dye Acid Yellow RR on C_1 & C_2 at different pH values. ◆C_1 7.06 ■C_2 7.06 ▲C_2 3.55 ▪C_2 10.

Table 2. Values of different constants for Langmuir Isotherm at various pH values.

Dye Name	Acid Yellow RR			
Parameters	pH			
	C_1 7.06	C_2 7.06	C_2 3.55	C_2 10
Q	20.340	8.530	11.546	3.618
B	0.053	0.064	0.067	0.035
r^2	0.838	0.903	0.963	0.922
SD	0.012	0.018	0.008	0.069
R_L	0.011	0.005	0.008	0.001

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 R^2 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 C_1 as compared to C_2. The linear plots of log q_e and log C_e for Freundlich isotherm are shown in **Figure 3**.

3.3. Adsorption Mechanism Explained

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. At acidic pH values the adsorbent tends to form an aqua complex to yield a positively charged surface, so there is an increase in H^+ ions in dye solution. The ionic dye releases colored dye: anions/cations in solution, which in turn is influenced by the solution pH agents. 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.

Lower adsorption at alkaline pH is 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.

4. CONCLUSION

As can be seen by the values of r^2 and SD, in **Tables 2** and **3**, the experimental data fit to Langmuir and Freundlich isotherm models demonstrated a good fit showing consistency in the dynamics analysis.

Granulated Activated Carbon sample C_1 and C_2 can thus 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.

Carbon sample C_1 showed high adsorption; above 70%.

Table 3. Values of different constants for Freundlich Isotherm at various pH values.

Dye Name	Acid Yellow RR		
Parameters	pH		
	C_1 7.06	C_2 7.06	C_2 3.55	C_2 10
K_F	2.21	1.414	2.099	0.000
N	2.07	2.597	2.765	1.000
r^2	0.96	0.967	0.987	1.000
SD	0.03	0.024	0.014	0.000
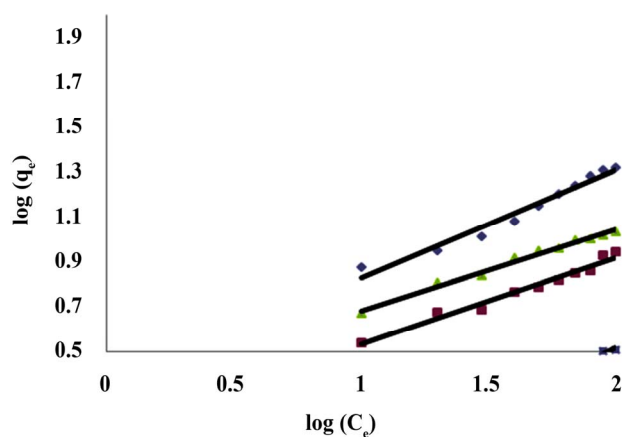
Figure 3. Freundlich Isotherm for dye Acid Yellow RR on C_1 & C_2 at different pH values. ◆C_1 7.06 ■ C_2 7.06 ▲C_2 3.55 ▪C_2 10.

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