REMOVAL OF CHROMIUM FROM STEEL PLANT EFFLUENT - A COMPARATIVE STUDY USING POLYMER AND METHOD OF ADSORPTION.

CIVIL ENGINEERING

PROJECT REPORT

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CERTIFICATE

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REMOVAL OF CHROMIUM FROM STEEL PLANT EFFLUENT - A COMPARATIVE STUDY USING POLYMER AND METHOD OF ADSORPTION.

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SYNOPSIS

Activated carbon adsorption and use of polymer is ascertained to be a promising technique for recovery of chromium from the pickling wastes. Hence a comparative study has been made using these two processes.

In view of the high cost and difficult procurement of commercial activated carbon, a need was sensed to evalve suitable alter natures which hold promise in treatment of pickling waste. As a prelude to this endeavour, a low-cost adsorption with Mango leaf & sawdust as the base material, was investigated for its adsorption potential of designated size (710 - 1400 microns) charred at 800^0 C. Column experiments were conducted varying different parameters. The collected samples where then tested using atomic adsorption spectrophotometer.

' Polyacryl amide ' a water soluable polymer was used for the recovery of chromium. Various concentration of polymer for a constant pH was used.

The recovery using both the processes are studied compared in this process.

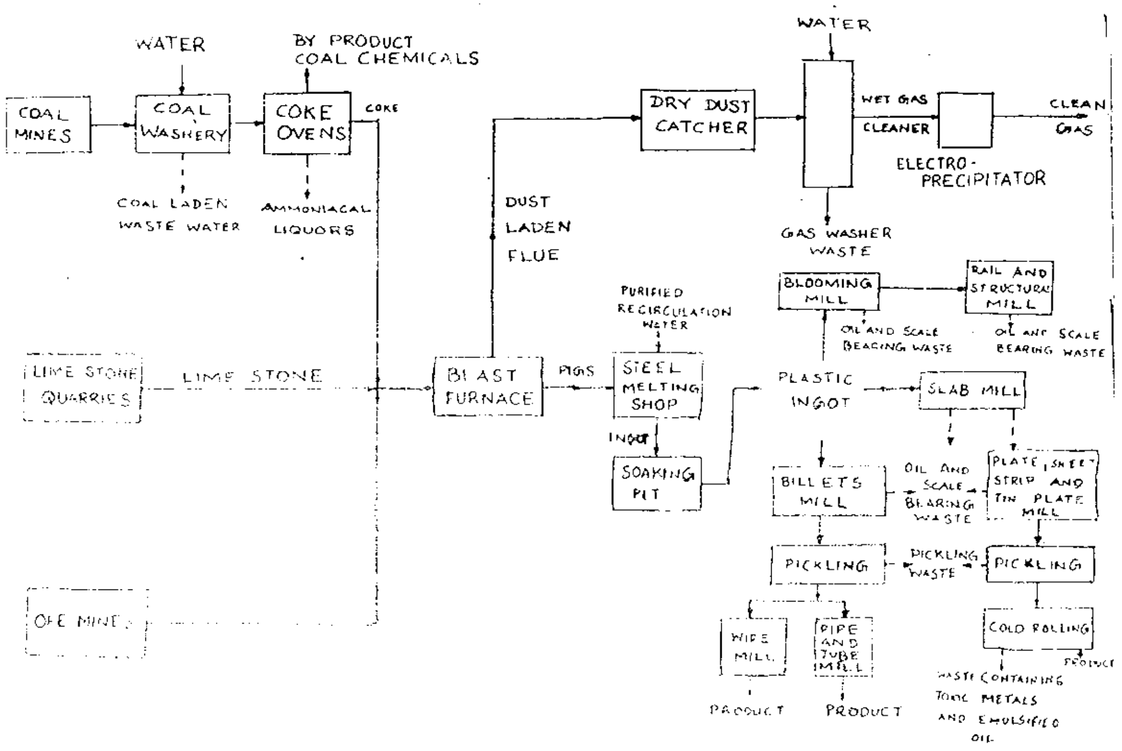
1. INTRODUCTION

With the growth in the production of high grade and alloy steels in the steel industry, a new problem has appeared requiring a solution. This originates from the face that an increase in the production of alloy steel leads to an increase in the content of elements like chromium, nickel, copper etc., of these in elements chromium is used more frequently for alloying in appreciable concentration.

Along with the steel produced, effluents also come out of a steel industry. In almost all the steel industries, the effluents are converted into their hydroxides or made in too less soluble compounds called sludge.

Utilization of these sludges creates problems of ecological and economical nature. In most of the cases, they are stored at various dumping sites and constitute, despite various protective measure, a substantial danger to the environment. With the phenomenal increase in steel production the liquidation of such waste dumps will become an unavoidable necessity sooner or latter.

A brief introduction about the steel making process will give an idea about the different wastes discharged at different stages.



FLOW DIAGRAM FOR MAJOR OPERATION IN A INTEGRATED STEEL PLANT

1.1 STEEL MAKING PROCESS AND WASTE COLLECTION

Integrated steel plants usually consists of five main units, namely.

1.1.1. Coal Washery
1.1.2. Coke oven
1.1.3. Blast Furnace
1.1.4. Steel Melting Shop
1.1.5. Hot and cold Rolling Mills

A flow diagram of an integrated steel plants is as shown in the figure.

1.1.1 Coal washery and its waste water

The coal needs some processing like crushing, screening and wet washing to remove solid foreign mater present in it to make it suitable for use in coke ovens.

Water, after being used for washing, contains solid particles in its like coal fines and other impurities like shale, clay, calcite, gypsum, kaolin, pyrites etc..

1.1.2 COKE OVENS AND THEIR WASTE WATER

The production of coke involves the carbonization of bituminous coal by heating in the absence of air at a temperature range of 900 - 1000^0 C in an oven, which drives off all the volatile portions in the coal. The gas which is evolved is collected through the stand pipes and is cooled in stages. In the first stage, the gas is cooled to about 800^0 C by spraying cold liquor over the gas, thereby producing mainly tar as the condensate. In the second stage by a further cooling to about 30^0 C, condensate containing additional tar and ammonia liquor is produced. The liquor after the separation of tar in a tar-decanter, are recycled as sprays in the first stage. The excess liquor known as "ammoniacal liquor" is subjected to distillation for the recovery of ammonia. In the third stage, the gas is compressed and cooled for further recovery of chemicals. This stage also includes a benzol washer for the recovery of light oils.

The coal after being corbonized is removed from the oven and quenched by cold water. The water after quenching contains coke fines and comes out as waste.

The waste water generated in this process are the ammonical liquor and benzol washer.

1.1.3 BLAST FURNACE AND ITS WASTE WATER

The blast furnace process consists of charging iron ore and coke as fuel with lime stone and dolomite as fluxing material. Pig iron is the metallic product of the process.

Large amount of water is used in blast furnace for cooling and cleaning operations. The cooling water normally remains uncontaminated and contains mainly suspended solids.

1.1.4 STEEL MELTING SHOP AND ITS WASTE

In the steel melting shops, the pig iron obtained from the blast furnace is oxidised to produce steel ingots. Water is required for cooling the furnace and as such this water remains uncontaminated and is reused.

1.1.5 ROLLING MILLS AND THEIR WASTE :-

The steel ingots obtained from the steel melting shop are rolled to different products in the rolling mills. However, the ingots are heated first in the soaking pits until they are plastic enough and are then rolled into blooms, billets or slabs depending upon the final product required. These are then cooled and stored and subsequently sent to another rolling mill, where these are re-rolled to produce final products.

The blooms, billets and slabs require reheating and this is accomplished in a continuous type reheating furnace where the blooms etc., are pushed over skid pipes, while they are heated and ultimately placed over the rool table.

During rolling, lots of scales are given off and are collected in the scale flume, below the roll tables. These scales are flushed down with high pressure water and are collected at the scale pit.

The rolls which gets heated up during the process are cooled with water which is then laden with oil and grease. This water also joins the waste water flow through the flume.

Some amount of water is also used to cool the skid pipes and furnace. This water is also sent to the common scale pit. Water is also used for de-scaling of fine end products which eventually increases the volume of the scale bearing waste.

When ever finer products like sheets,strips etc., are required the products from hot rolling mills are normally subjected to cold rolling. The surface oxides of the steel slabs must be removed before they are subjected to rolling.

The removal of hard black oxides formed on the surface of the products during the lot rolling is by a process known as "pickling", in which the steel slabs formed in the hot rolling mill are immersed in either sulphuric acid or hydrocloric acid or a mixture of hydrofloric acid and nitric acid. The acid reacts with the iron oxide scales and forms ferrous products depending upon the type of acid used. The used pickling liquor is then discharged and a then fresh batch of acid is taken.

Cold rolling generates that which is dissipated by the application of rolling solutions which are usually oils emulsified in water. The waste water generated contains significant amount of oil. In addition the waste from the cold rolling mill originates from the cleaning line, containing detergents.

1.2 TREATMENT OF WASTE DONE IN AN INTEGRATED STEEL PLANTS

1.2.1 TREATMENT OF COAL WASHERY WASTE

The suspended solids in the coal washery waste is removed in a clarifier with or without coagulation.

1.2.2 TREATMENT OF COKE OVEN WASTE :-

The coal washery waste is mixed with equal volumes of ammonical liquor and flocculated with lime in diariflocculator . The effluent of the flocculator is then given activated sludge treatment.

1.2.3 TREATMENT OF BLAST FURNACE WASTE :-

The blast furnace waste which contains mainly iron oxide and silica is treated in a clariflocculator with or without the addition of a coagulant like alum or lime.

1.2.4 TREATMENT OF THE SCALE PIT EFFLUENT :-

The scales produced in primary mills, like blooming mills etc., are coarse and mostly settle in the scale pit itself. A substantial quantity of finer scales produced in the process of rolling the billets, slabs etc., also gets settled. The effluent from the scale pit still contains fine scales, oil and grease and requires secondary treatment in clariflocculators using sodium hydroxide.

The iron content of the clarifier sludge is very high. As such the sludge is thickened, de-watered using vacuum filters and then sent to sintering plant so that it can be fed back to blast furnace. Thickening removes oil and grease from the sludge.

1.2.5 TREATMENT OF PICKLING WASTE :-

The waste generated during pickling operations may be contaminated with chromate, cyanide, fluoride, zink, tin, copper, acids and alkalis.

The pollution potential of this waste is very high and its disposal has always been a problem. The pollution due to this waste can be avoided if complete recovery of the waste is adopted. The pickling waste which is highly acidic in nature is treated with lime and converted into hydroxide. They are then dumped in lined pits.

2. CHARACTERISTICS OF EFFLUENT

2.1. NATURE OF WASTE

The picking waste is in the liquid form.

2.2. ODOUR

The liquid effluent does not have an offensive odour. The offensive odour is mainly due to micro-organism or other decaying substances, but as no such substances are present in the effluent hence is no decying odour.

2.3. COLOUR

The effluent bluishgreen in colour.

2.4. PH

The term pH is used to express the intensity of the acid or alkaline condition of a solution. It is the measure of the hydrogen ion concentration.

pH is defined as the logarithm (base 10) of the reciprocal of the hydrogen ion concentration. If the value is less than 7 them the nature of the sample is basic. The pH can be measured electrometrically or calorimetrically. Electrometric mehods are by far the most accurate and sufferes with little or no interference. The pH metres are available in various types commercially.

PROCEDURE :

The pH meters are usually standardized with a standard buffer solution.

Preparation of buffer solution :

Distilled water used should have a specified conductance less than 2 micro-ohms at 25% and a pH of 5.6 to 6.0

Care should be taken to complete dissolution of salts, otherwise pH may be incorrect.

PH 7 BUFFER SOLUTION :

1.36 g of Anydrous Potassium Dihydrogen Phosphate, and 1.42 g Anhydrous Disodium Hydrogen phosphate is dissolved in distilled water and made up to 1000 ml in a volumetric flask.

MEASUREMENT OF PH :

The manufacturer's instructions to operate the pH meter and to determine the pH of the sample is to be followed. Before the measurement of pH, the pH meter is standardized using the standard buffer solution. Now the meter has been calibrated.

Now the electrodes are introduced in to the sample to get the pH reading directy. The electorde response is checked occasionally by measuring the pH of another standard buffer solution of different pH. The pH of the sample was found out to he 1.4. hence the sample is acidic in nature.

2.5. TABLE GIVING THE CHARACTERISTICS OF EFFLUENT

Sl.No.	Parameter	Concentration
1	Colour	Dark bluish green
2	Odour	No effective odour
3	PH	1.4
4	Electrical conductivity (10 ml sample diluted with 130 ml distilled water)	1460 µs
5	Mineral acidity (ppm)	2240
6	Total acidity (ppm)	9920
7	CO_2 acidity (ppm)	7680
8	Total solids (mg / lt)	9.25
9	Volatile solids (mg / lt)	7.25
10	Non-volatile solids (mg / lt)	2.00

SAMPLING

The raw Effluent sample from the steel plant for different period of time was collected from the pickling acid process. Sample was also collected from various discharge points during the process. The effluent sample is collected before it is subject to any kind of treatment.

EQUIPMENTS AND CHEMICALS USED

The chemical and chemicals used for the determination and subsequent separation of chromium are :

4.1 EQUIPMENTS :

Physical balance

Silica crucible

Titration kit

Water bath

4.2 CHEMICALS

Ammonia buffer

Ammonium biflouride NH F . HF

Concentrated nitric acid, NHo_3

ION concentrated sulphuric acid, $H_2 SO_4$

EDTA Solution

Eriochrome Black - T Indicator (Solo Chrome Black)

Glass Beads

Hexamine

Lead Nitrate solution

Potassium Persulphate $K_2 S_2 O_8$

0.1N Silver Nitrate Solution, $AgNo_3$

0.1N Sodium thiosulphate, $Na_2S_2O_3 5H_20$

Starch Soluble, $(C_6H_{10}O_5)n$

Sulphamic Acid, NH_2SO_3H

Whatmen (Filter paper) Qualitative i number 40

Xylenol Orange Indicator

4.3. METHODS FOR SEPERATION OF CHROMIUM :

The possible methods for the separation of chromium are :

4.3.1. Carbon Adsorption method

4.3.2. Ion exchange method

4.3.3. Chemical method

- a. Roasting with sodium hydroxide
- b. Use of polymer

4.3.1.CARBON ADSORPTION METHOD :

The principle involved in this method is adsorption of metals on to the carbon surface. On passing the liquid containing chromium through a carbon column the chromium metal gets adsorbed on to the surface. However, this method is applicable only when chromium is in hexavalent form.

4.3.2. ION EXCHANGE METHOD :

In this method, the chromium if present in tricalent chromium is oxidised in to hexavalent chromium by electrochemical oxidation and the solution is passed through a highly acidiccations exchanger to retain all metal cations contained in the solution. The cations are then treated in a zeolyte bed to separate the chromium.

4.3.3.CHEMICAL METHOD :

Here, chemicals are made use of in the separation. This can be achieved either by roasting with sodium hydroxide or by the use of a polymer.

In the method of roasting, the waster is roasted with sodium hydroxide following by water leaching. The chromium from the leach liquor can be recovered utilising an oxidation - reduction reaction with pH adjustments to form a hydrous chromic oxide precipitate.

By the use if a polymer, chromium can be separated by adjusting the pH of the solution. The polymer used for the separation was poly acryl amide of strength 0.1%. Because of the "selective adsorption" properly of poly acrylamide it is used as a medium for recovery chromium.

By varying the pH, the polymer adsorbs metals like Iron, Calcium and Nickel without affecting chromium.

Considering the various facilitates that were available, the use of polymer for the recover was found to be the most feasible method.

4.4. DETERMINATION OF CHROMIUM CONTENT :

Chromium is present in two forms, hexavalent and tricalent forms.

PRINCIPLE

This method is based upon the oxidation of iodide and iodine by dichromate in acidic solution. The liberated iodine is titrated with standard thiosulphate solution using starch as indicator.

INTERFERENCES

Iron and nitrate interference :

Iron is innocuous by addition of ammonium biflouride and nitrate by the addition of sulphamic acid.

HEXAVALENT CHROMIUM

PROCEDURE

10 ml of the sample is taken is a conical flask and made to 100 ml by adding 90 ml distilled water.

To this 2m of 10N $H_2 SO_4$ 1 gm ammonium biflouride and 2gm sulphamic acid are added.

2gm sulphamic acid are added :

The flask is swirled to dissolve the chemicals added and 2 gms of potassium iodide is added to the flask and swirled again.

The flask is kept in a dark place for five minutes in an undisturbe position. To this a few drops of starch solution is added as an indicator. The colour of the solution turns blue.

This is titrated with standard 0.1N sodium thiosulphate solution where the end point is the disappearance of the blue colour.

Volume of thiosulphate used = 1.9ml

Normality of thiosulphate = 0.1V

Volume of sample = 100ml

Amount of chromium (VI) =

$$\frac{\text{Volume of thiosulphate x normality of thiosulphate x } 38.7 \text{ E}^{6}}{\text{Volume of sample x } 10^3}$$

$$= \frac{9 \text{ x } 0.1 \text{ x } 38.7 \text{ x } 10^6}{100 \text{ x } 10^3}$$

$$= \underline{348.3 \text{ mg / l}}$$

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and the sample is made up to 100 ml using distilled water. The following reagents are added to order with mixing after each addition.

5 ml of 10 Sulphuric acid

2 ml of 1N silvernitrate solution

2 gms of potassium persulphate

Sulfuric acid is added to acidify the solution (the solution become colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bank. The colour of the solution changes from wine red to pink.

100 ml distilled water is added to the cooled solution. 1 gm of Ammonium biflouride is added to the flask and swirled until all the salt is dissolved. 2 gms of potassium iodide is added to the above and the flask is swirled again. Now the solution becomes yellow in colour.

The flask is then kept in darkness for about five minutes. To this solution starch solution is added as an indicator. The colour of the solution changes to blue.

The obtained solution is titrated against 0.1N sodium thiosulphate solution taken in a burette and the end point is the disappearance of the blue colour.

Volume of This sulphate (ml)	Amount of chromium (mg / 500 mg.)
24.5	948.15

Volume of thiosulphate used = 24.5ml

Normality of thiosulphate = 0.1 N

Volume of sample = 100 ml

$$\text{Amount of chromium} = \frac{24.5 \times 0.1 \times 38.7 \times 10^6}{100 \times 10^3}$$

= 948.15 mg/l

Amount of Cr (III) =

[Total chromium - Amount of chromium (VI)]

= 948.15 - 348.3

= 599.85 mg/l

4.5 DETERMINATION OF CHROMIUM AFTER ADDITION OF 5 ML POLYMER

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and is made up to 100 ml using distilled water 5 ml of 1% strength polyacrylamide is added and mixed well with mixing after each addition.

5 ml of 10 N sulphuric acid

2ml pf 1 N Silvernitrate solution

2 gms of potassium Persulphate

Sulphuric acid is added to acidify the solution (the solution becomes colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bath. The colour of the solution changes from wine red to pink.

100 ml distilled water is added to the cooled solution. 1 gm of ammonium biflouride is added to the flask and swirled until all the salt is dissolved. 2 gms of potassium iodide is added to the above and the flask is swirled again. The solution becomes yellow in colour.

The flasks is then kept in darkness for about five minutes.
To this solution starch solution is added as an indicator. The colour of the solution changes to blue.

The obtained solution is titrated against 0.1N sodium thiosulphate solution taken in a burette and the end point is the disappearance of the blue colour.

Volume of thiosulphate used = 21.5 ml

Normality of thiosulphate = 0.1N

Volume of sample = 100ml

Amount of chromium = Normality of sample x Equivalent weight

= $0.0215 \times 38.7 \times 10^6 / 10^3$

= $\underline{818.06 \text{mg} / \text{l}}$

4.6 DETERMINATION OF CHROMIUM AFTER ADDITION OF 10 ML POLYMER

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and is made up to 100 ml using distilled water 10 ml of 1% strength polyacrylamide is added and mixed well with mixing after each addition.

5 ml of 10 N sulphuric acid

2ml pf 1 N Silvernitrate solution

2 gms of potassium Persulphate

Sulphuric acid is added to acidify the solution (the solution becomes colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bath. The colour of the solution changes from wine red to pink.

100 ml distilled water is added to the cooled solution. 1 gm of ammonium biflouride is added to the flask and swirled until all the salt is dissolved. 2 gms of potassium iodide is added to the above and the flask is swirled again. The solution becomes yellow in colour.

The flasks is then kept in darkness for about five minutes.

To this solution starch solution is added as an indicator. The colour of the solution changes to blue.

The obtained solution is titrated against 0.1N sodium thiosulphate solution taken in a burette and the end point is the disappearance of the blue colour.

Volume of thiosulphate used = 19.6 ml

Normality of thiosulphate = 0.1N

Volume of sample = 100ml

Amount of chromium = Normality of sample x Equivalent weight

= $0.0196 \times 38.7 \times 10^6 / 10^3$

= 759.18 mg / l

4.7 DETERMINATION OF CHROMIUM AFTER ADDITION OF 15 ML POLYMER

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and is made up to 100 ml using distilled water 15 ml of 1% strength polyacrylamide is added and mixed well with mixing after each addition.

5 ml of 10 N sulphuric acid

2ml pf 1 N Silvernitrate solution

2 gms of potassium Persulphate

Sulphuric acid is added to acidify the solution (the solution becomes colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bath. The colour of the solution changes from wine red to pink.

100 ml distilled water is added to the cooled solution. 1 gm of ammonium biflouride is added to the flask and swirled until all the salt is dissolved. 2 gms of potassium iodide is added to the above and the flask is swirled again. The solution becomes yellow in colour.

The flasks is then kept in darkness for about five minutes.

To this solution starch solution is added as an indicator. The colour of the solution changes to blue.

The obtained solution is titrated against 0.1N sodium thiosulphate solution taken in a burette and the end point is the disappearance of the blue colour.

Volume of thiosulphate used = 19.1 ml

Normality of thiosulphate = 0.1N

Volume of sample = 100ml

Amount of chromium = Normality of sample x Equivalent weight

= $0.0191 \times 38.7 \times 10^6 / 10^3$

= 740.32 mg / l

4.8 DETERMINATION OF CHROMIUM AFTER ADDITION OF 20 ML POLYMER

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and is made up to 100 ml using distilled water 20 ml of 1% strength polyacrylamide is added and mixed well with mixing after each addition.

5 ml of 10 N sulphuric acid

2ml pf 1 N Silvernitrate solution

2 gms of potassium Persulphate

Sulphuric acid is added to acidify the solution (the solution becomes colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bath. The colour of the solution changes from wine red to pink.

100 ml distilled water is added to the cooled solution. 1 gm of ammonium biflouride is added to the flask and swirled until all the salt is dissolved. 2 gms of potassium iodide is added to the above and the flask is swirled again. The solution becomes yellow in colour.

The flasks is then kept in darkness for about five minutes.

To this solution starch solution is added as an indicator. The colour of the solution changes to blue.

The obtained solution is titrated against 0.1N sodium thiosulphate solution taken in a burette and the end point is the disappearance of the blue colour.

Volume of thiosulphate used = 18.3 ml

Normality of thiosulphate = 0.1N

Volume of sample = 100ml

Amount of chromium = Normality of sample x Equivalent weight

= $0.0183 \times 38.7 \times 10^6 / 10^3$

= <u>709.50 mg / l</u>

4.9 DETERMINATION OF CHROMIUM AFTER ADDITION OF 25 ML POLYMER

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and is made up to 100 ml using distilled water 25 ml of 1% strength polyacrylamide is added and mixed well with mixing after each addition.

5 ml of 10 N sulphuric acid

2ml pf 1 N Silvernitrate solution

2 gms of potassium Persulphate

Sulphuric acid is added to acidify the solution (the solution becomes colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bath. The colour of the solution changes from wine red to pink.

100 ml distilled water is added to the cooled solution. 1 gm of ammonium biflouride is added to the flask and swirled until all the salt is dissolved. 2 gms of potassium iodide is added to the above and the flask is swirled again. The solution becomes yellow in colour.

The flasks is then kept in darkness for about five minutes.

To this solution starch solution is added as an indicator. The colour of the solution changes to blue.

The obtained solution is titrated against 0.1N sodium thiosulphate solution taken in a burette and the end point is the disappearance of the blue colour.

Volume of thiosulphate used = 20.1 ml

Normality of thiosulphate = 0.1N

Volume of sample = 100ml

Amount of chromium = Normality of sample x Equivalent weight

= $0.0201 \times 38.7 \times 10^6 / 10^3$

= <u>773.6 mg / l</u>

4.10. DETERMINATION OF CHROMIUM AFTER ADDITION OF 30 ML POLYMER

TOTAL CHROMIUM

10 ml of the sample is pipetted into a conical flask and is made up to 100 ml using distilled water 30 ml of 1% strength polyacrylamide is added and mixed well with mixing after each addition.

5 ml of 10 N sulphuric acid

2ml pf 1 N Silvernitrate solution

2 gms of potassium Persulphate

Sulphuric acid is added to acidify the solution (the solution becomes colourless). Silvernitrate solution and potassium persulphate are added as catalysts and as an oxidising agent respectively. The colour of the solution turns white and finally becomes wine red.

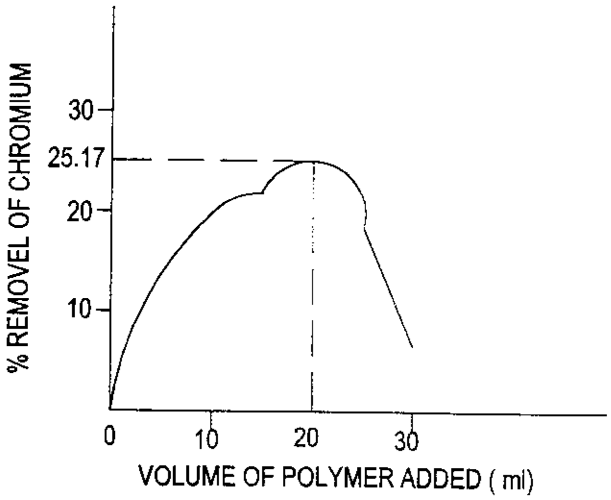
A few glass beads are added to the solution for proper mixing of the contents during boiling.

The solution is boiled for about 15 minutes and then cooled in a water bath. The colour of the solution changes from wine red to pink.

TABLE 4.1

TABLE GIVING THE PERCENTAGE RECOVERY OF CHROMIUM

Volume of polymer added (ml)	Amount of chromium present (mg/l)	% of recovery of chromium
0	948.15	-
5	818.06	13.72
10	759.18	19.93
15	740.32	21.92
20	709.50	25.17
25	773.6	18.41
30	884.81	6.68



OPTIMUM DOSAGE = 20ml OF POLYMER

MAX. % OF REMOVEL = 25.17%

5. ACTIVATED CARBON ADSORBTION

PRINCIPLES AND PRACTICES

5.1 CHEMISTRY OF ACTIVATED CARBON ADSORBTOION

5.1.1. ADSORBTION PRINCIPLES :

Adsorption is defined as the concentration of a solute at the surface or interface of a solid. Although the process can occur at any interface between two phases (liquid - solid, Liquid - liquid, gas - liquid) only liquid - solid interface is considered in this chapter. The material being concentrated or adsorbed is called adsorbate or solute and the adsorbing phase is the adsorbent.

Adsorption occurs at the solid surface because of attractive forces of the atoms and molecules that make up the surfaces. A layer of molecules of the solute accumulates at the surface of the solid (activated carbon) due to imbalance of the surface forces.

In the interior of the solid, molecules are completely surrounded by similar molecules and therefore subjected to balanced forces, as indicated by the arrows in fig. Molecules at the surface are subjected to imbalanced forces. Because these residual forces are sufficiently strong, they may imprison molecules of a solute with which the solid in contact. This phenomenon is called physical (van der waals) adsorption .

When chemical forces cause adsorption it is called " chemical adsorption " (chemisorbtion). Physical vs chemical adsorption.

Particles removed by physical adsorption are held to the adsorbent by relatively weak van der waals forces of attraction or by π - bonding under certain conditions. Physically adsorbed particles are assumed to be free to move on the surface of the adsorbent and adsorption is assumed to be multi layered with each new layer of molecules forming on top of previously adsorbed layers. Physical adsorption is thought to take place on the planar surfaces of carbon particles. These surfaces are uniform in nature and do not contain functional groups because the electrons of the carbon atoms are involved in covalent bonding. The large amount of surface area found in the micropores of carbon particles is probably of the planar surface type.

Chemical adsorption occurs as a result of chemical reaction between the adsorbate molecule and the adsorbent. This type of adsorption is thought to occur on the sides and corners of the microcrystallites that comprise the activated carbon, since these sites are characterised by the presence of various types of functional groups which participate is adsorption through electron - sharing reaction. (snoeyink and weber, 1967).

Most adsorption process in waste water treatment are neither purely physical nor chemical processes, but are a combination of the two. Adsorption capacity is directly related to the total surface of the adsorbent since the larger this surface is, the more residual (unbalanced) forces are available for adsorption. The overall rate of adsorption is controlled by the rate of diffusion of the adsorbate molecules within the capillary pores of the carbon particles.

5.1.2. ADSORPTION KINETICS :

Process kinetics describe the rate at which molecules are transferred from solution to the pores of the carbon particles. Three distinct steps must take place for adsorption to occur :

1. The adsorbed molecule must be transferred from the bulk solution phase to the surface of adsorbent particle. In doing so, it must pass through a film of solvent that surrounds the adsorbent particle. This process is referred to as film diffusion.

2. The adsorbate molecule must be transferred to an adsorption site inside the pore. This process referred is pore diffusion.

3. The particle must become attached to the surface of the solute i.e. be adsorbed.

The rate of adsorption determined the detention time required for treatment and thus the size of carbon contacting systems. The kinetics of carbon column adsorption is dealt within detail under section : 5.8.2.

5.3 ADSORPTION EQUILIBRIA :

When a solution is contacted with a solid adsorbent, molecules of adsorbate transfer from the fluid to the solid until the concentration of the adsorbate in solution is in equilibrium with the adsorbate on the solid. The equilibrium data at a given temperature are usually represented by an adsorption Isotherm, which is the relationship between the quantity adsorbed per unit mass of solid and the concentration of adsorbate in solution. Several mathematical relationships have been developed to describe adsorption equilibria which aid in the interpretation of adsorption data. Three of the most common are langmuir Isotherm, the fruendich Isotherm, and the Brunaur - emmett - teller (bet) Isotherm.

5.3.1. LANGMUIR'S ADSORPTION MODEL :

Langmuir's Isotherm is based on the assumption that :

a. Adsorption is limited to a single layer of solute molecules ;
b. Adsorbed molecules are not free to move on the surface; and
c. The enthalpy of adsorption is the same for the all molecules.

The Langmuir equation is commonly written as follows (Langmuir, 1918) :

$$x / m = \frac{q_m K_A C}{1 + K_A C}$$

where x = Amount of material adsorbed (mg or g)

m = Weight of adsorbent (mg or g)

q_m = Mass solute adsorbed / mass adsorbent for a complete monolayer.

C = Concentration of solute in solution, mass / volume

K_A = Constant related to enthalphy or adsorption.

The Langmuir Isotherm can be rearranged to the following linear form:

$$\frac{1}{x / m} = \frac{1}{q_m} + \frac{(1)}{(K_A q_m)} \frac{1}{C}$$

By plotting adsorption equilibrium data as shown in fig. The constant K_A and Q_M can be evaluated from the sloped and intercepts.

5.3.2. BET ADSORPTION MODEL :

The Brunauer - Emmett - Teller (bet) equation is used to describe multi layer adsorption. The assumptions in the bet model are :

a. Adsorbed molecule do not migrate on the surface ;

b. The enthalphy of adsorption is constant for all molecules in the given layer;

c. All molecules in layers beyond the first have equal energies of adsorption ; and

d. Layers need not be completed before next one starts. For adsorption from a liquid solution, the bet equation has the form:

$$\frac{X}{M} = \frac{q_m K_B C}{(C_S - C)(1 + (K_B - 1)(C / C_S)}$$

where C_S = Concentration of solute at saturation of all layers

K_B = Constant related to energy of adsorption

The BET equation can be rearranged to a linear form :

$$\frac{C}{(C_S - C)x/m} = \frac{1}{K_B q_m} + \frac{(K_B - 1)}{K_B q_m} \frac{C}{C_S}$$

The determination of the constants C_s K_B and qm is illustrated in fig.

5.3.3. FREUNDLICH ADSORPTION MODEL:

Freundlich developed an empirical equation for the adsorption Isotherm:

$$\frac{X}{m} = K_F\, C^{1/n}$$

Where k_F and n are constants and n is greater than one. By taking the logarithm of both sides, this equation is converted to a linear form;

$$\log x = \log K_F + \frac{1}{n} \log C$$

A plot of log x / m vs log c gives a straight line as shown in fig.

The freundlich equation most useful for dilute solutions over small concentration ranges. It is frequently applied to the adsorption of the impurities from a liquid solution into activated carbon. If the identity of the solute is not known, as in the adsorption of organics from waste streams, the concentrations can be expressed in terms of composite parameters such as COD and BOD.

5.3. FACTORS INFLUENCING ADSORPTION :

Many factors influence the rate at which adsorption reactions occur and the extent to which a particular material can be adsorbed. Several of the more important factors are :

a. Surface area,

b. Nature of the adsorbate

c. Hydrogen ion concentration (pH) of the solution,

d. Temperature

e. Mixed solutes, and

f. Nature of adsorbent

5.4.1. SURACE AREA :

Adsorption is a surface phenomenon and as such the extent of adsorption is proportional to specific surface area. Specific surface area can be define as that portion of the total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of a solid adsorbent greater, if the solid is more finally divided and more porous.

Webber and Morris in 1964 have found that for porous materials like activated carbon, the breaking up of large particles to form smaller ones can in some instances serve to open some tiny, sealed channels in the carbon which might then become available for adsorption. Thus possibly yielding dependence of equilibrium capacity of particle size. However. it also has been abserved that small GAC particles give increased resistance to flow, particularly in packed beds operated in down flow mode (Mc Carty et. al. 1979). Therefore the choice of particle size is often as compromise between the desire to optimize adsorption rates and minimize resistance to flow.

5.4.2. NATURE OF THE ADSORBATE

The nature of the adsorbate (molecular structure and solubility of the solute) is particularly important in dictating the degree of adsorption that can actually occur. As a rule branched - chain compounds are more sorbable than straight - chain compounds the type and location of the substituent (functional) group affects adsorbability, and molecules low in polarity and solubility tend to be preferentially adsorbed. unless physical blockage of the carbon pores actually occurs, large molecules are more sorbable than small molecules of similar chemical nature. This is attributable to more solute chemical bonds being formed. making desorption more difficult.

An increase in solubility acts to oppose the attraction to the adsorbate to carbon. Thus, polar groups with a high affinity for water usually diminish adsorption from aqueous solutions. The landelius rule states that an inverse relationship can be anticipated between the extent of adsorption of a solute and its solubility in the solvent from which adsorption occurs. Adsorption increases with decreasing solubility of the solute in the solvent. The greater the solubility, the stronger the solute - solvent bond and extent of adsorption.

5.4.3. HYDROGEN ION CONCENTRATION :

The P^H of a solution from which adsorption occurs influences the extent of adsorption. Because, hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the P^H of the solution.

The majority of coloured materials encountered in industry are negatively charged and ordinarily carbons will give greater decolourisation with increase in acidity of the solution. Both the carbon and the impurity to be removed carry electrical charges, and results show that in general the adsorption efficiency of carbons is dependent largerly upon the differences in electrical charges between the carbon and particle, colloid, or colour (or ion) to be adsorbed. The generalised curves in fig. show the relation between the acidity neutrality, and alkalinity of the solution and adsorption by carbons having various electrical properties.

Electronegative materials (colours like methylene blue, and most coloured impurities) are removed by there carbon most effectively in acid solutions.

Garten and weis 1957 have shown that acid and akali sorption can be related to surface functional groups which form during the preparation of the carbon. Alkali sorption occurs principally in carbons activated at temperatures near 400^0 C. carbons which sorb acid usually are activated at temperature near 1000^0 C.

The experimental plot obtained after adsorption in a column by webber 1966 indicated that the adsorption increases with time upon acidification. The P^H of the adsorbent itself is an important factor, as this may affect the P^H of the liquid. Frequently colour changes in indicators, which colour changes are functions of P^H and they are mistaken for adsorption effects.

5.4.4. TEMPERATURE :

Colour removal is usually greater at higher temperature. Temperature effect on adsorption equillibria are generally not significant over the range of temperature practically encountered in water and wastewaters. Thus small variation in temperature do not alter the adsorption process to any significant extent.

5.4.5 MIXED SOLUTES :

Most wastewater contain a myraid of compound that may mutually enhance, interface or act independently in the adsorption process. Webber and Morris, 1964 collected data for both rate of adsorption and adsorption capacities on carbon for mixed solutions and indicated that each solute competes in some way with the adsorption of the other. The degree of mutual inhibition of competing adsorbate should be related to the relative size of the molecules being adsorbed, to the relative adsorptive affinities and to the relative concentrations of the solutes. Fig. Illustrates the differences between the break - through curve (C/co vs T) for adsorption of a solute from its pure solution and from a mixer of solutes in a column carbon. It is readily apparent that the presence of the other solutes in the mixer adversely affects the adsorption of the first, leading to much more repaid break through of this material.

5.4.6. NATURE OF ADSORBENT :

The physiochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption . Adsorption ~~by activated carbon~~ is a surface phenomenon and is affected by the following parameters:

a. Surface functional groups;

b. Structural details.

Mattson et.al 1970 detected the presence of significant amount of carbonyl and carboxyl groups on activated carbon surfaces. The behavior of ~~activated~~ carbon as an adsorbent as to be related to the surface functionally of this material and the evidence for chemical interaction and the surface between carbonyl and cobroxyl groups and organic adsorbate is convincing. The adsorption capacity of ~~activated~~ carbon may well be accomplished by increasing the concentration of the appropriate functional groups.

5.5. MANUFACTURING OF ACTIVATED CARBON :

Activated carbons can be mode from a variety of carbonaceous materials including wood, coal peat, lignin, nutshells, bagasse (sugarcane pulp), sawdust lignite, bone, and petroleum residues. The current trend in the manufacturer of activated carbon is towards the potential utilisation of different wastes as raw materials, for example : waste lignin, sulfite, liquors, processing wastes from petroleum and lubricating oils, and carbonaceous solid waste.

Activated carbons can be classed in two groups ; powdered and granular. In waste water applications, powdered carbons or predominantly (60 - 75%) smaller than 325 mesh while granular carbons or typically larger than 40 mesh (0.42mm). powdered activated carbon is usually produced by activating lump material, or chips of wood charcoal, or lumps of paste prepared from sordust, and subsequently grinding the activated product. Depending on the method or grinding the shape of the particles can differ to a certain extent, and this may markedly influence the properties the product displays in industrial applications. Active carbon ground in ball mills has oval particles and that ground in hammer has elongated particles.

Granular carbons may be formed by either crushing or pressing. Crushed activated carbon is prepared activating a lump material, which is then crushed and classified to desired particle size. Pressed activated carbon is formed prior to activation. The appropriate strongly material is prepared in a plastic mass, then extruded from a die and cut in to pieces of uniform length. These uniform cylindrical shapes or then activated. The necessary hardness is acquired in the activation process. For activated carbons formed from pulverized materials, which are then bound together, the nature of blinding agent is a major factor in determining the hardness of the finished product.

requiring burnoff amorphous decomposition products (tars) at 750 - 900^0 C, plus enlargement of pores in the carbonised material. Burn off freeze the pore openings, increasing the number of pores, and activation enlarges these pore openings. Activation is achieved by two different process. Physical activation and chemical activation. Physical activation is normally achieved by treating char with mixers of CO_2, air and steam at temperatures of 750 - 900^0 C, so as to bur off the amorphous residues.

Pores spaces within the carbon are well developed following activation and can be classified according to size as follows : macropores, transitional pores, and mocropores according to dubinin et.al. (1964), Macropores have an effective radius of 5000 - 20000 A^0 and open directly to the outer surface of the carbon particle. Transitional pores with radii of 40 - 200 A^0 develop off the macropores. Micropores develop off the transitional pores with an effective ciably to the surface area of the carbon, but provide a passage way to the particle interior and the micropores. Pore size distribution determines the size distribution of molecules that can enter the carbon particle to be adsorbed. Particle size is generally considered to affect adsorption rate. But not the adsorptive capacity which is related to the total surface area. By reducing the particle size, the surface area of a given weight is not affected. Particle size mainly contributes to a system hydraulics, filterability and handling characteristics.

5.6 CHARACTERISTICS OF CARBON USED IN WASTE WATER TREATMENT :

There are several characteristics of activated carbon of importance in evaluating its suitability to waste water treatment which include the following.

1. Surface area : generally, the large the surface area, the more is the adsorption.
2. Apparent density : a measure of the regenerability of a caebon.
3. Bulk density : used to determine carbon quantities necessary to accomplish contain jobs.
4. Effective size, mean particle diameter, uniformity co-efficient : used to determine the hydraulic conditions of an adsorbent column.
5. Pore volume : can be used to determine the adsorbability of a particular waste entity.
6. Sieve analysis : used to check plant - handling effects on the carbon.
7. Pore size : used to obtained a carbon which can adsorb specific molecules.
8. Ash percent : shows activated carbons residue.
9. Phenol no. : used as an index of a carbon's ability to remove taste and order compounds.
10. Iodine no. : an important parameter to be determined. Because it can indicate a carbon's ability to adsorb low molecular weight substances (micropores having an effective radius of less than 2mm) and its

regenerability. The iodine no. is the milligrams of iodine adsorbed from a 0.02M solution at equilibrium under specified conditions.

11. Molasses no.: is an index of the adsorptive capacity of the carbon for colour bodies in a standard molasses solution as compared to a standard carbon. Molasses no. relates to the carbon's ability to adsorb high molecular weight substances (pores ranging from 1 - 50 mm)

The total surface can be measured by the bet method. Bet measures the activated carbon's adsorption and desorption of nitrogen under varying pressures. The procedures for determining the iodine and molasses nos. are given in the EPA manual. In general, high iodine nos. will be most effective on waste waters with predominantly low molecular weight organics, while high molasses no. will be most effective for wastewaters with a dominance of high molecular weight organics. Typical properties of four U.S. commercial granular activated carbons are given in EPA manual and are shown in table.

5.7. EVALUTION OF ACTIVATED CARBON :

The evaluation of activated carbon for a particular application is at present a difficult task. Evolution of activated carbon included determination of (1) adsorption rate and capacity (2) determination of attrition losses that will occur during carbon handling and regeneration. The rate of adsorption determines the detention time required for treatment and thus the size of carbon contacting systems adsorption capacity is the effectiveness of the activated carbon in removing the desired constituency such as CDS, colour, phenol, etc., from the wastewater. There is no precise method for predicting the performance of carbons founded on their basic properties of those of the adsorbing molecules. In wastewater substances to be removed such as colour. Order, COD, MBAS, and other refractory organics, are always a composite of ingredients of unknown identity.

Several tests have been employed to characterise adsorptive capacity. Simpler capacity tests such as phenol no., Iodine no., and molasses no, may also be of appropriate measures of adsorptive capacity. These tests are generally used for screening purposes. However, the adsorption capacity of a particular carbon is best determined experimentally with the wastewater of concern. The complex nature of wastewater males it necessary to empirically generate design data. Batch isotherm tests are useful to define the degree of treatment attainable by adsorption. Either a jar test assembly or a shake flask assembly can be employed. It has been shown that the batch isotherm results cannor be effectively scaled up to plant design and columnar studies should be conducted to determine the following for the plant scale use of granular activated carbon.

- carbon type, size, dosage ; bed dimensions
- effluent characteristic ; hydraulic characteristics
- dosage requirements ; contact time
- pretreatment requirements and other effects.

These other effects include bacterial growth on the carbon bed, filterability, hydrogen sulphide generation, and P^{H} and temperature effects pm adsorption. Breakthrough curves, a plot of wastewater constituent concentration vs wastewaters treated, are used in determining te durability of a carbon with respect to operating conditions it will encounter at a full-scale treatment facility.

5.6 BATCH ADSORPTION ISOTHERM TESTS

Batch adsorption isotherms are a generally accepted method of screening activated carbon to determine its relative capacity for a given waste. The adsorption isotherm is the relationship, at a given temperature between the amount of adsorbate adsorbed per unit weight of carbon and the concentration of the adsorbate remaining in solution. If a colour adsorption isotherm is taken as an example, the isotherm would consist of a curve plotted with residual colour in the wastewater as the abscissa, and the colour adsorbed per gram. The Isotherm gives the amount of colour adsorbed per unit weight of carbon, which is the carbon adsorptive capacity and a particular colour concentration and water temperature. In very dilute solutions, such as wastewater, adsorption data is usually co-related according to the freundlich isotherm (empirical) developed from batch tests. Generally, straight - line plots can be obtained by making use of the empirical and the freundlich equation :

$$\frac{X}{m} = K_F \, C^{1/n}$$

where x = Amount of colour adsorbed

m = Weight of carbon

x / m = Amount of colour adsorbed per unit weight of carbon

c = Unadsorbed concentration (equilibrium) of colour left in solution

K_F and n are constants and n is greater than one.

In logarithmic form, this equation is :

$$\frac{\text{Log } x}{m} = \log K_F + 1/n \log C$$

In which $1/n$ represents the slope of the straight line, isotherm.

Data for plotting isotherms are obtained by treating a fixed volumes of the liquid to be tested with a series of known weights of carbon. The carbon - liquid mixture is agitated for a fixed time at a constant temperature after the carbon has been removed by the filtration, the residual organic content of the solution is determined. From these measurements, all over the values necessity a plot an isotherm may be calculated.

The Isotherm tests may be performed room temperatures unless the anticipated plant operation will be at a significantly different one. To determine the needed contact time for the Isotherm, a preliminary experiment should be run in which fixed volumes of the wastewater are contacted with a fixed weight of carbon for 1,2,3, and 4 hour periods. A contact time sufficiently long to ensure a reasonable equilibrium should be chosen from these data for the Isotherm.

The P^H of the wastewater being tested will affect the carbon efficiency care should be taken to ensure that the P^H of the test sample is representative of the anticipated plant scale conditions.

5.8.1. ISOTHERM PROCEDURE :

A common procedure for conducting batch Isotherm is to use a carbon which has first been pulverized so that 90% of it passes through a 325 - mesh sieve. The pulverization, in tern, normally reduces the contact time to reach equilibrium by about 35 minutes to maintain a closer co-relation between the results of the batch Isotherms and that could be expected during a continuous flow column adsorber or barth reactor, these isotherm can also be performed using nonpulvarized carbon. This, however, necessitates a much longer contact time before equilibrium can be reached. The basic procedure for setting up each isotherm on nonpulvarised carbon is as closed :

each carbon should be rinsed vigorously first with distilled water to wash out ash much fine material as possible and then tried at 103^0 C for several hours before weighing. In performing Isotherm tests are nonpulvarised carbon, it is important to eliminate the inherent fines created during activation process or packaging of a carbon. If this is not done, those carbons containing more initial fines would have distinct advantage over those having fewer fines; i.e. greater exposed surface area / unit weight.

6. obtain a representative sample of the wastewater to be tested. Suspended matter should be removed by filtration.
7. Fill 6 - 8 flasks (for shaker assembly) or breakers (for jar test assembly) with a fixed volume of wastewater. The initial concentration (CO) of the parameter of concern (colour / Co) is to be determined.

8. Put varying weights of prewashed test carbon into each container. This value might range from 0.50 to 10 grams per 200ml.of wastewater. Other weights of carbon may be substituted if they are more appropriate for the wastewater being tested. If any volatile compounds are present in the wastewater which might be air stripped, then a "blank" (one container with wastewater but no carbon) should be included to correct for this organic removal.

9. Begin the agitation of the flasks (or mixing of the beakers) and monitor the organic concentration with time (15 minutes intervals). After the chosen contact time has elapsed, withdraw some test sample for analysis the total

sample withdrawn during the test should not exceed more than 5 % of the total liquid contents.

10. All samples withdrawn for analysis should be first filtered. Determine the organic contents of filtrate once the contaminant leave in the flask are beaker has stabilised, record the time to reach this level and note the equilibrium concentration.

11. Tabulate the data. The residual CO D/colour concentration (CO) is obtained from the filtrate analysis. The amount adsorbed on the carbon (x) is obtained by subtracting the value of Ce from CO, influent concentration. Dividing x by m, the weight of carbon used in the test, gives the amount adsorbed per unit weight of carbon.

12. On log paper plot Ce on the abscissa against x /m on the ordinate and draw the best straight line through the points, illustrated in fig.

5.8.2. INTERPRETATION OF THE ISOTHERM :

From the isotherm, it is apparent whether or not the desired degree of purification can be attained with particular activated carbon tested. Isotherm put a large amount of data into concise form for ready evolution interpretation. The chief value of the isotherm test lies in comparison of various types carbon and the ability to determine the quality of effluent achievable following carbon adsorption. The isotherm will also show the approximate adsorptive capacity of the carbon for the application, and provide a rough estimate of the carbon dosage required. Isotherm tests also afford a convenient means of studying the effects of P^H and temperature on adsorption fig. Shows the increase in adsorptive capacity with reduction of P^H due to change in solubility of the organics.

COMPARISON OF DIFFERENT CARBONS:

Isotherm obtained under identical conditions using the same test solution for two test carbons can be quickly and conveniently compared to reveal the relative merits of the carbons fig. And are presented to illustrate the interpretation of adsorption isotherm. If fig. the isotherm for carbon A is at a high level and has only a slight slope. This means that adsorption is large over the entire range of concentration studied. The face that the Isotherm for carbon B in fig. B is at a lower level indicates proportionately less adsorption, although adsorption improves at higher concentrations over that at low concentrations. But Isotherm having a steep slope indicates that adsorption is good at a higher concentrations but much less at low concentration. In general, steeper the slope of its isotherm the greater the efficiency of a carbon in column operation. In fig. C. carbon D is better suited to counter current column operation than carbon C. it has a higher capacity and the influent concentration, or more reserve capacity. Carbon C would be better than carbon D for batch treatment.

CALCULATION OF ADSORPTIVE CAPACITY :

If a vertical line is erected from the point on the abscissa corresponding to the influent concentration (CO) and the Isotherm is extra plotted to intersect that line, the x/m value at the point of intersection can be read from the ordinate.

This value (x/m)Co., represents the amount of COD/Colour adsorbed per unit weight of carbon when that carbon is in equilibrium with influent concentration. Since this should eventually be attained during column treatment, it represents the ultimate capacity of the carbon. However, experience has shown that it is difficult to predict the carbon dosage accurately from isotherm tests for plant scale carbon columns. Pilot carbon columns tests conducted over several weeks are the only accurate means of determining the required carbon dosage.

It is essential to realise that the lowest possible carbon usage rate is predicted by a properly run isotherm tests. If a lower usage is observed in a column tests or in the plant, then one or more of the following is true.

1. The isotherm test was not at equilibrium.
2. The interpretation of the isotherm was done in correctly
3. There was an error in the analytical techniques.
4. Carbon fines may not have been completely removed from the solution.

5. The liquid tested in the isotherm test and in the column tests were not identical.
6. There is a bacterial strain in the column which removes the adsorbate. This peonemenon is usually limited to water applications.

5.9 ADSORPTION STUDIES IN COLUMNS :

Plant scale use of granular activated carbons involves a dynamic system ; therefore, the rates of adsorption are as important as the equilibrium adsorption properties. The rate determinations can be best made by dynamic pilot test. The general range of variables to be investigated in granular adsorption systems are flow rates and bed depths. The diameter of the carbon columns can be scaled down by appropriate reduction in total flow and still simulate full scale plant conditions. If the laboratory cannot accommodate full high columns the same total bed depth can be provide by several shorter columns operated in series :

Prior to conducting a column test many things must be considered. Some of these are listed below.

1. Location of the test i.e. in the plant are in the laboratory :

2. Size and type of pilot system (i.e. column diameter, quantity of carbon and fixed or pulse bed).

In the laboratory columns are usually 2.5 to 5.0 cm in diameter by 1 - 1.5 meters deep. In the plants, the size is usually 5.30cm in diameter by 1 - 2 meters deep for fixed beds connected in series and 10 - 15 meters for pulse beds.

3. Carbon type and practical size :

The type of carbon to be used will have been determined usually during the isotherm testing. Since pore diffusion is a major contributor to the overall diffusion rate, the smaller the particle, the faster the diffusion and thus shorter the mass transfer zone.

4. linear velocity of the liquid in the carbon bed :

It is recommended that the pilot column tests be conducted at the rate expected to be used in the full - scale plant. The effect of the linear velocity on the diffusion through the film around the particle and the ratio of the magnitude of the film diffusion to the pore diffusion are the factors that determine what effect, if any occurs. It is obvious that the system at the high linear velocity, treats more liquid per volume of carbon at low concentrations leaves and the mass transfer zone (MTZ) is shorter.

5. Temperature :

As adsorption is a function of diffusion rate, and as diffusion is affected by the liquid viscosity, the columns should be operated at the plant process or isotherm temperature to eliminate this variable from data analysis.

6. P^H :

If the isotherm investigation indicated that a the same P^H adjustment should be made to the liquid before granular column studies.

7. Liquid pretreatment :

In cases where suspended matter is present in the test liquid, it should be removed by filtration before the liquid is pumped to the columns. If the test liquid has been stored at a low temperature for preservation purpose subsequent heating to room temperature or higher, may result in degassing the liquid. When these conditions exist in the liquid must be deaerated prior to pumping if through the carbon columns.

8. Carbon pretreatment :

Carbon should be deaerated prior to the adsorption tests. When this is not done, air pockets form in the columns and result in (1) channeling (2) high - pressure drops and (3) premature breakthrough of adsorbate. Therefore, the carbon should be prewetted prior to being placed in the test columns. The liquid used for prewetting can either be water, if it is compatible with the liquid to be treated, or a batch of a liquid to be treated which has been purified previously.

5.9.1. PILOT - SCALE CARBON COLUMNS :

The limitations of theoritical adsorption concepts relative to the practicalities of treatment requirements. For industrial wastewaters necessitate that comprehensive process simulation studies precede the final design. Breakthrough curves defining contaminant removal, (in terms of BOD, COD, TOD, colour, etc.) carbon capacities, and the influence of process variable on performance, should therefore be developed variable on performance, should therefore be developed using continuous - flow columns in pilot - scale testing. These pilot plant experiments serve he basis for the preferred design procedure, which is now described in detail.

1. Equipment required :

a. Three to six plexiglas carbon columns ;5.15 cm in diameter by approximately to M in depth, connecting piping, valves and pumps decide for serious column operation with back wash capacity : pressure gauges should be attached by each column.

b. Selected granular carbon.

c. Filtration (if required) using graded sand

d. Sample collection capacity from each column.

e. Flow measuring equipment ; such a pilot scheme assembly is shown in fig. both for down - flow and up - flow mode of contact.

EXPERIMENTAL PROCEDURE :

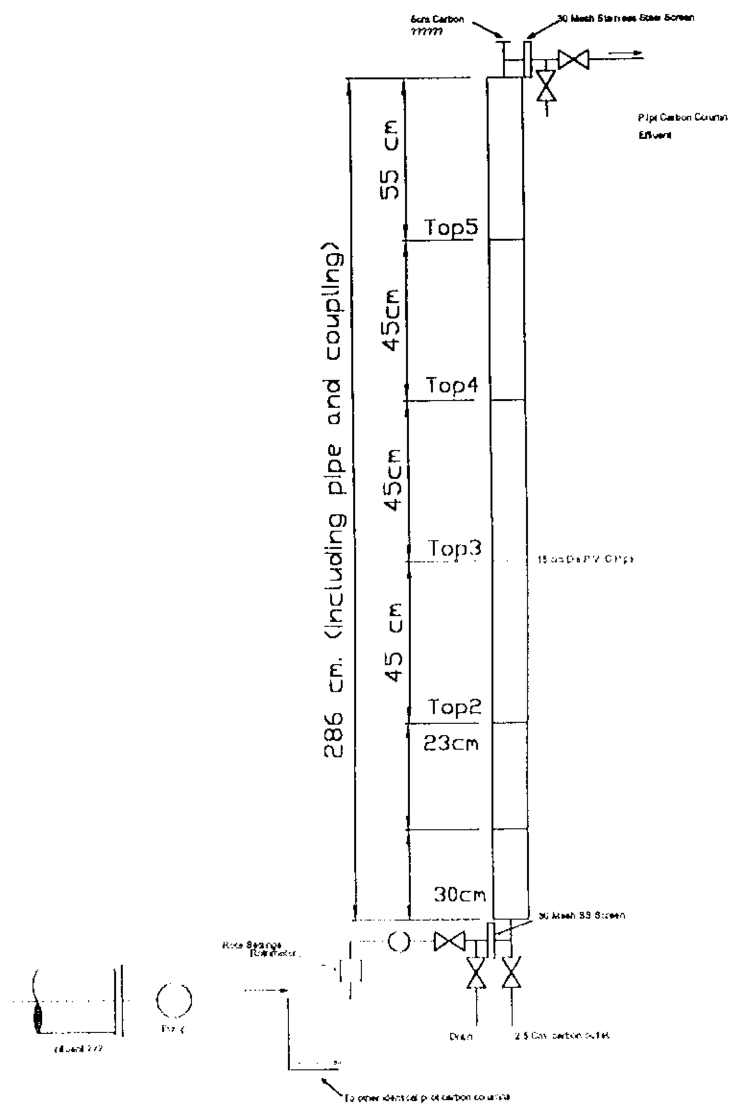
1. set up the plexi glass carbon columns in a manner similar to that in fig. they should be located close to the off feed water to minimize pumping losses - A variable - speed centrifugal pump is desirable for flexibility of operation. If the suspended solid or oil is high in the feed in wastewater (50 mg/1) then using one column has the prefilter will minimize backwashing.

2. The units should be piped or valued so that samples can be taken from each column and each column can be backwashed individually. Downflow operations are normally used, although the up flow mode of operation can be investigated if desired.

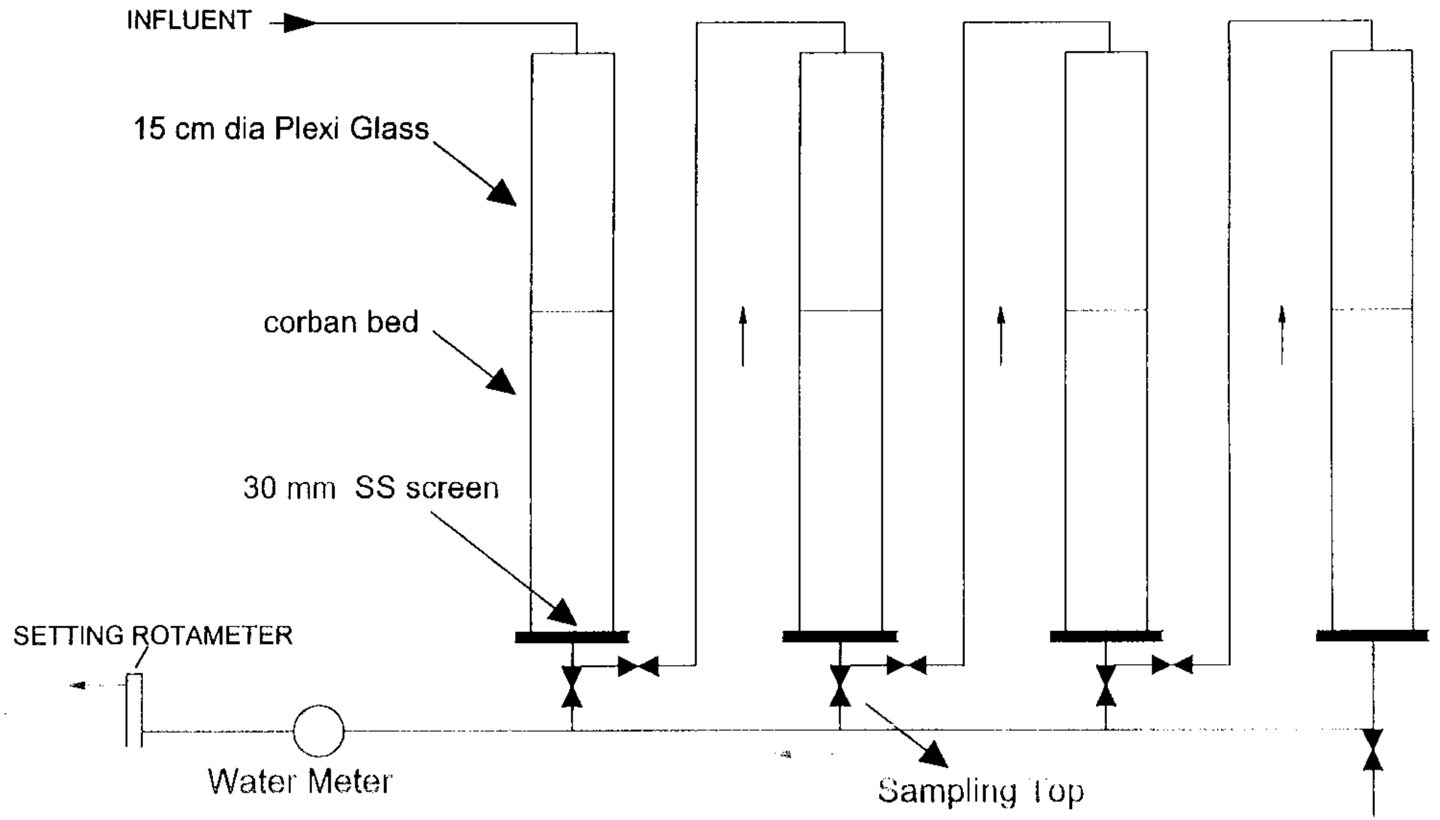
3. Load the columns with the required amounts of test carbon. Each column should have an equal amount. It may be helpful to paint the columns black or to cover them to prevent from sunlight penetration during the test run. This will minimize algal growth in the columns and reduce backwash frequency.

4. Begin the run at the prescribed linear flow velocity and initial conditions. Monitor the effluent quality of each column by withdrawing samples atleast once daily. The collected samples shall be analysed for the parameter of concerned.

UPFLOW PILOT CARBON COLUMN



DOWNFLOW PILOT CARBON COLUMN



5. The effluent from the last column should be connected in a 270 litre drum which can serve reservoir for backwash water Each column can be backwashed on a routine basis at a specified pressure drop through the column.

6. The test should be continued until the breakthrough curves are fully developed, i.e. the final column effluent concentration of the most [illegible] removed constituent approaches that of the firest column effluent concentration.

5.9.2. INTERPRETATION OF COLUMN DATA :

The intent of the column test is to obtained breakthrough curves showing how the concentration of the effluent various with volume of liquid treated. A family of curves can be developed as required (fig.) are for each column when the serious made is used. The carbon capacity is determined by taking the area between the column influent and effluent to the point of breakthrough divided by weight of carbon in the column. The capacity at complete column exhaustion can be determined by taking the total area to the point when the effluent plot joints the influents and dividing this value by the weight of carbon in the column. The carbon capacity and observed residual can then be compared to the batch isotherm values; however, the results of column study should govern when establishing effluent criteria.

Provided the wastewater charge to pilot - scale columns is representative and the process calculations are properly made ; the scaled up carbon capacity and organic change significantly. Since the prototype conditions are generally not known at the time of testing, a method for extra plotting data. To various conditions is need in order to reduce the no. of experiments. Hutchins has employed the Bohart Adams equation in the form of bed depth service time (BDST) for interpretation of column of data and process design including extrapolation to conditions other than tested. Such a concept is dealt within the succeeding sections under "design of column adsorption system ".

CARBON

5.10. CONTACTING SYSTEMS AND ADSORPTION OPERATION

Of particular importance in the application of carbon for large scale treatment of water and wastewater is the manner in which the carbon contacts. The solution to be treated. The particle may be contacted either through a batch flow system or through a continuous flow system of operations.

5.10.1. BATCH FLOW SYSTEM :

In a batch adsorption operation, the adsorbent is contacted with the wastewater in a tank until the pollutant level is decreased to a decide level. Absorbent is seperated from the wastewater by setting filtration or centrifugation and is then regenerated or discarded. The time required to approach equilibrium conditions depends upon the concentration of the obsorbate, the amount of solid, the particle size of adsorbent and the degree of agitation. For batch operations, the adsorbent is usually applied in powered form to increase the surface area and reduce the diffusional resistance inside the pores. With powered carbon a contact time of 10-60 minutes is often sufficient to approach equilibrium. Conversely with the use of large particles of carbon, requires ling periods of contact between the wastewater and absorbent necessitating large basins or tanks for treatment. Batch adsorption operations are usually limited to the treatment of small volume of effluence. Continues flow operations and has found the widest applications and hence, further discussion is limited to continuous flow system of operation.

5.8.2. CONTINUOUS FLOW SYSTEM :

Continuous flow granular carbon columns are most particle for the treatment of wastewaters containing high concentrations of organics to be removed because :

1. Separation of carbon from the wastewater after contact is not necessary.

2. The concentration of the adsorbed solute is in equlibrium with the influent concentration rather than effluent concentration and a greater flexibility of operation is attained.

5.10.2 THEORY OF COLUMN ADSORPTION :

The adsorption of organics on granular activated carbon columns is a diffusion process consisting of mainly three mechanisms. (1) film diffusion (2) pore diffusion and (3) adsorption on the surface.

If one step is much slower than the others under a given concentration gradient, it is called the ' rate determining step' or 'controlling resistance the transfer of adsorbate from bulk fluid to the outer surface of the carbon particle occurs by molecular convective diffusion. Transport of material through a boundry layer is often referred to as film diffusion. For a given weight of adsorbent the external surface are is inversely proportional to the particle diameter.

The transfer of adsorbate from the external surface to the interior of the particle occurs by diffusion in the void space of the pores or by migration along the pore surface. With fluid-phase pore diffusion, mass transfer precedes the adsorptive phase change whereas, with solid-phase pore diffusion, mass transfer occurs after adsorption on the surface. Since solid and pore diffusion in parallel the overall rate of internal transport is the sum of the two processes.

5.10.2.2. ADSORPTION RATE EXPRESSIONS :

Using the rationale, an expression for adsorption kinetics in column system can be developed.

$$V\, dc / dD = Km\, ar\, (Cs - C)$$

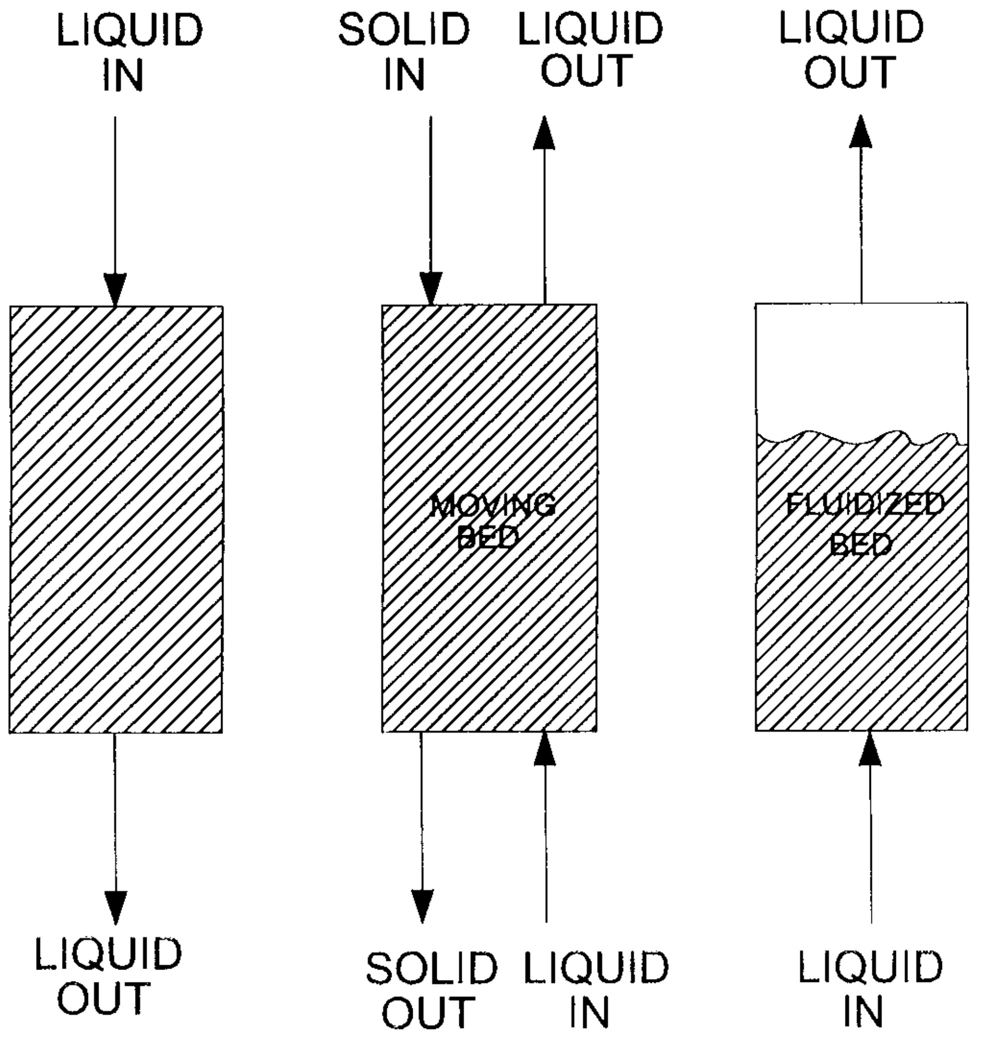
Where V = Flow rate per unit surface area (velocity)
C = Concentration of adsorbate
D = Adsorbent bed depth
Cs = Equilibrium adsorbate concentrations
Km = Overall mass transfer coefficient
ar = Surface area per unit volume of bed

A more convenient expression of the above equation is in terms of the adsorbate removal rate with respect to the weight to the adsorbent in the column is :

$$Q \times \rho_l \times dc / Dw = (Km \times a_r / \rho_s)\ (C_S - C_E)$$

where W = Wt of carbon in the column
Q = Flow rate (volume / unit time)
ρ_s = Packed density of carbon in the column
ρ_l = Liquid density

SCHEMATIC DIAGRAM OF FIXED, MOVING AND FLUIDIZED BEDS



A second one - stage model, originally proposed by Bohart and Adams in 1920, assumes that the adsorption rate is proportional to both the residual carbon capacity and the remaining adsorbate concentration. This is equivalent using a surface sorption reacting with second - order kinetics. Mathematically,

$$V \ d\ C/d\ D = \quad K (N_s - N) C$$

Where K = surface rate constant

N = carbon efficiency (wt. Of impurity / Wt. Of carbon)

Ns = carbon efficiency bed at saturation.

The Bohart - Adams model can be rearranged to yield service time bed depth relationship as discussed in chapter 5.

Unfortunately, adsorption theory as described by the above rate equations, applies only to binary solutions and ignores process variables such as temperature P^H, linear flow velocity, modes of wastewater - carbon contact, the complexity of industrial wastewaters and the extremes in adsorbability of various types of chemical compounds severally limit the industrial applicability of general rate quotations. From an operational point on view the rate of adsorption increases with :

1. an increase in adsorbate concentration.
2. A decrease in carbon particle size
3. A smaller adsorbate molecule and
4. An increase in surface of adsorbent

In most applications diffusion of the adsorbate controls or limits the overall rate which then becomes propotional to the square root of time of contact. For granular activated carbon, the adsorbate must penetrate the channels in the carbon, and a long time is required to attain equilibrium. Adsorption capacity may increase with :

1. An increase in adsorbate concentration
2. An increase in surface area of the adsorbent
3. An increase molecular weight of the adsorbate
4. A decrease P^H of the solution that changes the organic molecules into a less soluble form.

5.10.3. CONTINUOUS FLOW ADSORBERS.

Basically there are three types of granular certain adsorption system based on the most of carbon column operation. They are :

1. Steady - state moving bed or pulse adsorbers
2. Unsteady - state fixed - bed adsorbers and
3. Fluidised bed adsorbers.

These can be used singly, in parallel, or in combination of both. More than 95% of the systems now on - stream are either fixed or pulse beds. Either can be operated as packed or expanded beds. Of all, conventional fixed, bed adsorption techniques are widely used for water and wastewater treatment. Fig. represents the schematic diagrams of or fixed, moving and fluidised beds.

5.10.3.(1) STEADY-STATE MOVING-BED ADSORBERS :

In a steady - state moving - bed adsorber, the fluid and solid phases are fed at constant rates to opposites ends of column and flow counter current to each other through the column. At steady - state the compositions of the phases at any given point in the column do not change with time but there is a continuous gradient of concentrations in both phases along the column.

Continuous counter current adsorbers have been applied in the petroleum industry for seperating hydrocarbon gases. They are rarely used for treating wastewater because of the problems associated with moving solids continuously and uniformly through the column.

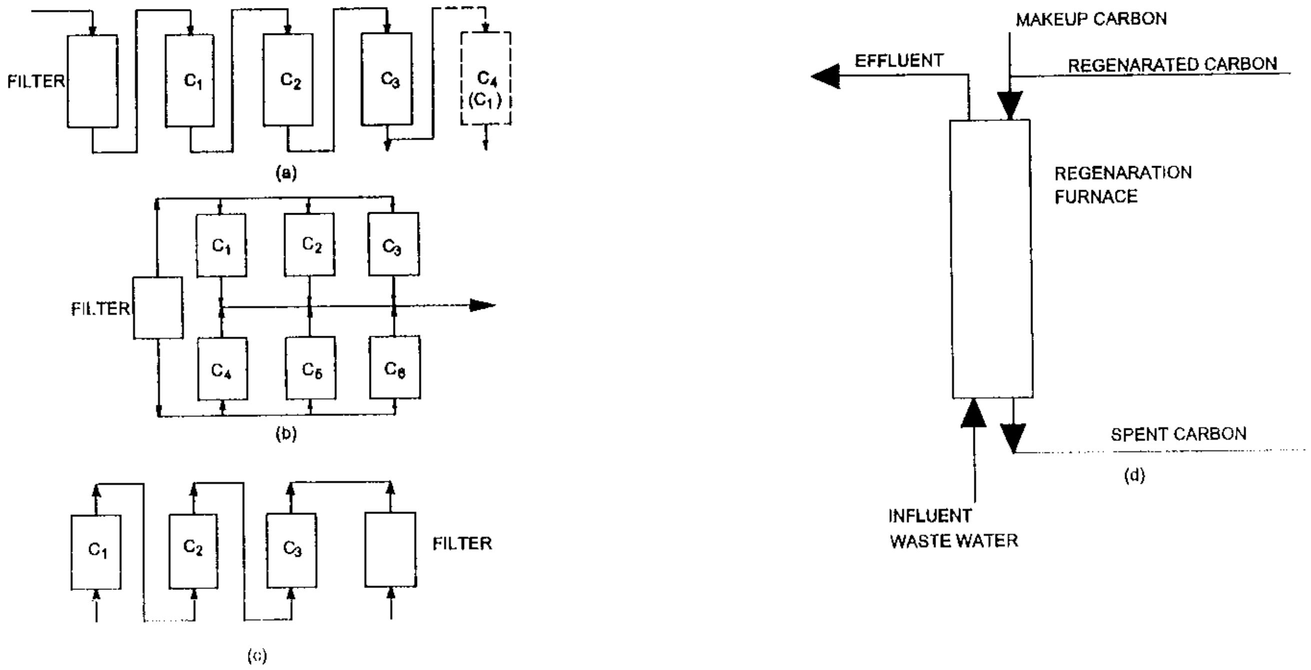
5.10.3. (2) FLUIDIZED - BED ADSORBERS :

In fluidized - bed adsorbers, the fluid flows upward through the solid particles at a velocity that is sufficient to suspend the particles but not high enough to carry them out of the bed. As fluid flow rate is increased to a fluidised bed, the bed the expanse and maintains a pressure drop that is essentially constant. For steady-state operations, solids may be continuously added to the top and removed from the bottom. In comparison with fixed - beds, fluidized beds have higher capital and operating costs but can be with higher feed rates and smaller particles without excessive pressure losses.

5.10.3. (3) FIXED BED ADSORBERS :

In practice, unsteady-state packed beds are used most often to treat large quantities of waste water. The liquid is fed continuously to either the top or the bottom of a stationary bed of adsorbent. The solid adsorbs increasing amount of solute with time and an unsteady - state condition prevails, when the adsorptive capacity of the solid is approached, it is regenerated for reuse. In liquid up flow operations, a portion of the adsorbent is usually removed periodically from the bottom and an equal amount of regenerated or virgin solid is added to the column.

CARBON COLUMN CONFIGURATION



The only reason for using a down flow fixed bed adsorber is to make it possible. To use the carbon for two purposes, adsorption of organics and removal by filteration of flocculated materials. The principle advantag[illegible] use of granular carbon is reduction in capital cost. The down flow bed may be fi[illegible]er in particle or in series.

5.10.4.ADSORBER CONFIGURATIONS :

Carbon column adsorbers c[illegible] be arranged i[illegible]us ways based on choice of influent characteristic, effluent criter[illegible]ate and economics. [illegible] of the common carbon column configurations are show in fig.

1. adsorbers in series (fixed-bed) : when [illegible]rough occurs in the last column the first column the first column is in equilibrium with the influent concentration (Co). in order to achieve a maximum carbon replacement in the first column it becomes the last column in the series. (fig.)

2. Adsorbers in parallel : multiple units are operated in parallel with the effluent blended to achieve the final desired quality. The effluent from a carbon column ready for regeneration or replacement, which is high in COD is blended with the other effluence from fresh carbon to achieve desired quality (fig.) this mode of operation is most adaptable to waters

in which the capacity at breakthrough / capacity at exhaustion is great (near 1.0).

3. Upflow -extended beds : These are used when suspended solids are present in the influent are when biological action occurs in the bed. (fig.).

4. Pulsed beds or moving beds : pulsed beds with spent carbon from bottom (in equilibrium with solute concentration) sent to regeneration. Regenerated and make up carbon is fed to top of the reactor (fig).

SELECTION OF SYSTEM CONFIGURATION :

Selection of a particular adsorber configuration is based upon the following factors :

a. single fixed bed :

1. The carbon exhaustion rate is low and the cost of replacing or reactivating the carbon is a minor operating expense.
2. The mass transfer zone is short, i.e. saturation of carbon occurs shortly after breakthrough.
3. The investment required for a multiple column system cannot be justified by the lower carbon make up rate.

b. fixed beds in series :

1. The performance is such that the saturation of the bed occurs a long time after breakthrough, i.e. the mass transfer zone is long.
2. It is economically attractive to have more stages to more completely exhaust the carbon.
3. Influent concentration fluctuates widely.

c. Fixed beds in parallel.

1. The floe rate is high and size of adsorbers in a single pass would be too large to be economical or feasible.
2. Space limitations prevent the use of large diameter or extremely high columns.
3. The adsorption process must be continuous.
4. It is necessary to operate with a minimum pressure drop.
5. Blending of products is desirable.
6. Fixed beds in parallel - series.
7. Flow rate of high.
8. It is desirable to have a lower carbon dosage than possible with parallel only operation.
9. Pulse beds.
10. There is an incentive for approaching the counter current operation, especially when the mass transfer zone is extremely long.
11. The capital investment is usually lower than for fixed beds in series.

12. There is a desire to minimize wide fluctuation in the effluent.

A continue flow granular carbon adsorption including regeneration is shown in fig.

5.11.CARBON REGENERATION SYSTEM :

To make activated carbon economically feasible wastewater treatment in most applications, the exhausted carbon must be regenerated and is reused. When the plant effluent quality reaches the minimum effluent quality reaches the minimum effluent quality standards or when a predetermined carbon dosage is achieved, spent carbon is removed from the columns to be regenerated.

There are four general methods for reactivating granular carbon. Solvent wash, acid or costic wash steam reactivation and thermal regeneration. With the use of a solvent which will dissolve the adsorbed material, the adsorbate is passed through the carbon in the direction to that of the service cycle of solvent and the regenerated carbon is ready to go back on stream. If an acid or caustic is more effective than a solvent in dissolving a particular adsorbate. It may be used in manner identical to that described for solvent washing. Adsorbates with low boiling points are sometimes are removed b stream. These first there methods do not appear to have application as primary methods for generation of activated carbon which has been used for the treatment of wastewater. The fourth method that is thermal regeneration is universally used for this purpose at the present time.

Juhols and Tupper, 1969 have shown that thermal regeneration of granular crbon consists of three basic steps :

1. Drying
2. Baking of adsorbate
3. Activating by exidation of the carbon residues from decomposed adsorbates.

The total regeneration process requires about 30 minutes. The first fifteen minutes is the drying period during which the water retained in the carbon pores is evaporated, (a 5-minute period) during which the adsorbed material is pyrolysed and a 10-minutes period during which the adsorbed material is oxidised and the granular carbon reactivated). Drying may be accomplish at $120^0 + 5^0$ C baking between 600^0 and 700^0 C and activating at carbon temperatures about 700^0 C - 800^0 C. all these steps can be carried out in a direct - fired multiple hearth furnace.

6. ADSORPTION SYSTEM DESIGN

Three types of activated carbon adsorption systems are in use ; Fixed bed down flow (Gravity flow), fixed bed upflow (pressure flow) and fluidised beds. All the three systems are nominal plugflow process and all three can be designed in the same fashion.

6.1 DESIGN CONSIDERATION :

Methodologies for designing activated carbon adsorption columns can be grouped into three distinct categories :

(1) Experience approach
(2) Micro approach
(3) Macro approach

The experience approach best described the technique presently used for the design of carbon column to treat wastewaters. This is, operating experience and design criteria employed at the existing installations are used as the basis for designing future installations. In this approach physical, chemical processes within the adsorption columns are not considered specifically. Present design of granular activated carbon columns is based on three criteria ; (1) volumetric flourate ; (2) detention time ; and (3) head loss. The expected volumetric flow rate is normally known. The theoretical dependention time of the wastewater within the bed of adsorbent is generally specified to be between 20 - 30 minutes. The detention time is the approximate time beyond which no further organic removal can be observed. Finally, the hydraulic head loss must be calculated (or measured in pilot studies) and minimized to prevent excessive pumping costs. Once the three criteria listed above are specified, the conceptual design is essentially completed.

Another general approach for the design of activated carbon columns is to develop a mathematical equation which describes the temporal and special distribution of the adsorbate within the adsorption column. In the micro approach, each resistance an adsorbate molecule encounters as it is transferred from the bulk solution phase to the surface of the adsorbent is described. Transfer steps for which mass transfer co-efficient must be determined include : (1) external diffusion (2) film diffusion (3) internal diffusion (4) site to site transport of the adsorbent surface and (5) adsorption on the carbon surface. The micro approach is advantages for two primary reasons.

1. The method can given insight in the mechanism (s) by which adsorption occurs.

2. Once a mathematical relationship is developed and programmed in a suitable, the influence of various experimental conditions on column performance is easily predicted.

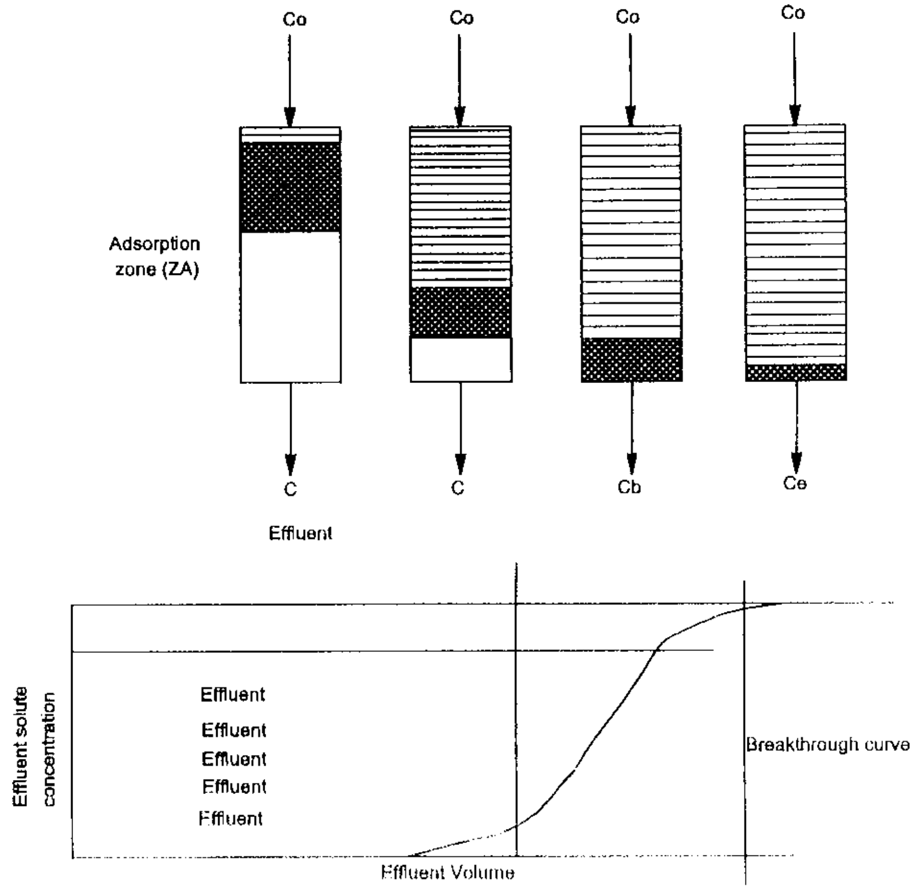
Defining each resistance step in the removal process is difficult and tedious task and represents a major obstacle in the micro approach. In most cases it is necessary to assume arbitrarily which one of the several transport steps represents the rate-limiting step, so that a mathematical solution can be derived.

The third general technique to design activated carbon columns is the macro method. This techniques of designing granular carbon columns is based on the mass transfer zone (MTZ) concept described by water and Lukchis. In contrast to the micro approach, only the overall resistance to adsorption is considered in the macro approach. The overall resistance to adsorption in a continues flow column is indicated viz. Its mass transfer wave (mass transfer front) which commonly characterized from breakthrough curves.

6.2. BREAKTHROUGH CURVES :

Adsorption processes are most easily designed through the use of back through curves obtained in pilot plant studies. These curves relate the effluent concentration to the volume of waste water treated and can be used to develop column characteristics.

Consider a down flow fixed - bed adsorber as shown in fog. Initially the feed solution (wastewater) is in contact with fresh adsorbent at the top of the column, progressively from the waste stream as it flows down the column. The length of the region were most of the adsorbate is removed is called the adsorption zone or mass transfer zone (MTZ).



Movement of adsorption zone for fixed-bed downflow adsorber

The length of the MTZ is somewhat arbitrary since it depends upon the value of adsorbate concentration selected for its lower boundary. Additional solute is removed as the waste water transverses the portion of the column below the adsorption zone. Because of equilibrium and kinetic factors however, some low concentration of solute escapes in the effluent. As more wastewater enters the column rapid adsorption occurs in uppermost layers in equilibrium with the influent concentration i.e. upper portion of column becomes saturated with adsorbate. With continuing flow, the saturated zone i.e. MTZ in equilibrium with the influent concentration moves down the column like a slowly moving wave preceded by a zone of active adsorption. When the lower edge of the MTZ reaches the bottom of the column, breakthrough occurs and the effluent concentration begins to raise rapidly. This point is called the breakpoint, defined as the volume of water passed through the bed before a maximum effluent concentration is reached. The plot of effluent concentration vs. time after breakpoint is defined as the breakthrough curve. Eventually, little additional adsorption occurs after the breakpoint since the entire column will be complete saturated and the effluent concentration (Ce) will approach influent concentration (Co) in practice the determination of breakthrough somewhat arbitrary, and usually either the effluent requirement, or 0.05 Co is used as a value, exhaustion is usually defined as Ce = 0.95 Co.

The breakpoint time decreases with ;

(1) decreased bed depth

(2) increasing practical size of a adsorbent

(3) increased flow rate

(4) increased initial solute concentration

If the adsorption isotherm where favorable and if the adsorption rate where infinite the breakthrough curve would approach straight vertical line. The breakthrough curves become less sharp as the mass transfer rates are decreased. Since the mass transfer rates are always finite, the breakthrough curves are diffused and exhibit an S shape. This S - shaped curve within the MTZ is usually described as master transfer wave or master transfer front.

When breakthrough occurs, the carbon in the adsorption zone is partially spent. For maximum economy, it requires that the spent carbon be in equilibrium with the influent waste water. The depth of carbon removed for regeneration (and hence the depth of total carbon system) will therefore depend upon the adsorption zone as shown in fig. In designing a column, the length of the adsorption zone represents the minimum bed depth needed to produce a low effluent concentration. The actual bed depth is usually greater than this minimum to allow a reasonable operating period of between regenerations of the adsorbent.

6.3 ADSORPTION COLUMN DESIGN :

To design an unsteady - state fixed-bed adsorber, a modelise needed that predicts the solute concentration in the bed as a function of time and position. As already discussed the x rate of adsorption depends upon external mass transfer, internal diffusion, and surface absorption. A general model for an adsorber involves a complex set of partial differential equations incorporating these kinetic process. Since a general model is very difficult to solve even with the aid of a computer, a no. of simplifying assumptions are usually made. The most common assumptions are ;

(1) The overall rate is controlled by only one of the rate steps and

(2) The equation for the equilibrium isotherm has a linear form. Even with simplifying assumptions, the solution of the quotations are often numerical rather than analytical.

6.3.1.MASS TRANSFER MODEL

This model assumes that an adsorption zone with constant shape and velocity moves through the bed and that the rate of adsorption is controlled by external mass transfer. Webber has found breakthrough curves predicted by this model may deviate from measured results in aqueous systems. Although more realistic models have been prepared, they are complex mathematically and lack adequate experimental confirmation with wastewaters.

Since the mass transfer model illustrates many of the concepts involved in predicting breakthrough curves, it is presented in this section.

6.3.1.1.MASS TRANSFER ZONE CONCEPTS :

The basics principles of the mass transfer zone are shown in fig. considering a fixed-bed adsorber treating wastewater at a volumetric flow rate. Q the influent and effluent concentrations are designated Co and Ce respectively. The lower portion of the fig. summarizes the transitional characteristics fo the granular carbon within the adsorber (column) and the effluent quality with time. Initially, the adsorbent is highly activate and the amount of solute adsorbed per unit weight of adsorbent. Is low fig 4.3a . At a later time 't' an analysis of the adsorber shows an adsorbate loading curve similar to the one presented in fig. three distinct zones within the bed of adsorbent are evident at this time :

(1) Equilibrium zone,

(2) Mass transfer zone, and

(3) Used bed zone.

In the equilibrium zone, the adsorbent is exhausted and is in equilibrium with the influent concentration of wastewater. The maximum adsorbate loading occurs within the equilibrium zone, the adsorbent is exhausted and is in equilibrium with the influent concentration of wastewater. The maximum adsorbate loading occurs within the equilibrium zone. In contrast, the adsorbate loading of the carbon near the effluent end of the filter is very low and is, essentially, the same as when first placed into the unit. It between the equilibrium zone and the unused zone the adsorbate loading of the absorbent changes from a maximum to minimum. This zone is characterized as the mass transfer zone because it is within the zone that the adsorbate is removed from the solution phase and adsorbed onto the surface of the adsorbate. The S-shape of the X vs Z plot within the MTZ is described as the 'mass transfer wave' or 'mass transfer front'.

As flow continues, the MTZ move down the column. When the physiochemical characteristics of the process are maintained constant, the velocity of the mass transfer wave is constant. Eventually, the unused the portion of the adsorber will be diminished. At this time , the leading edge of the mass transfer front is located at the bottom of the adsorbent. This is shown in fig. where the concentration of the adsorbate in the effluent is detected and breakthrough occurs. The mass transfer wave continues to move out of the adsorber as flow continues. When the trailing edge of the mass transfer wave reached the bottom of the column, the absorbent is totally exhausted, and the entire bed of carbon is in equilibrium with the influent. This situation if depicted in fig. the effluent concentration vs. time curve shown in fig. is defined as the breakthrough curve and can be used to design carbon columns.

FORMULATION OF ADSORPTION MODEL :

An idealized breakthrough curve for an adsorber is shown n fig. where c is the mass concentration of solute in the effluent viz. The total volume of solute free effluent per unit cross-sectional area. The breakthrough curve usually rises steeply between the breakpoint (C_B) and exhaustion point C_E are arbitrarily selected to include the major portion of the region in which adsorption is occurring. The main objective of this analysis is to predict the total quantity of effluent at the breakpoint, V_B and V_E i.e. the mass transfer wave. The time required for the adsorption zone MTZ to establish itself and move down the column and out of the bed is defined as the time to exhaustion t_E

$$t_E = \frac{V_E}{Q}$$

where V_E = total flow as exhaustion, M^3 waste

Q = Volumetric flow rate M^3 /day / M^2

The time needed for the MTZ to move its own height down, the column after it has been established is defined, t_A the time of passage through the adsorption zone.

$$t_A = \frac{V_E - V_B}{Q}$$

The velocity of the MTZ is given by

$$\underline{U}_A = \frac{Z_A}{t_A} \qquad \frac{Z}{tE - tF}$$

where Z_A = Height of MTZ

Z = Height of adsorbent bed (bed depth)

t_F = zone formation time, defined as the time required for initial formation of MTZ at entrance.

Eqn. Can be re-arranged to

$$\frac{ZA}{Z} = \frac{t\,A}{t\,E - t\,F}$$

The shaded area in fig. represents the amount of solute removed from the liquid in the MTZ between the breakpoint and exhaustion point i.e.

$$m = \int_{V_B}^{V_E} (Co - C)\, dV$$

If the adsorption zone (MTZ) were completely staturated, the adsorbent would contain

$$m_S = C_o (V_E - V_B)$$

when the effluent concentration reaches the breakpoint the MTZ is still within the column, and solute corresponding to the shaded area in fig. can be adsorbed before exhaustion.

Fractional capacity ' F ' is defined as the ratio of the quantity of solute (adsorbate) adsorbed in the MTZ from breakthrough to exhaustion (m) to the total capacity of the adsorbent zone (m_s)

$$\text{Therefore,} \quad 'F' = \frac{m}{m_S} \int_{V_B}^{V_E} \frac{(Co - C)\, dV}{Co (V_E - V_B)}$$

When ' F ' approaches 1,0, the adsorbent in the MTZ contains litres adsorbate and the time to form the zone is close to zero, and ideal plug-flow conditions are approximate. When channeling or mass transfer limitations prevail, the curve rises very quickly, following breakthrough until it nears C_E the exhaustion concentration. Under these conditions, m is small and f approaches zero i.e. the adsorbent in the zone becomes saturated and the time to form the zone t_F essentially the same as the time needed for the zone to move a distance equal its height ZA. The limiting cases can be expressed by

$$t_F = (1 - f)\, t_A$$

Thus, the lower the amount of solute in the adsorption zone, the shorter the time needed to form the zone initially. Substituting for t_F in eqn.

$$\frac{Z_A}{Z} = \frac{t_A}{t_E - (1 - f)\, t_A}$$

$$= \frac{(V_E - V) / Q}{(V_E / Q) - (1-f) - (V_E - V_B) / Q}$$

$$= \frac{(V_E - V_B)}{V_E - (1-f) - (V_E - V_B)}$$

$$= \frac{(V_E - V_B)}{V_B + f\ (V_E - V_B)}$$

If all the adsorbent in the column were completely saturated the mass of solute adsorbed would be,

$$M_S = Z\, \rho\, q_o$$

As the breakpoint, the section of the column upto the trailing edge of the breakthrough is saturated. The only section of the bed which has not been saturated, is the zone at the end of the column of depth Z_A, which has the fraction (1-F) of its saturation capacity.

Thus, the total sorption capacity at the breakpoint is,

$$M = (Z - ZA)\,\rho\, q_0 + ZA\,\rho\,(1-f)\,q_0$$

M = mass of solute adsorbed at equilibrium per unit cross sectional area m/l_2

Where ρ = apparent density of solid in the packed bed m/l_3

q_o = mass of solute adsorbed per unit mass of carbon at equilibrium

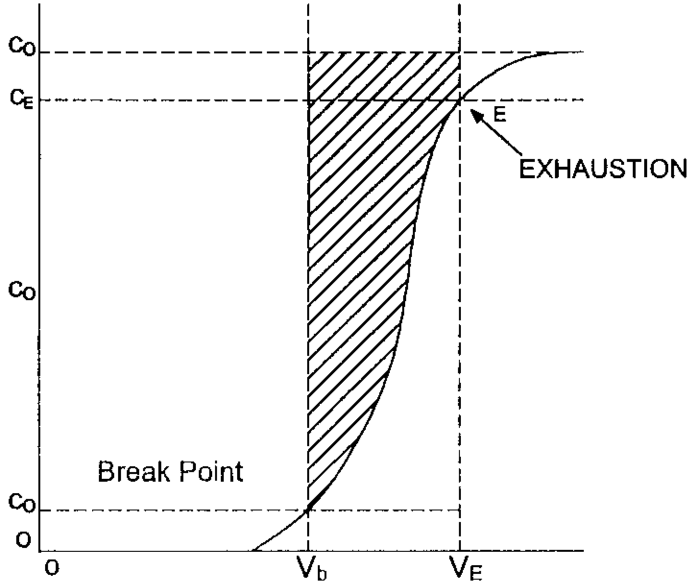
Z = concentration Co bed depth l_1

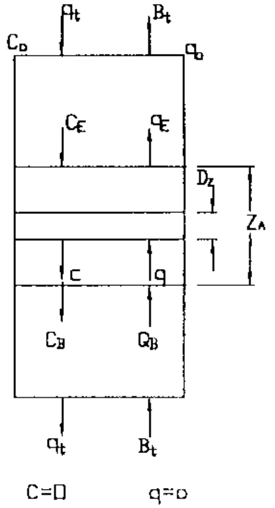
Eqn. can be combined to given the fraction of the column that is saturated Co in solute.

$$\text{Degree of saturation} = \frac{M}{M_S} = \frac{Z - FZ_A}{Z}$$

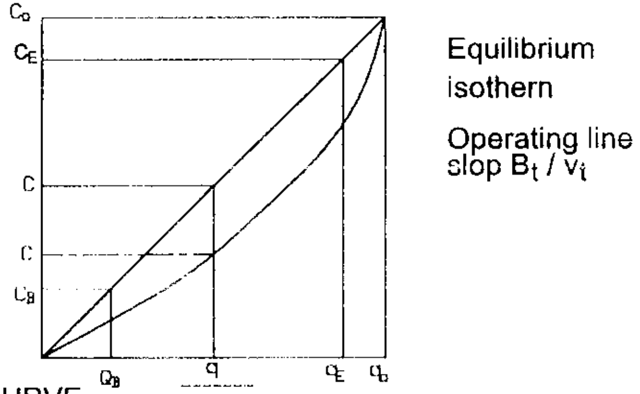
The effective sorption capacity of a column is clearly dependent upon the fractional capacity ' f '. As ' f ' decreases, Z_A increases in size and M decreases in magnitude.

Thus maximizing the fractional capacity of the adsorption zone is very beneficial.





SCHEMATIC DIAGRAM OF STEADY STATE ADSORPTION COLUMN



IDEAL BREAKTHROUGH CURVE

In a fixed bed adsorber, the adsorption zone moves down ward through the solid as time progresses. Since the motion of the solid and zone is relative, the solid can be visualized to move upward through the column at a velocity sufficient to maintain a stationary adsorption zone. Fig, illustrates a steady state adsorber with moving solid. The solid leaving the top is assumed to be in equilibrium with the entering liquid and all the solute is assumed to be removed from the effluent. Although these conditions would require infinitely tall column, the major concern of this analysis is the MTZ of height Z_A.

A material balance around the entire column of fig.

$$Q (C_o - O) = B_t (q_0 - o)$$

where B_t = flow rate of solid to maintains a stationary adsorption zone.

Similarly, a material balance between the lower end of the column and some arbitrary cross - section of the column is

$$Q (C - O) = B_t (q - o)$$

These material balances can be combined to give

$$\frac{B_t}{Q} = \frac{C}{q} = \frac{C}{q_0}$$

Thus, equation plotted on fig. as a straight line called an operating line, passes through the origin and the equilibrium curve at Co each point on the operating line represents the compositions of the liquid and solid streams passing each other at same cross section of the column.

As discussed earlier, the transfer of solute from a liquid to a solid involves several stops with differing resistances.

For this analysis the resistance to mass transfer will be combined into an overall co-efficient, K_L . for a differential section of the column dZ. the rate of transfer between phases is

$$Qdc = K_L\ a\,(C - C^*)\, dz$$

Where dz = differential column length

Overall mass transfer rate co-efficient $ML^{-2}T^{-1}$

a = External surface pf the adsorbent per unit volume of bd, L^{-1}

C^* = Equilibrium concentration of the organics adsorbed, x / m represented as q

As shown on fig. represents the vertical difference between the operating and equilibrium curves at a value of q. integration of eqn. Over the adsorption zone for constant K_L gives,

$$\int_{o}^{Za} \frac{K_L a}{Q} \, dZ = \int_{C_E}^{C_E} \frac{dc}{C - C^*}$$

$$\frac{K_L a Z}{Q} = \int_{C_B}^{C_E} \frac{dC}{C - C^*}$$

For any value of Z less than ZA corresponding to concentrations between C_B and C_E the quotation is

$$\frac{K_L a Z}{Q} = \int_{C_B}^{C_E} \frac{dC}{C - C^*}$$

Combining equation and gives,

Therefore, $$\frac{Z}{ZA} = \frac{V - V_B}{V_E - V_B} = \int_{C_B}^{C} \frac{dC}{C - C^*}$$

$$\int_{C_B}^{C} \frac{dC}{C - C^*}$$

If the co-efficient K_L is known, the snap of the breakthrough curve can be evaluated by graphical integration.

SURFACE REACTION MODEL :B

A useful and easily applied design method for fixed bed adsorber is presented by Eckenfelder and Hutchins model is based on the theory or Bohart and Adams who assumed that the rate of adsorption is controlled by the surface reaction between the adsorbate and unused capacity by adsorbent.

Consider a mass of adsorbent is residual capacity (N) diminishes at a rate given by the material balance equation.

$$\frac{DN}{t} = -KNC$$

$$\frac{DN}{t} = +KNC = 0$$

Where N = Residual adsorbing capacity per unit volume of bed, LM^{-3} (Kg/m^3)

t = service time, T (hr) i.e. the time required for the effluent to reach the specified breakthrough concentration C_3

K = Adsorption rate constant, $M^3\ M^{-1}\ T^{-1}$ (M^3 Kg.hr.)

C = Concentration of adsorbate in wastewater

t = 0, N = N_o = adsorptive capacity of carbon bed

Consider now the wastewater from which the adsorbate (contaminant) is removed by adsorption. Adsorbate concentration diminishes at a rate given by the material balance equation

$$\frac{\delta C}{\delta Z} = - KNC / v$$

$$\frac{\delta C}{\delta Z} = + KNC / v$$

Where Z = depth of adsorbent (bed depth $Z = Z_o$)

and v = L (m) hydraulic loading or linear flow velocity of wastewater paste the adsorbent LT^{-1} (m/hr)

Diffusion and accumulation terms where neglected in the liquid material balance.

Integrating the differential equations over the length of the bed and using the boundary conditions.

1. At t = o, N = no and
2. At z = o, C = Co (influent concentration) we get

$$\frac{1\, n\, (C_o - 1)}{C_B} = \frac{1\, n \left[(\exp\, (K\, NoZ)\right]}{V} -1$$

$$- KC_0\, t$$

This expression is known as Bohart and Adams equation since exp. $(K N Z / V)$ is usually much greater than one. Equations reduced to

$$t = \frac{C_0}{C_B} - 1 = \frac{KN_oZ}{V} - KC_0 t$$

Solving for breakpoint time (service time) yields

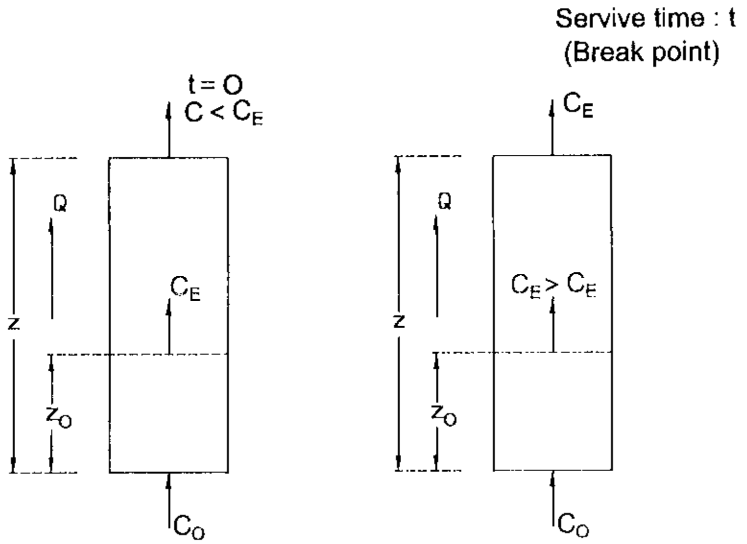
$$t = \frac{KN_oZ}{C_0 V} - \frac{1}{KC_0} \ln \frac{C_0}{C_B} - 1$$

This equation is the basis for determination of No and K from bench scale columns.

Hutchins has employed the Bohart and Adams equation in the form of bed depth service time (BDST) for interpretation of column data and process design, including extrapolation to conditions other than tested.

CONCEPT OF CRITICAL BED DEPTH :

In the operation of an activated carbon adsorption column wastewater with an influent concentration Co is fed into the column. It is desired to reduce the solute concentration. In the effluent to a value not exceeding C_E determined by water quality requirement.



Concept of critical bed depth(Z_o)

At time t = o, the theoretical depth of carbon which is sufficient to prevent penetration of concentration in excess of desired effluent concentration is defined as the critical depth Zc is less than, Z the actual bed depth fig.

An equation for Zc cane be derived from quotation by letting t = 0 and solving for Z (Z is equal to Zc at t = 0 and C_B - C_E

$$\ln \quad [C_0 / C_B \ - 1] \quad = \quad \frac{KNoZc}{V}$$

$$\text{Therefore, } Zc \quad = \quad \frac{V}{(Kno)} \ \ln \frac{C_0}{C_B} - 1$$

Adsorptive capacity (no.) is another important design variable. It is the maximum amount of containment solute that can be adsorbed by the carbon when saturation occurs - another parameter which enters Bohart - Adams's equation is the rate constant K - this assumes a first order adsorption rate r = Kc.

BDST ANALYSIS OF COLUMN DATA:

The procedure described by Hutchins for the use of breakthrough curves in the design of activated carbon columns is designated as BDST method. The data required to perofrm BDST analysis is normally obtained from pilot - scale experiments. In order to develop BDST co-relation, columns with different bed depths are evaluated in parallel. Each column is evaluated under the same set of physio chemical conditions. Samples are taken from each column at regular intervals and analysed for adsorbate concentration. The time at which the effluent from each column reached the breakthrough concentration (service time) is then plotted vs. bed depth to give a BDST graph as illustrated in fig. when the mass flow rate and other experimental conditions are maintained constant during the experiments the service time is a linear function of bed depth. The ? curve can be used to prediction how fast breakthrough will occur.

If the MTZ is arbitrarily defined as the carbon layer through which the liquid concentration various from 90 - 10 % of the feed concentration, the depth of this zone is given by the horizontal distance between these two lines in the BDST plot. As can be seen from fig. the depth of adsorption zone with time or bed depth.

EVALUATION OF PARAMETERS NUMBER, K AND ZC FROM BDST CURVE :

The BDST relationship shown in eqn. Can be expressed mathematically as

$t = aZ + C$

where t = service time

$\underline{a}$ = slope of the BDST graph hr/m

No / co. V

Z = Bed depth

$\underline{C}$ = The ordinate interrupt

= $-1 / CoK \ In (Co / C_B - 1)$

The slope of the BDST plot represents the time required to exhaust a unit length of adsorbent. i.e. to move the MTZ by unit length through the carbon under the test conditions. The horizontal intercept of the BDST curve gives the mass transfer zone, Z_A while the ordinate intercept gives the time required d for the MTZ to traverse its own length.

The values of parameters No, Zc and K are determined from equations. Many experimental factors can influence the numerical value of a and c. As such bench-scale experiments are typically conducted to define the experimental conditions under which the most favorable of a and c are obtained. Thereafter, pilot scale experiments are conducted to define a BDST equation which can be used in actual design calculations.

BDST ANALYSIS FOR MULTISTAGE COLUMNS :

Multistage columns ore us in an attempt to maximize carbon utilization whereby reducing the operating costs. This is accomplished by regenerating only the carbon that has been in contact with feed solution at its highest concentration thus approaching the maximum level of saturation, for given frrd. The advantage of multistage system over a single column is pronounced in he case of a deep adsorption zone as illustrated in fig. the figure shows the level of saturation along a single and a multistage system when the carbon is removed for regeneration. Whereas in the case of a shallow adsorption zone the carbon from both the system is highly saturated in the case of a deep adsorption zone the Carbon removed for regeneration in the multistage system is considerely move saturated compared to the single stage.

It should be emphasized that the best equation described above is only valid for a single stage column in which the feed is always applied to the head of the bed, and the entire bed is in service throughout the run. These conditions differ from the continuous operation of a multistage system since in the latter case the head section of the column is removed and a fresh section added to the tail end when the effluent quality is no longer acceptable. Hutchins suggested to use a modified BDST equation to calculate the forward velocity of the adsorption zone in the column of freshly added carbon. By assuming an experimental variation of concentration in the effluent from the last column in a series, and using the relationship of equation he calculated the adsorption zone velocity in the new column, from which he obtained the rate of carbon utilization in multi stage system.

The main advantages of this method that it is based on experimental data obtained during the early stage of operation that do not stimulate the conditions the prevail in a continuous operation of a multi stage system. A more reliable testing approaching would be to stimulate a multi stage operation by repeatedly removing the head column when the concentration C_b in the last column exceeds the acceptable level and adding a new column containing fresh or regenerated carbon at the tail end. Under these conditions a steady stage operation will be reached on which a reliable design can be based. The results of such an experiment can be presented in a BDST type plot as shown in fig. in this hypothetical plot the lines start at different slopes indicating a different velocity of the adsorption zone for different breakthrough level. However, after several cycles steady state is approached and the forward velocity of the adsorption zone is the same for all levels of breakthrough. Deviation from this behavior can be expected if the carbon adsorption capacity changes upon successive regenerations.

In order to design an adsorption system with maximum carbon utilization the carbon removed for regeneration should be in a high level of saturation. For practical design purposes a 90% breakthrough level may be selected as the minimum effluent concentration at which the carbon is regenerated. If the effluent quality requirements call for a 90% removal, the addition of a to the tail end of the series should coincide with a 10% breakthrough from the last column. Thus, the horizontal distance between 90 and 10 % breakthrough line in the BDST plot is taken as depth of the adsorption zone. This is the minimum bed depth in a moving bed system producing the desire effluent with maximum carbon utilization. For a multi stage system the no. of stage and the bed depth in each stage are related to the depth of the adsorption zone as follows :

$$N = \frac{Z_A}{Z} + 1$$

Where n = No. of stages in series (not including one stage in regeneration of stand-by)

Z_A = Depth of adsorption zone, FC

Z = is depth of single ft,

Selection of d should be based on practical considerations and should be an integer fraction of ${}^{z}A$. Selecting a small d will result in small size equipment with lower carbon inventory but a high no. of stages and consequently more costly equipment. A very low d approaches a moving bed operation a high value of d will result in simpler operation but higher carbon inventory and larger plant size.

The rate of carbon utilization can be calculated from the reciprocal of the slope of the BDST line. This value multiplied by the column's cross sectional area and the apparent density of the carbon is the rate of carbon utilization that is also equal to the required regeneration capacity. The preceding procedure may be applied directly for the design of systems operating under conditions similar to those in the experiment. If other operating conditions are contemplated extrapolation can be done although the accuracy such extrapolation is still not certain. The two most parameters to be extrapolated are the feed concentration Co and the hydraulic loading V. each of these parameters affects both the depth and the forward velocity of the adsorption zone. An increase in feed concentration will result in an increase in the forward velocity of the adsorption zone although not proportionately. As can be seen from equation the velocity of the a adsorption zone is directly proportional to Co and inversely proportional to N_o since N_o is related to Co the net effect of Co on the forward velocity of the adsorption zone depends on the Co to N_o co-relation. In system where no biological activity is present and the contact time is sufficiently, thus co-relation can be derived from isotherm data. The effect of Co on the depth of the adsorption zone can not be readily calculated. However, for equal percent removal it is reasonable to assume that the effect is in significant obviously, if equal effluent concentrations are required, the system operated with higher Co will require higher percentage of removal which in turn will lead to a deeper adsorption zone.

The hydraulic loading also affects both the depth and the forward velocity of the adsorption zone. The forward velocity is directly proportional to the hydraulic loading as can be seen from equation. It is assumed that the contact time long enough and N_o does not with hydraulic loading. Due to increased dispersion the depth of the adsorption zone will generally increase with hydraulic loading. The exact relationship between two is yet unknown.

7.2 METHODOLOGY

7.2.1. PREPARATION OF CARBON :

Activated carbons can be mode from a variety of carbonaceous materials including wood, coal peat, lignin, nutshells, bagass (sugarcane pulp), sawdust lignite, bone, and petroleum residues. The current trend in the manufacturer of activated carbon is towards the potential utilisation of different wastes as raw materials, for example : waste lignin, sulfite, liquors, processing wastes from petroleum and lubricating oils, and carbonaceous solid waste.

Activated carbons can be classed in two groups ; powdered and granular. In waste water applications, powdered carbons or predominantly (60 - 75%) smaller than 325 mesh while granular carbons or typically larger than 40 mesh (0.42mm). powdered activated carbon is usually produced by activating lump material, or chips of wood charcoal, or lumps of paste prepared from sordust, and subsequently grinding the activated product. Depending on the method or grinding the shape of the particles can differ to a certain extent, and this may markedly influence the properties the product displays in industrial applications. Active carbon ground in ball mills has oval particles and that ground in hammer has elongated particles.

Granular carbons may be formed by either crushing or pressing. Crushed activated carbon is prepared activating a lump material, which is then crushed and classified to desired particle size. Pressed activated carbon is formed prior to activation. The appropriate strongly material is prepared in a plastic mass, then extruded from a die and cut in to pieces of uniform length. These uniform cylindrical shapes or then activated. The necessary hardness is acquired in the activation process. For activated carbons formed from pulverized materials, which are then bound together, the nature of blinding agent is a major factor in determining the hardness of the finished product.

7.2.2. CARBON ACTIVATION :

Activated carbon is produced by a serious of process which include :

1. Removal of all water (dehydration)
2. Conversion of the organic matter to elemental carbon driving off the non carbon portion (carbonization)
3. Burning off tars and pour enlargement (activation).

In some cases zinc chloride are phosphoric acid may be used in addition to heat as dehydrating agent. Following dehydration, heating is continued, usually in the absence of air, at temperatures upto 400 - 500° C. this treatment known as carbonisation, converts the, organic material to elemental carbon which is a mixer of ash, (inert inorganics), tars, amorphous carbon, and crystalling carbon (elementary graphitic crystallities). Non carbon elements (H_2 and O_2) are removed in gaseous form, and the freed elementary carbons are grouped into oxidised crystalographic formations. the escape volatile substances (tars, methanols, acetic acid vapours , CO_2 , CO) causes pores to form within the materiel and leaves a product usually referred to as chair. Although surface area is opened up during carbonization, chars possess little adsorptive power due to the presence of amorphous residues (tars) blocking their pores. These residues are removed and the pores are, cleaned and enlarged by the process of activation, which is the final step in the production of activated carbon. Activation is essentially two phase process requiring burnoff amorphous decomposition products (tars) at 750 - 900^0 C, plus enlargement of pores in the carbonised material. Burn off freeze the pore openings, increasing the number of pores, and activation enlarges these pore openings. Activation is achieved by two different process. Physical activation and chemical activation. Physical activation is normally achieved by treating char with mixers of CO_2 , air and steam at temperatures of 750 - 900^0 C, so as to bur off the amorphous residues.

Pores spaces within the carbon are well developed following activation and can be classified according to size as follows : macropores, transitional pores, and mocropores according to dubinin et.al. (1964). Macropores have an effective radius of 5000 - 20000 A^0 and open directly to the outer surface of the carbon particle. Transitional pores with radii of 40 - 200 A^0 develop off the macropores. Micropores develop off the transitional pores with an effective ciably to the surface area of the carbon, but provide a passage way to the particle interior and the micropores. Pore size distribution determines the size distribution of molecules that can enter the carbon particle to be adsorbed. Particle size is generally considered to affect adsorption rate. But not the adsorptive capacity which is related to the total surface area. By reducing the particle size, the surface area of a given weight is not affected. Particle size mainly contributes to a system hydraulics, filterability and handling characteristics.

7.2.3. EXPERIMENTAL PROCEDURE

1. Set up the plexi glass carbon columns in a manner similar to that in fig. they should be located close to the off feed water to minimize pumping losses - A variable - speed centrifugal pump is desirable for flexibility of operation. If the suspended solid or oil is high in the feed in wastewater

(50 mg/1) then using one column has the prefilter will minimize backwashing.

2. The units should be piped or valued so that samples can be taken from each column and each column can be backwashed individually. Downflow operations are normally used, although the up flow mode of operation can be investigated if desired.
3. Load the columns with the required amounts of test carbon. Each column should have an equal amount. It may be helpful to paint the columns black or to cover them to prevent from sunlight penetration during the test run. This will minimize algal growth in the columns and reduce backwash frequency.

4. Begin the run at the prescribed linear flow velocity and initial conditions. Monitor the effluent quality of each column by withdrawing samples atleast once daily. The collected samples shall be analysed for the parameter of concerned.

METHODOLOY FOR TESTING USING ATOMIC ADSORPTION STECTRO PHOTO METER.

The method used can be analytical technique use for the qualitative and quantitative determination o f an element in a sample. in this method the sample in the form of a and chemical reactions create free atoms capable of adsorbing, emitting of fluorescing at characteristic wave length. Flame spectroscopy can be divided the different processes occurring, to give us.

- Flame emission Spectroscopy
- Atomic flourescence Spectroscopy
- Atomic adsorption Spectroscopy

In emission spectroscopy thermal energy is used to excite the atoms to higher levels. This suffers from a major disadvantage that emission Spectra are complex due to emission by other species in the sample by the flame, causing considerable interferences.

The process of fluorescence is similar to atomic adsorption. In this the detector is placed at right angles to the radiation source to observe fluorescence.

In atomic adsorption Spectrophotometer, a light source emitting a narrow spectral line of the characteristic energy is used to excite free atoms formed in the flame. The decrease in energy in hen measured.

The similarity between atomic adsorption spectrophotometry and flame photometry is, in flame photometry an atomic adsorption system consists of a flame unit, a prison to disperse and isolate the emission lines and a detector with appropriate amplifiers. In addition, the adsorption system has a light source which emits a stable and intense light of a particular wave length. Each element has characteristic wave length which it will readily absorb.

The advantage of atomic adsorption Spectrophotometry is that it is quite specific for many elements. Adsorption depends upon the presence of free unexcited atoms in the flame and these are in much greater abundance than excited atoms. Thus elements such as (Zn), Magnesium (Mg), which are not easily excited in flames and so give poor results with the flame photometer, can be readily measured by the atomic adsorption method.

A relatively new addition to atomic adsorption spectrophotometer is the graphite furnace, which allows analysis for many heavy metals in the microgram per litre range. Here the atomizer burner is replaced with a small cylindrical graphite tube which can be programmed through a series of different temperatures. The radiation from the cathode lamp source passes through the open ends of the horizontal cylinder and selected wave lengths are measured by the phototube as with the atomizer - burner method. A small quantity of a water sample is inserted into the cylinder through a hole in the side and the temperature program is initiated. The temperature first rises to just other 100^0 c to allow the sample to evaporate, leaving the metal containing salt behind. The temperature then increases to several hundred degree celcius which volatilizes the cations so they fill the cylindrical space and the particular cation to be determined adsorbs the characteristic radiation from the carbon cathode tube.

In atomic adsorption spectrophotometer, the adsorption is proportional to the concentration of free atoms in the flame, it is given by Lambers - Beer Law that

$$\text{Adsorbence} = \log_{10} \frac{I_o}{I_t} = K.C.L.$$

I_o = Intensity of incident radiation emitted by the light source

I_t = Intensity of transmitted radiation (amount not adsorbed)

C = concentration of sample (free atoms)

K = constant (determined experimentally)

L = Path length

PRINCIPLE OF WORKING OF ATOMIC SPECTROMETER

Figure (1) shows a line diagram to explain the working principle of atomic adsorption spectrometer.

A liquid sample to be analysed is sprayed under controlled conditions into a flame where the water evaporated, leaving inorganic salts behind as minute particles. The salts decompose into constituent atoms or radicals and may become vaporized. The vapours containing the metal atoms are excited by the thermal energy of the flame and also by a light source which emits a stable and intense light of a particular wave length of particular metal. This causes electrons of the metallic atoms to be raised to higher energy level. When electrons fall back to their original position or to a lower level they give off discrete amount of radiant energy. The emitted energy is passed through a prism which seperates the various wave length so that the desired region can be located.

OPTIMIZATIONS :

Most elements can be analysed at more than are wave length, the choice of which depends as a varietry of factors.

LAMP CURRENT OPTIXMIZATION

Recommended currents given by the lamp manufacturer are generally the best settings to use. The use of as low an operating current as possible is advised in order to prolong the life of the lamp and to optimize curvature due to self absorption.

BAND PASS OPTIMIZATION :

The band pass is set tot the maximum possible that does not cause excessive curvature by the introduction of ray and unadsorbable radiation. In general, the narrower the band pass the greater the adsorbence and the more linear the calibration curve.

OPTIMIZATION OF SAMPLE INTRODUCTION SYSTEM :

Sample introduction system camprises : - Nebulizer, impact bead, spray chamber, burner and flame. After optimizing the wave length and zeroing the adsorbence reading, the burner is adjusted by wrong the horizontal rotational and vertical controls.

Quick and approximate optimization of burner position without the flame running, raises the burner until it starts to block the light path. Using a white card,trace the light path along the burner. Lower the burner until it just does not intesfere. Final optimization is performed for maximum adsorbence with the flame irnited and standard aspirating.

Flame optimization is performed by aspirating a standard and adjusting the fuel control for optimum adsorbence.

CALIBRATION

CALIBRATION CURVE

This is the most common method where interference effects are known to be absent usually atleast three standards and a blank are used to cover the range. 0.1 to 0.8 Abs. The calibration is performed by using the blank solution to zero the instrument. The standards are then analysed with the lowest concentration first, and the blank run between standards to ensure the base line has not changed, samples are these analysed and their adosrbence are recorded. A graph of concentration Vs adsorbence is plotted.

For the metals analysed (Mn, Fe. Cu, Zn. Pb and Cd standards at different known concentration were prepared and calibration curve is plotted.

The details of preparation, of standard. Solution and standards for calibration, for different metals are given seperately.

SENSITIVITY

The concentrations of an element that will produce a transmittance of 99 per cent (adsorbence of 0.0044)

EXPERIMENTSAL PROCEDURE :

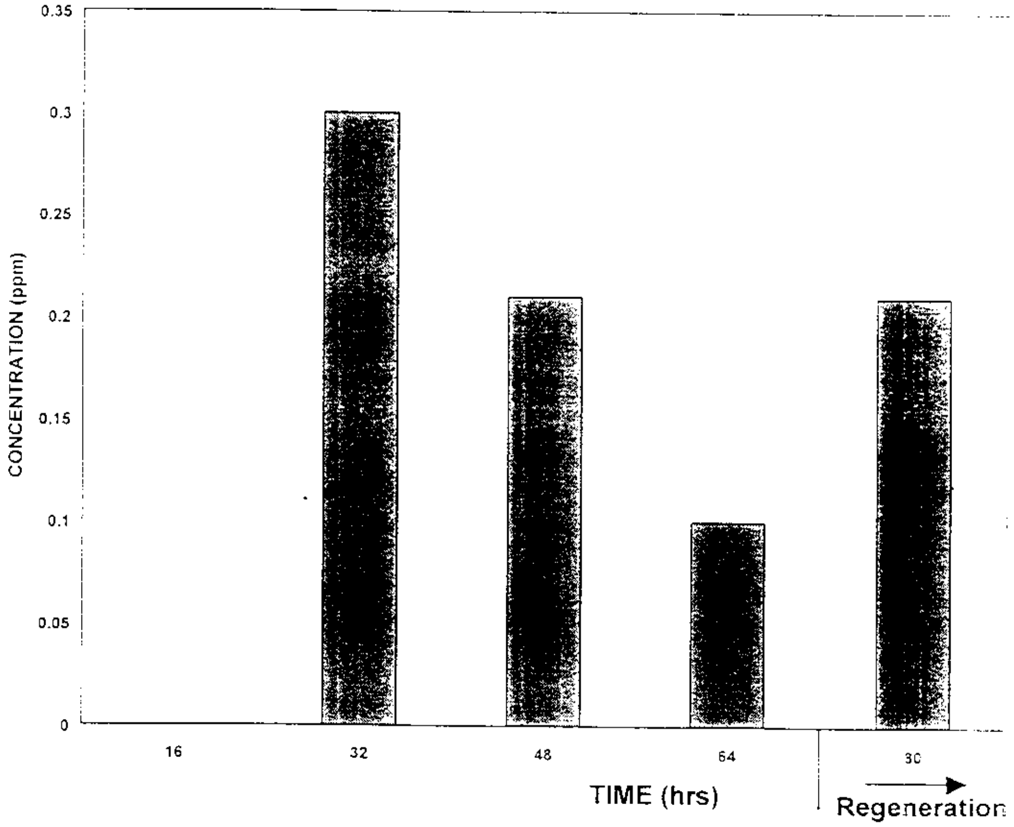
Instrument is switched on and left for 10 minutes to warm up. The cathode lamp of particular metal to be tested is fixed in positions. Lamp current is fed so that lamp is on. The appropriate wave length and slit width are chosen.

The preliminary adjustments are done as explained in the operational procedure. Then the instrument is calibrated for the particular metal using standard solution of known concentrations.

Now a blank solution is aspired and zero is set. The samples to be tested for the particular metal is fed, the readings are directly printed on the printer which is connected to the equipment. The same procedure is conducted for the other metals. The details of operational procedure is furnished.

TABLE 8.1

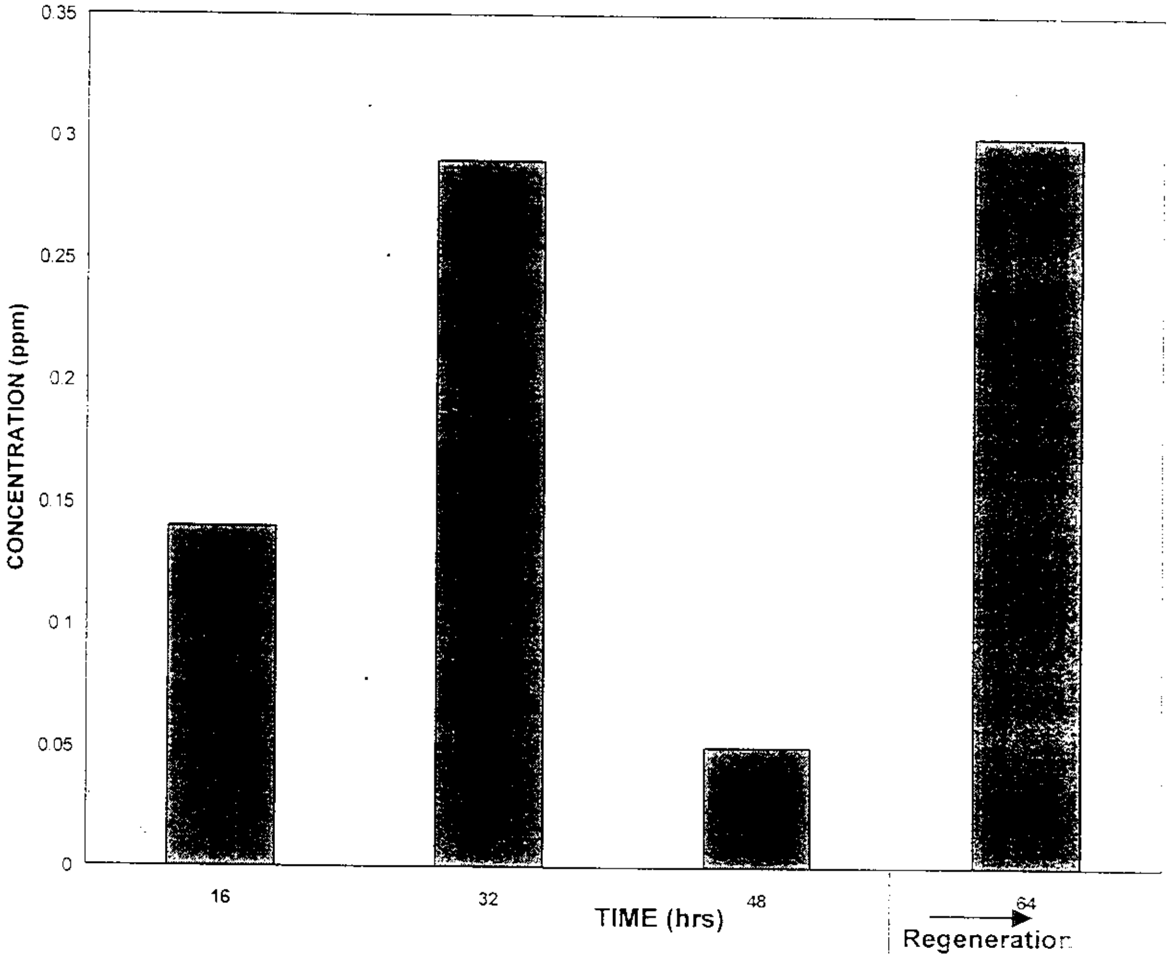
Absorbent	Carbon
Dia	3.5 cm
Rate of flow	25 ml/hr
Head	16 cm
Intervals	16 hrs x 5
Weight of Carbon	137.7 gms



TIME (hrs)	16	32	48	64	80
CONCENTRATION (ppm)	0	0.3	0.21	0.1	0.21

TABLE 8.2

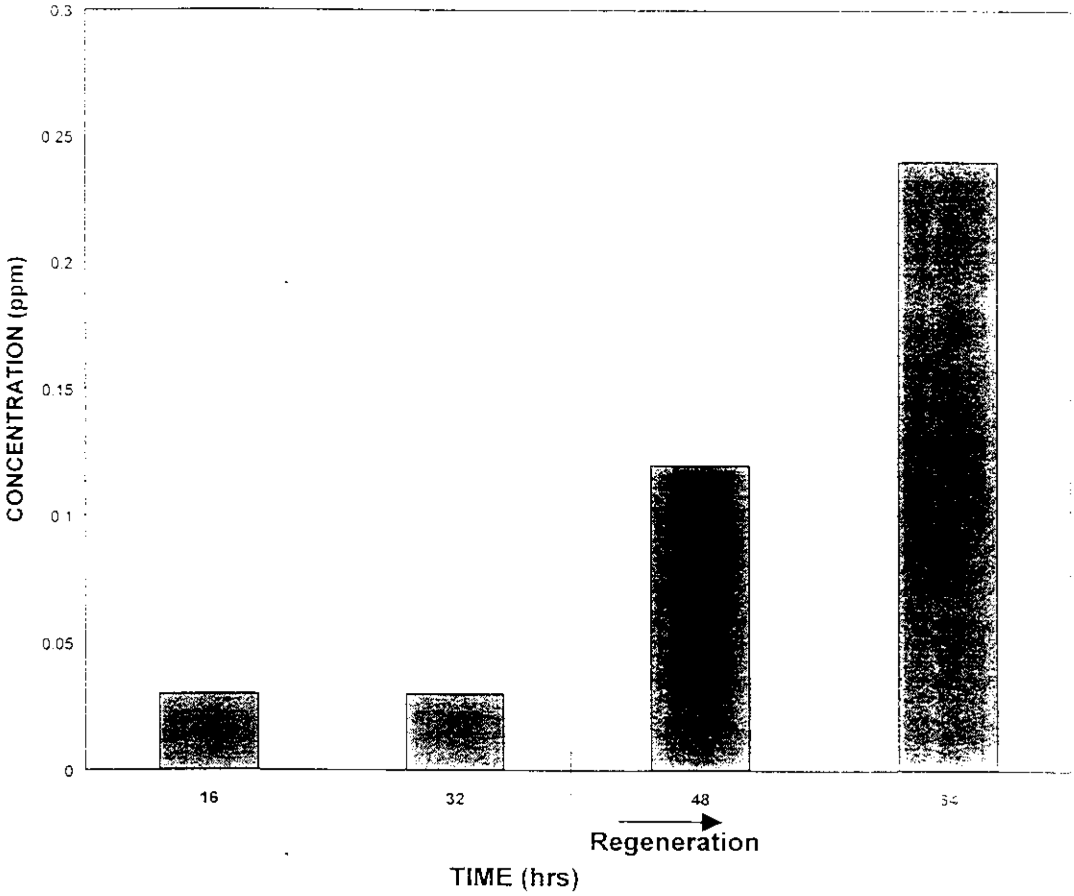
Absorbent	Carbon
Dia	3.0 cm
Rate of flow	25 ml/hr
Head	75 cm
Intervals	16 hrs x 4
Weight of Carbon	97.41 gms



TIME (hrs)	16	32	48	64
CONCENTRATION (ppm)	0.14	0.29	0.05	0.3

TABLE 8.3

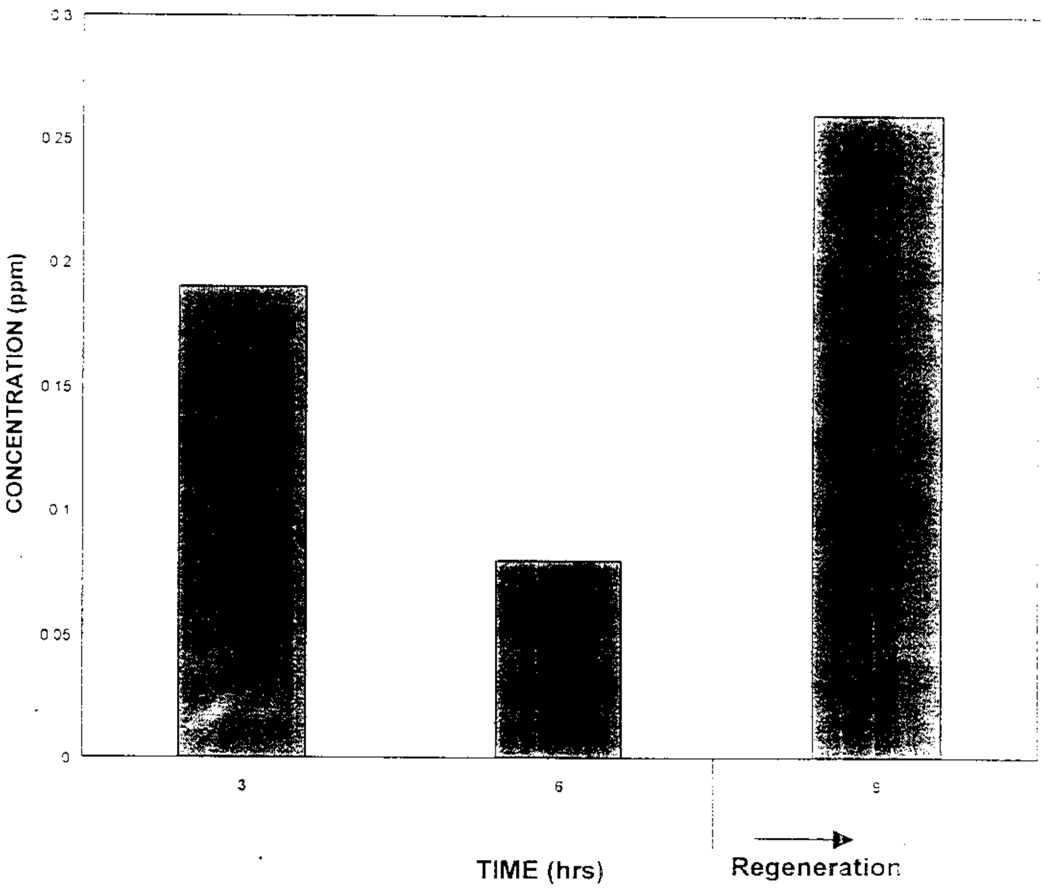
Absorbent	Carbon
Dia	2.5 cm
Rate of flow	25 ml/hr
Head	75 cm
Intervals	16 hrs x 4
Weight of Carbon	26.29 gms



TIME (hrs)	16	32	48	64
CONCENTRATION (ppm)	0.03	0.03	0.12	0.24

TABLE 8.4

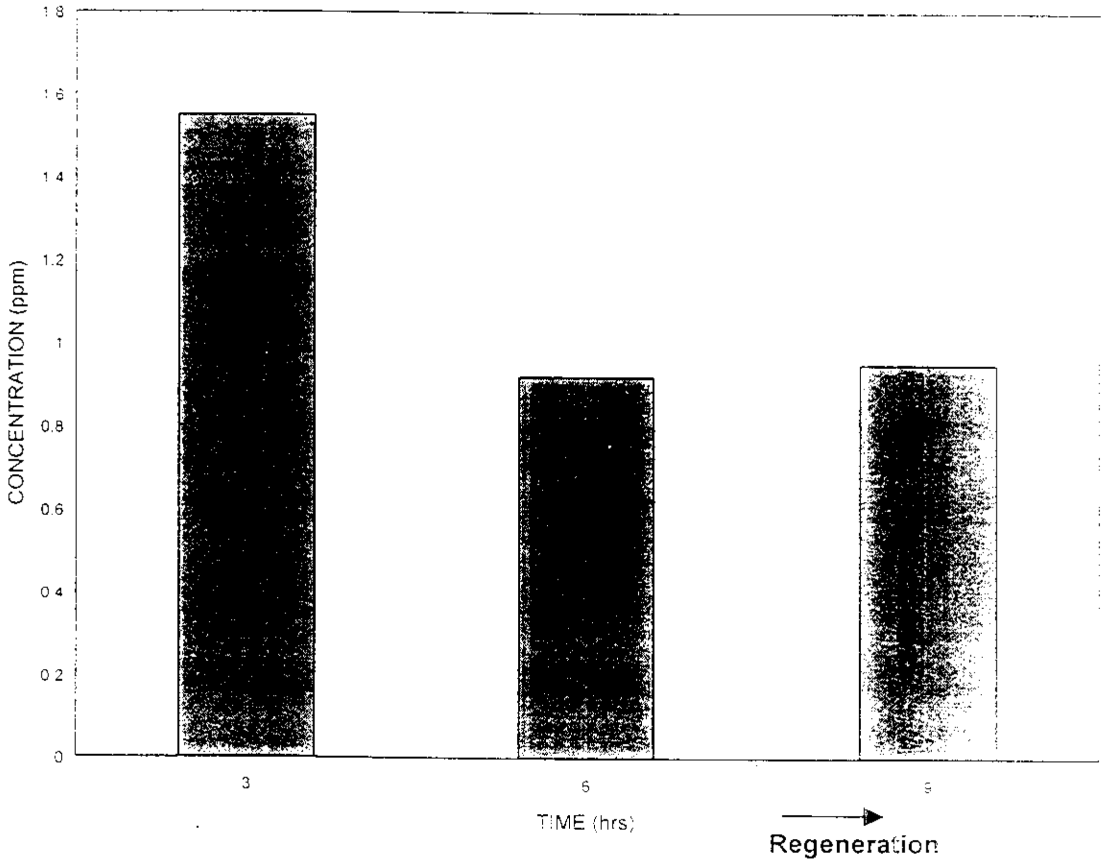
Absorbent	Saw dust
Dia	3.5 cm
Rate of flow	50 ml/hr
Head	75 cm
Intervals	3hrs x 3
Weight of Saw dust	125.36 gms



TIME (hrs)	3	6	9
CONCENTRATION (ppm)	0.19	0.08	0.26

TABLE 8.5

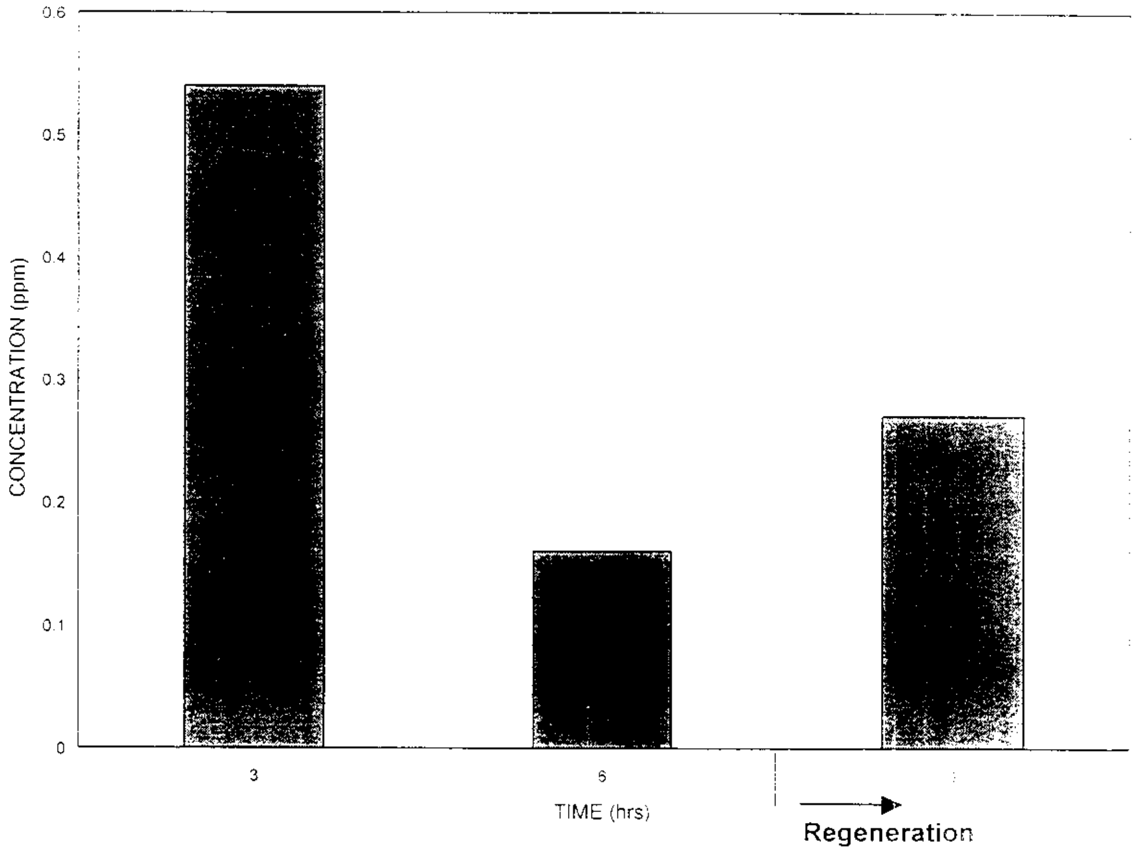
Absorbent	Saw dust
Dia	3.0cm
Rate of flow	50 ml/hr
Head	75 cm
Intervals	3hrs x 3
Weight of Saw dust	109.34 gms



TIME (hrs)	3	6	9
CONCENTRATION (ppm)	1.55	0.92	0.95

TABLE 8.6

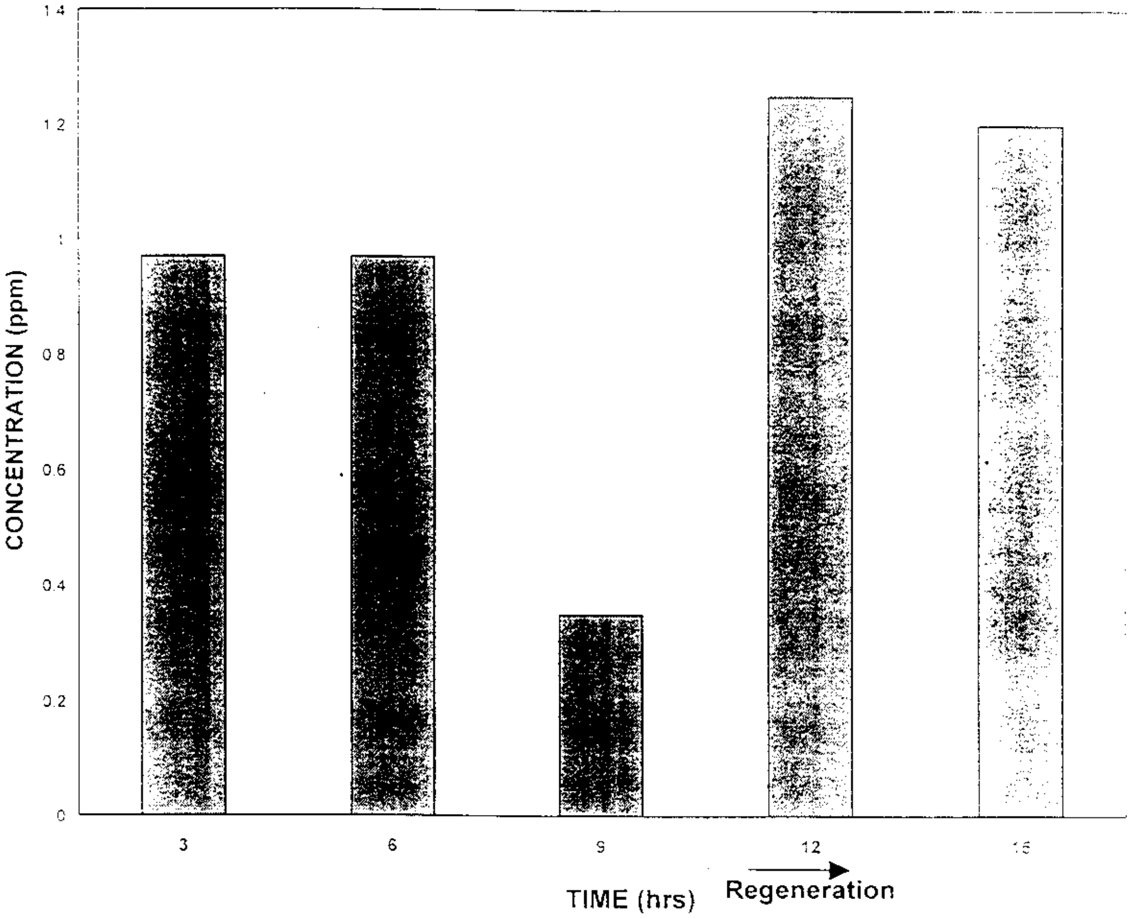
Absorbent	Saw dust
Dia	2.5 cm
Rate of flow	50 ml/hr
Head	75 cm
Intervals	3hrs x 3
Weight of Saw dust	71.12 gms



TIME (hrs)	3	6	9
CONCENTRATION (ppm)	0.54	0.16	0.27

TABLE 8.7

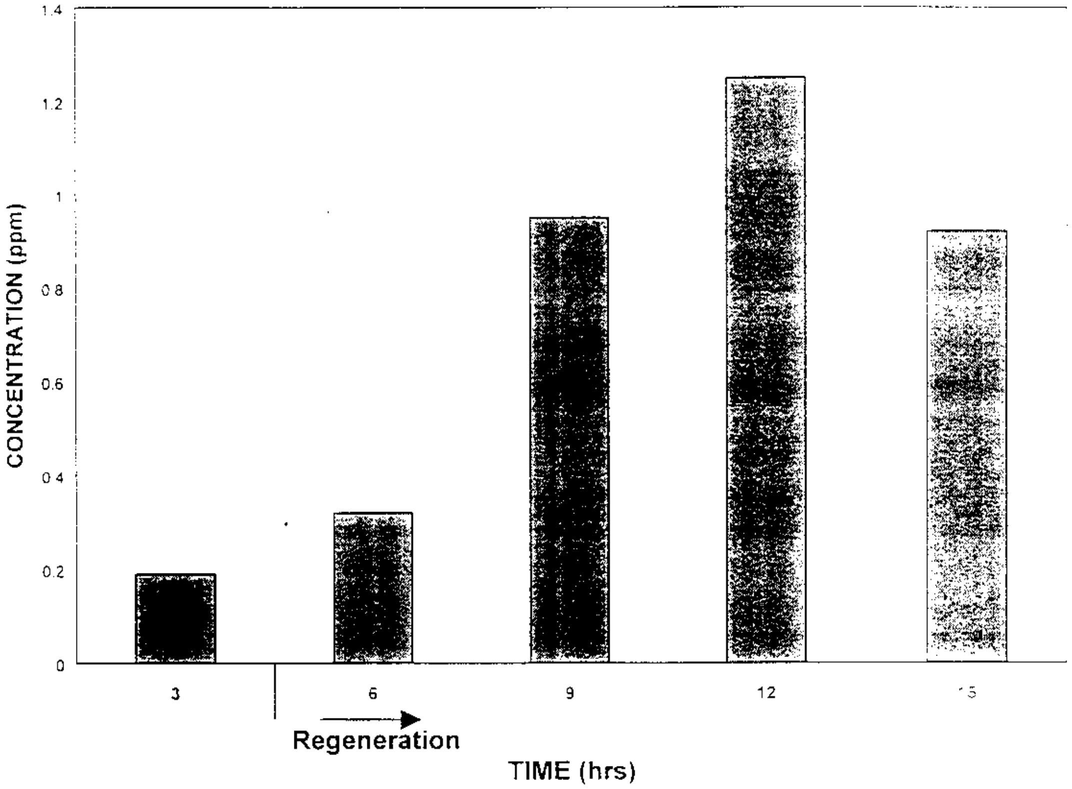
Absorbent	Mango leaf
Dia	3.5 cm
Rate of flow	25 ml/hr
Head	75 cm
Intervals	3hrs x 5
Weight of Mango leaf	136.99 gms



TIME (hrs)	3	6	9	12	15
CONCENTRATION (ppm)	0.97	0.97	0.35	1.25	1.2

TABLE 8.8

Absorbent	Mango Leaf
Dia	3.0 cm
Rate of flow	50 ml/hr
Head	75 cm
Intervals	3hrs x 5
Weight of Mango leaf	109.06 gms



TIME (hrs)	3	6	9	12	15
CONCENTRATION (ppm)	0.19	0.32	0.95	1.25	0.92

RESULTS AND CONCLUSION :

Results from the tests conducted by both the methods are tabulated and compared.

Removal of chromium content using polymer was studied. it was found that percentage of chromium removed. Using this method was not that significant. The reasons are studies and found the if the pH value is increases that removal will be better, but interference of Iron comes into picture at higher level of pH. Hence the method can be improved by eliminating the interference of iron.

By method of carbon adsorption two parameters were eliminated. the colour of the effluent (greenish blue) was removed 100 % and also chromium was removed upto a level of 99.5% since, commercial activated carbon is costly derived out of saw dust and mango leaf were use. The results got using this are commendable.

Hence from the studies made it is concluded that the method of adsorption is successful in the removal colour as well as chromium from effluent and the effluent after this treatment can be disposed.

FUTURE SCOPE OF STUDY

The adsorption process can be studies with the use of carbon from other materials such as groundnut shell, coconut coir, etc.

Iron exchange process can also be studies since it has also been a promising process for removal of chromium.

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