CHAPTER 4

STUDIES ON THE VARIOUS ADSORBENTS FOR THE COD REMOVAL IN INDUSTRIAL EFFLUENTS
RESUME

A comparative study for the removal of COD by various adsorbents from the dye industry effluents is described. The adsorbent materials used were poly styrene-p-carboxo hydroxamic acid, poly acrylo calix[6]arene hydroxamic acid, neem leaf ash, neem bark ash, coconut kernel, coconut shell and bagasse. Combination of various adsorbents materials viz., charcoal-poly acrylo calix[6]arene hydroxamic acid, coconut shell ash-bagasse ash, etc. were also tried to check their effectiveness. The bagasse ash was found to be the most effective.
INTRODUCTION

Conventional wastewater treatment consists of preliminary, primary and secondary treatment processes (Fig.1)(1). Primary treatment consists of pumping, screening and sedimentation, which includes grit removal and primary settling this enables the removal of large and heavy solids and floatable materials. In secondary treatment, biological aeration is used to metabolize and flocculate colloidal and dissolved organics. Tertiary or advanced treatment is an additional step applied only after the wastewater has undergone conventional primary and secondary treatment process.

A. Preliminary treatment:

The first level of wastewater treatment includes the physical processes of screening and sedimentation, which remove large floating objects and settleable solids. These account for about 60% of the total suspended solids (TSS) and approximately 35% of the BOD.

Raw wastewater first undergoes coarse screening. Bar screens made of long narrow metal bars spaced 1 in (25mm) apart retain floating debris and bulky objects. The bar screens are cleaned manually or by an automatic mechanical device.

B. Primary treatment

Wastewater contains suspended matter that has a high specific gravity than the liquid and is in a relatively quiescent state, the particles will settle out because of gravity. Grit chambers remove grit, including gravel, sand and heavy particulate matter such as corn kernels, bone chips, broken glass, etc. After grit removal, the wastewater still contains suspended solids, which are then removed by sedimentation.

1. Grit removal

For design purposes, grit is defined as 0.2mm particles with a specific gravity of 2.65 and a settling velocity of 0.0225m/sec. Most of the gritty material settles out of the wastewater flow of 0.6m/sec, by gravity if the velocity is reduced from the grit chambers is high in organic content. A counter flow grits washer before its disposal.
Fig:1 FLOWSHEET OF A WASTEWATER TREATMENT PROCESS
into a landfill then washes the grit. The waste organics are returned to the plant influent Primary settling tanks are used to remove the readily settleable solids preceding further treatment. With chemical treatment and flocculation the primary settling tank (clarifier) can remove a significant amount of colloidal particles. Intermediate and final settling tanks are used to remove the settleable solids following biological treatment processes.

Fig. 2 shows the four zones- inlet, settling, outlet and sludge storage. The inlet zone distributes the flow evenly across the cross section of the settling zone. It consists of the inlet pipes and baffles. Wastewater enters at the centre behind a stilling baffle and travels down and outward toward the effluent wier. The inlet line usually terminates near the surface, but the wastewater must travel down behind the baffle before it enters the actual settling zone. The baffle reduces the velocity and forces downward motion of solids.

Following the inlet zone is the settling zone. The flow velocity decreases in the settling zone, suspended solids settle out and accumulate in the sludge zone. Mechanically cleaned tanks have bottom scrapers in which the sludge is continuously scapped to the hopper from which it is pumped out. The tank bottom has a 1% slope in the direction of the sludge removal point. The sludge hopper is designed with sides at a vertical-to-horizontal slope of between 1.2:1 and 2:1.
The function of the outlet zone is to remove the settled water from the basin without carrying particles with the effluent. In the design of a sedimentation tank, the settling velocity \( (V_s) \) of the particles to be removed should be greater than the overflow rate \( (V_0) \).

C. Secondary Treatment (Biological)

Physical treatment of wastewater by sedimentation removes most of those pollutants that will either float or settle out by gravity, which accounts for only approx. 35% of the BOD. The major purpose of secondary treatment is to remove nonsettleable (colloidal and dissolved) solids in the wastewater. Secondary treatment usually treats 85% of BOD. Secondary treatment processes are almost always biological systems. Biological treatment systems are living systems that rely on mixed biological cultures to break down waste organics and remove organic matter from the solution. A biological waste treatment system provides an artificial and controlled environment suitable for the growth of microorganisms that can stabilize the organic pollutants in the wastewater. These living microorganisms, including bacteria and protozoa, consume the organic pollutants as food. They metabolize the biodegradable organics, converting them into carbon dioxide, water and energy. Aerobic metabolism requires oxygen for the processes of metabolism and synthesis. When the supply of biologically available energy is exhausted, the processes of metabolism and synthesis cease.

To keep the microorganisms productive in their task of wastewater treatment, they require an ample supply of oxygen, suitable temperatures and pH, a nontoxic environment and other favourable conditions.

Trickling filters and activated sludge are the two most commonly used biological treatment systems.

1. Trickling Filters

A trickling filter consists of a bed of coarse material, such as stones, slats or plastic media, over which wastewater is applied. A widely used design is a bed of stones approximately 5-7 ft deep; it is usually circular and may be as large as 200 ft in diameter. The primary effluent is sprayed on a bed of crushed rock or other media coated with biological films. The slime layer consists of bacteria, protozoans and fungi. Sludge worms, rotifers, filter-fly larvae and other higher animals also grow in
this environment. As the wastewater flows over the microbiological film, the soluble organics are metabolized and colloidal organics are absorbed onto the surface, thus removing organic substances from the wastewater. Air circulating through the void spaces in the bed of stones provides the oxygen for stabilization of the organics by the microorganisms.

The rocks in the trickling filter are usually approximately 3 in. in size to provide a large surface area for the biological growths, and the large voids allow air circulation.

As the microorganisms grow and multiply, the slime layer thickens. Due to its weight and the flushing action of the flowing wastewater, the slime is washed off in the underdrain system, from where it flows to a sedimentation tank called a secondary clarifier.

To maintain a uniform flow rate through the trickling filter and to keep the distributor arm rotating during periods of low wastewater flow, a portion of the effluent is pumped back to the trickling filter inlet. Recirculation also improves the treatment efficiency of the trickling filter. The amount of recirculation is characterised by a recycled flow to wastewater flow,

\[ R = \frac{Q_r}{Q} \]

where,

- \( R \) = recirculation ratio
- \( Q_r \) = recirculation flow rate, \( m^3/sec. \)
- \( Q \) = wastewater flow rate, \( m^3/sec. \)

The recirculation ratio is generally in the range of 0-3.0. The rate at which the wastewater flow is applied to the trickling filter surface is the hydraulic load. It depends on the recirculated flow \( Q_r \); the total flow through the trickling filter is equal to \( Q + Q_r \)

\[ \text{Hydraulic load} = \frac{Q + Q_r}{A_s} \]

\( A_s \) is the trickling filter surface area in sq. m. The hydraulic load can be expressed in cubic feet per sq. m. per day or millions of gallons per acre per day.

The rate at which the organic material is applied to the trickling filter is expressed as BOD load.

\[ \text{Organic load} = \frac{Q \times \text{BOD}}{V} \text{Kg/(m}^3 \text{.day)} \]

where, \( \text{BOD} \) is the biological oxygen demand of the primary effluent in mg/L and \( V \) is the volume of the trickling filter bed in cubic meters.
2. Activated Sludge

The activated sludge process is a biological wastewater treatment technique in which a mixture of wastewater and microorganisms is agitated and aerated. Wastewater is fed continuously into an aerated tank, where the microorganisms metabolize and biologically flocculate the organics using oxygen provided in the compressed air.

Organics + oxygen $\rightarrow$ CO$_2$ + H$_2$O + Energy

Aeration and mixing are achieved by continuously injecting compressed air into the mixture through mechanical devices such as propeller-type mixtures located at the liquid surface are used. The propeller blades mix air with the wastewater and keep the contents of the tank in suspension.

The aerobic microorganisms in the tank grow and multiply, forming an active suspension of biological solids called activated sludge. The mixture of the activated sludge and the wastewater in the aeration tank is called mixed liquor. In most cases the aeration period is 6-9 hr. The biological solids are subsequently separated by gravity from the mixed liquor in the secondary clarifier. The settled sludge is pumped out from the hopper bottom and a portion of it is returned to the aeration tank so that active, acclimatized microorganisms can absorb and metabolize organics more efficiently. The excess sludge is diverted to the sludge handling unit for treatment and disposal.

General loading and operational parameters for the activated sludge process is listed in Table 1.

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>LOADING (BOD/Day/lb MLSS)</th>
<th>AERATION (hr)</th>
<th>EFFICIENCY OF BOD REMOVAL (%)</th>
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<tr>
<td>High rate</td>
<td>1-2</td>
<td>4</td>
<td>80-85</td>
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<tr>
<td>Conventional</td>
<td>0.2-0.5</td>
<td>6</td>
<td>85-90</td>
</tr>
<tr>
<td>Extended aeration</td>
<td>0.05-0.2</td>
<td>30</td>
<td>90-95</td>
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</tbody>
</table>

An important factor in the operation of activated sludge systems is the food/microorganism (F/M) ratio. The "food" or the BOD in the influent wastewater
An important factor in the operation of activated sludge systems is the food/microorganism (F/M) ratio. The "food" or the BOD in the influent wastewater (without regard to return sludge) is expressed in pounds or kg/day of liquid volume in the aeration tank. The concentration of the suspended solids, which mainly consists of active microorganisms, is called mixed liquor suspended solids (MLSS). F/M can be computed from the formula,

\[ \frac{F}{M} = \frac{\text{BOD} \times Q}{\text{MLSS} \times V}, \]

where \( \text{BOD} \) = applied 5 day BOD in ppm

\( Q \) = wastewater flow rate mg/day or mL/day

\( \text{MLSS} \) = mixed liquor suspended solids

\( V \) = volume of the aeration tank, mL.

Operation and Control of Activated Sludge Process

Operation of an (A.S.) treatment plant is regulated by the quantity of air supplied, the rate of activated sludge recirculation and the amount of excess sludge withdrawn. The settleability of the mixed liquor in the final clarifier governs the rate of activated sludge recirculation. Poorly flocculated particles and filamentous growths that do not separate by gravity in the final clarifier contribute to the BOD and SS in the effluent. Excessive carryover of floc is called sludge bulking. This condition can be controlled by appropriate adjustments in the mixed liquor suspended solids concentration and F/M ratio. Sludge bulking may be caused by excessive agitation or insufficient aeration.

The settleability of mixed liquor is defined by the sludge volume index (SVI), which is equal to the volume occupied by 1 g of settled sludge and is expressed in (mL/g). To determine SVI, a sample of mixed liquor from the aeration tank is allowed to settle for 30 min in a 1L graduated glass cylinder. The volume of the settled sludge is read and the MLSS is also measured. The SVI, is then computed as

\[ \text{SVI} = \frac{V \times 1000}{\text{MLSS}}, \]

where \( V \) = volume to settled sludge, mL/L,

\( \text{MLSS} \) = mixed liquor suspended solids, mg/L.
D. Advanced Treatment

A wide variety of methods are used in advanced waste treatment to remove

(1) suspended solids
(2) BOD
(3) plant nutrients
(4) dissolved solids
(5) toxic substances.

These methods may be introduced at any stage of the total treatment process as in the case of industrial wastewater or may be used for the complete removal of pollutants after the secondary treatment. For the removal of dissolved organic substances the most popular method used is adsorption on activated carbon.

**ADSORPTION ON ACTIVATED CARBON**

Adsorption is a surface phenomenon wherein the dissolved substances in wastewater are attracted to and adhere to the surface of the adsorbent. The attractive forces holding the molecules at the surface may be either physical (physical adsorption) or chemical (chemisorption) in nature. In physical adsorption process the pollutants adhere to the surface of the adsorbent by weak interactions like vander waal's forces or hydrogen bonding and is accompanied by evolution of heat. The adsorbed material can be removed or desorbed by reducing the pressure or by increasing the temperature. Thus the process is reversible. Chemisorption, which is the result of a chemical interaction between the pollutant and the adsorbent, is usually irreversible with the heat of adsorption being much higher than that for physical adsorption. The pollutants are held to the solid surface by chemical bonds and the original material undergoes a chemical change.

Adsorption onto activated carbon is a physical sorption process. The adsorption occurs in several stages. The first stage is the diffusion of the pollutant from the bulk phase to the external surface of the solid. The second stage is the diffusion of the solid, and the third stage is the actual adsorption on the active sites in the pores. The third stage is relatively fast compared to the first two stages and it is these earlier stages that determine the rate of adsorption. The rate of adsorption of a substance depends on the concentration of the substance around the adsorbent, the
most economical and technically attractive method available for removing soluble organics, such as phenols, chlorinated hydrocarbons, surfactants, colour and odour producing substances from wastewater.

Adsorption system based on granular activated carbon can either be of fixed-bed type (flow down) or expanded-bed type (flow up). The adsorbers can be arranged in several different process configurations as shown in the figure 3.

In series operation, the wastewater enters the first column and leaves the second column receives the same feed and the effluents from each column are combined to form a composite product. When the carbon bed is saturated with pollutants, it is regenerated. In the series operation the first column is removed from service when the bed is exhausted and a fresh column is placed at the end of the series. The second column then becomes the lead column. In parallel operation the beds become saturated simultaneously and are replaced by a fresh batch.

After the bed becomes saturated, it is necessary to regenerate it for reuse. In thermal regeneration the activated carbon is dewatered and then passed through a multiple hearth furnace where the adsorbed organics are oxidised at temperatures of 815 to 925°C. Steam regeneration of activated carbon is also one of the popular methods used today.

Thus adsorption is a simple decontamination method which gives a sludge free operation. Most of the commercial adsorption systems currently use activated carbon and although it is the most popular and widely used adsorbent, there are problems associated with its use; viz., activated carbon is expensive and the higher the quality greater is the cost. Although regeneration of an adsorbent is possible, it is usual that upto 15% is lost in the process. Thus there is a search for a cheaper alternative to activated carbon, which should have a high enough quality and can be utilized in wastewater treatment systems.

E. Waste Water Sludge, Its Treatment And Disposal

In the process of removing pollutants from wastewater during treatment, sludge accumulates in the settling tanks and must be withdrawn, treated and disposed off. The amount of solids generated in a wastewater treatment system is a function of the degree of treatment provided and the amount of chemicals added. Land disposal
of sludge or sludge incineration is usually preceded by some type of treatment to render it easier and less effective to handle and reduce its volume. Sludge is treated prior to ultimate disposal for two reasons:

1) Volume reduction
2) Stabilization of organics

The common methods to accomplish the two objectives include thickening, biological digestion, dewatering and incineration. When incineration is used, there is no need to stabilize the sludge.

1. Thickening

Thickening serves to increase the solids concentration in the sludge. It is accomplished in one of the two ways:

- the solids are floated to the top of the liquid (floatation)
- or are allowed to settle to the bottom (gravity thickening)

2. Stabilization

The stabilization of sludge is accomplished by a sludge digestion process in which organic solids are biochemically decomposed. The organics converted into simpler and more stable products. Digestion reduces odors of the sludge, makes it less putrescible and easier to dewater and destroy pathogens. Sludge may be digested under anaerobic or aerobic conditions.

**Anaerobic digestion**

In modern anaerobic systems, the digestion process takes place in two covered circular tanks about 25m in diameter and 15m deep. The sludge in the first tank is heated to a temperature of 35°C and the contents thoroughly mixed. The digestion occurs in two stages. The first stage is commonly referred to as acid fermentation. In this stage organic material is converted into organic acids, alcohols and new bacterial cells and in the second stage the end products of the first stage are converted into gases, mainly methane and carbon dioxide. This stage is called methane fermentation. The digestion process in the first tank is completed within 10-15 days of detention time. The sludge then flows to the second tank for settling and storage. The digestor supernatant is pumped to the inlet of the treatment plant. Digested sludge is removed from the bottom of the second tank for further processing and final disposal.
Aerobic digestion

In aerobic sludge digestion, the sludge is aerated in an open tank similar to the activated sludge aeration tank. The sludge is aerated for a long period (approx. 30 days or more), during which most organics are stabilised and the amount of sludge is reduced. The aerobic digestor is followed by a settling tank unless the liquid is to be disposed of by land. The supernatant (effluent) from the clarifier is recycled back to the head end of the plant.

3. Conditioning

Conditioning of sludge facilitates the separation of the liquid and solids. Chemical conditioning involves addition of coagulants such as lime, ferric chloride, or organic polymers. This facilitates the neutralisation of the charges on the sludge particles so that they can collide and form larger and heavier particles to facilitate separation from the water. These conditioning chemicals (coagulants) are mixed into the sludge just before dewatering.

Dewatering

The process of removing water from the sludge is dewatering or drying even though the dewatered sludge may still be 70-75% water. The most popular method of dewatering is the use of sludge drying beds. The beds usually consist of 6-9in. of coarse sand supported on a graded gravel bed. The digested sludge is spread on an open bed of sand, where drying takes place by a combination of evaporation and drainage. A piping system with open joints placed in the gravel or crushed stone bed collects the water that drains from the sludge. Recently the use of vacuum filters and centrifuge has increased because of the faster dewatering.
4. Incineration

The dewatered sludge can be incinerated to convert it into inert ash. The exhaust gases from the incinerator must be treated to meet air quality standards.

In a multiple hearth-furnace, dewatered sludge passes through a series of hearths, where it is dried and heated to the ignition stage. Fuel burners provide the heat for start-up; afterwards sludge serves as a fuel to keep incineration going.

SLUDGE DISPOSAL

The dewatered or incinerated sludge may be applied to plots of land for the purpose of recovering nutrients or reclaiming spoiled land. Application rates are controlled by characteristics and intended crops.

Sludge landfill is a planned burial of wastewater solids, which may include screenings, grit, processed sludge, and ash, at a suitable site. A trench is excavated, and solids are put in it and covered with a layer of soil that does not permit water to percolate.

Effluents from dye industries are highly coloured and also have high amounts of dissolved organic content (2). There has always been a pressing need for low cost treatment techniques for treating effluents from dyes and chemical industries. The extent of contamination of the water with such effluents has raised much concern because of the potential health hazards associated with the entry of these substances into the food chain. Certain dyes have been found to cause nausea, haemorrhage, ulceration of skin and mucous membrane, dermatitis, perforation of nasal septum and severe irritation of respiratory tract (3). Unless and otherwise properly treated, these dyes may significantly affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of metals, chlorides etc. in them (4). The primary concern in any case is the impact of dye colour upon the aesthetics of a receiving water body (5).

Dyes are highly stable molecules, which often resist degradation by light, chemical, biological and other exposures (6). While both biological and physico-chemical methods have been employed for dye removal, the former has not been successful, due to the essential non-biodegradable nature of most of the dyes (7-9). Advanced wastewater treatment methods are usually needed to achieve effluent
quality requirement (2). These include some combination of biological, chemical and physical processes. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal, cost-effective alternative to the conventional expensive methods.

The preparation of low cost adsorbents for water purification has recently been reviewed by Pollard et al. (10). For example a wide range of lignocellulose agricultural by-products have successfully been converted into activated carbons including coconut coir (11), jute stick (12), sarkanda grass (13), palm tree corbs (14), rice husk (15) and tamarind nut shells (16-18). The suitability of these precursors is determined by their local and bulk availability, carbon content and the presence of inherent microstructure within the substrate itself (19). Viability of their ultimate use may be determined as much by these factors as by the adsorptive capacity, regenerative characteristics and physical form to the subsequent carbon product.

The present study is aimed at studying the adsorption capacities of locally available, low cost adsorbents. The adsorbents selected, were easily available and were waste materials like the neem leaf, neem bark, coconut kernel, coconut shell and the sugarcane bagasse having no commercial value and problems of their disposal. Synthetic polymers like a hydroxamic acid and calixarene were also tried for their effectiveness. The performance of these adsorbents was evaluated against activated charcoal for the removal of the organic substances from the effluent. The batchwise column studies were conducted on a laboratory scale using a composite effluent sample of the dye industries. The COD of the samples, before and after passing through the column was measured.
EXPERIMENTAL

MATERIALS AND METHODS

The double distilled water used was prepared by the method described elsewhere (20). A. R. grade reagents were used of BDH and E. Merck unless otherwise specified. A poly styrene p-carboxo hydroxamic acid (21) and a poly acrylo calix[6]arene hydroxamic acid (22) were obtained which were synthesised by the methods developed in the laboratory. Neem bark, neem leaves, coconut kernel, coconut shell and sugarcane bagasse were procured from their respective waste generation sites.

The leaves and bark of Azadirachta indica (neem) were collected and washed several times with distilled water to remove surface adhered particles and water solubles. It was than dried. The leaves and bark were heated at 300 - 350°C in a muffle furnace in a inert atmosphere for 3 hr, cooled to room temperature and sieved to obtain the 60 mesh size fraction. The products neem leaf ash and neem bark ash were dried and kept in a dessicator for further use.

The coconut kernel (husk) was seperated from the fruit and was shredded into fine pieces, in a laboratory grinder. It was then thoroughly washed with distilled water and dried for further use until a clear decantate is obtained. The sherdded coconut husk was dried and stored in a dessicator for further use. The unshredded kernel and the hard coconut shells were washed several times with distilled water and dried. It was then heated in a muffle furnace at 330°C for 4 - 5 hr and sieved. A 60mesh product was separated and stored in a dessicator for further use.

Sugarcane waste (devoid of juice) was obtained and washed several times with distilled water and dried. This was then burnt in a muffle furnace at 300°C for hr. The bagasse ash thus obtained was sieved into 60 mesh size fraction and stored in a dessicator for further use.

DETERMINATION OF PHYSICAL PROPERTIES OF THE ADSORBENTS

Physical properties of adsorbents like bulk density, moisture (%), fixed carbon content, Ash (%), Matter soluble in water (%), matter soluble in acid (%), ion exchange capacity, were determined by standard methods (23, 24).
Bulk density of swollen adsorbent was determined by filling 1g of fully swollen adsorbent in a measuring cylinder filled with water and pounded with hard rubber till the volume of polymer did not change. The stationary volume was read and expressed as g/m³.

The moisture content of the adsorbents was determined by weighing 0.5 g of the material in an oven at 140°C. It was cooled in a dessicator and weighed and the % moisture was calculated.

The ash (%) is usually determined as the residue after ignition at 650 ± 25°C. The watersoluble or acid soluble part of the ash is determinned by dissolving the ash in water or acid (25).

The ion exchange capacity is determined by placing 0.5g of the material in a dry stoppered conical flask. Added 25mL of 0.25 N sodium bicarbonate solution and allowed to stand for 24 hr. The solution was filtered and 25 mL of 0.25N hydrochloric acid was added and boiled to expel the carbon dioxide and titrated with 0.25N sodium hydroxide solution.

DECONTAMINATION COLUMN

A glass column of length 20 cm and internal diameter 1cm was packed with 1 gm of the adsorbent material. The columns were filled with double distilled water when not in use.

Effluent used for the decontamination studies was obtained from the Kharicut canal in Vatva GIDC Phase II. COD determination of influent and effluent column samples was used as a basis of the decontamination of the industrial effluent with respect to organics. Twenty mL of well-shaken sample was passed through the column with a flow rate of 1ml per minute. Ten mL of sample is collected in a clean and dried beaker was used for the COD estimation. From the difference in the COD of the sample before and after passing through the column, the % COD reduction efficiency was calculated for each adsorbent.

In case of the combined adsorbent material study, the two adsorbents in equal proportion (0.5g + 0.5g) were packed into the glass columns one above the other. In the two column study of bagasse ash, two columns were filled with 1g each of the bagasse ash. The sample was passed through the columns so that the effluent from column 1 was the influent of column 2 and the final COD reduction was determined.
RESULTS AND DISCUSSION

A comparative study of activated carbon with other adsorbents like sawdust, activated alumina, molecular sieves and diatomite have been carried out which showed that activated carbon (GAC, PAC) has a higher COD reduction efficiency (1).

The process of adsorption is necessarily a mass transfer process of solute from the solvent to the surface of a solid adsorbent. Since virtually all the useful surface area is within the pores, the overall rate of adsorption is dependent on the particle size. The rate of adsorption varies reciprocally with the square of the particle diameter (26). The smaller pore size of the charcoal enables it to entrap greater amount of organic substances.

Characteristics of various activated carbon materials studied in the present investigation are given in Table 2. The COD reduction efficiencies of various adsorbents are summarised in Table 3. The activated charcoal is having the efficiency of 49% while the coconut shell-bagasse ash combined column shows an efficiency of 47.3%. The bagasse ash column shows an efficiency of 48.1%. Thus a two column study was carried out by passing the effluent twice through two fresh bagasse ash columns to have a better adsorption of COD. This combined column gave 70.5% reduction in COD (Table 3).

In the case of poly styrene-p-carboxo hydroxamic acid, the COD reduction is 45%. The functional group of a hydroxamic acid present in the Poly styrene backbone enables to entrap certain ionic or metallic components present in the dye molecules, for which this resin is highly selective. Thus it is able to entrap the dye molecules by a chemical interaction and shows a COD reduction efficiency of 45%.

The other polymer (poly acrylo calix[6]arene hydroxamic acid) gives a reduction efficiency of only 29% which may be due the absence of a strongly polar group for attracting anionic or cationic dyes in the effluents. More over it may not be able to act as a resin for physio-sorption because of the larger effective pore size of the particles.

The neem bark ash and the neem leaf ash both were found to be ineffective giving 28 and 33% reduction efficiency, respectively. Neem bark has a greater amount of lignocellulosic material thus the possibility of uncombustioned products in the ash is greater. This has effected the pore size of the adsorbent prepared and so gives a lesser efficiency than the neem leaf adsorbent.
## TABLE 2

PHYSICAL CHARACTERISTICS OF ACTIVATED CARBON OBTAINED FROM VARIOUS MATERIAL

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>1</td>
<td>Bulk density</td>
<td>0.72</td>
<td>0.70</td>
<td>0.66</td>
<td>0.67</td>
<td>0.38</td>
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<td>Moisture %</td>
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<td>-</td>
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<td>99.53</td>
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<td>4</td>
<td>Ash %</td>
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<td>0.65</td>
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<td>Matter soluble in water (%)</td>
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<td>0.01</td>
<td>0.18</td>
<td>0.20</td>
<td>1.48</td>
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<td>Matter soluble in acid (%)</td>
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<td>Ion exchange capacity (m eq./g)</td>
<td>3.76</td>
<td>2.78</td>
<td>1.00</td>
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<td>0.08</td>
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<td>No.</td>
<td>COLUMN COD OF SAMPLE (ppm)</td>
<td>COD AFTER PASSING THROUGH THE COLUMN (ppm)</td>
<td>REDUCTION IN COD (ppm)</td>
<td>% REDUCTION</td>
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<td>3</td>
<td>Poly acrylo calix[6]arene H. A.</td>
<td>1288</td>
<td>912</td>
<td>376</td>
<td>29.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Charcoal-Poly acrylo calix[6]arene H. A.</td>
<td>1760</td>
<td>960</td>
<td>800</td>
<td>45.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Neem leaf ash</td>
<td>1008</td>
<td>680</td>
<td>328</td>
<td>33.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Neem bark ash</td>
<td>1152</td>
<td>829</td>
<td>323</td>
<td>28.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Coconut kernel (shredded)</td>
<td>1152</td>
<td>1024</td>
<td>128</td>
<td>11.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Coconut kernel ash</td>
<td>1152</td>
<td>808</td>
<td>344</td>
<td>29.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Coconut shell ash</td>
<td>1021</td>
<td>801</td>
<td>220</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Bagasse ash</td>
<td>1021</td>
<td>528</td>
<td>492</td>
<td>48.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Coconut shell ash-bagasse ash</td>
<td>836</td>
<td>440</td>
<td>396</td>
<td>47.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Bagasse ash</td>
<td>836</td>
<td>246</td>
<td>590</td>
<td>70.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The coconut kernel was shredded in a grinder but due to the lesser rpm of a laboratory grinder the particle size was not uniform. Thus no improvement in the efficiency of the reduction efficiency was found. The coconut kernel ash has an efficiency of 30% as compared to the coconut shell ash (21.5%). The fibrous structure of the coconut kernel resulted in a more porous ash as compared to that of the coconut shell ash. Thus the difference in the reduction efficiency is observed.

**BATCH ADSORPTION STUDIES**

The sorption was measured by equilibrating 1.0g/L of the adsorbent carbon material with 50mL of sample with known COD in glass stoppered bottle of 300 mL capacity. These were agitated in a temperature controlled rotary mechanical shaker bath for a particular period of contact time. After equilibration, the bottles were taken from the shaker and carbon was separated from solution by filtration. The filtrate was analysed for COD content. The desired pH of the solutions was adjusted with NaOH and HCl solutions and measured with systronics pH meter 303. Kinetics experiments were also conducted and the rate constant calculated by the conventional rate equation. The distribution co-efficient $K_d$ (mL/g) was estimated from the expression,

$$K_d = \frac{(A - B)}{B \times V/m}$$

where, $A$ and $B$ are the COD content of adsorbate solution at time zero and at equilibrium respectively. $V$ is the volume of the adsorbate solution (mL) and $m$ is the mass of the adsorbent (g).

The adsorption of the COD on the bagasse activated carbon was examined at different initial concentration of 0.25 - 1.0 mg/L. The experimental results are shown graphically as a plot of % COD removal versus time in Fig.3. It can be seen that the time growth of adsorption of COD is very fast, with most of the sorption occurring within the first few minutes. The complete adsorption equilibrium between two phases is not the same for studied concentrations. Equilibrium time for 0.25 mg/L is about 1.0 min., while 1.0 mg/L found nearly about 1.5 min. It is quite apparent form Fig.4, that the extent of COD adsorbed at the equilibrium as well as prior to equilibrium increases with increase in adsorbate concentration. Numerically the amount adsorbed at equilibrium increased from 0.2 to 0.4 mg/g with the change in COD concentration from 0.1 to 1.0 mg/L.
% COD Adsorbed

Time (min) →

[I - 0.25 mg/L, II - 0.50 mg/L, III - 0.75 mg/L, IV - 1.0 mg/L]

Fig: 3 ADSORPTION OF COD ON THE BAGASSE ACTIVATED CARBON AT VARIOUS CONCENTRATIONS
Fig 4: ADSORPTION ISOTHERMS OF COD ON DIFFERENT ADSORBENTS

- BAGASSE, POLYSTYRENE-p-CARBOXO H. A.,
Fig 5: LANGMUIR ISOTHERM PLOT OF COD ON VARIOUS ADSORBENT SYSTEMS

- BAGASSE,
- POLYSTYRENE-p-CARBOXO H. A.,
- NEEM LEAF ASH
It was found to obey Langmuir adsorption isotherm. This isotherm can be represented by

\[ \theta = \frac{b_p}{1 + p} \]

Where, \( \theta \) is the fraction of the surface covered

\[ \theta = \frac{C}{C_0} \]

\[ \frac{C}{C_0} = \frac{1}{K_p} + \frac{p}{K_0 p} \]

Where \( C_0 \) is the amount adsorbed per unit weight (mg/g), \( C \) is the concentration of COD at equilibrium (mg/L), \( K_p \) and \( b \) are Langmuir constants indicating sorption intensity (mg/g) and energy of sorption (L/mg) respectively. A linear plot of \( C/ C_0 \) versus \( C \) for different activated carbon systems suggests the applicability of the above model and is shown in Fig. 5.

The bagasse (waste sugarcane) is a highly porous, lignocellulosic material. Thus the ash prepared from this material shows a higher porosity, uniform particle dimensions and thus greater reduction efficiencies (48.1%) than the other materials used in the present study. To combine the COD reduction efficiency of the coconut shell ash and bagasse ash, respectively the sandwich column of both the adsorbents together was prepared but the COD reduction efficiency did not vary to a greater extent, but colour removal was achieved. The two-column study was carried out for the bagasse ash to observe the viability of its use in a series connection in effluent treatment systems. This column thus can be used in wastewater treatment systems.

Figure 6 shows the reduction in the COD of the effluents by different adsorbents. Here the COD of the sample (COD S) and the COD of the sample after passing through the column of the particular adsorbent (COD T) are shown as different columns for each of the adsorbent.

Figure 7 compares the COD reduction efficiency of the adsorbents, where it clearly depicts that the bagasse ash has reduction efficiency equal to that of the activated charcoal and the series column of bagasse ash can reduce COD of a effluent sample to around 70.5%.
Fig 6: REDUCTION IN COD USING DIFFERENT ADSORBENTS
Fig. 7: COD REDUCTION EFFICIENCY OF VARIOUS ADSORBENTS
REFERENCES


