



RESEARCH ARTICLE

ADSORPTION OF BISMARCK BROWN ONTO ACTIVATED CARBON FROM CORN COBS

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ABSTRACT

Adsorption of a basic dye, Bismarck brown, from aqueous solutions onto acid activated corncobs was investigated. Various experiments were undertaken in a batch adsorption technique to study the effect of the process variables, which include initial pH, adsorbent dosage, initial dye concentration, particle size, temperature and agitation speed. The adsorption of Bismarck brown on to the adsorbent was found to improve with the increase in adsorbent dosage, finer the mesh size and at a neutral pH (value ranging from 6-8). It was observed that the adsorption was better with increasing temperatures and the process was endothermic with a ΔH value of 35.698KJ/mole and the kinetics followed was first order in nature. The results showed that both Langmuir and Freundlich isotherms fit the equilibrium data. Also, the results revealed that activated carbon from corncob, a waste material, proved to be an excellent low-cost sorbent.

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INTRODUCTION

Colored compounds comprising pigments and dyes are used widely in textile and leather dyeing, paper, printing, pharmaceutical and cosmetic industries. 10,000 different dyes weighing about 0.7 million tons are produced annually for various industrial processes (Zollinger, 1987). A percentage of these dyes are lost in the effluent during the dyeing process. Many of these are toxic or even carcinogenic (Rnmin Gong *et al.*, 2005). Discharge of these into water bodies would pollute the water

and make it unfit for aquatic life by their toxicity. Further, the dyes would color the water and make penetration of sunlight to the lower layers impossible. So, it is not possible for aquatic plants to perform photosynthesis (Reife and Fermann, 1996). Polluted water not only damages plants and animals but also harms the environment. Majority of these dyes are stable to light and oxidation. They are immune to aerobic digestion. Biological treatment may remove BOD, COD and suspended solids but remains ineffective in removing the color of dyes. Many physical methods such as adsorption, coagulation, precipitation and filtration have been attempted for treatment of dye

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containing effluent. Chemical methods such as oxidation have also been used. Biological methods would be economically simple but most dyes are resistant to bacterial degradation (Reife and Fermann, 1996).

The potential of various methods have been explored and adsorption of the chemical dyes has been found to be the most effective. Commercially available activated carbon as an adsorbent has yielded excellent results (Walker and Weatherly, 1998). However, taking into account the high costs involved in such a process, feasibility of alternate adsorbents have been studied. These include industrial as well as agricultural byproducts. Industrial waste products include slurry from fertilizer plant and blast furnace slag. A variety of agricultural products have been used namely rice straw, coconut husk, rice husk, bagasse and tree bark (Gupta *et al.*, 2003). In a country like India where agriculture is the primary occupation, corncobs, an agricultural waste is abundantly available. There is need to develop cost effective low cost adsorbent from waste biomass. The area under maize cultivation in India is 6.5 million hectare with a production of 11.8 million tons (Anon, 2004). Dissection of five maize plants of single variety shows that grain represents 38% of the biomass (dry weight basis), 16% cobs and ear husks, remaining 46% consists of leaves, sheaths and stalks (Anon, 2004). Presently, the cobs alone are used in making paper, light packing material, fuel, smoking products and as a source of charcoal. Here we are reporting preparation of low cost active adsorbents from corncobs waste biomass and its utilization in removal of color (Bismarck brown as a model dye) from simulated dye bath effluents.

MATERIALS AND METHODS

Materials

Bismarck brown a cationic dye was supplied by S.D.Fine Chemicals, India. Sodium hydroxide, hydrochloric acid, and sulfuric acid were received from E.Merck Limited Mumbai, India. Preparation of activated carbon from corn cobs biomass. Corncobs, which has been used as the sorbent in this study was obtained from local agricultural field

(after grains being removed) and the waste cob alone was cut into pieces and activated by soaking it in concentrated sulfuric acid 1:2 (w/v) for 48 hours. The charred material was then removed, washed several times to remove the excess acid and soaked in distilled water for 24 hours till its wash water attained neutral pH. The water was then drained off and the material was dried in a hot air oven at a temperature of 110°C till moisture was completely removed. The dried material was then ground using mortar and pestle. The activated carbon thus obtained was then sieved into three different sizes, which are, 100 mm size, 36 mm size and 18mm sizes. These samples were stored in separate airtight containers free from moisture until further use.

Batch adsorption experiments

Stock solution of 5000 ppm was prepared by dissolving appropriate amount of Bismarck brown and further dilutions were made to get particular concentrations of adsorbate in the batch experiments. Adsorption experiments were conducted in a batch reactor system. An orbital shaker, Orbitek, Scigenics (Biotech. Pvt Ltd, Chennai, India) was used for the experiments. The temperature was set at 30°C and the agitation speed was set at 100 rpm. Experiments on pH variation, adsorbent dosage and variation in concentration were carried out for 100 mm size, 36 mm size and 18 mm sizes. Different pH solutions ranging from 1-12 pH were prepared in separate flasks using distilled water. 0.1 N HCl and NaOH solutions were used to adjust the pH of the solution accordingly. A known weight of adsorbent of 100 mm size was added to each of the flasks and was kept in the shaker for 24 hours. After a period of 24 hours, the samples were centrifuged and analyzed in the UV spectrophotometer. The absorbance measured was then converted to concentration and the percentage removal was assessed. The amount of adsorbent (100 mm size) used was varied in the 12 flasks having equal amounts of dye solution of the same concentration. The adsorbent dosage varied from 0.001g, to 1g. After 24 hours the samples were withdrawn and analyzed. The experiment was repeated for 36 mm size and 18 mm sizes. The optimum adsorbent

dosage in each mesh size was thereafter standardized. To understand the maximum uptake of the adsorbent and its behavior at very high dye concentrations, solutions of various concentrations ranging from 1 ppm to 5000 ppm were prepared in separate 100ml conical flasks. The standardized adsorbent dosage of 100 mm size was transferred into each of the conical flasks. These flasks were placed in the orbital shaker for 24 hours and the readings were taken after centrifuging. To study the effect of agitation, agitation speed was varied from 50 rpm to 200 rpm for a single concentration of dye of the same volume. Samples were withdrawn at intervals to understand the rate at which equilibrium is reached.

Adsorption Kinetics

Kinetic Study is important to study the rate of the adsorption process and understand when the steady state condition is reached after equilibrium. 250 ml Bismarck brown dye solution of varying concentrations, 50 ppm, 100 ppm, and 300 ppm were prepared and transferred into separate 250 ml conical flasks. The standardized adsorbent dosage of 100 mm mesh size adsorbent was transferred into each of the conical flasks and kept in an orbital shaker. Samples were withdrawn for every 5 minutes initially and centrifuged. The time gap for the withdrawal of successive samples was increased to 15 minutes, half an hour, 1 hour, and 2 hours and so on. The flasks were kept in the shaker for a total period of 360 minutes, to allow complete equilibration even for high concentrations. The samples thus obtained were withdrawn and centrifuged. The percentage removal of dye from solution is then analyzed

Analysis of dye

The concentration of Bismarck brown dye before and after the adsorption processes were monitored using UV-visible spectrometer (Shimadzu 2101 PC) at λ_{\max} 516 nm.

RESULTS AND DISCUSSION

Variation in pH

pH studies are initially done to standardize the pH at which the adsorption studies should be carried out.

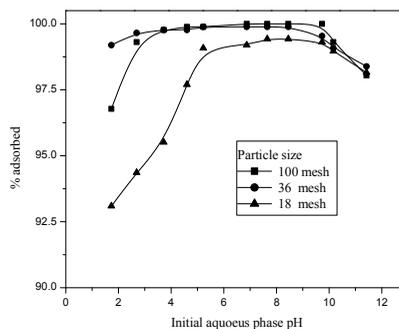


Fig. 1. Effect of pH with initial concentration of 10 ppm, 10 ml solution, 30°C, 100 rpm

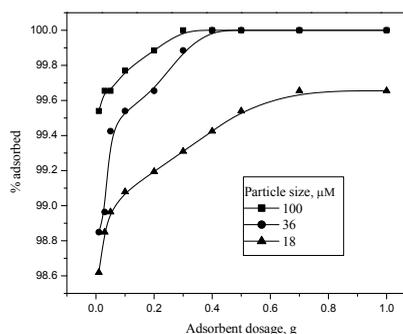


Fig. 2. Variation in adsorbent dosage with initial dye concentration of 10 ppm, 10 ml solution, 30°C, 100 rpm, neutral pH.

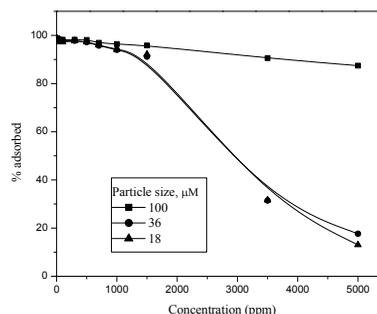


Fig. 3. Variation in initial dye concentration, 0.2g sizes, 1 ml solution, adsorbent for 100 mm, 0.3 g for 36 mm and 0.5 g for 18 mm 30°C, 100 rpm, at neutral pH.

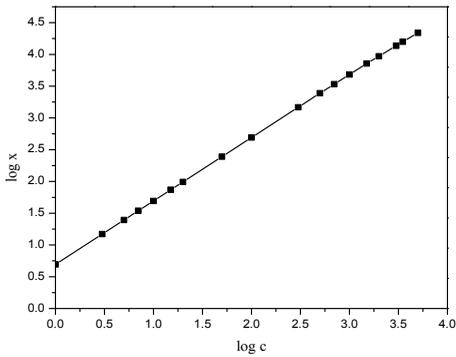


Fig. 4. Freundlich Isotherm

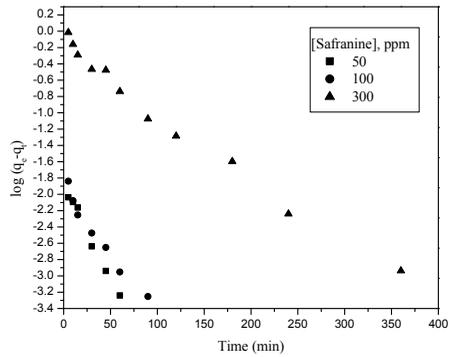


Fig. 7. Pseudo first order kinetics, 100 rpm, 250 ml, neutral pH, 5g adsorbent, neutral pH.

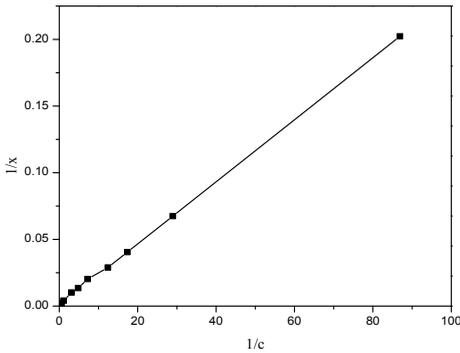


Fig. 5. Langmuir Isotherm

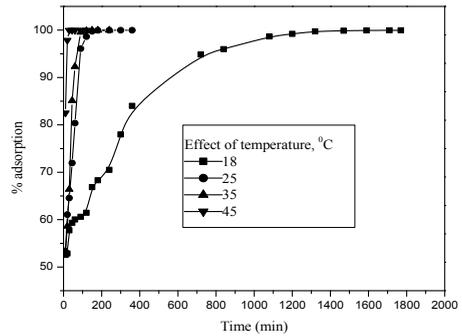


Fig. 8. Effect of temperature, 300 ppm, 100 rpm, 5g adsorbent, neutral pH

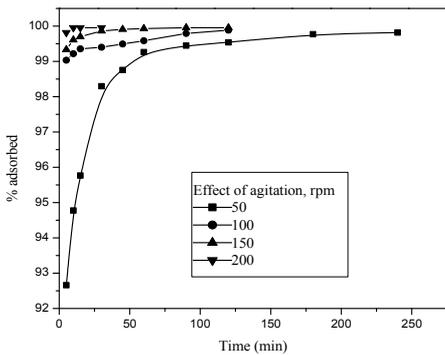


Fig. 6. Effect of agitation speed, 100mm size, 5g adsorbent, 300 ppm.

It was evident that the adsorbent showed best adsorption in neutral pH ranging from 6 to 8 as shown in graph. The experiment was repeated for 36 mm size and 18 mm sizes and a similar trend was seen in both the cases. Hence it was concluded that the adsorbent worked best in a neutral pH range. The reason could be because the basic dye becomes protonated in acidic medium and deprotonization takes place as the pH is increased. It remains almost constant for a pH range from 6-8 and thereafter there is a fall in the percentage removal. A similar kind of result is seen in literature (Gupta *et al.*, 2003).

Variation in adsorbent dosage

Increasing the adsorbent quantity provides more adsorption sites for the dye. As the adsorbent dosage increases, the available sites increase and consequently better the adsorption. However, review of literature reveals that with increasing dosage, the efficiency is not observed to increase in linear proportion. Records show that only up to certain stage there is linear relationship, beyond which there is only marginal raise in the percentage of dye removal. It is in this context, optimum adsorbent dosage requires standardization (Khanidtha Marungrueng and Prasert Pavasant, 2005). It was seen that 0.2g for 100 mm size, 0.3g for 36 mm size and 0.5 g for 18 mm mesh size for 10ml dye solution of 10 ppm was the optimum adsorbent dosage. This amount of adsorbent was standardized for further experiments.

Variation in initial concentration

The adsorbent had the capacity to remove up to 90% color even for a concentrated solution of 3000 ppm for the adsorbent mesh size of 100 mm. Almost 50% color removal was seen for 3000 ppm when the adsorbent mesh size used was 18 mm. The adsorbent was capable of color removal at very high concentrations as shown in graph.

Adsorption Isotherms

The two isotherms used to describe the adsorption process are Langmuir and Freundlich. The Langmuir model is based on the assumption that maximum adsorption corresponds to saturated monomolecular layer of dye molecules on the surface of the adsorbent. Langmuir isotherm is applicable to homogeneous sorption where the sorption onto each active site has equal activation energy. Freundlich isotherm is an empirical. It assumes that the sites on the surface of the adsorbent have different binding energies. It is employed to describe heterogeneous systems.

Langmuir Isotherm is given as:

$$Q = \frac{Q_{max} b C_f}{1 + b C_f} \quad (1)$$

Where Q_{max} is the maximum dye uptake (mg/g), C_f is the equilibrium dye concentration (mg/l) solution and b is the Langmuir equilibrium constant (dm^3/mg) which relates to adsorption energy. For fitting the experimental data, the Langmuir model is linearized as follows (Langmuir, 1916).

$$1/Q = 1/Q_{max} + 1/b Q_{max} C_f \quad (2)$$

The Freundlich model is given by:

$$Q = K C_f^{1/n} \quad (3)$$

where K (dm^3/mg) and n are constants indicative of adsorption capacity and intensity respectively. For fitting the experimental data, the Freundlich model is linearized as follows, $\ln Q = \ln K + 1/n \ln C_f$ (Freundlich, 1906). The data for variation in concentration fitted both the above mentioned isotherms and the values of the Langmuir and Freundlich isotherms are as reported in Table1. The fit for Freundlich and Langmuir isotherms are as shown in Fig.4 and Fig. 5.

Effect of particle size

Finer the particle size, larger the surface area, better the area of contact between the adsorbate and adsorbent and hence better the adsorption capacity. There is a tendency that smaller particles take shorter time to equilibrate (Freundlich, 1906; Vasanth Kumar *et al.*, 2005; Reyad *et al.*, 2003). It is evident that 100 μ m mesh size when compared to 36 mm size and 18 mm sizes showed better adsorption characteristics.

Kinetics study

The kinetic study for any experiment provides useful data regarding the efficiency of the process and feasibility for scale up operations. It represents the rate of adsorbate uptake by the adsorbent (Vasanth Kumar *et al.*, 2005). The pseudo first order rate equation (Lagergren, 1898) is used to describe the process and given as follows:

$$Dq_t/dt = k_1(q_e - q_t) \quad (4)$$

Where q_e and q_t are the adsorption capacities at equilibrium and time t respectively (mg/g) K_1 is the rate constant of pseudo I order expression. On

integration with limits from $t=0$ to t and $q_1=0$ to q_t , we have

$$\log(q_c - q_t) = \log(q_c) - ((k_1/2.303) * t) \quad (5)$$

The values of k for the varying concentration are as shown in Table 2. Also, the fit for pseudo First order reaction is as shown in Figure 6.

Effect of agitation

Varying the speed of agitation can always vary the rate of adsorption. By increasing the speed, the randomness increases which results in better contact between the adsorbate and adsorbent and hence enhancing faster rate of adsorption. It is quite obvious that adsorption should be better at higher speeds (Namasivayam *et al.*, 2004). A similar trend was followed in this case. The effect of agitation is as shown in Figure 8.

Effect of adsorption with temperature

Whether a process is endothermic or exothermic, it depends on the value of ΔH . Here, the value of ΔH was found to be positive and hence the reaction involved is endothermic. Also the negative value of ΔG indicates the spontaneous nature of adsorption of Bismarck brown on corncobs. The rate of adsorption at 18°C, 25°C, 30°C, 35°C and 45°C temperatures was studied by withdrawing samples at specific time intervals. Interestingly, it was seen that as temperature increases the rate of adsorption got quicker. The process was hence concluded to be endothermic and spontaneous. The effect of temperature is as shown in Figure 7.

Thermodynamics of adsorption

The kinetics of the rate of adsorption was assessed at different temperatures of 20°C, 30°C and 40°C. Thermodynamic parameters ΔG , ΔS and ΔH were calculated using the following equations and the values are as shown in Table 3. The negative values of ΔG^0 indicate the spontaneous nature of adsorbent on the dye. The positive values of ΔH^0 confirm the endothermic nature of adsorption (Gupta *et al.*, 2003).

$$\Delta G^0 = -RT \ln K \quad (6)$$

$$\Delta H^0 = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{K_2}{K_1} \right) \quad (7)$$

$$\Delta S^0 = (\Delta H - \Delta G) / T \quad (8)$$

where K_1 and K_2 are the Langmuir constants corresponding to the temperatures 20°C and 40°C.

Determination of activation energy for adsorption process.

The rate of a reaction depends on the temperature in which it is carried out. As the temperature increases, randomness increases and hence the molecules tend to collide more frequently. The molecules also carry more kinetic energy. In 1889, Svante Arrhenius showed that the relationship between temperature and the rate constant for a reaction obeyed the following equation.

$$k = Z e^{-E_a / RT} \quad (9)$$

where k is the constant for the reaction, Z is a proportionality constant that varies from one reaction to another, E_a is the activation energy for the reaction and R is the universal gas constant in J/mole K, T is the temperature in Kelvin. This equation can be used to determine the activation energy for the adsorption process. On taking natural logarithm on both sides we get,

$$\ln k = \ln Z - E_a / RT \quad (10) \quad \text{or}$$

$\ln k = (E_a / RT)(1/T) + \ln Z$. A plot of $\ln k$ vs $1/T$ should give a straight line with a slope of $-E_a / R$ as shown in Figure 9. The value of E_a hence calculated was found to be 114.62 KJ/mole.

Conclusions

The studies revealed that activated corncobs proved to be a good low-cost adsorbent. Freundlich and Langmuir isotherms fitted the data well. The thermodynamic studies showed that the process was endothermic and spontaneous and the kinetic data showed that the adsorption followed first order kinetics

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