

The Removal of Cationic Dyes Using Coconut Husk as an Adsorbent

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ABSTRAK

Eksperimen tentang penggunaan sabut kelapa sebagai satu penjerap bagi metilena biru telah dijalankan. Parameter yang dikaji termasuk kepekatan larutan pewarna masa tindakan, dos penjerap dan pH larutan. Keputusan menunjukkan bahawa isoterma Langmuir boleh digunakan pada sistem metilena biru – sabut kelapa. Di samping itu sabut kelapa adalah suatu bahan penjerap yang sesuai bagi metilena biru. Satu siri eksperimen mengenai padatan tetap telah dilakukan dan keputusan yang didapati dibandingkan dengan suatu model tinggi padatan/masa servis untuk penjerapan turus. Kesahan model ini juga dibincangkan.

ABSTRACT

The ability of coconut husk to remove methylene blue from solution was investigated. Factors such as initial dye concentration, contact time, adsorbent dosage and pH of solution were studied. Results show that Langmuir isotherm can be successfully applied to the methylene blue – coconut husk system and that coconut husk is a suitable adsorbent for such a dye. Maximum adsorption capacity is 99 mg g⁻¹ moss as derived from Langmuir isotherm. A series of fixed bed experiments was carried out and the results were applied to a bed-depth/service time model for column adsorption. The validity of such a model is discussed.

INTRODUCTION

The discharge of colour materials from industrial wastewaters into streams and rivers constitutes one of the major sources of water pollution. Owing to its colour, it is the most easily recognisable pollutant. Although it may be present in minute quantities, its presence is still clearly undesirable from the aesthetic point of view. The treatment of dyes in industrial wastewaters poses several problems as the dyes are generally stable to light and oxidation and hence they cannot be treated by conventional methods of aerobic digestion.

The adsorption process provides an attractive alternative especially if the adsorbent is inexpensive and readily available. The use of activated carbon for treatment of colour effluents has been investigated extensively (Molvar 1970; McKay, 1982). Fullers earth and bauxite have also been reported to be

successful in removing colour on a laboratory scale (Pearson 1913; Thorton and Moore, 1953).

Recently the use of low cost materials to remove colour has been reported by several workers. Poots and co-workers found that peat and wood can be successfully used to remove acid and basic dyes (1976, 1978). The sorption of ionic dyes on wool carbonizing waste was reported to be feasible (Perineau, 1980). The removal of cationic dyes using natural mosses was also reported by Lee (1987).

Coconut husk, a byproduct of coconut, is being used for the production of charcoal, fuel and brooms. According to the Department of Statistical Malaysia (1985), Malaysia produced a total of 120,195,000 coconuts in 1984. As the husk is readily available, we investigated the potential of such a material in removing dyes from solution.

The bulk of coconut husk is made up of cellulose and lignin (60%). The hydroxyl groups in these two polymeric substance provide sites for adsorption of dyes. Preliminary investigation showed that cationic dyes like Astrazone Red GTLN, Astrazone Pink FG, Astrazone Blue BG and methylene blue could be readily adsorbed on the husk. However, neutral dyes like methyl blue orange and phenol red showed no such activity.

In this paper, the adsorption characteristics of methylene blue-coconut husk system on a laboratory scale has been investigated. Parameters studied included adsorptive equilibria as function of concentration, dosage and pH. A series of fixed bed experiments was also undertaken and the results were applied to a bed-depth/service time (BDST) model for column adsorption. (Hutchins 1973).

MATERIALS AND METHODS

Sample Preparation

Coconut husks collected from a nearby estate were dried at room temperature. After removing the outer layer, the husk was ground and then treated with a mixture of formaldehyde/HCl according to the method of Randall (1978) for the treatment of peanut shell. It was then sieved in succession into various fractions after drying at 80°C. The largest fraction (55% by weight) of size 300–850 μ was used in all the experiments. Methylene blue of 82% purity (British Drug House) was used without further purification.

Contact Time Experiments

In all contact-time experiments, except where the effect of dosage of adsorbent was studied, 0.5 g of husk was shaken in 100 ml methylene blue solutions of varied concentrations. Aliquots of 1 ml solution were withdrawn at regular intervals for the analysis of the dye using a Shimadzu UV-160 spectrophotometer. All measurements were recorded at λ_{\max} 665 nm at room temperature.

In the study of the effect of adsorbent dosage on dye uptake, the weight of sample was varied from 0.25 to 1.5 g while the dye concentration was maintained at 250 mg l⁻¹.

The effect of initial concentrations was studied by varying the dye concentration of the dye solution from 50–500 mg l⁻¹.

The influence of pH was conducted under an equilibrium condition. The pH of the solution was adjusted by dilute HCl or NaOH before experimentation. A contact time of three hours with constant shaking was maintained. In order to eliminate the effect of pH on colour, all solutions were adjusted to the same pH that is 5.20 before measurements were recorded.

The reproducibility of the experiments was established by shaking four replicates of 100 ml 500 mg l⁻¹ methylene blue solution with 0.5 g coconut husk.

Adsorption Isotherms

Adsorption isotherms were obtained by shaking 0.25 g of coconut husk with 100 ml of dye solution for four hours. The concentration of the dye solution was varied from 250–1000 mg l⁻¹.

Fixed-bed Study

In the flow studies, vertical glass columns of internal diameter of 2.2 cm were used. The husk was packed to a height of 3, 6, 12, 18 cm corresponding to 0.625, 1.25, 2.50 and 3.75 g of samples respectively. Flow rate was controlled by means of a clip attached to the bottom of the column. Dye solution of 50 mg l⁻¹ was passed through the column and 250 ml-fraction were collected and analysed for methylene blue. The flow rate was varied between 25–75 ml min⁻¹.

RESULTS AND DISCUSSION

Reproducibility

The reproducibility of the experiments was established by shaking four replicates of 100 ml 500 mg l⁻¹ methylene blue solution with 0.5 g coconut husk. The relative standard deviation was found to be less than 4%.

Effect of pH

The effect of pH on the uptake of methylene blue by coconut husk is shown in *Fig. 1*. The adsorption capacity increased with increasing

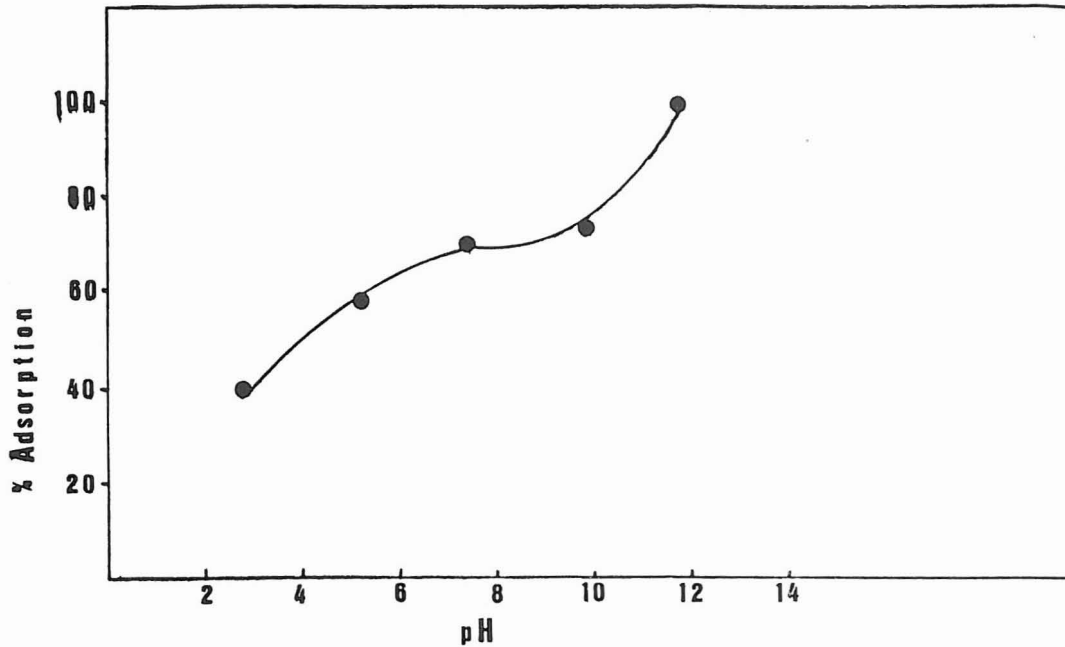


Fig. 1: Effect of initial pH on the uptake of methylene blue.

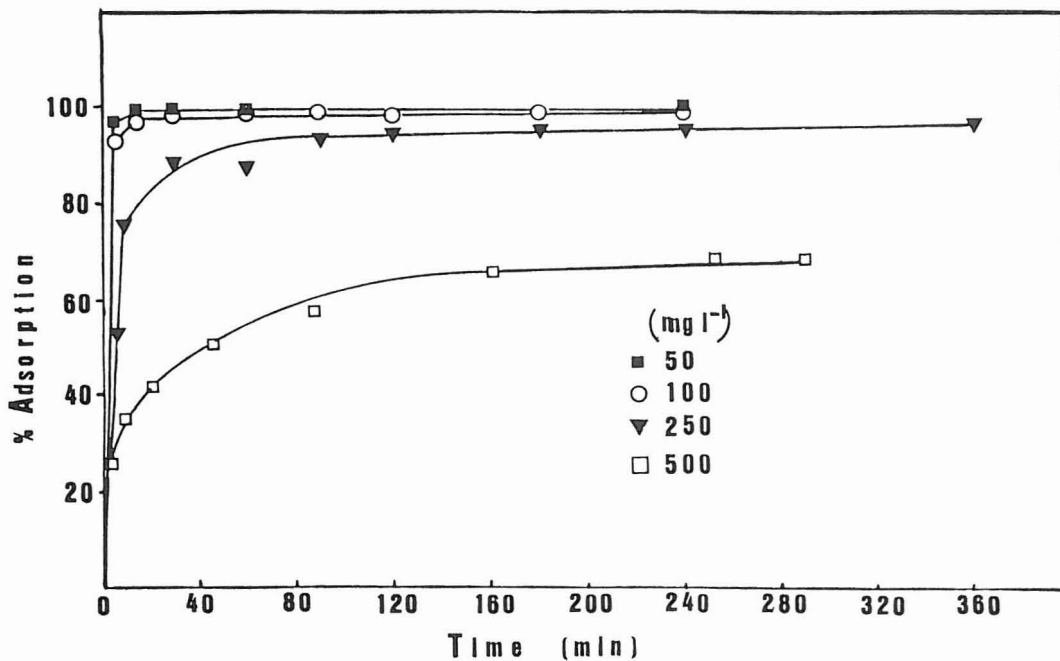


Fig. 2: Effect of concentration on the uptake of methylene blue. Condition: 0.5 g husk/100ml solution.

pH. At pH 12, almost 100% adsorption was achieved. This is attributed to the increasing electronegative charge of the adsorbent as the pH of the solution increases. A similar observation was also reported by Perineau and co-workers (1980) in their study of dye uptake by

wool carbonizing waste. However, subsequent experiments were performed without adjusting the natural pH of the solution, which was 5.20.

Effect of Initial Concentration

The influence of initial concentration on the

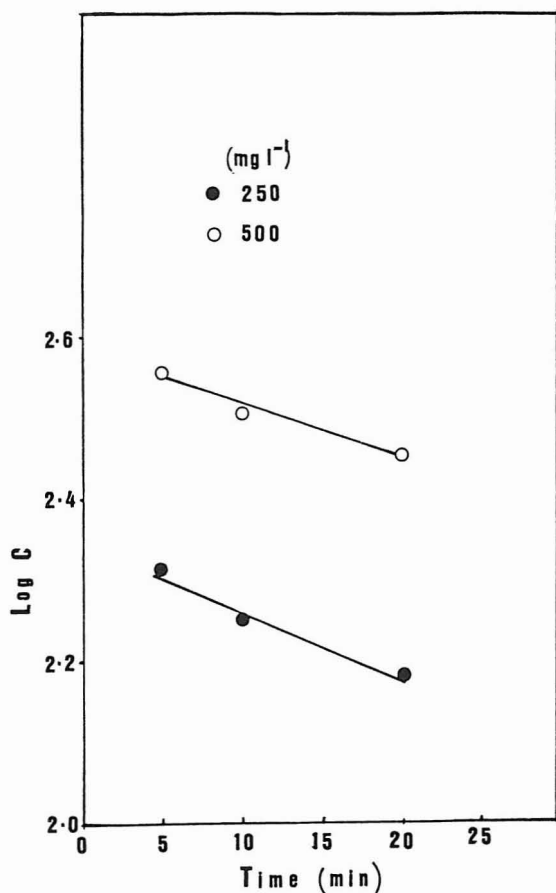


Fig. 3: Plots of log C against time.

adsorption of dye on coconut husk is shown in Fig. 2. The time taken to reach equilibrium increased with increasing concentration. For an initial dye concentrations of less than 100 mg l⁻¹, saturation was attained in less than 20 minutes. This was increased to about three hours when the concentration reached 500 mg l⁻¹. The initial rapid adsorption of dye could be attributed to ion-exchange with surface cations on the husk followed by a gradual uptake which could be due to cation exchange at the inner surface. Poots and co-workers (1978) in their study on removal of Astrazone Blue by wood, reported that initial concentration of dye has very little influence on the time of contact to reach equilibrium. The reason for such an observation is not clear. For a given mass of adsorbent, the amount of dye it can adsorb is fixed. The higher the concentration of the dye, the smaller the volume it can remove.

The kinetics of adsorption appears to be first order. Plots of log C against time for 250 and 500 ppm solutions for the first twenty minutes of contact time yielded straight lines (Fig. 3). No attempts were made to determine the kinetics of solution with concentration less than 100 mg l⁻¹ as equilibrium time was too rapid.

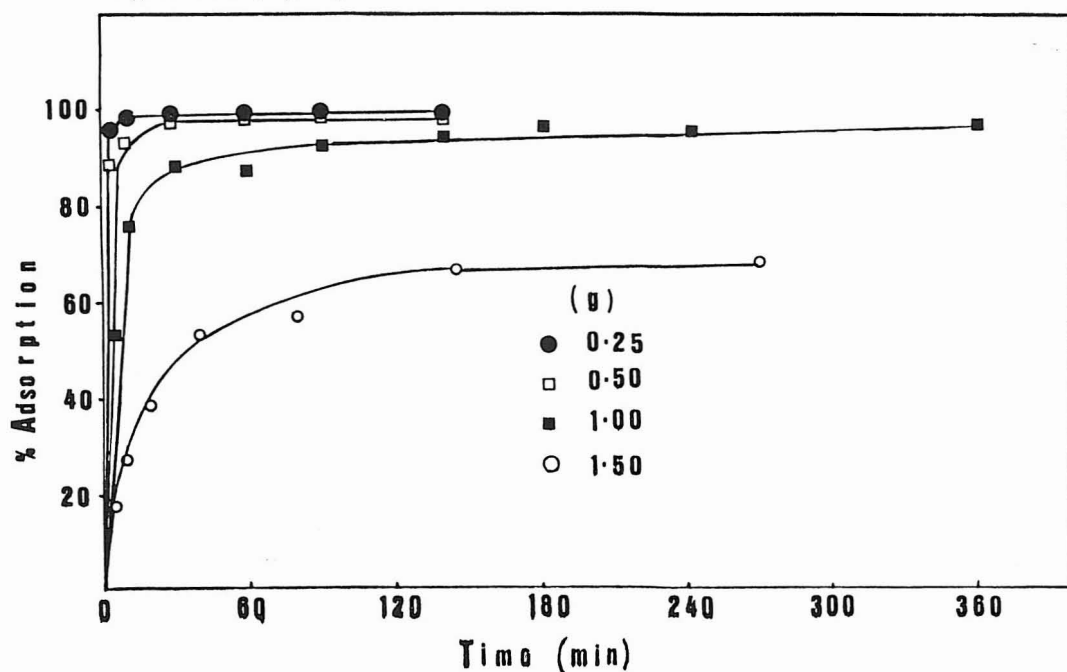


Fig. 4: Effect of adsorbent dosage on the uptake of methylene blue. Condition: ml 250 µg l⁻¹ methylene blue solution.

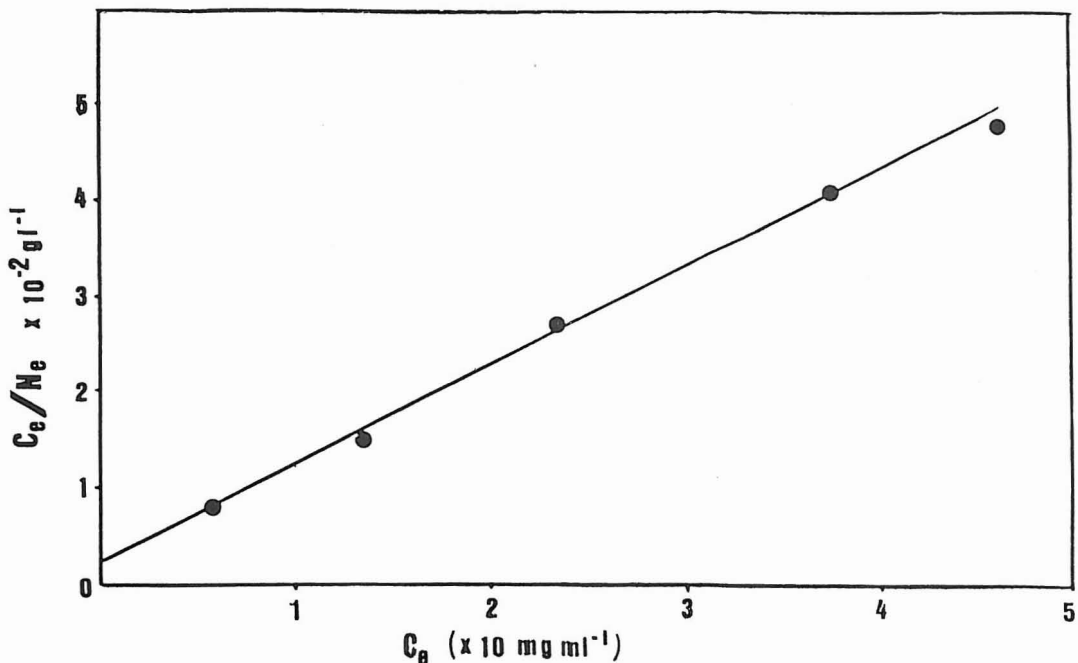


Fig. 5: Langmuir isotherm for the adsorption of methylene blue on coconut husk.

Effect of Adsorbent Dosage

The effect of the amount of adsorbent on the adsorption of a fixed quantity of methylene blue is shown in Fig. 4. The rate of adsorption and the percentage adsorption of the dye increased with increasing the amount of husk. This is due to the increase in binding sites in the adsorbent.

Adsorption Isotherm

The results from adsorption studies at equilibrium can be used to determine the maximum of dye adsorbed by the husk by using a modified Langmuir isotherm shown below (Zimdahl and Skogerboe 1972).

$$\frac{C_e}{N_e} = \frac{1}{N^*b} + \frac{C_e}{N^*}$$

where N_e is the amount of dye adsorbed per gram of husk at concentration C_e . A plot of C_e/N_e against C_e is shown in Fig. 5. The coefficient of correlation of such a plot is 0.996 indicating the general validity of the equation when applied to the adsorption of dye on coconut husk. The maximum adsorption of the system (N^*) is 99 mg g $^{-1}$. This compares

favourably with the experimental value of 102 mg g $^{-1}$. In a similar study using natural moss as an adsorbent, a value of 252 mg g $^{-1}$ was reported by Lee and Low (1987). Despite its lower adsorptive power, coconut husk, a cheap agricultural by product, could still be used to remove methylene blue from wastewaters.

Column Study

Adsorption isotherms are useful in providing information on the effectiveness of the adsorption system. However, the isotherms are obtained under equilibrium conditions. In most industrial treatment applications, the contact time is not sufficiently long for equilibrium to be achieved. In order to establish the suitability of coconut husk in removing methylene blue on a continuous basis, some flow studies using columns were conducted. For column operation, the husk is in constant contact with a fresh solution and hence equilibrium is unlikely to be attained. The usefulness of a column is related to the length of time before renewal or regeneration is necessary. For this purpose, the determination of breakthrough curve at different bed depths and flow rates is necessary. Fig. 6 shows a series

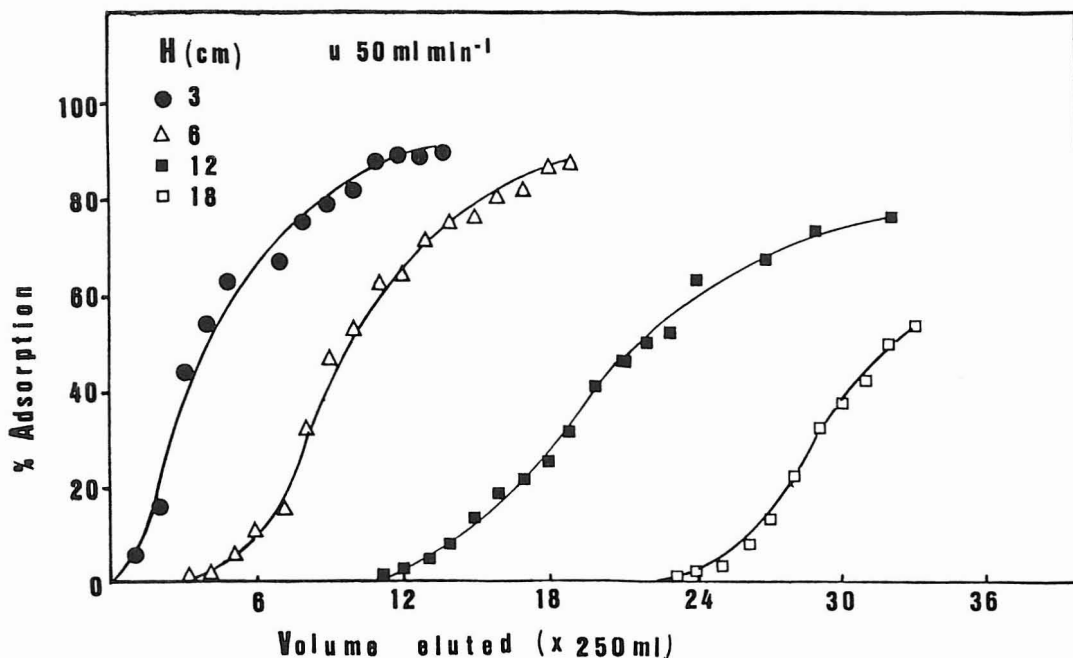


Fig. 6: Breakthrough curves for different bed-depths of coconut husk at a constant flow rate of 50 ml min^{-1} .

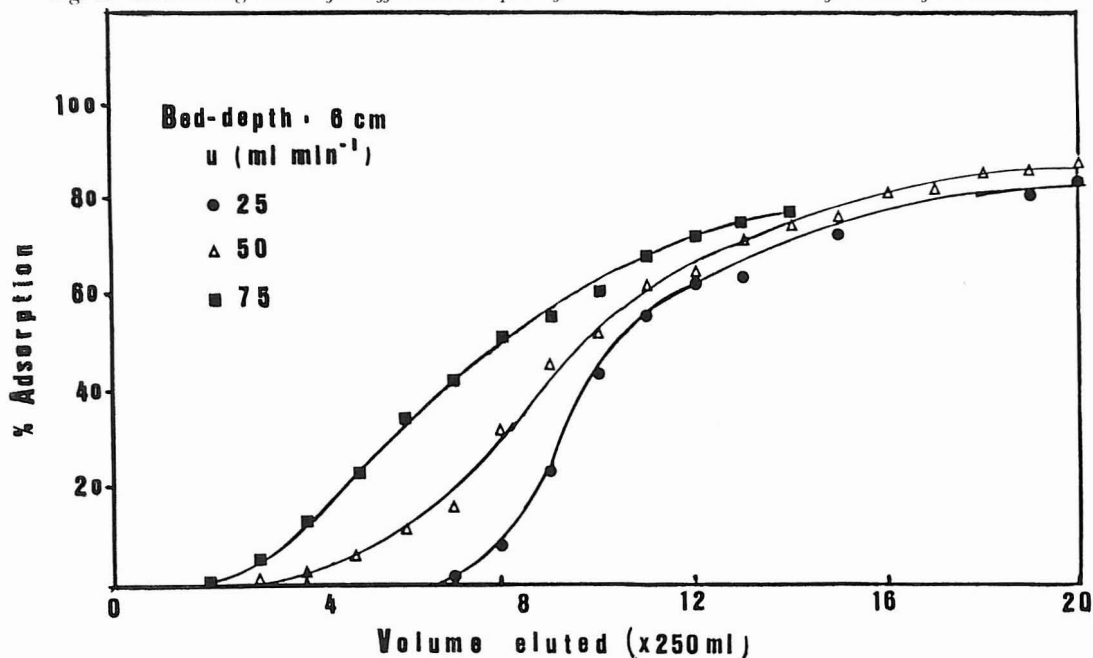


Fig. 7: Breakthrough curves for different flow rates at a fixed bed depth of 6 cm.

of breakthrough curves at different bed heights (H) of coconut husk at a flow rate (u) of 550 ml min^{-1} . Other flow rates of 25 and 75 ml min^{-1} show similar trends of breakthrough curves.

For a small bed mass which is proportional to the bed height, the 50% breakthrough rises

rapidly and this breakthrough time ($t_{1/2}$) becomes larger with increasing mass. Reducing the flow rate increases the volume of dye treated before 50% breakthrough occurs. This is illustrated in Fig. 7 where the height was fixed at 6 cm and the flow rates varied from

25 to 75 ml min⁻¹.

The results obtained from the break-through curves are applied to a bed-depth/service time model as proposed by Hutchins (1973). It predicts the service time of a column with operation variables. The equation of such a model is given below:

$$t = ax + b$$

where

- t = service time at breakthrough, min
- a = slope = (N₀/C₀v), min cm⁻¹
- b = ordinate intercept = 1/(kC₀)ln(C₀/C-1), min
- N₀ = adsorption capacity, mg adsorbate per cm³ adsorbent
- C₀ = initial concentration of methylene blue mg l⁻¹
- v = linear flow rate ml min⁻¹ cm²
- k = rate constant for adsorption l mg⁻¹ min⁻¹
- C = eluant concentration mg l⁻¹

The slope a of the line is the time required to exhaust the length of the fixed bed under trial conditions, or the time required for the wave front to move through 1 cm of the bed. The intercept of the abscissa is the critical bed depth x₀, defined as the minimum depth for maintaining satisfactory effluent at time zero under the trial conditions. The ordinate intercept, b, is a measure of the adsorption rate and is defined as the time required for the adsorption wave front to pass through the critical bed depth. Plots of BDST at 50% adsorption against bed-depth at various flow rates are shown in Fig. 8. The plots are linear indicating the general validity of the model. After obtaining a BDST equation from column studies for one particular flow rate, the equations for the other flow rates can be calculated. Using a flow rate of 50 ml min⁻¹ as a reference, equations for 25 and 75 ml min⁻¹ were calculated and shown in Table 1.

Variation between calculated and experimental values are less than 10%, indicating that the BDST model could be satisfactorily applied to the methylene blue-coconut husk system.

In most treatment processes for the removal of dyes, it is necessary to regenerate and reuse the adsorbent once it becomes

TABLE 1
Experimental and calculated BDST equations for flow rates based on u = 50 ml min⁻¹

u (ml min ⁻¹)	Experimental (t _{1/2})	Calculated (t _{1/2})	Variation (%)
25	17.9 x -3.67	18.8 x -7.09	6
50	9.4 x -7.09	-	-
75	5.8 x -6.04	6.3 x -7.09	8

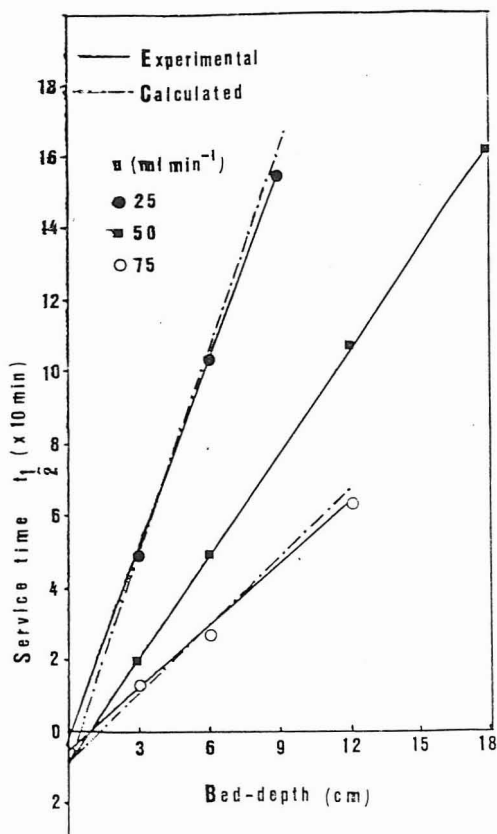


Fig. 8: Experimental and calculated BDST (50% break-through) curves for different flow rates.

saturated. This is especially so if the adsorbent is expensive. However, in this case, coconut husk is a cheap agricultural byproduct. It can be burned with the adsorbed dyes and used as a source of energy.

CONCLUSION

The study shows that coconut husk, a cheap

and easily available agricultural by product, can be effectively used to remove methylene blue from solution. Results of the column studies show that the rate at which the husk has to be replaced once it is saturated with the dye, can be predicted quite satisfactorily by the Hutchins BDST model.

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