CHAPTER 8

SUMMARY AND CONCLUSIONS

8.1 SUMMARY

8.1.1 Introduction

Adsorption of most organics and some inorganic materials including heavy metals from water and wastewater using activated carbon is gaining acceptability all over the world. But the cost of activated carbon limits its use to some specified applications only. The purpose of the present study is to develop a cheap carbon derived from paddy husk which is commercially available in large quantities as an agriculture waste in India and to evaluate its characteristics and performance capability with regard to colour and phenol removal. The present study was carried out at the Centre for Environmental Studies, College of Engineering, Guindy, Anna University, Madras. Activated carbon was prepared by means of dehydrating, simple chemical activation with calcium carbonate and charring at 800°C of raw paddy husk collected from nearby rice hulling mills where it was available in large quantities.

Powdered carbon has excellent adsorptive capacities but due to lack of an efficient regeneration system and the complexity in application and handling it is being replaced by granular carbon. Moreover the PHAC in powdered form is very fine and is likely to be washed away with the effluent and the loss could be very high. Capturing the spent carbon from the effluent requires additional units such as coagulation tanks which will
effluent requires additional units such as coagulation tanks which will increase the scheme cost to a great extent. It was therefore decided to mix the carbon with clay and make pellets so that these pellets form a granular structure making handling simpler.

8.1.2 Characteristics

8.1.2.1 PHAC

The characteristics of the paddy husk carbon manufactured in the laboratory were evaluated and compared with those of the commercial carbon. The parameters studied for this purpose included moisture, ash content, apparent density, matter soluble in water, matter soluble in acid, pH, decolourising power, phenol number, hardness, adsorption isotherms and surface area.

The results on evaluation of the characteristics of carbon revealed that the paddy husk activated carbon prepared in the laboratory compared fairly well with those of the commercial activated carbon as indicated below:

1. The moisture content of PHAC was 4.2 percent by mass, which was slightly less than that for CAC which was 5.0 percent by mass. As the moisture content dilutes the carbon and necessitates the use of additional weight of carbon, lesser moisture content is desirable. Hence PHAC was better than CAC.

2. The ash content of PHAC was 8.403 percent by mass while that of the CAC was 5.895 percent by mass indicating that the PHAC had relatively less carbon content than the CAC. The lower ash content of CAC indicated that it was derived from wood base.

3. The apparent density was 0.248 and 0.436 g/ml for PHAC and CAC respectively. It indicated the space that would be occupied
by the material of the carbon. In other words, for a given weight, carbon of PHAC would occupy more volume than CAC.

4. The matter soluble in water was 9.127 and 4.876 percent by mass and the matter soluble in acid was 1.870 and 1.265 percent by mass for PHAC and CAC respectively.

5. The low decolourising power of 85 mg/g and the high value of phenol number of 40 showed that PHAC had less adsorption characteristics for organics compared to CAC which had values of 195 mg/g and 26 respectively. This was also reflected by the surface area which was found to be 264.22 m²/g for PHAC as against 483.93 m²/g for CAC.

6. The Isotherm tests conducted on phenol adsorbance revealed that PHAC adsorbed 0.009 mg/mg as against 0.026 mg/mg for CAC which indicated that PHAC had about 3 times lesser adsorption capacity than that of CAC.

7. Hardness or abrasion resistance was also significant in the case of regenerable carbons as it was subjected to alternate cycles of exhaustion and reactivation with minimum material loss. The hardness number was 84.0 and 94.8 for PHAC and CAC respectively and were comparable.

8. From sieve analysis the particle size of PHAC was between 0.4 and 1.18 mm. Approximately 40% by weight of carbon was obtained from the raw paddy husk.

8.1.2.2 PHAC Pellets

Characteristics of PHAC pellets based on ‘Phenol’ as the organic pollutant were also determined.

9. From the phenol adsorption data for different carbon to clay mix pellets, it was found that the carbon to clay ratio of 1:0.2 was optimum.
10. The minimum contact time for 90% absorbance of phenol for PHAC pellets and CAC was 60 minutes, and 87.0g of PHAC pellets and 34.3g of CAC were required for the same.

11. The optimum pH of the solution for maximum adsorption of phenol by PHAC pellets and CAC was in the range of 4.8 to 5.5 and 6.3 to 6.9 respectively.

8.1.3 Colour removal
8.1.3.1 Batch adsorption experiments with PHAC and CAC

Methylene Blue

Studies on PHAC and CAC were undertaken for the removal of colour using methylene blue based on colour as the characteristic parameter. Batch reactors were employed in these experiments wherein predetermined quantities of the coloured waste were agitated either using a Jar test apparatus or wrist arm shaker continuously and samples taken and residual concentration monitored at appropriate time intervals. The following results were observed.

For 99% adsorbance of methylene blue, using 1 litre methylene blue solution with a concentration of 1500 mg/l, the minimum contact time required was found to be 60 minutes and the quantity of carbon required was 333g PHAC and 200g CAC. In other words to achieve the same degree of efficiency 67% more of PHAC was required compared to CAC.

Textile Dye Waste

In order to study the colour removal efficiency of the carbon, a composite textile dye waste was collected from a reputed textile printing and dyeing centre near Madras. Preliminary experiments were conducted to characterise the dye present in the dye waste. The textile dye waste was sampled at the time of maximum colour concentration to make the study more representative.
The evaluation of paddy husk carbon chosen for colour removal of textile dye-waste was done with a batch reactor to assess the parameters influencing the adsorption process such as contact time, kinetics of dye colour adsorption, equilibrium characteristics (adsorption isotherm), pH and kinetics of colour adsorption for different initial dye concentrations. The results are as follows.

1. It was found that the dissolved solids in the dye waste amounted to 78.3% of the total solids thus implying the presence of dyes in the dissolved state.

2. The COD of the dyewaste was about 12 times its BOD indicating the presence of bioreistant organics.

3. The waste was alkaline and red in colour. The presence of colour in dissolved state and the higher load of bioreistant organics suggested, physicochemical processes for colour removal of textile dye waste.

4. From the time adsorption study, the percent colour removal from textile dye waste was found to increase with contact time. For a dosage of 40 g/l the percent colour removal was found to be 27.65 after 75 minutes and this increased to 31.40 after 150 minutes. There was steep increase in the percent colour removal for the first 75 minutes of contact time and the rate of increase decreased for the next 75 minutes.

5. The adsorption capacity of PHAC was measured by determining the adsorption isotherm experimentally. The isotherm test data was found to be in confirmity with Langmuir adsorption isotherm. The Langmuir adsorption constants were $q_m = 0.0247$, $K_a = 1.0449 \times 10^{-3}$ and $R_l = 0.504$ indicating a favourable isotherm behaviour for PHAC as an adsorbent for colour removal.

6. The percent colour removal increased with decrease in pH and the increase was not apparent upto a pH of 2 (47.74 to 31.91%). But a steep increase in colour removal (68.42%) was seen at a pH of 1. There was a decrease in residual pH from its initial value
and this was probably due to the chemical activation of PHAC which was likely to aid in the process of colour removal. Hence pH adjustment was not carried out. After the prescribed contact time the pH was raised to the original pH of the waste i.e. 9.42 and it was got confirmed that colour did not reappear.

The percent colour removal was found to increase with decrease in initial concentration of colour for a given contact time and carbon dosage. For a contact time of 150 minutes at a dosage of 50 g/l the percent colour removal was 38.29 and 85.71 at initial concentrations of 940 mg/l and 210 mg/l respectively.

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8.1.3.2 Coloumn studiess

Column experiments were taken up to make the study more representative and were conducted in single fixed bed down flow continuous columns of 2.5 and 4.0 cm internal diameter. The treated effluent was monitored at regular time intervals and the corresponding effluent concentration was determined using appropriate analytical techniques.

VARYING FLOW RATES AND CONSTANT BED DEPTH

Column adsorption tests were conducted using textile dye with flow rates varying from 1 to 6 ml/minute, at a constant bed depth of 20 cm. Breakthrough curves were plotted to illustrate the variation in volume treated with residual colour. From the above experiments the following conclusions were drawn.

1. The volume treated was found to decrease with increase in flowrate.
2. The breakthrough curves relating variation in volume treated with residual colour were analysed to evaluate the optimum flow rate at various break points of 30 to 70% and set of breakthrough curves were plotted, from which the optimum flow rate for a fixed bed
depth could be evaluated based on the effluent requirement. For example for 70% breakthrough the volume treated was 630 ml at a flow rate of 1 ml/minute and this value decreased to 252 ml at a flow rate of 6 ml/minute. For a bed depth of 20 cm the optimum flow rate was evidently 1 ml/minute.

### VARYING BED DEPTH AND CONSTANT FLOW RATE

To illustrate the influence of bed depth on colour removal of textile-dye waste with PHAC as adsorbent, column adsorption studies were conducted with bed depths of 20 to 80 cm at a constant volumetric flow rate of 4 ml/minute and the results were plotted to obtain breakthrough curves.

From the above studies, the following conclusions were arrived at

1. The volume of wastewater treated was found to increase with increase in bed depth.
2. From the results it was also observed that in general the volume of waste treated and the time taken increased with increase in bed depth for a particular breakthrough concentration.

### BDST RELATIONSHIP

The Bed depth-Service time (BDST) relationship established between bed depth and volume treated upto breakthrough was found to follow a linear path.

For 70% breakthrough the BDST relationship was found to be

\[
t_{0.7} = 4.545Z + 15
\]

where

- \( t_{0.7} \) = Service time in minutes upto 70% break through concentration
- \( Z \) = bed depth in cm.
The BDST expression could be extrapolated to conditions other than those encountered in the experiments. For example, the volume treated up to 70% breakthrough for a 150 cm depth of column was found to be 2.8 litres. Similarly, the BDST expressions developed corresponding to various breakpoints could be used to predict the time of exhaustion of column bed for a particular depth and the designed breakthrough concentration of the effluent. From the BDST relationship, we can choose the optimum bed depth for the required effluent specification.

8.1.3.3 Studies on regeneration of PHAC

The spent carbon was regenerated after exhaustion by keeping it in contact with concentrated $\text{H}_2\text{SO}_4$ for about 24 hours. After acid treatment the carbon was washed, oven dried and used. Two sets of experiments were conducted with regenerated carbon, first using a flow rate of 2 ml/minute for a 20 cm bed depth and subsequently at 4 ml/minute for 40 cm bed depth. The studies on regeneration of PHAC indicated the following.

1. The regeneration of spent PHAC was possible with about 40% loss in efficiency.
2. At a bed depth of 20 cm and flow rate of 2 ml/minute to attain a residual colour concentration of 75 mg/l, the volume of waste treated was 150 ml for PHAC and 90 ml for regenerated PHAC.

8.1.3.4 Multiple column studies using PHAC

Further column adsorption studies were conducted with multiple columns in series to study the effect of flow rate and influent concentration on colour removal efficiency. Flow rates of 10000, 8000 and 4000 l/m²/day were adopted. The dyewaste was prepared at a dilution ratio of 1:250 for all the experiments. PHAC of 6.5 g corresponding to 5 cm depth of carbon
was taken in each column. Experiments were initially carried out using a single column, then using two columns in series, then with three columns in series and finally with four columns in series. Each time the effluent was collected from the last column in series and absorbance values measured. The breakthrough curves for the different experiments were drawn.

In the present study an adsorbance value of 0.01 corresponding to a dye concentration of 0.00055 μg/ml was selected as the breakpoint, since the effluent having a value of 0.01 absorbance was found to be colourless. The following conclusions were drawn based on multiple column studies using PHAC.

1. Considering a flow rate of 8000 l/m²/day as an example for comparing the performance of the carbon columns, it was observed that when two columns were operated in series, the volume of wastewater treated till breakthrough was reached was about 21% more than the volume of wastewater that would have been treated when two columns were operating independently.

2. When three columns were operated in series, about 19.5% more wastewater was found to be treated than when the columns were operated independently.

3. For four columns operating in series, the improvement in efficiency was found to be 22.3%. This implied that operating carbon columns in series for adsorption studies yielded better results.

4. The volume of wastewater treated by the carbon columns till breakthrough was reached did not vary much at flow rates of 4000 and 8000 l/m²/day (154.9 ml and 172.8 ml respectively) whereas at a flow rate of 10,000 l/m²/day, it was much less (99.5 ml only).

5. It was observed that at flow rates of 4000 and 8000 l/m²/day the absorbance value of the effluent changed according to the quantity of dye deposited on carbon, whereas at a flow rate of 10,000 l/m²/day
the absorbance values were much less than that for 4000 and 8000 l/m²/day. This showed that at a flow rate of 10000 l/m²/day complete adsorption was not taking place and the influent was just washed through the column. Hence it was inferred that at flow rates of 8000 l/m²/day or less the full adsorptive capacity of the carbon was utilised. This explained the ability of carbon columns to treat shock loads with little change in effluent quality. This showed that adsorption was basically an integrative process whereupon they tended to sum up the total input over a period of time. A carbon column thus had a finite capacity and must be taken out of operation when that capacity has been reached. Upto that point the input rate has little effect within a fairly wide range of values.

8.1.4 Phenol Removal

In the present study, the phenol removal efficiency of the PHAC was determined using a fixed bed down flow continuous column for various influent concentrations of phenol. Experiments were also carried out to study the regeneration efficiency using organic solvent acetone to desorb the phenol from the exhausted carbon bed. The above regeneration efficiencies for repeated cycles of adsorption and desorption using the same bed were studied, one cycle consisting of one adsorption followed by one desorption.

The residual phenol concentrations in the effluent were obtained at equal intervals of time for each influent concentration of phenol and the breakthrough curves were drawn. From the breakthrough curves the total quantity of phenol adsorbed were worked out for each influent phenol concentration. From the observations, it was found that
1. The total quantities of phenol adsorbed for 19.472 g of PHAC used was 30.43, 44.39 and 60.81 mg for the influent phenol concentrations of 25, 50 and 100 mg/l respectively.

2. The PHAC showed good performance with regard to phenol removal and the adsorption capacity increased with increase in influent phenol concentration.

3. Subsequent to loading the column with phenol, a solvent desorption phase was initiated using acetone. During the first cycle of adsorption, exhausting the virgin carbon with 25 mg/l of influent phenol concentration at a flow rate of 10 ml/minute, it was observed that 30.43 mg of phenol was adsorbed until complete breakthrough occurred. Then the first cycle of desorption was carried out. It was found that 200 ml of acetone was required to remove 27.35 mg of phenol from the exhausted bed out of the 30.43 mg of phenol adsorbed, which was about 90% of the adsorbed phenol.

4. In the second cycle of adsorption followed by the first cycle of desorption, it was found that the first regenerated carbon adsorbed about 24.89 mg of phenol which showed that the phenol adsorption efficiency was about 82% of that of the virgin PHAC. In the second cycle of desorption the same 200 ml of acetone removed about 24.78 mg of phenol from the exhausted bed.

5. In the third cycle of adsorption the second regenerated carbon adsorbed about 23.75 mg of phenol with 78% efficiency of the virgin carbon and was 4% less than the adsorption efficiency of the second cycle of adsorption. In the third cycle of desorption the same 200 ml of acetone removed about 23.6 mg of phenol, from the exhausted bed.

6. In the fourth cycle of adsorption, the third cycle regenerated bed adsorbed 23.28 mg of phenol. This showed that the phenol adsorption efficiency of the third cycle regenerated carbon was about 76.5% of that of the virgin carbon and about 1.5% less than the adsorption efficiency of the third cycle of adsorption. It was observed that the
rate of decrease in efficiency was reduced with increase in the cycles of operation.

7. The acetone used for removing the phenol from PHAC columns can be separated by distilling it and collecting the fraction boiling at 56°C. The recovered acetone can be reused repeatedly for removing phenol from the PHAC column.

8.1.5 Pelletisation

Based on 'Colour' as the characteristic parameter the study was continued. To arrive at the minimum contact time fixed volumes of methylene blue solution of known concentration was mixed with different weights of the material under study and agitated well in a wrist arm shaker for a fixed time. From the adsorption results it was observed that

1. The minimum contact time for 99% absorbance of methylene blue solution was 60 minutes and 10g of PHAC pellets and 6g of CAC were required for the same.

2. To achieve the same efficiency 67% more of PHAC pellets was required than CAC.

3. The optimum pH of the solution for maximum adsorption of methylene blue by PHAC pellets and the CAC was 1. The methylene blue adsorbed by PHAC pellets and CAC were 10.75 and 12.5 mg/g respectively.

4. The residual colour concentration against colour adsorbed per unit weight of carbon yielded straight lines in a log log sheet thus establishing agreement with the Freundlich isotherm equation used for comparison of carbons in water and wastewater treatment.

The isotherm equations for PHAC pellets and CAC are

\[
q_e = 1.0098 C^{0.043} \quad (8.1)
\]

\[
q_e = 1.0089 C^{0.12} \quad (8.2)
\]

respectively.
It was observed from the isotherm curve that the CAC possessed higher adsorption capacity than PHAC over the entire range of methylene blue studied which is indicated by the slope 0.12 for CAC as against 0.043 for PHAC pellets and its position over the isotherm curve for PHAC pellets.

The amount of methylene blue adsorbed from the solution with initial concentration of 1500 mg/l for the PHAC pellets and CAC was 5.8 mg/g and 8.25 mg/g respectively. These values indicated that the PHAC pellets had approximately 1.4 times less adsorption capacity compared to CAC.

Thermal regeneration of the spent carbon was adopted in the present study. The apparent densities of the regenerated PHAC pellets and those of the CAC obtained after first, second, third and fourth regenerations revealed that the apparent density decreased with successive regeneration for both PHAC and CAC. (i.e.) from 0.491 to 0.431 g/ml and from 0.443 to 0.300 g/ml for regenerated PHAC pellets and CAC respectively.

The loss of carbon on regeneration for the PHAC pellets was in the range of 2.2 to 10.2 percent while for that of CAC was in the range of 9.33 to 30.33 percent by mass to the virgin carbon initially taken for the test. These values indicated that the PHAC pellets had a very good regeneration capacity compared to that of CAC.

8.1.6 Cost Analysis

Based on their relative performance, cost comparison between the material cost alone of paddy husk activated carbon, commercial activated carbon, and paddy husk activated carbon pellets developed was made. The cost analysis was carried out for 90% phenol and 99% methylene blue adsorption efficiency based on the material cost of carbon alone. The analysis reveals the following.
1. The material cost of PHAC, CAC and PHAC pellets were Rs. 29.00, Rs. 95.00 and Rs. 42.50 per kg respectively.

2. The material cost of PHAC was the cheapest per kg of carbon compared to CAC and PHAC pellets suggesting thereby PHAC could be employed as an alternative.

3. Based on phenol adsorption efficiency of fresh carbons, the cost per 100 mg of phenol adsorbed worked out of Rs. 1.04, Rs. 2.51 and Rs. 2.76 for PHAC, CAC and PHAC pellets respectively indicating a ratio of costs of 1:2.41 : 2.65.

4. Based on methylene blue adsorption efficiency for fresh carbons, the cost per 100 mg of methylene blue adsorbed worked out to Rs. 0.64, Rs. 1.27 and Rs. 0.94 for PHAC, CAC and PHAC pellets respectively which indicates a ratio of costs of 1:1.98 : 1.47.

5. In the case of phenol and methylene blue adsorption efficiencies the PHAC was having the lowest benefit index whereas CAC was better than PHAC pellets so far as phenol adsorption efficiency was concerned but PHAC pellets were better than CAC with regard to methylene blue adsorption efficiency.

6. PHAC pellets prepared by the present process might not be economical compared to PHAC.

7. Studies using PHAC provide a strong basis for justifying the development of the paddy husk carbon in place of CAC.

8.2 CONCLUSIONS

Carbon adsorption is ascertained to be a promising technique for the removal of refractory organics. In view of the high cost and difficult procurement of commercial carbon, a need was sensed to evolve a suitable alternative material. As a prelude to this endeavour, a low cost adsorbent, with paddy husk as the base material was investigated for its adsorption potential by chemically activating the paddy husk charred at 800°C. The
evaluation of PHAC was made using static and dynamic tests. Static tests were conducted to assess the influence of the fundamental parameters such as contact time and weight of adsorbent, equilibrium characteristics, pH and initial colour concentration etc on the adsorption process. In the dynamic tests downflow columns were employed to assess the flow rate and bed depth as these were the two main guiding factors. The costs of the carbon could be further minimised by regenerating the carbon.

The evaluation of properties and adsorptive capabilities for PHAC was conducted based on phenol and methylene blue adsorbance in the present study. However the entire evaluation may further be studied considering COD or TOC as the guiding parameter.

The PHAC produced in a laboratory was comparable to the carbon available in the market. However in the powdered form PHAC is very fine and is likely to be washed along with the effluent. This may lead to unnecessary loss of carbon and its frequent replacement thus increasing the cost of the process. Hence it was decided to mix the carbon with clay and prepare pellets so that these pellets form a granular structure making handling simpler. A carbon to clay mix ratio of 1:0.2 was found to be optimum for pellet preparation. These pellets were also evaluated for the adsorption of colour and phenol. However the pellets has a comparatively low efficiency for colour & phenol removal and hence to achieve a desired degree of removal, they proved to be uneconomical.

The present studies provide a strong basis for justifying the development of new activated carbon from paddy husk in place of CAC.

In the light of the results of this study, the carbon derived from paddy husk is found to be capable of not only removing colour and phenol from wastewater but also comparatively cheaper and therefore could serve as an alternative to other adsorbents now in use in our country.