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Adsorptive Treatment of Azo Dyes from Aqueous Solution Using PVA Coated Carbon Black as An Adsorbent

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The paper concerns with the adsorptive treatment of dye 1-brilliant yellow and dye 2-benzoazurin G in aqueous solution on polyvinyl alcohol (PVA) coated carbon black as an adsorbent. The effect of pH, concentration and time on adsorption process was investigated and adsorption equilibrium isotherms reported. The adsorption equilibrium data fitted to both Freundlich and Langmuir isotherms equally well. Batch adsorption studies were conducted at room temperature (30 ºC). The per cent removal of benzoazurin G was 80 % and brilliant yellow was 84 %.

Key Words: Adsorption, Adsorbent, Dyes, Isotherms, Waste waters.

INTRODUCTION

The pollution of water due to various types of synthetic dyes has been a major cause of concern since long. The dye bearing wastewater discharged into water contributes negatively and upset aquatic life. The discharge from the textile industries[1] is solution of complex chemicals. The colour is due to unfixed dye. Nature of dyes and dying process affect the concentration of unused dye. It is unfit for recycling without proper treatment. The chronic risks of colorants are carcinogenicity. Reactive dyes are the principal dyes used in the cotton industry which makes up 50 % of the world's fiber consumption.They are commonly used in the textile industry because of their bright colours, excellent colourfastness and ease of application. A large number of reactive dyes are azo compounds which are linked by an azo group. Many reactive dyes are toxic to some organisms and may cause direct destruction of aquatic life due to the presence of aromatic and metal chlorides. It has been reported that some azo dyes are able to produce carcinogenic aromatic amines in the process of reductive degradation. Their high solubility, synthetic origin and complex aromatic molecular structure make their removal a very difficult task.

The removal of colour from wastewater can be accomplished by flotation, chemical coagulation, chemical oxidation and adsorption[2]. Adsorption hold promise in the treatment of wastewater, as it is inexpensive, simply designed, easy to handle and provides sludge-free cleaning operations. Activated carbon has long been used in industry as a standard adsorbent for removing colour. However, although it is the most widely used adsorbent for the removal of colour and the treatment of textile effluents, it is not used on a large scale on account of its high price. Therefore, the development of low-cost alternative adsorbents has been the focus of recent research[3,4].

The objective of the work is to develop a better method for the removal of synthetic dyes using low cost adsorbent. Poly vinyl alcohol is a good hydrophilic polymer and has water-adsorbing capacity. The carbon black used for adsorption is furnace black. The furnace black is obtained from the burning of furnace oil in absence of sufficient oxygen at higher temperature. This carbon black (commonly named furnace black) is in the form of very fine particles.

EXPERIMENTAL

Preparation of activated carbon from *Crotolaria burhia*: The activated carbon is prepared from the naturally dried stems of the plants *Crotolaria burhia*, a desert plant material. It was cut into small pieces. These were then treated with concentrated sulphuric acid (five times its volume) and kept in oven at 150 °C for 24 h. It was filtered and washed with distilled water repeatedly to remove sulphuric acid (washing tested with two drops of barium chloride solution) and finally dried and powdered using mortar and pestle. The adsorbent is sieved to 40-60 mesh size and heated at 150 °C for 2 h. This adsorbent is also added to polyvinyl alcohol coated carbon black to form a new adsorbent having a fine particle size for removing dyes.

Preparation of poly vinyl alcohol (PVA) coated carbon black: 1 g of PVA is dissolved in 10 mL hot water (10 % solution) as a result gel formation occurs. Now 1.5 g of furnace black is added in it to form a thick paste. This paste is then mixed with activated carbon obtained from the dried stem of *Crotolaria burhia*. Now the thick paste obtained is then dried to form lumps. The lumps are further grinded into fine powder. This powder (PVA coated carbon black) is used as an adsorbing material.

Adsorption experiment: The adsorbent-adsorbate system was established at ambient temperature and in Batch mode using stock solution. A comparative study of adsorption of dyes on the adsorbent poly vinyl alcohol coated carbon black at different pH is studied. In the adsorption measurement dyes solutions at different concentrations (from 10 to 40 ppm) and pH of 2, 4, 6, 8 and 10 were used. The desired pH was maintained using dilute NaOH/HCl solutions.The adsorbent dose between 1.00 to 1.75 g was used. During experiment the system was continuously stirred and at the end of each experiment the solution was centrifuged and filtered using whatman filter paper.

The concentration of dye was measured by UV-Vis spectrophotometer between the time intervals 30 to 240 min. The concentration of dye in solution was measured at the wavelength of abs. max. 5690 Å (benzoazurin-G), abs. max. 5430 Å (brilliant yellow). The pH was measured by pH meter.

Langmuir adsorption isotherm: The Langmuir equation is derived from simple mass-action kinetic, assuming chemisorption.This model is based on two assumptions that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site and no further sorption takes place. The saturation value is reached beyond which no further sorption takes place. The saturation monolayer can then be represented by the expression:

$$C_e/q_e = 1/Q_ob + C_e/Q_o \quad (1)$$

where, C_e is equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium time per unit adsorbent (mg/g) and Q and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L. It is defined by

$$R_L = 1/(1 + bC_o) \quad (2)$$

where C_o is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (mg/L).Values of dimensionless equilibrium parameter R_L show the adsorption to be favourable ($0 < R_L < 1$).

TABLE-1
LINEAR REGRESSION DATA AND CO-RELATION COEFFICIENT FOR LANGMUIR ISOTHERM FOR ADSORPTION OF DYE 2 AT 30 ºC

Adsorbent dose (g)	Langmuir isotherm (Linear equation)	Co-relation coefficient (R)
1.00	y = 0.0097x + 0.1958	0.9930
1.25	y = 0.0143x + 0.1753	0.9694
1.50	y = 0.0241x + 0.1315	0.9892
1.75	y = 0.0335x + 0.1011	0.9847

Freundlich adsorption isotherm: The Freundlich equation is used for heterogeneous surface energies in which the energy term, Q_o in the Langmuir equation varies as a function of the surface coverage, q_e strictly due to variations in the heat of adsorption:

$$q_e = k_f C_e^{1/n} \quad (3)$$

The linear form of the eqn. 1 or the log form is:

$$\log q_e = \log k_f + 1/n \log C_e \quad (4)$$

k_f and n are Freundlich constants; n gives an indication of the favourability and k_f the capacity of the adsorbent. Value of n between 1 and 10 indicates good adsorption.

TABLE-2
LINEAR REGRESSION DATA AND CO-RELATION COEFFICIENT FOR FREUNDLICH ISOTHERM FOR ADSORPTION OF DYE 1 AT 30 ºC

Adsorbent dose (g)	Freundlich isotherm (Linear equation)	Co-relation coefficient (R)
1.00	y = 0.817x + 0.6537	0.9998
1.25	y = 0.766x + 0.6777	0.9992
1.50	y = 0.6962x + 0.9937	0.9968
1.75	y = 0.6595x + 0.9916	0.9958

The equilibrium concentration was calculated using following formula:

$$C_e = C_o - (\% \text{ adsorption} \times C_o / 100) \quad (5)$$

The amount of dye adsorbed per unit weight of an adsorbent 'q' was calculated using following formula:

$$q = (C_o - C_e) \times V/m \quad (6)$$

where C_e is the equilibrium concentration (mg/L), C_o is the initial concentration (mg/L), m is the mass of the adsorbent (g) and V is the volume of the solution (L).

The Langmuir and Freundlich constants increase with the rise in temperature. The values of the n lie between 1 to 10 indicating good sorption potential of the sorbent. The co-relation coefficient (r) for Freundlich and Langmuir isotherms are merely equal. Therefore from the present adsorption study it can be stated that Freundlich and Langmuir adsorption equations are found to be better fitted (r = 0.999).

RESULTS AND DISCUSSION

In adsorption system, the contact time plays a vital role irrespective of the other experimental parameters. The data obtained during the adsorption studies made here to evaluate the effect of contact time and initial dyes concentration on the removal of dyes from synthetic wastewater has been analyzed.

Effect of contact time: The effect of contact time on the percentage removal of dyes at different concentration of different pH showed that with increase in contact time the percentage adsorbance of dye increases rapidly up to 3 h after that the rate of adsorption of dye increases very slowly with increase in contact time up to 4 h. The plot in Fig. 1 represents the percentage removal of dyes *vs.* the contact time for the 30 ppm initial dye concentration.

Effect of dose: The effect of adsorbent dose on % removal was studied by keeping the pH, concentration and contact time constant as shown in the Fig. 2. Results showed that the percentage adsorbance of dyes increases with increase in adsorbent dose from 1.0 to 1.75 g this is due to the enhanced surface area of the adsorbent. But after a certain dose of adsorbent the maximum adsorption is attained due to the saturation capacity of the adsorbent.

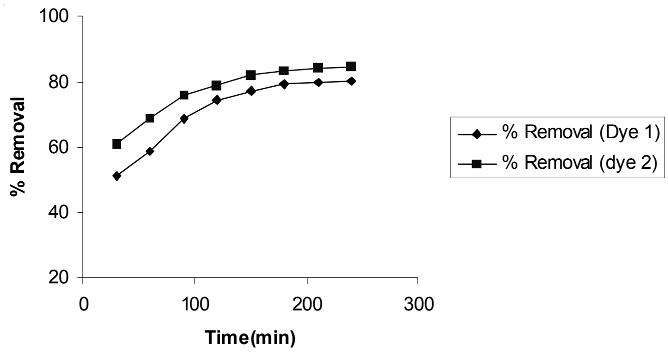

Fig. 1. Time *vs.* % removal of dyes

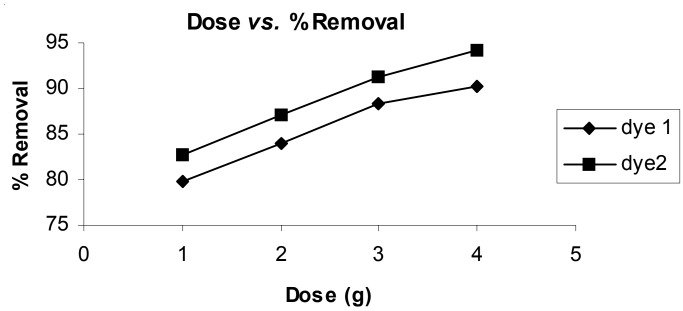

Fig. 2. Dose *vs.* % removal of dyes

Effect of initial dye concentration: The effect of initial dye concentration is presented in Fig. 3. The observations reveal that the % removal of dyes decreases with an increase in the concentration of dyes from 10 to 40 ppm.

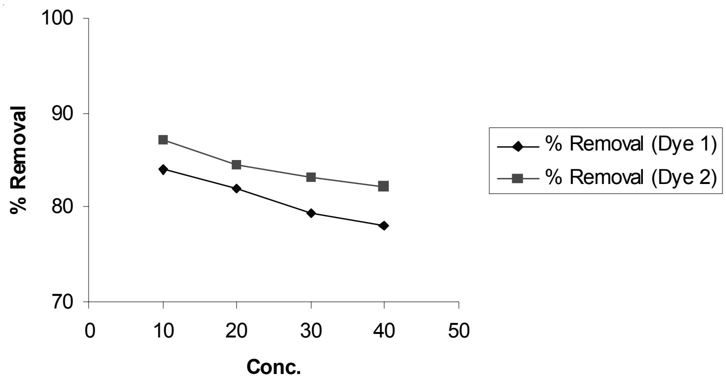

Fig. 3. Concentration *vs.* % removal of dyes

Effect of pH: The pH of the aqueous solution is an important controlling parameter in the adsorption process[5]. The effect of pH was studied at room temperature by varying the pH from 2-10. The maximum adsorption was observed at pH 8 due to the increase in deprotonation of the adsorbent surface, leading to decrease in H^+ ion on the adsorbent surface. This creates more negative charge on the adsorbent surface which favours adsorption of positively charged species and the positive sites on the adsorbent surface[6-8].

Conclusion

In this study, it was observed that with the decreasing pH and dyes concentration the adsorption rate and the amount of dyes adsorbed by adsorbent increases. The series of batch experiment showed that adsorbent PVA coated carbon black have ability to adsorb dye solution. The dye uptake capacities showed order benzoazurin G < brilliant yellow.

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