5 DISCUSSION

5.1 Characteristics of the adsorbents

The adsorbent characteristics show that both the carbons possess nearly same apparent density. The decolourising power of CAC is higher when compared with that of CHC which may be due to the higher surface area of CAC. The higher value of surface area of CAC compared with that of CHC may be due to the carbonization process involved. The surface area of carbon prepared from Calymperes delessertii Besch, moss is reported to be 190 m²/g (Lee and Low, 1987) which is comparable with CHC.

5.2 Batch type experiments

5.2.1 Effect of initial dye concentration and agitation time on dye removal

The figures show that initially the uptake of dyes was rapid and after reaching the maximum percent removal, it remained constant. The contact time needed for the maximum removal of Procion Brilliant Blue MR, Procion Orange M2R and Taupe was very short. Relatively short contact time i.e., 2 hours has been reported by Poots et al. (1978) for the removal of Astrazone blue (basic dye) on wood. The authors stated that the short contact time confirms that the chemisorption may be the predominating mechanism and the regeneration may be fairly difficult. The results of the present study suggest that the mechanism involved
may be chemisorption. Though the regeneration may be difficult, the cheapness of the adsorbent makes us neglect this fact.

Similarly, very short contact time has been reported by Sethuraman and Raymhashay (1975) for the colour removal of methylene blue, a basic dye solution using kaolinite and montomorillonite clays in 5 min and 2 hours respectively. Similar type of curves was reported by Low and Lee (1990) for the removal of methylene blue on coconut husk carbon.

The maximum percentage removal of Brilliant Blue MR on cashewnut hull carbon decreased from 93.7% to 85.6% with an increase in concentration from 50mg/L to 175 mg/L and on commercial activated carbon it decreased from 98.0% to 90.3%. A similar trend was noted for all the dyes and the mixture. This showed that the dye removal is concentration dependent whereas the equilibrium time was not concentration dependent.

5.2.2 Adsorption dynamics

The rate constants obtained for the removal of Brilliant Blue MR on cashewnut hull carbon and on commercial activated carbon were higher than the rate constants for Yellow MGR and Orange M2R. But the values do not show any increase or decrease with the increase in initial dye concentration.
A similar trend has been observed by Deo and Ali (1993) for the adsorption of Congored on paddy straw. The values were $2.16 \times 10^{-3} \text{ min}^{-1}$, $3.68 \times 10^{-3} \text{ min}^{-1}$, $4.73 \times 10^{-3} \text{ min}^{-1}$, and $1.58 \times 10^{-3} \text{ min}^{-1}$ for an initial dye concentrations of 20, 40, 60 and 100 mg/L respectively. For the adsorption of Victoria blue on fly ash-wollastonite mixture, the rate constant was observed as $6.6 \times 10^{-2} \text{ min}^{-1}$ (Khare et al., 1987). Gupta et al. (1988a) reported the rate constant of adsorption of chromedye on fly ash to be $1.8 \times 10^{-2} \text{ min}^{-1}$ at 30°C.

5.2.3 Intraparticle diffusion studies

The plots of amount of dye adsorbed $q$ (mg/g) versus $\sqrt{\text{time (min)}}^{1/2}$ for all the three dyes and the mixture for the removal on cashewnut hull carbon and commercial activated carbon have same general feature. The plots do not pass through the origin showing that intraparticle diffusion is not the only rate controlling mechanism for the removal of dyes, but also boundary layer diffusion has taken place in the initial stage of dye adsorption on the carbons.

The $k$ values were found to increase with the increase in initial dye concentration in all cases. Similar results were recorded by Deo and Ali (1993) for the adsorption of congo red
on paddy straw, for the concentration of 20, 40, 60, 100 and 200 mg/L. The k values have increased from $4.5 \times 10^{-2}$ mg.g$^{-1}$ min$^{-1}$ to $23.4 \times 10^{-2}$ mg.g$^{-1}$ min$^{-1}$. Similar plots were shown by Gupta et al. (1988a). Lee and Low (1987) reported k values to be 46 to 83 mg.g$^{-1}$ min$^{-1}$ for the adsorption of Astrazone red violet at different temperature on moss, Calymperes delessertii, Besch and for the adsorption of methylene blue at different temperatures it was 50 to 150 mg.g$^{-1}$ min$^{-1}$.

Gupta et al. (1988a) reported 'k' values for the removal of chrome dye by fly ash to be $0.03$ mg.g$^{-1}$ min$^{-1}$ at $30^\circ$C. In the plots, the linear portion was attributed to the intraparticle diffusion.

5.2.4 Adsorption isotherm

The plot of $C_e/q_e$ vs $C_e$ resulted in a linear relation indicating the applicability of the Langmuir equation for the removal of Procion Brilliant Blue MR, Procion Yellow MGR, Procion Orange M2R and Taupe on cashewnut hull carbon and commercial activated carbon.

The capacity to adsorb, Procion Brilliant Blue MR and the mixture of dyes by both cashewnut hull carbon and commercial
activated carbon was relatively higher when compared with the capacity to adsorb Procion Yellow MGR and Procion Orange M2R.

As mentioned earlier, in the mixture of dyes the dyes are in the following ratio: PBBMR : PYMGR : POM2R = 0.598: 0.177: 0.225 which shows the higher concentration of Procion Brilliant Blue MR, which could be the reason for the higher adsorption capacity of cashewnut hull carbon and commercial activated carbon to adsorb Taupe.

For CAC, $Q^0$ values decreased in the following order:

Taupe > PBBMR > POM2R > PYMGR.

For CHC, $Q^0$ values decreased in the following order:

Taupe > PBBMR > PYMGR > POM2R

The $Q^0$ values for the adsorption of congored on paddy straw was around 2.4 mg/g (Deo and Ali, 1993). The $Q^0$ values at 30°C for the adsorption of Astrazone blue on silica were found to be 20.8 mg/g by Mckay et al. (1980b). For the adsorption of Victoria blue on flyash and wollastonite mixture $Q^0$ values were reported to be 0.801 mg/g at 30°C (Khare et al., 1987) and $b$ values for the same temperature was 0.074 L/mg.

For the adsorption of basic dyes Astrazone blue and Maxilon red and acidic dyes Erionyl red and Telon blue on maize
the Q° values were 160, 94.5, 47.7 and 41.4 mg/g respectively (ElGeundi, 1991). Similarly Low and Lee (1990) have reported that the maximum adsorption capacity of coconut husk to adsorb methylene blue was 99 mg/g and of natural moss was 252 mg/g (Low and Lee, 1990).

Gupta et al. (1988a) have reported the Q° value of flyash to remove Omega chrome red ME dye was 0.72 at 30°C and the 'b' value was 2.1960 at the above said temperature.

Nassar and ElGeundi (1991) reported the maximum adsorption capacity of activated carbon to adsorb Maxilon red, Astrazone blue and Telon blue as 790, 648 and 120 mg/g and Q° values for the adsorption on clay as 326, 378 and 39 mg/g, on maize cob it was 94, 160 and 41 mg/g and finally on bagasse pith it was 76, 167 and 23 mg/g.

Mall and Upadhyay (1995) reported the Q° values for the adsorption of methylene blue on boiler bottom ash as 4.732 mg/g at 30°C and for malachite green it was 4.12 mg/g at 30°C.

McKay (1982) studied the adsorption capacity of activated carbon to adsorb victoria blue, deorlene yellow, disperse blue 7 and Telon blue and reported as 5.5, 200, 25 and 175 mg/g respectively.
The $R_L$ values listed indicate favourable adsorption of dyes on cashewnut hull carbon and on commercial activated carbon since the values lie in the range of $0<R<1$.

The values of $n$ were within 10 for the removal of Procion Brilliant Blue MR, Procion Yellow MGR and Procion Orange M2R on cashewnut hull carbon and commercial activated carbon which suggest that the adsorption is good and the values of $1/n$ were less than one indicating favourable adsorption. The values of $n$ in the range of 2-10 represents good adsorption (Helby, 1952).

But the $n$ values obtained for the mixture of the dyes, Taupe on cashewnut hull carbon and commercial activated carbon were greater than 10. Similarly, McKay et al. (1985) have reported the $n$ values for adsorption of Astrazone blue on fuller's earth to be 28.5 and the $n$ values for adsorption of Astrazone blue, Direct orange and Telon blue on fired clay were 1.4, 3.57 and 6 respectively.

Generally, the $k_f$ values stand as a measure of adsorption capacity of the adsorbent (Kannan, 1991). The rate constants obtained were comparable with previous reports.
The $k_f$ values were 500 mg/g, 32 mg/g for the adsorption of Astrazone blue and Telon blue on fuller's earth and for Astrazone blue, Direct orange and Telon blue on fired clay it was 1.35, 2.1 and 1.6 mg/g respectively (McKay et al., 1985).

Manjunath and Mehrotra (1981) have reported $k_f$ values for the removal of reactive dyes on sludge and on a mixture of alum and sludge as 0.4 and 1.0 mg/g respectively. And the $1/n$ values to be 1.27 and 1.22 respectively. McKay et al. (1980b) have reported the \( n \) values for the adsorption of Astrazone blue on silica. The values were reported to be 3.12, 2.50, 2.27, 2.07, 1.90 and 1.37 while the particle size was in the range of 355-500, 500-710, 710-850, 850-1000, 1000-1700 and 1700-3350 respectively.

Deo and Ali (1993) reported the $1/n$ and log $k_f$ values for the adsorption of congored on paddy straw as 0.13 and 0.68 respectively. Allen et al. (1989b) worked on the removal of basic dyes namely Basic red 22 and Basic yellow 21 on lignite and reported the $n$ values as 0.327 and 0.347 respectively.

Mall and Upadhyay (1995) have reported the $n$ and $k_f$ values for adsorption of methylene blue on boiler bottom ash at 30°C as 7.568 and 4.276 mg/g and for malachite green at 30°C it was 3.172 and 2.942 mg/g respectively.
Activated carbon was used to adsorb various dyes like Victoria blue, Deorlene yellow, Disperse blue 7 and Telon blue by McKay (1982) and the 'n' values obtained were 3.1, 6.9, 5.0 and 9.3 and the 'k_f' values were 3.1, 112, 2.8 and 110 mg/g respectively.

5.2.5 Effect of adsorbent dosage on percent dye removal

The effect of adsorbent dosage on the removal of Procion Brilliant Blue MR, Procion Yellow MGR, Procion Orange M2R and Taupe showed that the removal of all the dyes and the mixture increased with the increase in dosage of cashewnut hull carbon, whereas on commercial activated carbon the maximum removal was reached at about 750 mg after which the curve reached equilibrium.

Since in our experiments, particle size was kept constant, the surface area available for adsorption will be proportional to the mass of the adsorbent. Similar results have been shown by McKay (1982) for the adsorption of Telon blue and Deorlene yellow on activated carbon, by Lee and Low (1987) for the adsorption of Astrazone red violet 3R on moss, by El-Geundi (1991) for the removal of Erionyl red on maize cob and by Low and Lee (1990) for the removal of methylene blue on coconut husk.
5.2.6 Effect of pH on percent dye removal

The removal of all the dyes and the mixture on cashewnut hull carbon was pH independent. The percentage remained the same for all the pH values and a slight reduction was noticed for pH 12 and the mechanism seems to be complex. This shows the suitability of cashewnut hull carbon irrespective of the pH of the effluent.

Similarly, the pH of 2 to 10 has not shown any marked effect on the removal of methylene blue and red violet 3R on natural moss. The percentage removal has remained more or less the same (Lee and Low, 1987).

Commercial activated carbon shows a higher percentage removal of all the dyes and the mixture at an acidic pH 2 and showed a decline in percentage removal as the pH increases to 12, which may be due to the fact that as the pH increases, the adsorbent surface becomes negatively charged and therefore it repels the dye anions, resulting in low adsorption at high pH. Similarly Kannan and Vanangamudi (1991) reported the highest percentage removal of Cr (VI) on lignite coal at pH 2 and removal decreased with increase in pH. Gupta et al. (1988a) have reported a higher percentage removal of chrome dye using fly ash at a pH 2. But removal of Telon blue on activated carbon has shown no change with pH (Mckay, 1982).
5.2.7 Batch type desorption studies

It is necessary to know the nature of the process by which the dye remains adhered to the surface of the adsorbent. The adherence may be physical or chemical. The nature of bonding could be decided on observing the results of desorption studies.

The percentage of desorption for all the dyes using cashewnut hull carbon and commercial activated carbon was very less. The very low values show the absence of weak bonds of attachment between dye molecule and sorbents i.e. physisorption. Desorption was negligible from both adsorbents for all the dyes when $H_2SO_4$ was used, so ion-exchange was also ruled out. The other mechanism, namely, chemisorption might be responsible for sorption of dye on the adsorbents. Similar results were presented by Mittal and Venkobachar (1989) for the removal of Rhodamine B and Sandolan Rhodine by sulfonated coal and Ganoderma lucidum.

5.2.8 Dyeing industry effluent treatment studies

As observed from the characteristics of the wastewater, the higher content of suspended solids emphasizes the need of sedimentation, which can reduce the content. Further the COD of the effluent was higher than the BOD, implicating the presence of bioresistant organics.
For our studies, "Colour removal" was chosen as the main parameter, since it is the critical pollutant as far as dyeing effluent is concerned. Though the effluent warrants some pretreatment prior to adsorption studies using activated carbon, plain sedimentation was considered, since it may prevent the clogging of the columns during fixed bed studies. So the effluent was subjected to sedimentation for 48 hours and the analysis revealed a less reduction in total suspended solids and chloride, and no change was seen in other parameters.

5.3 Fixed bed experiments

The adsorption capacities of the carbons (CHC and CAC) obtained from fixed bed experiments were slightly higher than the \( Q^0 \) values obtained by batch type experiments. The long time of contact between the carbon and the adsorbate may be the reason for higher value obtained during fixed and bed experiments. The adsorption capacity of commercial activated carbon was found to be higher than that of cashewnut husk carbon.

The \( N_0 \) values lie in the order of 5-12 mg/cm\(^3\) for all the dyes for 60% removal of the dyes. Mall and Upadhyay (1995) have reported a value of 2.208 mg/cm\(^3\) for the removal of methylene blue on bottom ash for 90% removal.
The nature of plots are linear which showed the applicability of BDST for both the carbons. But not all the plots for 50% dye removal has passed through the origin as said by Poots et al. (1978). Similar type of curves were presented by Lee and Low (1987) and Low and Lee (1990) for the removal of methylene blue on Calypomes delessertii Besch, moss and on coconut husk respectively.

The plots of $C_t/C_0$ vs effluent volume were of typical sigmoidal shape, which confirm that the mass transfer rate are finite.

In the design of fixed bed absorption columns contact time is the important parameter and bed depth and flow rate are the major design parameters. Though there are many other parameters such as dye concentration, pH, temperature, adsorbent characteristics such as particle size, porosity etc. which could be altered and experimented, in our work the application of BDST model to bed depth is considered mainly after optimising the flow rate. As mentioned earlier, the data fits in the BDST model well.
5.4 Effect of untreated dyeing industry effluent and carbon (CHC and CAC) treated effluent on growth and bio-chemical characters of (*Zeamays* L.) var. CO-1.

The gradual decline in germination percentage of the seeds subjected to treatment with different dilutions of the effluent may be due the high salt concentration in the effluent (Kittock and Law, 1968; Hadas 1976) whereas the seed germination remained unaltered at different dilutions of carbon treated effluents.

The increasing concentration of total dissolved solids, total suspended solids, chloride, sulphate and nitrates may be destabilizing the chloroplast which may deplete the pigment content and has resulted in the gradual decline in the total chlorophyll content with the increase in effluent concentration. The chlorophyll content of the seedlings treated with carbon treated effluents has shown a reduction along with the increase in the carbon treated effluents concentration. This may be due to the presence of unremoved pollutants.

The reduction in the production of carbohydrates has resulted a reduction in shoot and root length along with a reduction in fresh and dry weight of the seedlings treated with higher concentration of the effluent. The values obtained for the
seedlings treated with carbon treated effluents were not statistically significant. The values were comparable with that obtained for the control. Similar results were reported by Ozoh and Oladimeji (1984), Rajaram et al. (1988) and Nirmalarani and Janardhanan (1988, 89).

Considering all the above facts it may be stated that the cashewnut hull carbon or commercial activated carbon treated effluents can be employed for irrigation since it is devoid of disagreeable colour and they may not reduce the productivity of maize (Zea mays L.) var. Co-1 variety.

5.5 Effect of untreated dyeing industry effluent and carbon (CHC and CAC) treated effluents on bacterial population of soil

The bacterial populations were found to increase up to 30 days when the soil was treated with untreated and carbon treated effluents. But the population was observed to reduce after 30 days for the soils treated with 10%, 25%, 50% and 100% dilutions of dyeing industry effluent.

Maximum bacterial population was recorded for 10% effluent concentration and may be the tolerance limit for the soil bacteria. The reduction may be due to the adverse effect of BOD and COD of the effluent.
The bacterial population in the soil treated with CHC and CAC treated effluents showed a similar pattern as noticed for the control soil. Similarly Maleeka (1996) has reported an increase in bacterial population upto 30 days and then a declination in soils treated with congo red and neolon grey.

The results of this study indicate the necessity of treatment of the dyeing industry effluent before being discharged in the soil.

5.6 Dye tolerance studies

The bacterial strains isolated from the soil treated with the untreated dyeing industry effluent and carbon (CHC and CAC) treated effluents have shown higher resistance to Procion Brilliant Blue MR, Procion Orange M2R and Taupe when compared with that to Procion Yellow MGR.

Out of these strains, which showed resistance to different concentrations of the dyes and their mixture, Bacillus and Pseudomonas have shown higher tolerance. Similarly, Maleeka (1996) has reported the dominance of Bacillus in soils treated with neolon grey and chromium (III) and sensitive to congo red. Pseudomonas was resistant in soils treated with neolan grey and chromium (III) whereas Vibrio was the dominant strain in soils treated with congo red.
However these results indicate the possibility of using certain strains of bacteria such as Bacillus and Pseudomonas for the sorption of dyes due to their higher resistivity to the reactive dyes.

5.7 Reuse of CHC treated taupe solution for fabric dyeing process

The possibility of reuse of CHC treated taupe solution was checked by dyeing a fabric in original taupe and CHC treated taupe solution.

Since the dye uptake by any fabric is directly proportional to the Kubelka-Munk function, the original dyed sample and the sample dyed in treated Taupe solution were said to have same colour, since the K/S value for Taupe A was 2.994 and Taupe B was 3.016. This study confirms the possibility of reusing the treated dye solution for even dyeing the fabric.

5.8 Cost-analysis

Though the mass(kg) of CHC needed to remove 1 kg of Procion Brilliant Blue MR, Procion Yellow MGR, Procion Orange M2R and Taupe is higher than the amount of CAC needed, the relative cost of CHC needed is nearly five times lesser than the cost of CAC needed, which proves that using CHC is quite economical.
Mckay et al. (1984a) have reported that wood was the cheapest adsorbent to remove Acid Blue 25 and Basic Blue 69 and it was followed by peat and the carbon is said to be 65 times more expensive. Nassar and El-Geundi (1991) reported that the relative cost of adsorbents like clay, maize cob and begasse pith are relatively lesser than the relative cost of carbon to adsorb Maxilon Red, Astrazon Blue and Telon Blue.