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## Removal of Indigo Carmine from Aqueous Solution by Using Activated Carbon

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### ABSTRACT

In this work, we reported the feasibility of removal of Indigo carmine dye by using activated carbon prepared from *Delania regia*. Batch adsorption studies were carried out for removal of indigo carmine as a function of initial concentration of the dye, pH, contact time, particle size, adsorbent dosage, and temperature. Freundlich, Langmuir isotherm models have also been applied to the equilibrium adsorption data. The adsorption capacity of oxidized carbon adsorbent was systematically studied by varying the initial concentration of dye solution between 100-500 mg/L and at optimized condition 4.0 g of dose, 35 min contact time and 3.0 pH of the reaction media.

**Keywords:** Indigo carmine, adsorption, Activated carbon, Equilibrium studies

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## INTRODUCTION

Organic dyes constitute one of the larger groups of pollutants in wastewater released from textile and other industries. The discharge of highly colored wastewater into the ecosystem involves environmental problems like aesthetic pollution, and perturbation of aquatic life. Among the most useful dyes, there is indigo carmine or 5,5'-indigodisulfonic acid sodium salt, is a pH indicator with the chemical formula  $C_{16}H_8N_2Na_2O_8S_2$ .

Apart from its use as textile colouring agent and additive in pharmaceutical tablets and capsules as well as in confectionery items, indigo carmine is also used for medical diagnostic purposes. In conjunction with acetic acid the dye facilitate diagnosis of Barrett's esophagus [1]. It can also help to target biopsies even better, since in homogeneously stained or unstained areas seem to correlate with intraepithelial neoplasia[2]. Indigo carmine, however, is not readily metabolized but is rather freely filterable by the kidneys. Giving intravenous injection of indigo carmine for intra-operative cystoscopy is a safe technique that can detect otherwise undetected intra-operative compromise of the urinary tract [3]. It also contributes to intra-vital staining for contrasting and accentuating changed mucosal processes [4].

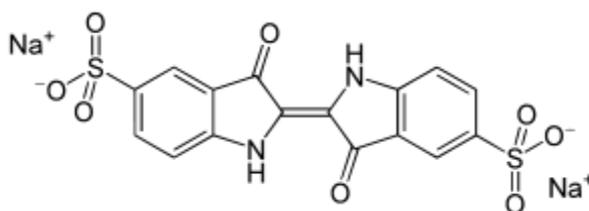


Figure 1: Structure of Indigo carmine.

The dye indigo carmine is considered a highly toxic indigoid class of dye and its touch can cause skin and eye irritations to human being. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye can also prove fatal, as it is carcinogenic in nature and can lead to reproductive, developmental, neuro and acute toxicity [5]. It has also been established that the dye leads to tumors at the site of application [6]. When administered intravenously to determine potency of the urinary collecting system, it has also been reported to cause mild to severe hypertension, cardiovascular and respiratory effects in patients [7-10]. It may also cause gastrointestinal irritation with nausea, vomiting and diarrhea [10, 11]. The toxicity tests of the dye revealed long-term toxicity in mice [11] and short-term toxicity in the pig [13].

The adsorption abilities of activated carbons are mainly determined by their physico-chemical nature of surface [28-30]. In the case of liquid adsorption systems, chemical properties of surface groups influence the adsorption equilibria to a large extent [31-34]. Adsorption affinity of activated carbons towards solutes of different polarity depends on the chemical character of carbon surface. A significant role is described to the surface functional groups containing various hetero atoms (mainly oxygen). The influence of surface oxides of activated carbon on adsorption uptake was analyzed; the magnitude of adsorbate preferential adsorption was related to the number of surface species of appropriate polarity [31]. Its physical properties are more important in the industry due to how it is classified; commercially made activated carbon is separated into several categories, defined by their

physical attributes. However, due to the properties of activated carbon, it only binds with certain chemicals. Correct pore size distribution is necessary to facilitate the adsorption process by providing adsorption sites and the appropriate channels to transport the adsorbate. The properties of activated carbon are mainly derived from its high surface area and porosity, which can only be observed with a microscope. The surface area is able to expand if combined with a plausible chemical.

The developed method for the removal of indigo carmine from aqueous solution has been found easy, versatile and economic because of easy operation, simple design and less investment. The data reported in the present study include equilibrium uptake of dye at a particular concentration, pH, temperature and adsorption kinetics etc.,

### MATERIALS AND METHODS

All the chemicals used are of analytical reagent grade and all reagents were prepared by using redistilled water. The reagents prepared are: Stock solutions of Indigo Carmine (1000 mg/L) were prepared and suitably diluted to the required initial concentrations. The Elico – pH Meter, model number L1-1201 was used to measure the pH of the solutions. Adsorption experiments were carried out at room temperature ( $30\pm 1^\circ\text{C}$ ) under batch mode. The initial concentrations ( $C_i$ ) of dye solutions were obtained by measuring Optical Density at 707 nm for Indigo Carmine using UV–visible spectrophotometer or colorimeter method.

Exactly 100 ml of dye solution of known initial concentration ( $C_i$  range: 100-250 mg/L) was shaken at the constant agitation speed (200 rpm) with a required dose of carbon (range 0.5–5.0 g/L), of a fixed particle size (pan size) for a specific period of contact time (range: 10–60 min) in a thermostatic orbit incubator shaker (magnetic stirrer), after noting down the initial pH of the solution (pH=3.0). The pH of the solutions were adjusted to the required value (range: 3.0–10.0) by adding either 1M.HCl or 1M.NaOH solution. After equilibration, the final concentrations ( $C_e$ ) were measured at 707 nm for Indigo Carmine by colorimeter method.

The percentage removal of dye and amount adsorbed (mg/g) were calculated using the following relationships:

$$\text{Percentage removal of Indigo Carmine} = 100 \frac{(c_i - c_e)}{c_i} \quad \dots\dots\dots 1$$

$$\text{Amount adsorbed} \quad q_e = \frac{(c_i - c_e)}{m} \quad \dots\dots\dots 2$$

Where  $C_i$  and  $C_e$  are the initial and final concentrations (mg/L) of dye, respectively and  $m$  is the mass of carbon (mg/L). Blanks containing no dye were used for each series of experiments as controls. The average values of duplicate runs were obtained and analyzed. Error in data:  $\pm 1-2\%$  for percentage removal  $\pm 0.005-0.01$  mg/g for amount adsorbed.

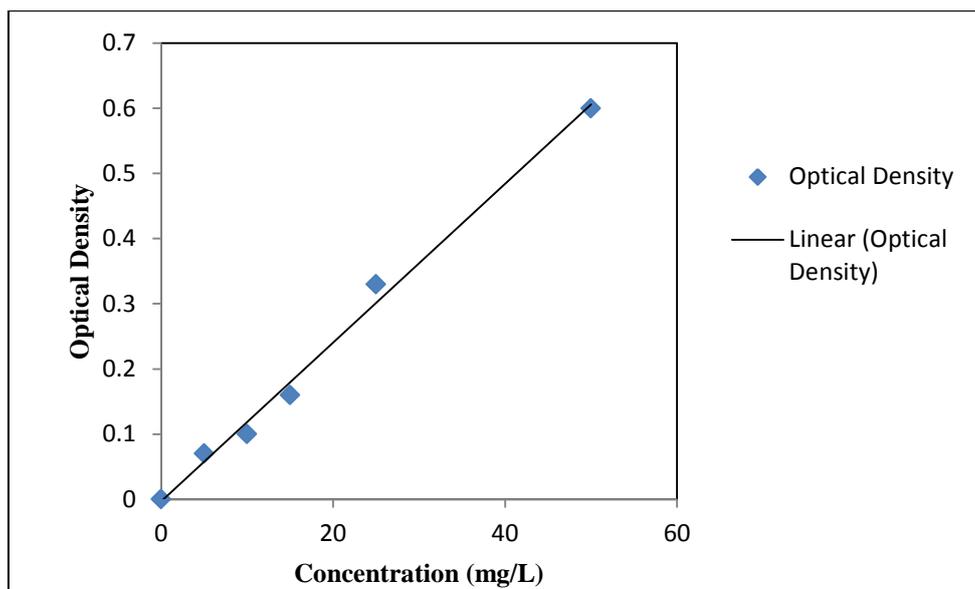


Figure 2: Calibration Chart

## RESULTS AND DISCUSSION

### Effect of Dye Concentration

For a strict adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial dye concentration. The adsorption capacity of oxidized carbon adsorbent was systematically studied by varying the initial concentration of dye solution between 100-500 mg/L and at optimized condition 4.0 g of dose, 35 min contact time and 3.0 pH of the reaction media. The percent removal with respect to the initial concentration of dye is represented in Figure 3.

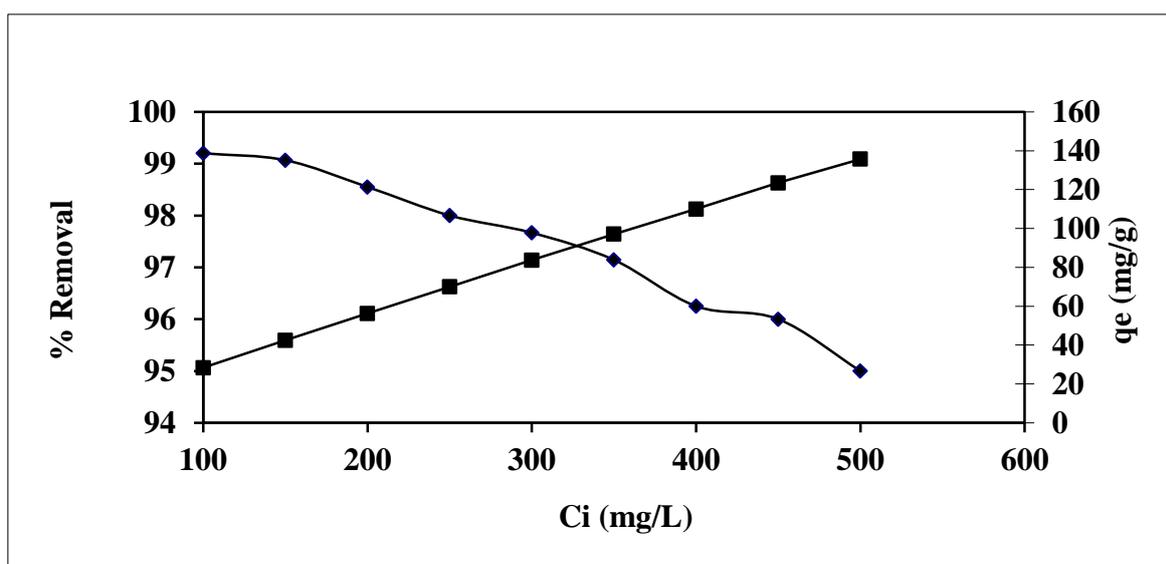


Figure 3: The plots showing the relationships between percent removals and amount adsorbed of dye by adsorption with prepared carbon.

The amount adsorbed exponentially increase while the percentage removal exponentially decrease with the increase in initial concentration of the dye. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface, compared with the relatively large number of active sites required for the high initial concentration of dye.

### Effect of pH

The pH of the aqueous solution is an important controlling factor in the adsorption process and thus the role of hydrogen ion concentration is examined at different pH levels of 3-10, which is maintained by adding 1M solutions of HCl and NaOH with 100 ml of standard dye solutions of 100 mg/L of with a contact time of 35 min., and a dose of 4.0 g/L for IC adsorbent carbon that are treated. The influence of the pH on the sorption rate is shown in Figure 4.

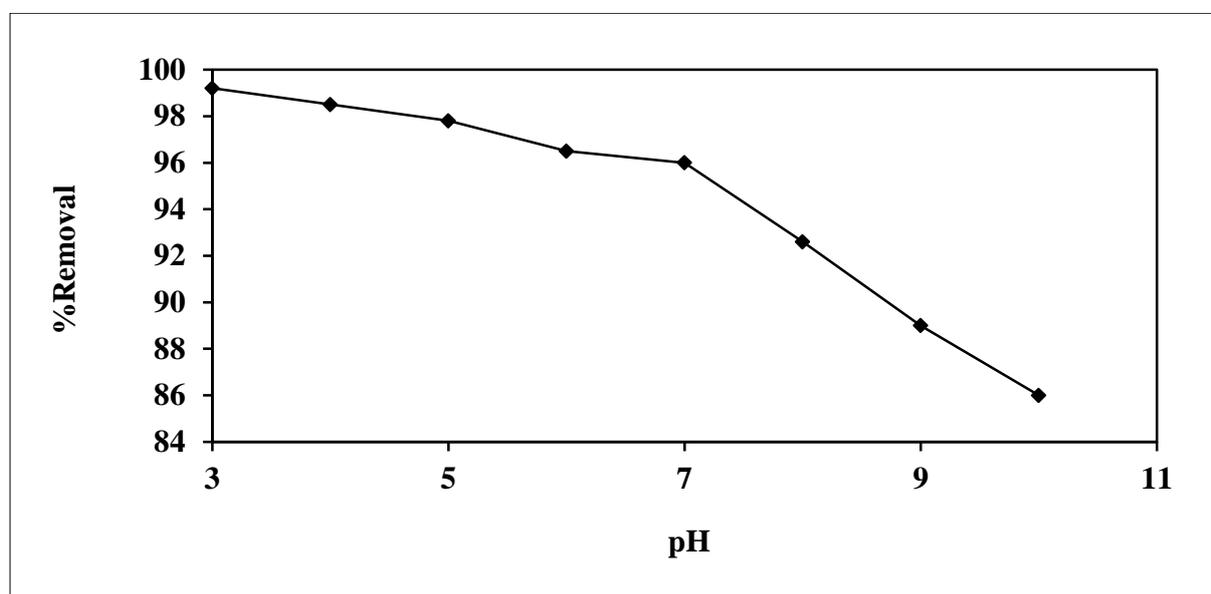


Figure 4: Plots showing the relationship between pH of initial dye solution and % removal of Indigo Carmine by adsorption with adsorbent carbon.

It is observed that from the figure that the percent removal is pH dependant. The results obtained show that the maximum efficiency of Indigo Carmine removal in decreases with increase pH value i.e. from acidic media to alkaline media and the maximum absorption 3.0, but the dye removal capacity is negligible after 9.0. The results agree well with those reported by others in the study of Indigo Carmine. Hence further studies were conducted with this pH value.

### Effect of agitation time

In the adsorption system contact time place a vital role, irrespective of the other experimental parameters that affect the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of dye by adsorbent, the adsorption experiments are conducted

and the extent of removal of dye is conducted by varying the contact time (range: 5-60 min) at optimum conditions.

The percentage dye removal at different time was worked out using equation 1 and a plot was prepared between the percentage dye removal and contact time Figure 5. It can be noted that the percentage dye removal is increasing with time and attained almost an equilibrium condition (at which the rate of adsorption of solute is equal to the rate of desorption).

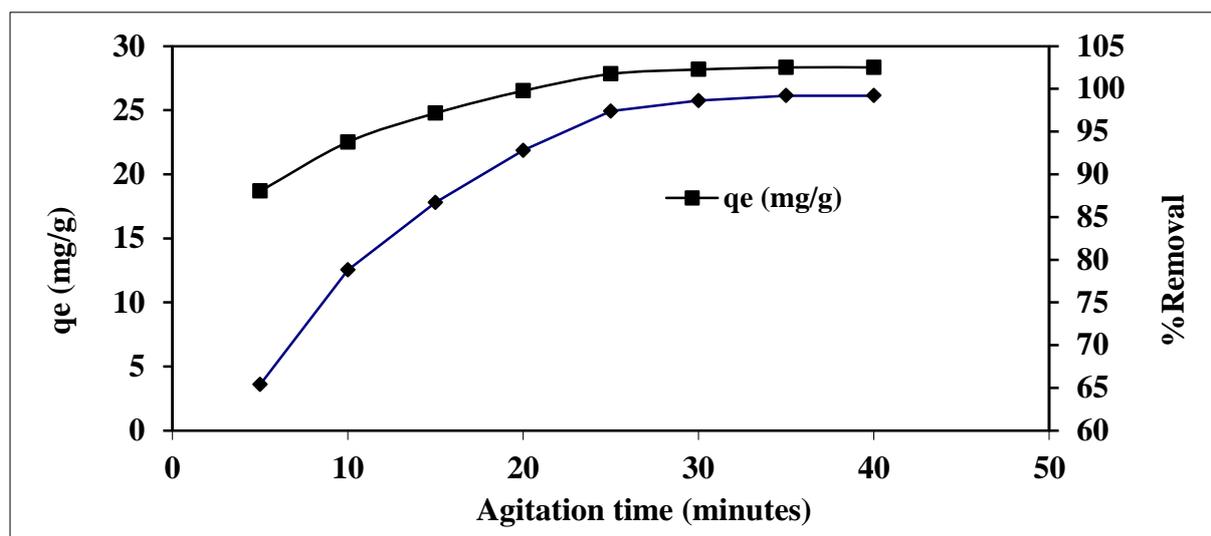


Figure 5: The Effect of Agitation Time on the percentage Removal and Amount adsorbed of dye.

In about 35 minutes the decreasing removal rate, particularly towards the end indicates a possible monolayer of dye on the outer interface of the carbon and pore (Intraparticle) diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitation maintained during the experiments. The data also indicate the removal of dye by this adsorbent sample is rapid at the initial period but becomes slow and almost stagnates with the increase in the contact time. The relative increase in the extent of removal of dye is substantially low after 35 min of contact time and it is negligible after 40 min, which is fixed as the optimum contact time. This indicates that the rate of removal of dye is higher in the initial stage due to the availability of adequate surface area of the adsorbent. With increase in contact time and due to the decrease in the availability of active sites the adsorption process decrease. Though equilibrium of the adsorption process was found to be attained in about 35 minutes, the particle contact time for the adsorption process under the condition chosen may be taken as 35 minutes as most of the dye ions are absorbed by them. The higher initial rate of removal may be occurring due to the vacant adsorption sites, high solute concentration gradient and the electrostatic affinity between the adsorbent and the solute.

### Effect of adsorbent quantity

The percentage removal of dye by adsorption with the selected adsorbent is obtained with various doses of adsorbents (range: 0.5 – 6.0 g/L), with optimum initial concentration of Indigo Carmine (100 mg/L) and contact time (35 min) at  $29 \pm 1^{\circ}\text{C}$ . Dye

uptake by selected adsorbent as a function of adsorbent concentration is depicted in Figure 6.

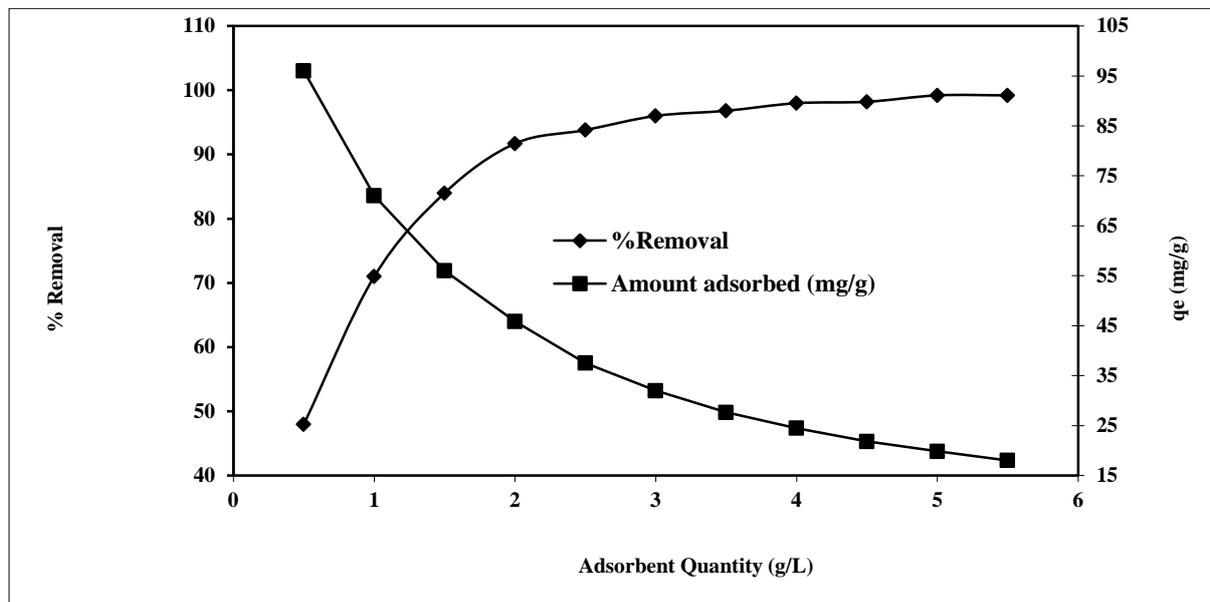


Figure 6: The Effect of Adsorbent dosage on the percentage Removal and Amount adsorbed of dye.

The percentage removal of dye increase with increase in dose of adsorbent and it is due to the increase in the availability of number of active sites owing to the increase in the effective surface area resulting from the increase in dose of adsorbent and conglomeration of the adsorbent particles, especially at the higher doses of adsorbent.

In the present investigation relative percentage removal of Indigo Carmine is found to be insignificant after a dose of 4.0 g/L in Indigo Carmine, so which is fixed as optimum dose of adsorbent and this variations of requirement of doses may be expected from variation in sorption activity of two dye.

### Effect of temperature on adsorption process

Temperature has important effects on the adsorption process. As the temperature increase, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increase. Changing to temperature will change the equilibrium capacity of the adsorbent for particular adsorbate. Figure 7 shows effects of different temperatures for Indigo Carmine adsorption on activated carbon. The removal of Indigo Carmine by adsorption on carbon adsorbent increase slightly from 27.98 to 28.56 mg/g for Indigo Carmine, when concentration is 100 mg/L, and increasing the temperature of the solution from 298 to 318 K, indicating the process to be endothermic.

### Effect of particle size

Experiments were conducted to evaluate the influence of the adsorbent particle size for a constant weight on the removal of Indigo Carmine. Particle size analysis was conducted on prepared carbon and the percentage composition of particle size is investigated. The

results obtained with the variation of adsorbent particle size and percent removal ions are graphically represented in Figure 8. The uptake of Indigo Carmine at different adsorbent mesh sizes increased with decreased in the particle diameter. The presence of larger number of smaller particles provides the sorption system with larger surface area available for Indigo Carmine removal and also it reduces the external mass transfer resistance. Also the time required for 50 % of the total adsorption is also less with the particles of smaller size. This also gives some idea of rate limiting step of the adsorption process. In the present investigation the largest mesh size of 150 and pan particle size the percent removal was found to be almost 100%. Small particle provides more active surface area and hence such results were observed.

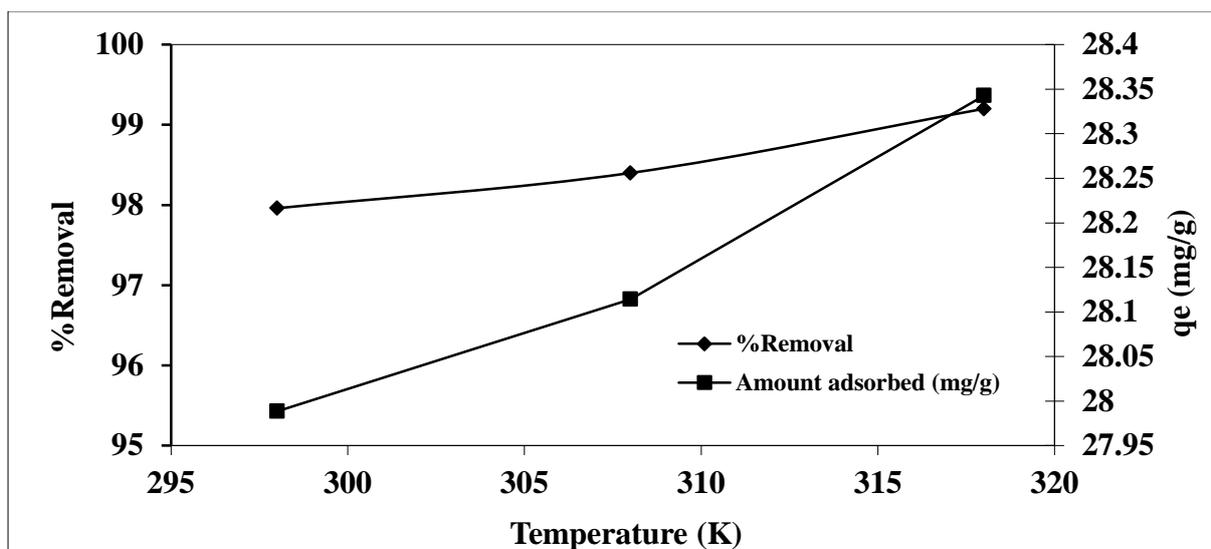


Figure 7: The Effect of temperature on the % removal of dye ( $C_i$ = Conc.100 mg/L, Time 35 min, and pH = 3.0)

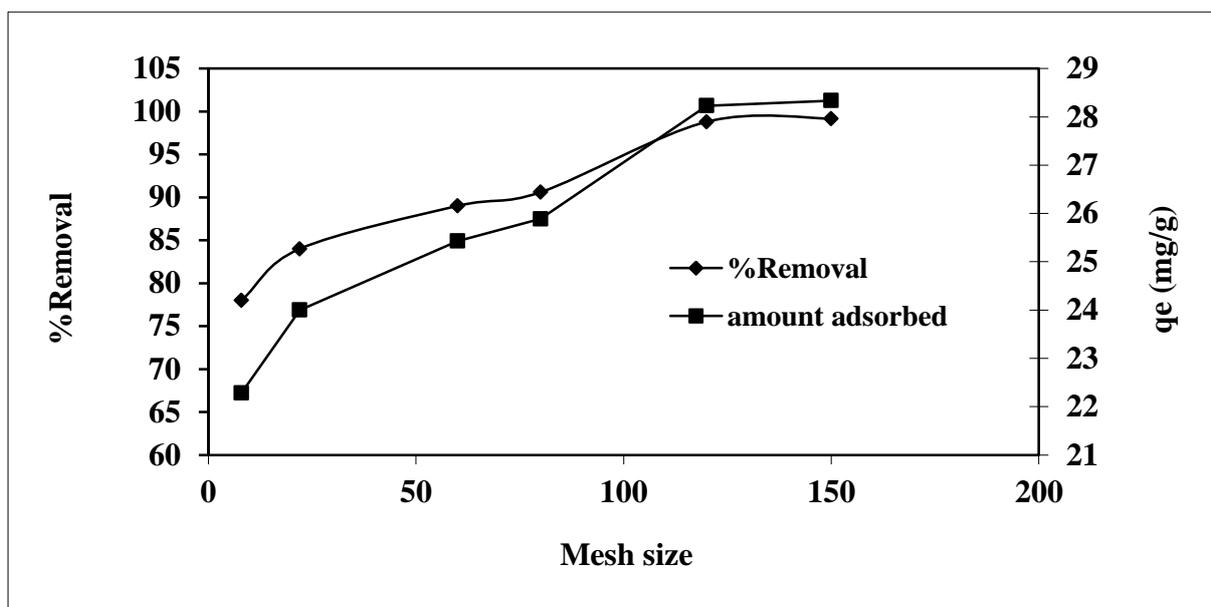


Figure 8: The Effect of particle (mesh) size on the % removal and amount adsorbed dye.

## Isotherms and Kinetics

### Freundlich Isotherm

The linearised Freundlich adsorption isotherm, which is of the form

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \dots\dots\dots 3$$

Where,  $K_f$  and  $1/n$  are the Freundlich constants,  $q_e$  is the amount of dye adsorbed per unit weight of the adsorbent (in mg/g), and if  $1/n < 1$  bond energies increases with surface density, if  $1/n > 1$ , bond energy decreases with surface density and if  $1/n = 1$ , all surface sites are equivalent, related to sorption capacity and sorption intensity respectively. In the present adsorption study these  $1/n$  value is 0.37 for Indigo Carmine adsorption. The results indicate  $1/n < 1$  i.e bond energies increases with surface density.  $C_e$  is the equilibrium concentration of dye (in mg/L). The isotherms exhibited the Freundlich behavior,  $R^2$  0.98 for the IC dye, which indicates a heterogeneous surface binding. Linear plots of  $\log (C_e)$  Vs  $\log (q_e)$  at different dye concentrations are applied to confirm the applicability of Freundlich isotherm model for the removal of dyes is shown in Figure 9.

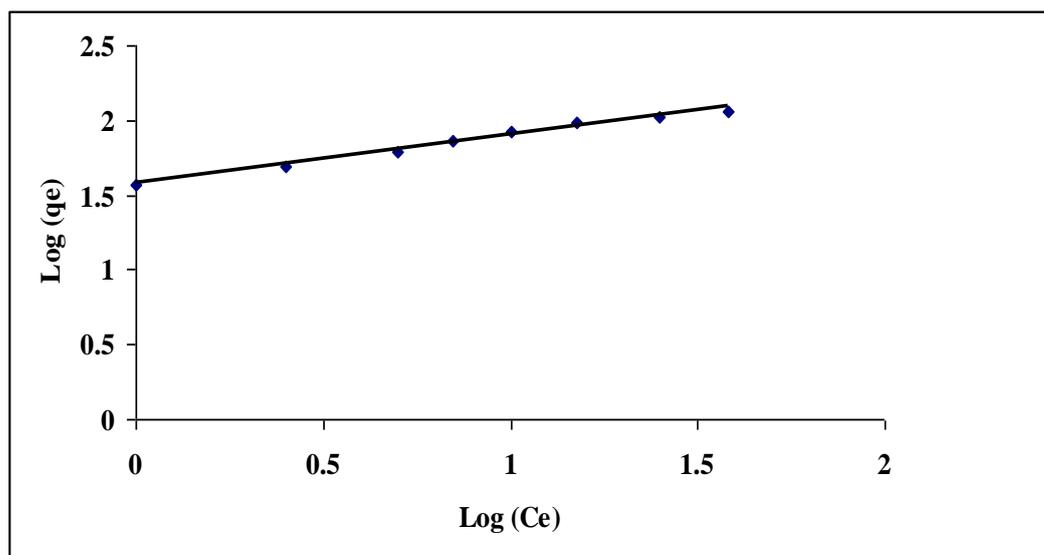


Figure 9: Freundlich isotherm for the removal of IC by adsorption with prepared carbon

### Langmuir Isotherm

The Langmuir adsorption isotherm has been successfully applied to many adsorption processes and it has been used here to explain the sorption of cationic dye onto carbon. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place. Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities

for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as

$$\frac{C_e}{q_e} = \left( \frac{1}{Q_0 b} \right) + \frac{C_e}{Q_0} \dots 4$$

Where  $q_e$  is the amount adsorbed (mg/g) and  $C_e$  is the equilibrium concentration of adsorbate (mg/L),  $Q_0$  and  $b$  are the Langmuir constants related to capacity and energy of adsorption, respectively. When  $C_e$  is plotted against  $C_e/q_e$ , a straight line with slope  $1/b$  is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Figure 10.

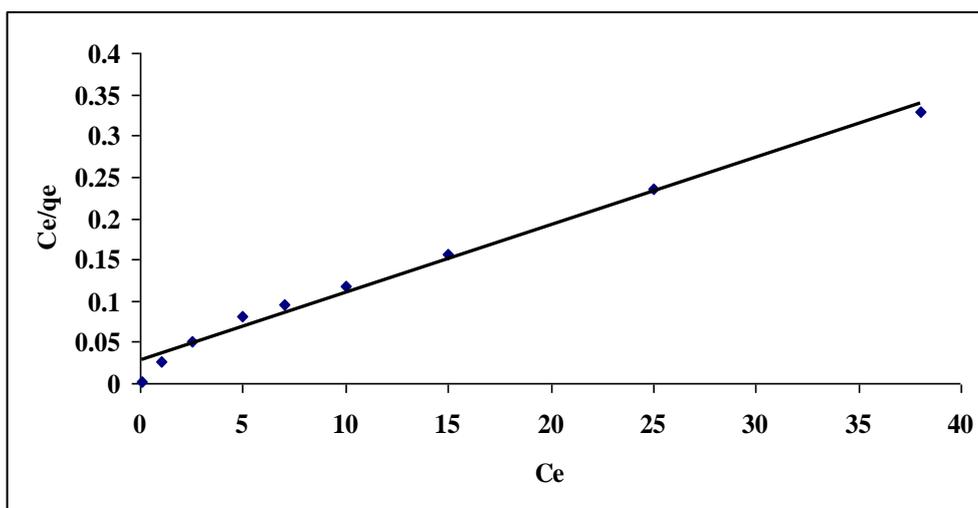


Figure 10: Langmuir isotherm for the removal of Indigo Carmine by adsorption with prepared carbon

### CONCLUSIONS

The studies indicate that adsorbent activated carbon can be successfully used for the removal of hazardous dye, indigo carmine from aqueous solutions. The results of the experiments have shown that the percentage of Indigo Carmine removal has increased with the increase of contact time, temperature and dosage of adsorbent. On the contrary, the percentage of removal has decreased with the increase in initial concentrations of standard Indigo Carmine solution, pH and increase in particle size of the adsorbent. The adsorbent process validate Langmuir and Freundlich adsorption isotherms and thermodynamic parameters obtained by the adsorption isotherm data confirm the feasibility of the process .

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