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ADSORPTION OF CRYSTAL VIOLET ONTO HIBISCUS ROSA SINENSIS

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ABSTRACT:

The removal of the textile dye, crystal violet (CV), from aqueous solutions was studied by adsorption on *Hibiscus rosa sinensis*. Batch adsorption studies were conducted by varying the initial concentration of the adsorbate, adsorbent dosage, contact time, and pH. The effect of pH on adsorption of crystal violet onto *Hibiscus rosa sinensis* was studied at pH 4. The percentage removal of dye was measured as a function of both the concentration of the dye (10 - 30 ppm) and the temperature (303 – 323 K). The experimental data were fitted into the Freundlich and Langmuir adsorption isotherm equations. The values of their corresponding constants were determined. Thermodynamic parameters like free energy, enthalpy and entropy of the systems were calculated using Freundlich constant. The present study shows that nearly80% removal of crystal violet was observed and hence *Hibiscus rosa sinensis*was found to be an efficient adsorbent for the removal of the basic dye crystal violet from aqueous solutions.

Key words : Crystal violet, Adsorption, *Hibiscus rosa sinensis*.

INTRODUCTION

Dyes and pigments are widely used, mostly in the textiles, paper, plastics, leather and cosmetic industry to colour products. Most commercial dyes are chemically stable and are difficult to be removed from waste water [1]. Environmental pollution due to industrial effluents is of major concern because of their toxicity and threat for human life and the environment. Effluents from industries such as food, paper, plastics and textiles generate considerable amount of colour due to dyes and cause serious water pollution, which affects the nature and sunlight penetration into the stream and reduces the photosynthetic action [2]. Synthetic dyes are extensively used for dyeing and printing in a variety of industries. Over 10,000 dyes with an annual production over $7X10^5$ metric tons worldwide are commercially available and 5-10% of the dye stuff is lost in the industrial effluents [3].

Crystal violet or gentian violet is a triarylmethane dye.The dye is used as a histological stain and in Gram's method of classifying bacteria. Crystal violet has antibacterial, antifungal, and anthelmintic properties and was formerly important as a topical antiseptic. The medical use of the dye has been largely superseded by more modern drugs, although it is still listed by the World Health Organization (WHO). When dissolved in water, the dye has a blue-violet colour. Crystal violet is a potent cationic (basic) dye with an absorbance maximum at 590 nm. It is a mutagen and mitotic poison and may cause cancer. It is known to be responsible for severe eye irritation, when it is used in contact with skin [4]. Therefore the treatment of effluent containing such dye is of interest due to its impacts on receiving waters.

Many treatment processes like coagulation and flocculation [5,6] membrane separation [7], ultra chemical filtration [8], activated carbon adsorption [7] *etc*. have been applied for the removal of dyes from waste water. Adsorption onto activated carbon is proven to be very effective in treating textile wastes. However, in view of the high cost and associated problems of regeneration, there is a constant search for alternate low cost adsorbents. Such types of adsorbents include coir pith [9], date pits [10], almond shell [11], cassava peel [12], orange peel [13], jute fiber [14], and rice husk [15] *etc*.

The objective of this work is to obtain the equilibrium relationship and a model that described the contact time of the adsorption of the dye crystal violet on *Hibiscus rosa sinensis* as adsorbent. The common name of the plant *Hibiscus rosa sinensis*is Hibiscus, and it is also called Semparuthi (in Tamil). The adsorbent carbon (HC) was prepared from the plant Hibiscus. The plant Hibiscus is medicinally significant and soothes internal and external wounds and sores. It also soothes alimentary tract and relieves inflammation. The molecular structure of crystal violet is shown in Figure 1.

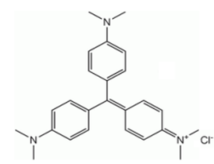

Fig.1. Molecular structure of crystal violet

MATERIALS AND METHODS

Reagents

Reagents include crystal violet (Merck), sulphuric acid (Merck), hydrochloric acid (Merck) and sodium hydroxide (Merck). All chemicals used in the present investigation were spectroscopic grade. They were of ultra high purity. The carbon was finely crushed and sieved through 75, 150, 300 and 425 μm sieves. The chemical analysis of carbon was done by standard methods [16].

Experimental

Batch adsorption experiments were conducted by shaking 0.1g of Hibiscus carbon (HC) with 50 mL aqueous solution of dye at different concentrations, temperatures and pH values. The pH values ranged from 2 to 10. 1.0 N HCl and 1.0 N NaOH were used for pH adjustment. The adsorbent was removed by filtration and the concentration of dye in the supernatant liquid was determined spectrophotometrically.

RESULTS AND DISCUSSION

Effect of contact time

The time dependent behaviour of the dye adsorption was examined by varying the contact time between CV and HC in the range of 10 to 60 min. The concentration of CV was kept as 10 ppm while the amount of adsorbent added was 0.1 g of HC. The amount of dye adsorbed (in mg/g and per cent) is given in Table 1.

The dye removal capacity was plotted as a function of contact time is shown in Figure 2 which indicates that the equilibrium between dye and the adsorbent was attained within 60 min. Therefore, 60 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent experiments. Figure 2 reveals that the curves are smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the carbon surface [17]. The percentage removal of CV observed was 80 for HC.

Effect of adsorbent dosage

The effect of various adsorbent dosages of HC on CV was studied keeping other parameters, like contact time (60 min), initial dye concentration (10 ppm) and pH 4 as constant at 303 K. The amount of dye adsorbed (in mg/g and per cent) is given in Table 2. The dye removal capacity was plotted as a function of adsorbent dosage is showed in Figure 3.A significant increase in percentage removal of CV with increase in adsorbent dosage was observed as expected. This has been attributed that the increase in the adsorbent dosage increases the surface area of carbon which provide more adsorption sites which in turn enhanced the percentage of dye removal [18]. The rate of adsorption depends on the driving forces per unit area in this case since the increase in the adsorbent dosage increases the surface area available for adsorption; hence percentage removal of CV increases. The percentage removal for initial concentration of 10 ppm of CV for contact time of 60 min with a dosage of 0.1 g of HC was 85.5.

Effect of *p*H

Adsorption is also affected by the pH change of the dye solution. The initial *p*H of dye solution was adjusted to *p*H 2, 4, 6, 8 and 10. The amount of dye adsorbed (in mg/g and per cent) is given in Table 3.Dye adsorption was determined by fixing the other parameters as constant and results are given in Figure 4. The *p*H of the working solution was controlled by adding HCl or NaOH solution. It is apparent from the figure that the percentage removal of CV was increasing with increase in acidity and no significant increase in the dye removal while increasing the alkalinity [19]. Hence, throughout the study, the pH of the medium was maintained at *p*H 4.

Effect of dye concentration

The effect of concentration of CV on the HC was studied at constant contact time, temperature and *p*H. The percentage removal of dye gets increased with increase in concentration of the dye. The initial CV concentrations were taken from 10, 20, 30, 40 and 50 ppm with adsorbent dosage of 0.1 g for contact time of one hour. The percentage removal of CV gets increased gradually with the increase in dye concentration.

Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important ways for characterizing carbonaceous adsorbents. In this manner, the Langmuir and Freundlich isotherm equations were used to interpret the mechanism of the adsorption.The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The observed data on the adsorption of the dye at different temperatures have been analyzed on the basis of the Langmuir isotherm model.The linear plot of C_e/q_e vs C_e(Figure 5) confirms that in the present investigation, Langmuir isotherm model is suitable in explaining the adsorption process and also indicates the monolayer coverage of the dye CV onto the outer surface of the HC [20]. The Q_0 and b values, as given in Table 4, are obtained from the slope and intercepts of the linearized plots of the Langmuir isotherm. The values of correlation coefficient, r, obtained from linear plot (Figure 5) are listed in Table 4. The values are very close to unity which indicates the applicability of Langmuir isotherm model. The equilibrium adsorption data at different dye concentrations are fitted with Freundlich isotherm model [21].

where n and K_f (mg/g) are Freundlich constants related to the intensity of adsorption and adsorption capacity, respectively. The plot of log q_e against log C_e is shown in Figure 6. The values of K_f and n are calculated from the intercept and slope of these linearized plots and are listed in Table 5 along with the r values. The r values are very close to unity, which indicate that Freundlich isotherm is applicable.

The values of K_f, the Freundlich constants decrease with increase in temperature, showing the temperature dependence of the rate of sorption. The decrease in adsorption with increase in temperature suggests weak adsorption between the surface and sorbents, which supports physisorption. From the r values, it is found that both the Freundlich and Langmuir models are the best-fit models for the adsorption of CV onto HC.

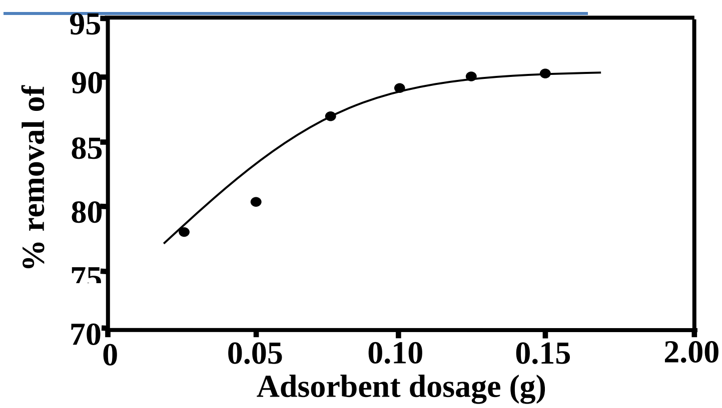

Figure 3. Effect of adsorbent dosage on the removal of CV

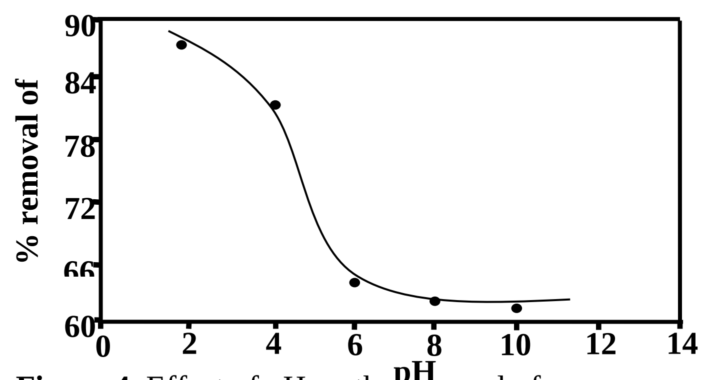

Figure 4. Effect of pH on the removal of CV

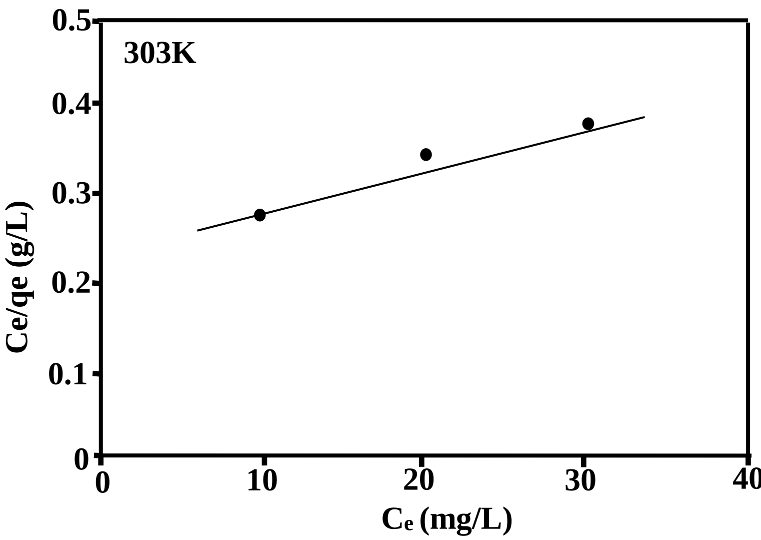

Figure 5. Langmuir isotherm of sorption of CV on HC at 303K

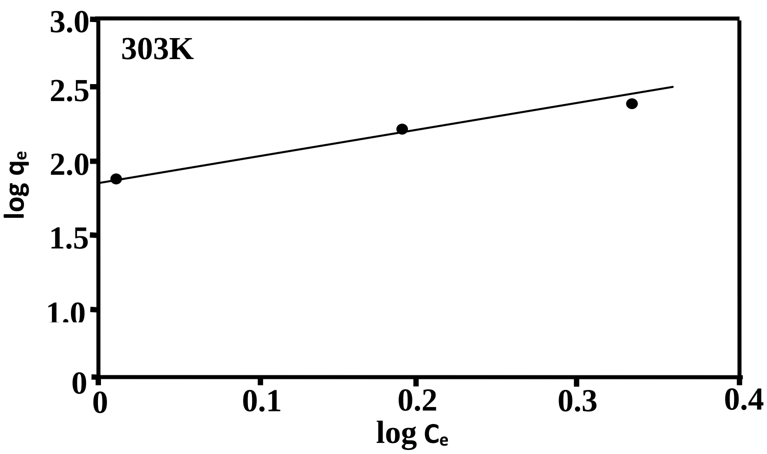

Figure 6. Freundlich isotherm of sorption of CV on HC at 303K

CONCLUSION

The present study shows that the Indian Hemp carbon is an effective adsorbent for the removal of crystal violet from aqueous solution. In batch mode adsorption studies, the adsorption was dependent on contact time, solution pH, and adsorbent dosage. Adsorption followed both the Langmuir and Freundlich isotherm models. The adsorption capacity was found to be more than 80 percent. Since the adsorbent used in this study is a cheap, readily available and medicinally significant, it can be used as an alternative for more costly adsorbents used for dye removal in wastewater treatment process.

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