

# MODELING OF FIXED BED ADSORPTION COLUMN FOR THE REMOVAL OF PHENOL IN WASTE WATER

A DISSERTATION

*Submitted in partial fulfillment of the  
requirements for the award of the degree*

*of*

**MASTER OF TECHNOLOGY**

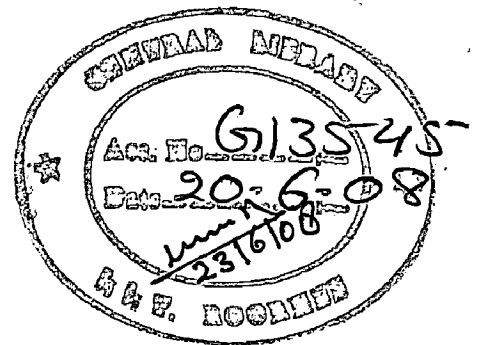
*in*

**CHEMICAL ENGINEERING**

**(with specialization in Computer Aided Process Plant Design)**

By

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JUNE, 2007**

## **CANDIDATE'S DECLARATION**

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I hereby declare that the work which is being presented in this dissertation entitled **“MODELING OF FIXED BED ADSORPTION COLUMN FOR THE REMOVAL OF PHENOL IN WASTE WATER”**, in partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization **COMPUTER AIDED PROCESS PLANT DESIGN** of Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during the period from July 2006 to June 2007, under the guidance of **Dr. (Mrs.) SHASHI**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

I have not submitted the matter presented in this dissertation for the award of any other degree.

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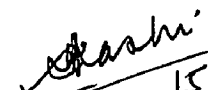
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## **CERTIFICATE**

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

  
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## ABSTRACT

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Phenol is a target pollutant to be removed from waste waters from different industries because of its toxicity. The kinetic behavior of a fixed-bed adsorber can be explained and the characteristic break through curve for the adsorption of phenol in waste water onto Amberlite XAD16 can be obtained through mathematical models. Langmuir isotherm model is used to fit the equilibrium data. For modeling adsorption kinetics a linear driving force approximation was used. The LDF rate constants accounting for film mass transfer resistance, macro pore diffusion and adsorption were grouped in an overall mass transfer coefficient. The proposed mathematical model for fixed-bed adsorption is solved by implementing a computer algorithm in MATLAB (V.7.3) software and compared with experimental data in literature. The effects of important and influencing parameters such as flow rate and temperature are studied.

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## NOMENCLATURE

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$C_0$	Initial concentration of adsorbate in solution (mg/ l)
$C_e$	Concentration of adsorbate in solution at equilibrium (mg/ l)
$D_{ax}$	Axial dispersion ( $m^2 \text{ min}^{-1}$ )
$d_p$	Diameter of the particle of the adsorbent (m)
$\Delta H_L$	Enthalpy of adsorption for the Langmuir isotherm ( $J \text{ mol}^{-1}$ )
$k$	Constant in Radke–Prausnitz isotherm (l /g)
$K$	Constant in Radke–Prausnitz isotherm $(\text{mg/ l}) / (\text{mg/ l})^{1/p}$
$K_L$	Parameter in the Langmuir isotherm model ( $L \text{ mg}^{-1}$ )
$K_L^\infty$	Equilibrium constant corresponding to the Langmuir model ( $L \text{ mg}^{-1}$ )
$M_B$	Molecular weight of solvent B ( $\text{g mol}^{-1}$ )
$p$	Constant in Radke–Prausnitz isotherm (–)
$Pe$	Peclet number
$q_e$	Amount of adsorbate adsorbed at equilibrium (mg/g)
$q_m$	Amount of adsorbate adsorbed per gram of adsorbent at 24 h (mg/g)
$q$	Amount of adsorbate adsorbed per gram of adsorbent at any time $t$ (mg/g)
$r$	Radius of activated carbon particle (m)
$R$	Universal gas constant ( $J/\text{mol}$ )
$Sc$	Schmidt number
$Sh$	Sherwood number
$S_e^\infty$	Monolayer adsorption capacity parameter in Toth isotherm (mg/g)
$u_0$	Superficial velocity ( $\text{m min}^{-1}$ )
$u_i$	Interstitial velocity
$V$	Solution volume (l)
$V_A$	Molar volume of solute a at its normal boiling temperature ( $\text{cm}^3 \text{ g mol}^{-1}$ )
$t$	Time (h)
$T$	Absolute temperature (K)
$th$	Constant in Toth isotherm (–)

## Greek symbols

$\alpha_1$	Constant in Fritz–Schlunder isotherm (mg/g)/(mg/l) <sup><math>\beta_1</math></sup>
$\alpha_2$	Constant in Fritz–Schlunder isotherm (mg/g)/(mg/l) <sup><math>\beta_2</math></sup>
$\varepsilon_p$	Porosity of the adsorbent
$\eta$	Viscosity of the solution (Pa s <sup>-1</sup> )
$\eta_B$	Viscosity of solvent B (cp)
$\rho$	Density of the adsorbent (g L <sup>-1</sup> )
$\phi$	Dimensionless association factor of solvent



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INTRODUCTION

Waste water may be defined as a combination of liquid or water carried wastes from residences, institutes, commercial and industrial establishments. Together with such ground water, surface water and storm water as may be present. This water has been adversely affected in quality by anthropogenic influence. Increased no. of stringent environmental laws enforces the treatment of this waste water according to the norms specified by State and Central pollution Control Board (CPCB). In this thesis, the treatment of waste water consisting of physical adsorption processes employing modeling concept is discussed.

**1.1 Waste water characterization**

Waste water is characterized in terms of its physical, chemical and biological composition. The composition of industrial waste water is quiet varied, its constituents ranging from organic solvents, oils, suspended solids to dissolved chemical compounds. No. of polluting chemical substances released by different industries. Most of the chemicals are toxic, some are even suspected of cancer, some are valuable enough warrant recovery. The principal physical properties and the chemical and the biological constituents of waste water and their sources are listed in table.

Table 1: Physical, chemical and biological characteristics of waste water and their sources.

Characteristic	source
<i>Physical properties</i>	
Color	Domestic and industrial wastes
Odor	Decomposing waste water, industrial wastewaters
Solids	Domestic water supply, domestic and industrial wastes ,soil erosion
Temperature	Domestic and industrial wastes

<b><i>Chemical constituents</i></b>	
<b><i>Organic</i></b>	
Carbohydrates	Domestic, commercial and industrial wastes
Fats, oils and grease	Domestic, commercial and industrial wastes
Pesticides	Agricultural wastes
Phenols	industrial wastes
Proteins	Domestic, commercial and industrial wastes
Priority pollutants	Domestic, commercial and industrial wastes
Surfactants	Domestic, commercial and industrial wastes
Volatile organic compounds	Domestic, commercial and industrial wastes
other	Natural decay of organic materials
<b><i>Inorganic</i></b>	
Alkalinity	Domestic wastes, domestic water supply, ground water infiltration
Chlorides	Domestic wastes, domestic water supply, ground water infiltration
Heavy metals	Industrial wastes
Nitrogen	Domestic and agricultural wastes
pH	Domestic, commercial and industrial wastes
Phosphorous	Domestic, commercial and industrial wastes, natural run off
Priority pollutants	Domestic, commercial and industrial wastes
Sulfur	Domestic, commercial ,industrial wastes, domestic water supply
<b><i>Gases</i></b>	
Hydrogen sulfide	Decomposition of domestic wastes
Methane	Decomposition of domestic wastes
Oxygen	Domestic water supply, surface-water infiltration
<b><i>Biological constituents</i></b>	
Animals	Open water course and treatment plants
plants	Open water course and treatment plants

Protists	Domestic wastes ,surface-water infiltration
Eubacteria	
Archaeobacteria	
Viruses	Domestic wastes

## 1.2 General Standards for discharge of environmental pollutants [32]

### Effluents

Table.2 General Standards for discharge of environmental pollutants

S. No.	Parameter	Inland surface water	Public sewers	Land for irrigation	Marine/coastal areas
1	Colour and odour	All efforts should be made to remove colour and unpleasant odour as far as practicable.			
2	Suspended solids mg/l, max.	100	600	200	(a) For process waste water (b) For cooling water effluent 10 per cent above total suspended matter of influent.
3	Particle size of suspended solids	shall pass 850 micron IS Sieve	-	-	(a) Floatable solids, solids max. 3 mm (b) Settlable solids, max 856 microns
4	pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
5	Temperature	shall not exceed 50°C above the receiving water temperature			shall not exceed 50°C above the receiving water temperature

6	Oil and grease, mg/l max,	10	20	10	20
7	Total residual chlorine, mg/l max	1.0	-	-	1.0
8	Ammonical nitrogen (as N), mg/l, max.	50	50	-	50
9	Total kjeldahl nitrogen (as N); mg/l, max. mg/l,	100	-	-	100
10	Free ammonia (as NH <sub>3</sub> ), mg/l, max.	5.0	-	-	5.0
11	Biochemical oxygen demand (3 days at 27°C), mg/l, max.	30	350	100	100
12	Chemical oxygen demand, mg/l, max.	250	-	-	250
13	Arsenic (as As).	0.2	0.2	0.2	0.2
14	Mercury (As Hg), mg/l, max.	0.01	0.01	-	0.01
15	Lead (as Pb) mg/l, max	0.1	1.0	-	2.0
16	Cadmium (as Cd) mg/l, max	2.0	1.0	-	2.0
17	Hexa valent chromium (as Cr <sup>+6</sup> ), mg/l, max.	0.1	2.0	-	1.0
18	Total chromium (as Cr) mg/l, max.	2.0	2.0	-	2.0
19	Copper (as Cu) mg/l, max.	3.0	3.0	-	3.0
20	Zinc (as Zn) mg/l, max.	5.0	15	-	15
21	Selenium (as Se)	0.05	0.05	-	0.05
22	Nickel(as Ni)max mg/l	3.0	3.0	-	5.0

23	Cyanide (as CN) mg/l, max.	0.2	2.0	0.2	0.2
24	Fluoride (as F) mg/l, max.	2.0	15	-	15
25	Dissolved phosphates (as P), mg/l, max.	5.0	-	-	-
26	Sulphide (as S) mg/l, max.	2.0	-	-	5.0
27	Phenolic compounds (as C6H5OH) mg/l, max.	1.0	5.0	-	5.0
28	Radioactive materials: (a) Alpha emitters micro curie mg/l, max. (b) Beta emitters micro curie mg/l	10 <sup>-7</sup> 10 <sup>-6</sup>	10 <sup>-7</sup> 10 <sup>-6</sup>	10 <sup>-8</sup> 10 <sup>-7</sup>	10 <sup>-7</sup> 10 <sup>-6</sup>
29	Bio-assay test	90% survival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% effluent
30	Manganese (mg/l)	2	2	-	2
31	Iron (as Fe) (mg/l)	3	3l	-	3
32	Vanadium (as V) (mg/l)	0.2	0.2	-	0.2
33	Nitrate Nitrogen (mg/l)	10	-	-	20

### 1.3 Industrial waste water treatment

Industrial facilities that send their wastes to municipal treatment plants must meet certain minimum standards to ensure that the wastes have been adequately pretreated and will not damage municipal treatment facilities. Increased no. of stringent environmental laws enforces the treatment of waste water according to the norms specified by Central Pollution control Board (CPCB). Advanced waste water treatment encompasses several individual unit operations, unit processes used separately or in combination with other process to achieve very high overall treatment efficiencies. The unit operations and processes grouped together to provide various levels of treatment. They are as follows:

- Preliminary waste water treatment
- Primary waste water treatment
- Secondary waste water treatment
- Tertiary waste water treatment

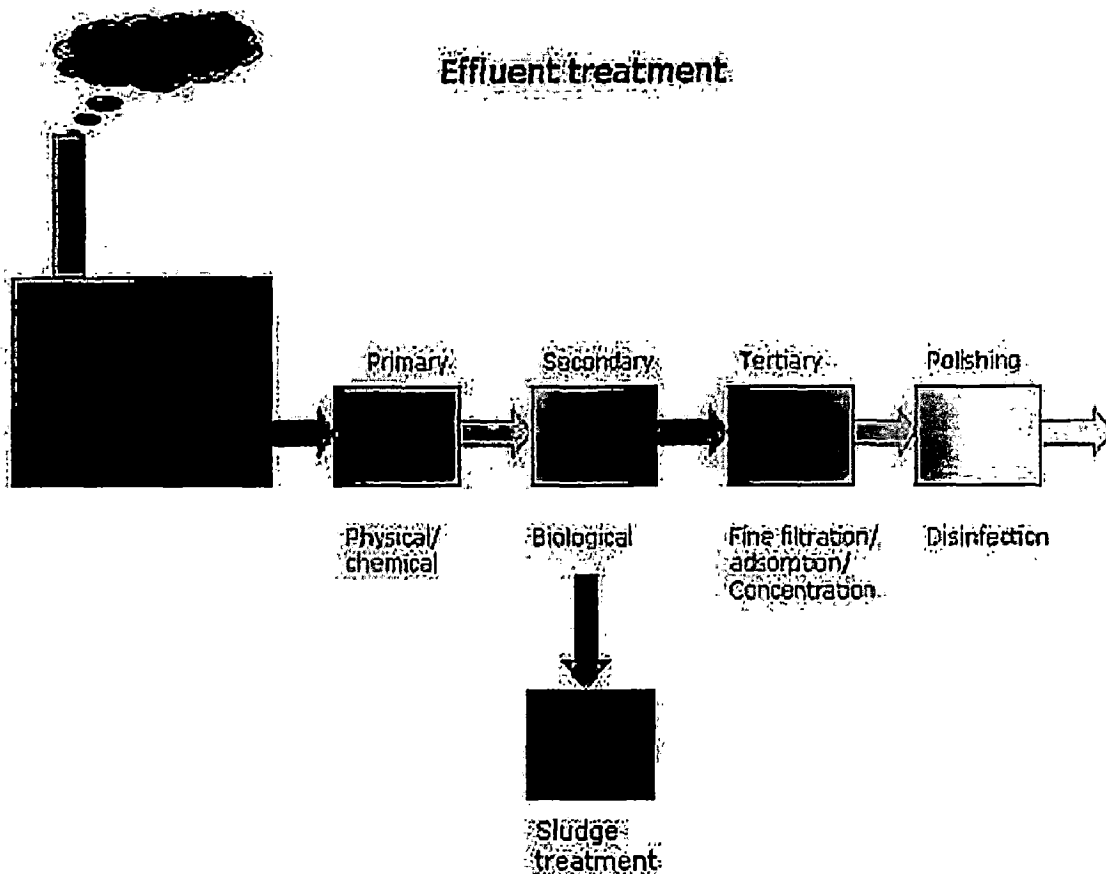


Fig.1.1 Industrial waste water treatment process



**Preliminary waste water treatment:** It is defined as the removal of waste water constituents that may cause maintenance or operational problems with treatment operations, processes and ancillary systems [19].

Examples of preliminary operations are screening and comminution for the removal of debris and rags, grit removal for the elimination of coarse suspended matter that may cause wear or clogging of equipment, and flotation for the removal of large quantities of oil and grease.

**Primary waste water treatment:** In this a portion of suspended solids and organic matter is removed, usually accomplished with physical operations. The effluent from primary treatment will ordinarily contain considerable organic matter and will have relatively high BOD.

The preliminary/primary treatment refers to the Physical unit operations.

**Secondary waste water treatment:** This is directed principally toward the removal of biodegradable organics and suspended solids. This refers to the chemical and biological unit processes.

**Tertiary waste water treatment:** This is to remove constituents of concern including nutrients, toxic compounds, and increased amounts of organic material and suspended solids. This refers to the combination of all physical unit operations, chemical and biological unit processes.

**Physical unit operations:** Treatment methods in which application of physical forces predominate are known as physical unit operations. Screening, mixing, sedimentation, flotation, filtration and gas transfer are typical unit operations.

- Screening is removal of coarse solids by use of a straining device
- Sedimentation is gravity settling of pollutants out of waste water
- Flotation is the use of small gas bubbles injected into the waste water which cause pollutant particles to raise to the surface for subsequent removal

- Air stripping is removal of volatile and semi- volatile organic compounds from waste water by use of air flow.

**Chemical unit processes:** Treatment methods in which removal or conversion of contaminants is brought about by addition of chemicals or by other chemical reactions are known as chemical unit operations. Precipitation, adsorption, coagulation and disinfection are the most common examples used in waste water treatment.

- Neutralization is adjustment of alkalinity and acidity to the same concentration (pH =7).
- Precipitation is addition of chemicals which produce chemical precipitates that will settle out during sedimentation.
- Coagulation is use of chemicals to cause the pollutants to agglomerate and subsequently settle out during sedimentation.
- Adsorption onto chemical solids on which pollutants adhere to the surface and we can separate them by desorption process. It is used especially when solutes are valuable compounds.
- Disinfection is selectively destroy disease causing organisms by chemicals
- Break point chlorination is the addition of chlorine to the level that chloramines will be oxidized to nitrous oxide and nitrogen, and chlorine will be reduced to chloride ions.

**Biological unit processes:** Treatment methods in which removal of contaminants is brought about by biological activity are known as biological unit processes. It is used to remove biodegradable organic substances (colloidal or dissolved) and nutrients (nitrogen and phosphorous) .The organic substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by settling [19].

- Air activated sludge is an aerobic process in which bacteria consume organic matter, nitrogen and oxygen from the waste water and growth occurs. The bacteria are suspended in aeration tank by mixing action of air blown into the waste water.

- High purity oxygen activated sludge is an aerobic process similar to air activated sludge except that pure oxygen is injected.
- Aerated pond /lagoon is also similar except mechanical agitators are used to air.
- Trickling filter is fixed film aerobic process .A tank containing media with a high surface to volume ratio is constructed waste water is discharged at the top of tank and trickles down through the media. Bacteria growth occurs by utilization of organic matter and nitrogen from waste water.
- Rotating biological contactor (RBC) is similar to trickling filter except that the media is supported horizontally across the tank and is rotated so that it is alternately in the waste water and the air.
- Oxidation ditch is an aerobic process similar to the activated sludge process. Physically it is ring –shaped and is equipped with mechanical aeration devices.

Table.3 Waste water constituents and its removal by various methods

<b>Constituents</b>	<b>Removal methods</b>
Suspended solids	Screening and comminution, Filtration, Flotation, Grit removal, Chemical polymer addition, Coagulation, Natural systems(Land treatment)
Biodegradable Organics	Activated sludge variations, Fixed film reactors (Trickling filters),Lagoon variations, Rotating biological contactors, Intermittent sand filtration, Physical-chemicalsystems, Natural systems
Volatile organics	Air stripping, Off gas treatment, Carbon adsorption
Pathogens	Chlorination, Hypo chlorination, Bromine chloride, Ozonation U V Radiation, Natural Systems.
<b>Nutrients</b>	
Nitrogen	Suspended growth nitrification& denitrification variations, Fixed film nitrification& denitrification variations, Ammonia stripping, Ion exchange, Break point chlorination, Natural systems.
Phosphorous	Metal-salt addition, Lime coagulation/sedimentation, Biological

	phosphorous Removal, Biological-chemical phosphorous removal, Natural systems.
Nitrogen & Phosphorous	Biological nutrient removal
Refractory Organics	Carbon adsorption, Tertiary Ozonation, Natural systems.
Heavy metals	Chemical Precipitation, Ion exchange, Natural Systems
Dissolved organic solids	Ion exchange, Reverse osmosis, Electro dialysis.

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**ADSORPTION**

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**2.0 Adsorption**

A separation process in which solids are used for the removal of substances from either gaseous or liquid solutions known as adsorption, it involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

Two key parameters:

- Amount of the surface area. The more the merrier.
- "Residence time" of fluid within adsorbing media.

Examples:

- Decolorization of sugar solutions using charcoal.
- Solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

**2.1 Types of Adsorption**

There are two types of Adsorption:

- Physical adsorption
- Chemisorption

### **Physical adsorption:**

A reversible phenomena, is the result of vanderwaals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. The adsorbed substance penetrates with in crystal lattice of the solid and does not dissolve in it but remains entirely upon the surface. In industrial operations the types we shall consider depend upon the reversibility of adsorption for recovery of adsorbent for reuse, for the recovery of adsorbed substances, or for the fractionation of mixtures.

### **Chemisorption:**

Adsorption phenomena as a result of chemical interactions between solid and adsorbed substance. The strength of chemical bond may vary considerably and identifiable chemical compounds in the usual sense may not actual form, but the adhesive force is generally much greater than that found in physical adsorption. The heat liberated is usually large and is of the order of the heat of chemical reaction. The process is frequently irreversible and on desorption of the original substance will often be found to have undergone a chemical change [28].

The same substance which under the conditions of low temperature will undergo substantially only physical adsorption upon a solid will some times exhibits chemisorption at higher temperatures, and both phenomena may occur at the same time.

## **2.2 Adsorbents**

The solid surface on which the adsorbate is going to be adsorbed is called adsorbent. The adsorbents are characterized first by surface properties such as surface area and polarity .A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. A Adsorbents are mostly micro porous, high specific surface materials (200 - 2000 m<sup>2</sup>/g) The size of the micro pores

determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micro pores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called "hydrophilic" and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, non polar adsorbents are generally "hydrophobic". Carbonaceous adsorbents, polymer adsorbents and silicalite are typical non polar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water. If the solid is highly porous, containing many fine capillaries, the adsorbed substance will penetrate these interstices if it wets the solid.

#### **Nature:**

Adsorbent solids are usually used in granular form, varying size from 12mm in diameter to as small as 50 $\mu$ m. The solids must possess certain engineering properties depending on the application to which they are put. For example in the fixed bed adsorption in which liquids or gas is to flow they must not offer too great pressure drop for flow nor must they easily be carried away by flowing stream. They must have adequate strength and hardness so as not to be reduced in size during handling or crushed in supporting their own weights of beds of required thickness.

#### **Physical adsorbents:**

The most commonly used adsorbents are Alumina, Silica gel, Zeolite molecular sieves, highly specific, single pore size may be fine-tuned: cations + structure type of organo-modified materials, Mordenite, other natural zeolites Silicalites, Active carbon, Carbon molecular sieves (narrow pore distribution), impregnated carbons clays (natural and pillared clays) resins, polymers (biological, ions, large molecules) carbon nano tubes.

Perforated plate has a structure so that activated carbon does not fall to lower stages because of the angle of repose when water flow is off. This makes it possible to run and stop raw waste water pump. New activated carbon is loaded into a weighing tank and fed by treated water to the top of tower under pumping force.

The raw waste water is fed from the bottom of the tower and moves towards the top through perforated plates. When the waste water contact with the fluidized activated carbon, organic substances in it get adsorbed. When water feed is stopped and the valve at the bottom of the tower is opened to remove old activated carbon in it, and flows to the bottom along with the water stage-by-stage and is released from the bottom of the tower.

**Moving bed adsorption column:**

It is very effective when the length of adsorption bed is long. Waste water is supplied through a nozzle on the bottom of tower and discharged as treated water from a screen on the top (Fig.2.4).

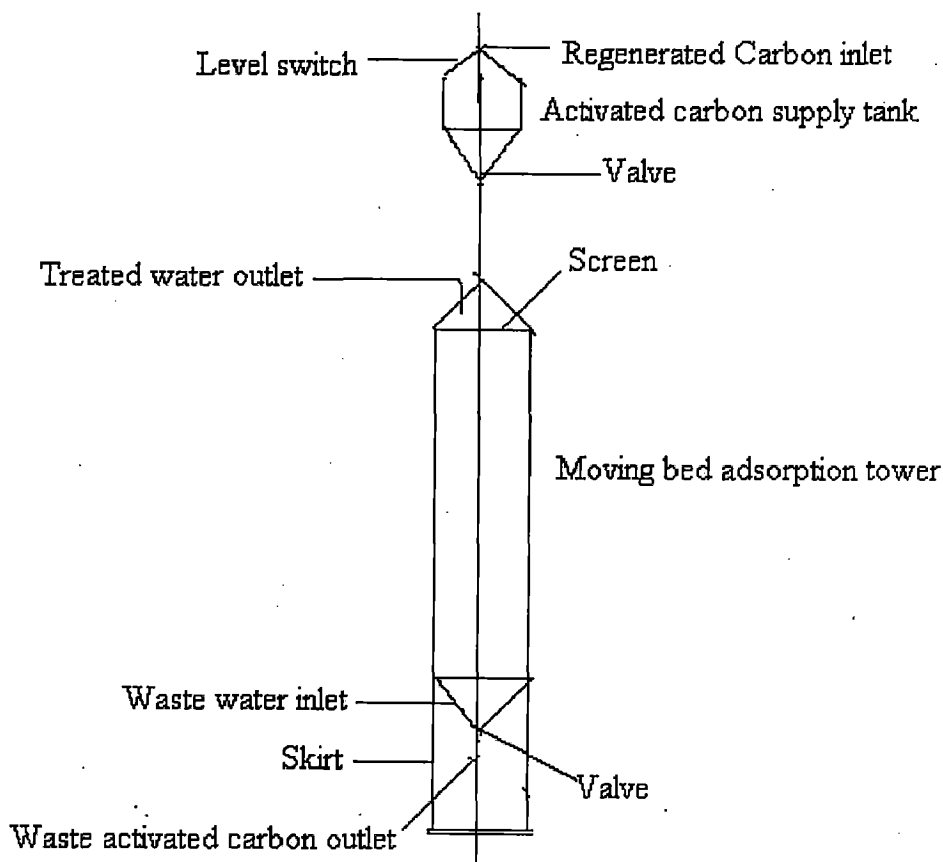


Fig.2.4 Moving bed adsorption tower.



Activated carbon: It is the trade name for a carbonaceous adsorbent which is defined as follows: Activated carbons are non-hazardous, processed, carbonaceous products, having a porous structure and a large internal surface area. These materials can adsorb a wide variety of substances, i.e. they are able to attract molecules to their internal surface, and are therefore called adsorbents.

Fuller's earth: These are natural clays chiefly magnesium aluminum silicates in the form of minerals attapulgite and montomorrillonite. The clays are particularly useful in decolorizing, neutralizing, and drying. By washing and burning the adsorbed organic matter accumulating upon the clay during use, the adsorbent can be reused many times.

Activated clays: These are bentonite or other clays which show essentially no adsorptive ability unless activated by treatment with sulfuric or hydrochloric acid. It is particularly useful for decolorizing petroleum products and is ordinarily discarded after a single application.

Bauxite: A certain form of naturally occurring hydrated alumina which must be activated by heating to temperatures varying from 230 to 815<sup>0</sup> C in order to develop its adsorptive ability.

Alumina: This is a hard, hydrated aluminum oxide which is activated by heating to drive off the moisture. The porous product is available as a granules or powders, used as a desiccant for gases and liquids. It can be reactivated for reuse.

Bone char: This is obtained by destructive distillation of crushed, dried bones at temperatures in the range 600 to 900<sup>0</sup>C. It can be reused after washing and burning.

Synthetic polymeric adsorbents: These are porous spherical beads, 0.5 mm diameter, and each bed of collection of micro spheres 10<sup>-4</sup>mm diameter. The material is synthetic, made from polymerizable monomers of two major types. Those made from unsaturated aromatics such as styrene and vinyl benzene are useful for adsorbing nonpolar organics from aqueous solution. Those made from acrylic esters are suitable for more polar solutes. They are used principally for treating water solutions and are regenerated by leaching with low molecular weight alcohols or ketones.

Silica gel: This is a hard, granular, very porous product made from the gel precipitated by acid treatment of sodium silicate solution. It is revived for reuse by evaporation of the adsorbed matter.

Molecular sieves: These are porous, synthetic zeolite crystals, metal aluminosilicates. The “cages” of the crystal cells can entrap adsorbed matter, and the diameter of the passage ways, controlled by the crystal composition, regulates the size of the molecules which can enter. They are used for dehydration of gases and liquids, separation of gas and liquid hydrocarbon mixtures, and in a great variety of processes. They are regenerated by heating or elution [28].

Table.4 Representative Commercial Liquid Phase Adsorption Separations

<b>Liquid Bulk Separations (b)</b>	
<b>Separation (a)</b>	<b>Adsorbent</b>
Normal paraffins / isoparaffins, aromatics	Zeolite
p-Xylene/o-xylene, m-xylene	Zeolite
Detergent-range olefins/paraffins	Zeolite
p-Diethyl benzene/isomer mixture	Zeolite
Fructose /glucose	Zeolite
<b>Separation (a)</b>	<b>Adsorbent</b>
H <sub>2</sub> O/organics, oxygenated organics, chlorinated organics, etc.	Silica, alumina, zeolite
Organics, oxygenated organics, chlorinated organics, etc./H <sub>2</sub> O	Activated carbon
Odor, taste bodies/drinking H <sub>2</sub> O	Activated carbon
Sulfur compounds/organics.	Zeolite, others
Various fermentation products/fermentor effluent	Activated carbon
Decolorizing petroleum fractions, sugar syrups, vegetable oils, etc.	Activated carbon

## 2.3 Activated carbon adsorption

Organic contaminants from industrial waste streams that seriously threaten human health and environment. Activated carbon is widely used for removing organic pollutants from water. The porous nature of this adsorbent material and its high surface area are suitable properties for adsorption. The volume of pores of the activated carbons is generally greater than  $0.2 \text{ ml g}^{-1}$ . The internal surface area is generally greater than  $400 \text{ m}^2 \text{ g}^{-1}$ . The width of the pores ranges from 0.3 to several thousand nm.

All activated carbons are characterized by their ramified pore system within which various meso pores ( $r = 1\text{-}25 \text{ nm}$ ), micro pores ( $r = 0.4\text{-}1.0 \text{ nm}$ ) and sub micro pores ( $r < 0.4 \text{ nm}$ ) branch off from what we call macro pores ( $r > 25 \text{ nm}$ ) (Figure I). Specific surface area is 500 to  $1500 \text{ m}^2/\text{g}$ . It offers strong adsorption power it mainly comes from vander walls forces.

**Types and features of activated carbon:** There are many types of activated carbon. Therefore it is necessary to select one among them according to objective..

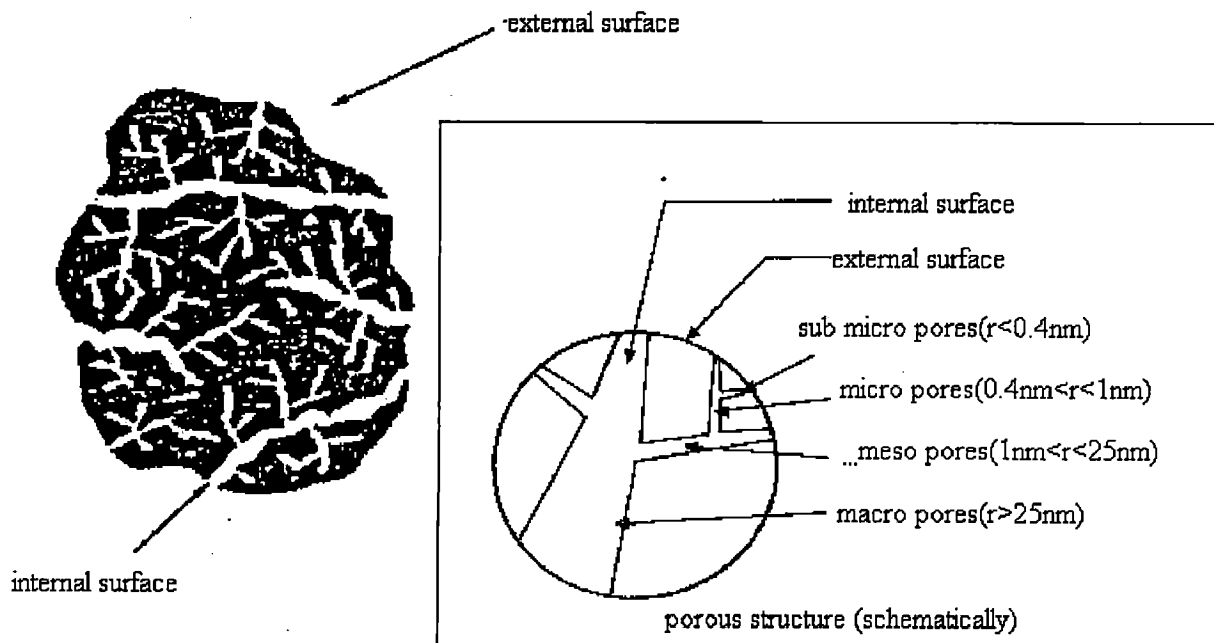


Figure.2.1 Schematic activated carbon model

The main raw materials are coal, wood, coconuts and petroleum pitch. Properties are generally depending upon activation conditions when making them from raw materials.

Activation is done using high temperature steam of about 900<sup>0</sup> C. In case of wooden raw material, it is carbonized after soaking in chemicals such as zinc chloride. Activated carbon is divided into two types, namely powder and granules the powder cannot be easily regenerated and is usually discarded after use. The granular type is generally used in waste water treatment because of continuous use, easy handling and repeated regeneration. It comes from crushing or sintering but crushed carbon is ordinarily used.

### **Factors contributing to activated carbon adsorption:**

Activated carbon has the following tendencies in general.

1. **Solubility:** It is hydrophobic Therefore it readily adsorbs hydrophobic substances. In aliphatic compounds, the longer the alkyl group, the more hydrophobic it is .it does not readily dissolve in water. So adsorption amount of it increases.
2. **Size of the molecule:** In general the larger the molecular weight, the larger is the adsorption amount. However, molecular diffusion velocity in the pores is slow when molecular weight is large. Therefore it may be effective to decrease molecular weight to some extent, by biological decomposition or oxidation by ozone prior to adsorption.
3. **pH:** Removal rate of organic substances can be improved by decreasing the pH of waste water to about 2 to3 .Because ionization rate organic substances in waste water is low at low pH range like this.
4. **Concentration:** In general, as the concentration of organic substances in the waste water increases, adsorption amount increases too. However in case of chemical substances such as surface active agents, adsorption amount is constant regardless of concentration.
5. **Water temperatures:** Unlike gas phase water temperature has less effect on adsorption in ordinary waste water.

## **2.4 Adsorption Equilibria**

The great bulk of experimental data pertaining to the adsorption represents equilibrium measurements. The apparent adsorption of given solute depends on temperature,

the solvent, and the type of adsorbent. The extent of adsorption of a given solute practically always decreases at increased temperature and usually greater the solubility in the solvent. It is usually reversible, so that the same isotherm results whether solute is adsorbed or desorbed.

### **Adsorption isotherm:**

It shows the equilibrium relation between sorbent and sorbate are described by sorption isotherms, the ratio between the amount sorbed and that remaining in the solution at a fixed temperature at equilibrium. It takes equilibrium concentration as the axis of ordinate and the weight of solute adsorbed per unit weight of adsorbent as the axis of abscissa. The equilibrium sorption isotherm is crucial is fundamentally very crucial in design of sorption system. The adsorption isotherms described by different isotherm models

- Langmuir isotherm
- Freundlich isotherm
- Redlich–Peterson isotherm
- Linear sorption isotherm.
- Tooth isotherm
- Radke-prausnitz
- Fritz-Schluder isotherm
- Temkin isotherm
- Brunauer-Emmett-Teller isotherm

Langmuir isotherm: The Langmuir sorption isotherm has been widely applied to many pollutants sorption process. It has produced good agreement with a wide variety of experimental data for the sorption of a solute from a liquid solution.

A basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites in the sorbent. Moreover, when a site is occupied by a solute, no further sorption can take place at that site. It has the form of

$$s_e = \frac{K_L S_m C_e}{1 + K_L C_e} \quad (1)$$

Where  $S_e$  is the amount adsorbed on solid at equilibrium (mg/kg),  $C_e$  is the equilibrium liquid concentration (mg/L),  $S_m$  is the adsorption capacity or adsorption maximum (mg/kg), and  $K_L$  is the adsorption intensity or Langmuir coefficient (L/mg). Eq. (1) can be rearranged to the following linear form:

$$\frac{C_e}{S_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \quad (2)$$

**Freundlich isotherm:** If the concentration of solution at equilibrium,  $C_e$ , was increased to the power of  $1/n$ , the amount of solute sorbed being  $S_e$ , then the  $C_e^{1/n}/S_e$  was a constant at a fixed temperature. This experimental model can be applied to non ideal sorption on heterogeneous surfaces as well as multi-layer sorption and is expressed by the following equation:

$$S_e = K_F C_e^a \quad (3)$$

Assumption: An exponentially decaying sorption site energy distribution.

This equation can be rearranged in the linear form by taking the logarithm of both sides as

$$\log S_e = \log K_F + a \log C_e \quad (4)$$

The Freundlich constant  $a$  is a measure of deviation from adsorption linearity. If  $a$  is equal to unity the adsorption is proved to be linear, which means that adsorption sites are homogeneous or these sites of the adsorbent are not limiting in quantity and are not modified by the adsorption process itself. If  $a$  is less than unity, this implies that increased adsorption modifies the adsorbent, giving rise to an increase in the adsorption capacity, such as forming new adsorption sites on the adsorbent surface. If  $a$  is greater than unity the adsorption bond becomes weak, and the  $q_e$  changes significantly, with small changes in  $C_e$ .

**Redlich–Peterson isotherm:** It has three parameters and incorporates the features of both the Langmuir and Freundlich equation. It has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$S_e = \frac{AC_e}{1 + BC_e^g} \quad (5)$$

Where  $A$ ,  $B$  and  $g$  ( $0 < g < 1$ ) are the isotherm constants. At low concentrations, it approximates to Henry's law and at high concentrations its behavior approaches that of the Freundlich isotherm. It has two limiting case that can be summarized:

$$S_e = \frac{AC_e}{1+BC_e} \quad (6)$$

Where  $g = 1$ , i.e. the Langmuir form results.

$$S_e = \frac{AC_e}{1+B} \quad (7)$$

Where  $g = 0$ , i.e. the Henry's law form results. Although a linear analysis is not possible for a three-parameter isotherm, a trial and error procedure has previously been applied to a pseudo-linear form of Redlich–Peterson isotherm to obtain values for the isotherm constants. Eq. (5) can be converted to a pseudo-linear form by taking logarithms:

$$\ln\left(A\frac{C_e}{S_e} - 1\right) = g \ln(C_e) + \ln(B) \quad (8)$$

This method involves varying the isotherm parameter,  $A$ , to obtain the maximum value of correlation coefficient for the linear regression of  $\ln(C_e)$  against  $\ln(A(C_e/S_e) - 1)$ .

Linear sorption isotherm: The sorption of NOCs to an organic rich substrate can obey a linear sorption isotherm or Henry's equation with the following form:

$$C_s = K_d C_w \quad (9)$$

Where  $C_s$  is the amount of solute sorbed (mg/kg),  $C_w$  the equilibrium aqueous solute concentration (mg/L), and  $K_d$  is the linear sorption coefficient.  $K_d$  is related to  $f_{oc}$ , the fractional organic carbon content of the sorbent, and  $K_{oc}$  the organic carbon-based partition coefficient of the NOC, by the following equation:

$$K_d = K_{oc} f_{oc} \quad (10)$$

For a certain NOC,  $K_{oc}$  is reasonably constant and thus  $K_d$  increases linearly with respect to  $f_{oc}$ . In a partitioning process, the NOC distributes itself between two immiscible phases. The partition coefficient  $K_{oc}$  reflects the ratio of NOC concentrations in the organic phase ( $C_{oc}$ ) and the aqueous phase ( $C_w$ ):

$$K_{oc} = \frac{C_{oc}}{C_w} \quad (11)$$

Since  $f_{oc}$  is dimensionless and  $K_{oc}$  has the same unit as  $K_d$ ,  $C_{oc}$  has the unit of (mass of NOC) / (mass of bound organic carbon).

Tooth isotherm: 
$$S_e = S_e^{\infty} C_e / [a + C_e^{th}]^{1/th} \quad (12)$$

Radke-prausnitz isotherm:  $1/S_e = 1/KC_e + 1/KC_e^{1/p}$  (13)

Fritz-Schluder isotherm:  $S_e = \alpha_1 C_e^{\beta_1} / (1 + \alpha_2 C_e^{\beta_2})$  (14)

Brunauer-Emmett-Teller isotherm:  $\frac{p/p_0}{q(1 - p/p_0)} = \frac{1}{q_m C} + \frac{p(C - 1)}{p_0 q_m C}$  (15)

Temkin isotherm:  $q_e = \frac{RT}{b} \ln(K_T C_e)$  (16)

## 2.5 Adsorption columns

There are mainly three kinds of equipments, namely fixed bed adsorption column, moving bed adsorption column and fluidized column. It is necessary to remove suspended solids as pretreatment regardless of type of tower.

**Fixed bed adsorption column:** Adsorption in fixed bed is unsteady state process. In its analysis of basic importance is the space and the time distribution of the adsorbate.

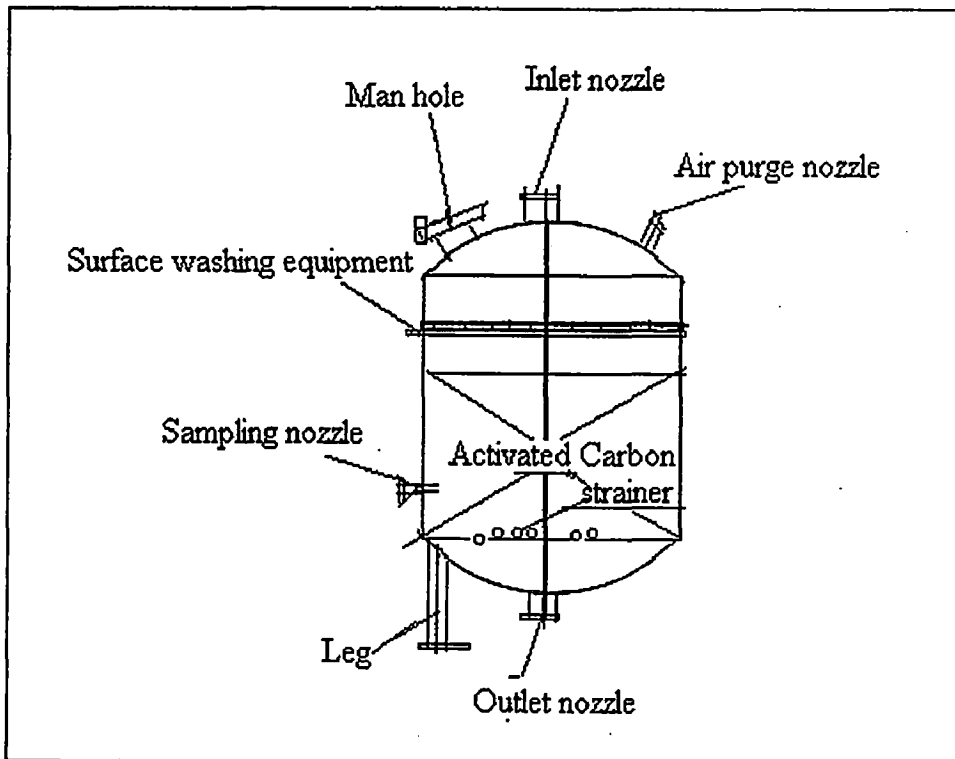


Fig.2.2 Fixed bed adsorption column.



A graphical representation of the bed operation is a break through curve i.e the dependence of adsorbate concentration in the effluent from the column on process duration. Break through time determines the period of protective action of the bed [12].

Conventional fixed bed processes involve a saturation, adsorption or loading step, followed by desorption, elution or regeneration steps. It comprise two drawbacks, one is the low efficiency of the fixed bed operation, since only a fraction of the adsorbent is used and the other is the use of a chemical regenerant to get an operative bed, with the associate waste disposal and a new pollution problem [2].

**Fluidized bed adsorption column:**

A multi stage fluidized bed adsorption tower is introduced. There are multiple stages partitioned by perforated plates in a tower fig.2.3. There are many nozzles on perforated

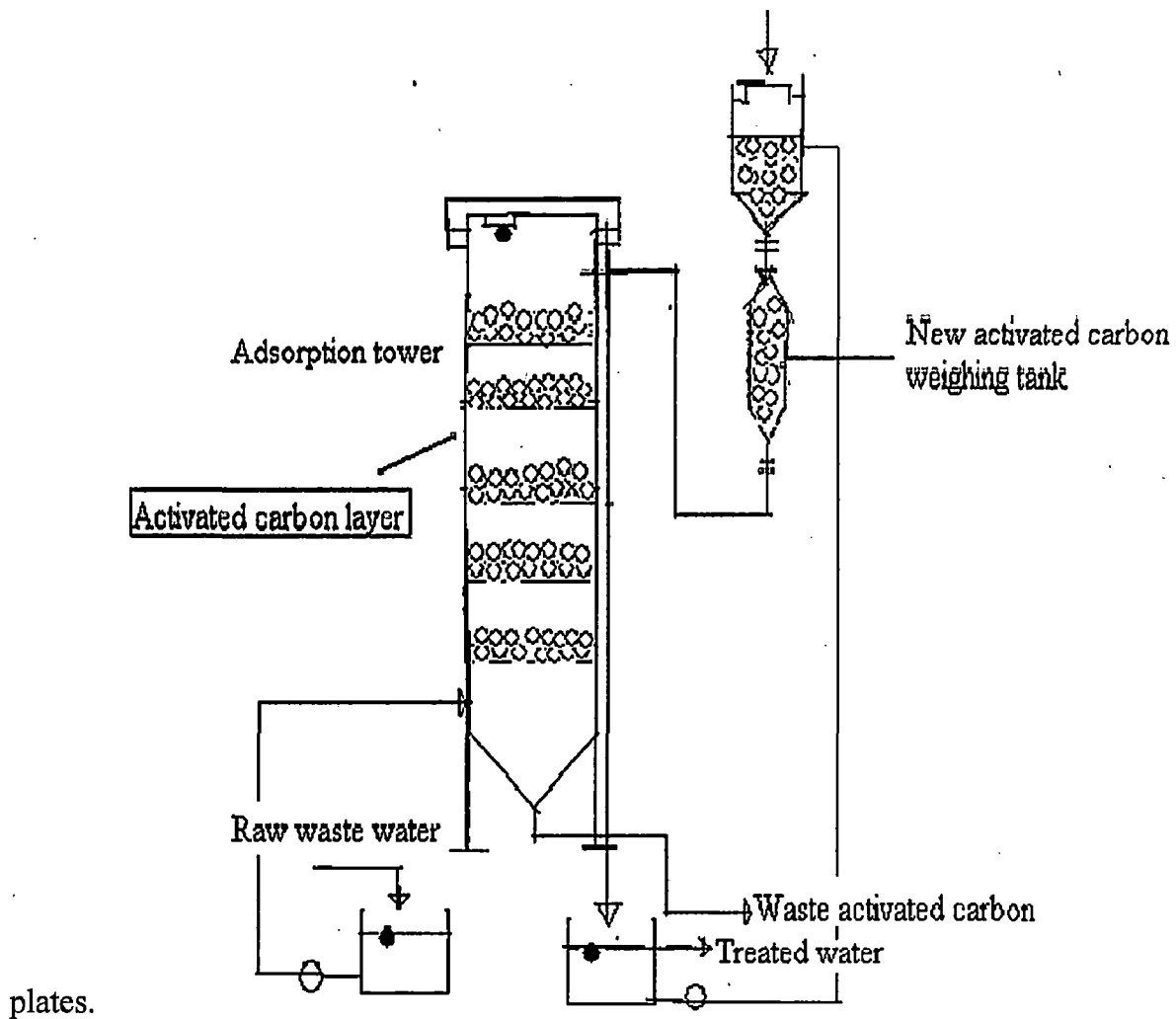


Fig.2.3 Fluidized bed adsorption column.

### **2.5.1 Fixed Bed Adsorption Column:**

In most case adsorption is carried out in fixed bed mode. This is unsteady state process. A graphical representation of the bed operation is a break through curve is dependence of adsorbate concentration in the effluent from the column on process duration. Break through time determines the period of protective action of the bed [12].

Conventional fixed bed processes involve a saturation, adsorption or loading step, followed by desorption, elution or regeneration steps. It comprise two drawbacks, one is the low efficiency of the fixed bed operation, since only a fraction of the adsorbent is used and the other is the use of a chemical regenerant to get an operative bed, with the associate waste disposal and a new pollution problem [2].

#### **2.5.1.1 Adsorption Uptake rate:**

Important and integral to adsorption calculations and model formulations is the prediction or estimation of adsorbate uptake rates by adsorbent pellets. For the transport of adsorbates from the bulk of the fluid phase to the interior of a pellet before adsorption takes place, the following mass-transfer process may be present:

- a) Inter pellet mass transfer: It refers to the diffusion and mixing of adsorbates in fluid occupying the spaces between the pellets. It is significant in fixed bed because adsorption treated solution is contacted with adsorbent pellets in relative motion.
- b) Inter phase mass transfer: It refers to the transfer of adsorbate across the fluid pellet interface.
- c) Intra pellet mass transfer: It refers to the diffusion of adsorbates with in the pellet. It often takes place simultaneously with adsorption.

#### **Inter pellet mass transfer:**

In fixed bed adsorption, diffusion and mixing of adsorbates in fluid occurs as a result of adsorbate concentration gradients and non uniformity of fluid flow. This effect gives rise to dispersion of adsorbates, which takes place along both direction of main fluid flow (axial dispersion) and the direction transverse to the main flow direction(radial dispersion). Although the effect of axial dispersion is undesirable, since it reduces the separation efficiency, radial dispersion is usually considered helpful. Radial dispersion tends to equalize the differences in concentrations of small fluid elements at the same axial location;

consequently, the undesired axial dispersion effect may be reduced. For liquids the axial Peclet number approaches the theoretical value of 2.0 as the Reynolds number approaches 1000. For lower Reynolds number, Peclet number is of the order 0.3 to 1.0. i.e the dispersion effect is more significant.

### **Inter phase mass transfer:**

It is an important step in the overall take up process. For single species adsorption with spherical particles, the inter phase mass transfer rate may be expressed as

$$\frac{\partial \bar{q}}{\partial t} = k_f a (C_b - C_s) = \frac{3k_f}{a_p \rho_p} (C_b - C_s) \quad (17)$$

The magnitude of  $k_f$  mass transfer coefficient depends on the flow conditions around the pellet and many empirical correlations are available in literature.

### **Intra pellet mass transfer:**

The adsorbent materials are micro porous and their void is occupied by the fluid to be treated by adsorption, adsorbate may diffuse through pore fluid because of the presence of radial concentration gradient. This implies the existence of a similar concentration gradient in the adsorbed phase which, in turn causes the diffusion of the adsorbed molecules. Both types of diffusion may be operative simultaneously or individually. These two different mechanisms are pore and surface diffusion.

Pore diffusion: It is due to the diffusion of adsorbate molecules through the pore fluid. For the simple case of single species adsorption and assuming that Fick's law applies, the macroscopic conservation equation is given as

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ D_p r^2 \frac{\partial c}{\partial r} \right] \quad 0 \leq r \leq a_p \quad (18)$$

Where  $c$  and  $q$  are the adsorbate concentrations in the pore fluid and of the adsorbed phase corresponding to any given point within the pellet. Both pore diffusion and molecular diffusion involves the migration of adsorbate molecules in fluid phases. The semi empirical relation between pore diffusivity ( $D_p$ ) and molecular diffusivity ( $D_m$ ) may be expressed as

$$D_{pe} = \frac{\varepsilon_p D_m}{\tau} \quad (19)$$

where  $\tau$  is tortuosity factor of adsorbent which accounts for the fact that diffusion takes place zigzag wise rather than along the radial direction [35].

In the limiting case in which the pores are small (to the extent that pore radius is less than the mean free path of the fluid molecules), collisions of fluid molecules with the pore surface dominate resulting in an entirely different type of diffusion, known as Knudsen diffusion. In the pore both molecular and Knudsen diffusivity ( $D_K$ ) may be operative simultaneously  $D_p$  should be replaced by  $\overline{D_p}$  which is defined as

$$\frac{1}{\overline{D_p}} = \frac{1}{D_p} + \frac{1}{D_K} \quad (20)$$

Surface diffusion: It is the case in which the intra pellet mass transfer is affected through the diffusion of adsorbed molecules, for single species adsorption with spherical pellets and assuming that Fick's law applies, and is described by the following equation:

$$\left( \frac{\varepsilon_p}{\rho_p} \right) \frac{\partial c}{\partial t} + \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ D_s r^2 \frac{\partial q}{\partial r} \right] \quad (21)$$

Here the term  $\left( \frac{\varepsilon_p}{\rho_p} \right) \left( \frac{\partial c}{\partial t} \right)$  is much less than  $\partial q / \partial t$  so it can be easily solved with appropriate initial and boundary conditions. The parameter  $D_s$  vary with both temperature and extent of surface coverage ( $q$ ). For the liquid systems it is found to be in the range of  $10^{-9}$  to  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ .

Combined pore and surface diffusion: For more general description of intra pellet mass transfer, it is appropriate to assume that both pore and surface diffusion are operative. The corresponding macroscopic conservation equation for a spherical pellet becomes

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ D_p r^2 \frac{\partial c}{\partial r} \right] + \frac{\rho_p}{r^2} \frac{\partial}{\partial r} \left[ D_s r^2 \frac{\partial q}{\partial r} \right] \quad (22)$$

For physical adsorption, since the actual adsorption step occurs much faster than does mass transfer step, the pore solution concentration and the adsorption concentration may be assumed equilibrium i.e  $q = f(c)$  is the isotherm expression. And  $dq = f'(c) dc$ . Substituting and rearranging one has

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{\rho_p}{r^2} \frac{\partial}{\partial r} \left[ D_e r^2 \frac{\partial q}{\partial r} \right] \quad (23)$$

where effective intra particle diffusivity  $D_e$  is defined as

$$D_e = \frac{D_p}{f'(c)} \frac{1}{\rho_p} + D_s \quad (24)$$

In the limiting case either pore diffusion or surface diffusion dominates.

#### **Intra pellet mass transfer:**

It refers to the diffusion of adsorbates within the pellet. It often takes place simultaneously with adsorption.

In physical adsorption of adsorbate from the solution phase onto adsorption site occurs due to the difference between the adsorbates chemical potential in the solution and adsorbed phases. In most cases, it occurs much faster than various transport steps and can therefore be ignored when formulating the overall rate expression [33].

#### **2.5.1.2 Intra pellet diffusion-Linear driving force model:**

Regardless of the diffusion mechanism is used to describe the transport of adsorbate, a quantitative representation of adsorbate uptake rate requires the solution of the appropriate intra particle diffusion equation. To simplify calculations, the so-called lumped parameter model has been developed. In essence, it is postulated that the uptake rate of adsorbate by pellet is linearly proportional to a driving force, defined as the difference between the surface concentration and the average adsorbed-phase concentration can be written as

$$\frac{d\bar{q}}{dt} = k_p (q_s - \bar{q}) \quad (25)$$

where  $k_p$  is particle phase transfer coefficient,  $\bar{q}$  and  $q_s$  are the average adsorbed phase concentration and the adsorbed phase concentration at the exterior surface of the pellet.

$$k_p = \frac{15D_e}{a_p^2} \quad (26)$$

$D_e$  is effective particle diffusivity when both surface and pore diffusivity's are present. In the limiting cases that either pore or surface diffusion is the controlling mechanism we will have

$$k_p = \frac{15D_s}{a_p^2} \quad \text{for surface diffusion} \quad (27)$$

$$k_p = \frac{15D_p}{a_p^2 f'(c) \rho_p} \quad \text{for pore diffusion} \quad (28)$$

### 2.5.1.3 Break through curve :

Adsorption is unsteady state process. A graphical representation of the bed operation is a break through curve is dependence of adsorbate concentration in the effluent from the column on process duration. Break through time determines the period of protective action of the bed [12]. To remove the phenol, the waste water flows through adsorption bed. Fig.2.5 shows the idealized breakthrough curve as a function of the liquid volume to be treated. After short working time the adsorbent bed is subdivided into three zones:

- On the inlet side of the adsorber the equilibrium load corresponding to the inlet concentration  $c_0$  is achieved.
- Next follows the adsorbate reduction in the so called adsorption or mass transfer zone (MTZ).
- The outlet zone of the adsorber filling is still unloaded at this time.

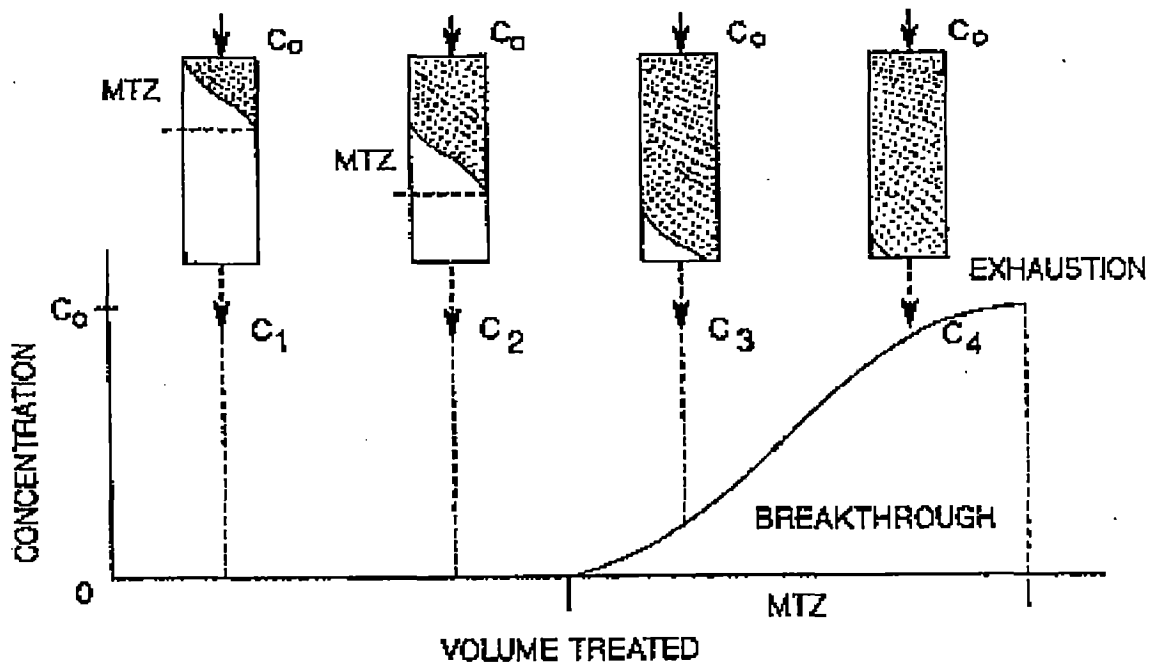


Fig.2.5 Idealized breakthrough curve of a fixed bed adsorber.

With increasing adsorption time the adsorption zone moves through the bed. If the top of the MTZ reaches the adsorber end breakthrough occurs. The adsorption step will be stopped if a pre-determined solvent concentration in the exhaust liquid is exceeded. Then the bed has to be regenerated. If the passage of the fluid is continued on still further, the exit concentration continues to rise until it becomes the same as the inlet concentration.

The shape and time of appearance of break through curve greatly influence the method of operating a fixed bed adsorber. The curves generally have an S-shape, but they may be steep or relatively flat and in some cases considerably distorted. If the adsorption process were infinitely rapid, the break through curve would be a straight vertical line in the lower part of figure. The actual rate and mechanism of adsorption process, the nature of adsorption equilibrium, the fluid velocity, the concentration of solute in the feed, and the length of the adsorber bed (particularly if the solute concentration in the feed is high) all contribute to the shape of the curve produced for any system. The break point is very sharply defined in some cases and in other cases poorly defined.

Generally the break time decreases with decreased bed height, increased particle size of adsorbent, increased rate of flow of fluid through the bed, and increased initial solute content of the feed. There is a critical minimum bed height below which the solute concentration in the effluent rise rapidly from the first appearance of effluent. In planning new processes it is best to determine the break point and break through curve for a particular system experimentally under conditions resembling as much as possible those expected in the process.

## **2.6 Description of the Problem**

Aromatic compounds such as phenols occur in wastewater of a number of industries such as high temperature coal conversion, petroleum refining, resin, pharmaceutical, plastic, and pesticidal chemical industries. Such aromatic hydroxy compounds can be toxic when present in elevated levels and are known or suspected to be carcinogens. However, phenol is toxic to aquatic life and humans even at low concentrations ( $5\text{--}25\text{ mg L}^{-1}$ ). Phenol is listed as a priority pollutant by the United States Environmental Protection Agency (EPA) and results in oxygen demand in receiving waters and objectionable tastes to drinking water. Chronic toxic effects due to these reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances. Thus, the removal of such chemicals from industrial effluents is of great importance. The MOEF has set a maximum concentration level of  $1.0\text{mg/l}$  of phenol in the industrial effluents for safe discharge into surface waters, WHO recommends the permissible phenolic concentration of  $0.001\text{mg/l}$  in potable waters [29].

Current methods for removing phenolics from wastewater include microbial degradation, adsorption on activated carbon, chemical oxidation (using agents such as ozone, hydrogen peroxide or chlorine dioxide), incineration methods, solvent extraction and irradiation. The choice of system depends on economic and other factors [24]. Biodegradation of phenol occurs very slowly or does not occur at all lead to setting up of rigid limits on the acceptable level of phenol in the environment. Adsorptive processes are widely used as secondary or polishing treatment in purification of such polluted streams and diluted waste waters.

Phenol, a derivative of benzene, is an important raw material in petrochemicals, oil refineries, leather, paint, steel industries, pharmaceuticals, plastic and pesticide industry [29]. Phenol is usually used to synthesize chemical products in basic solution .because of its low solubility in acidic and neutral solution. Therefore, the effluents from these chemical plants containing phenol are basic.

Properties of phenol: It is highly soluble in water ( $98\text{ g/l}$ ).Melting point:  $181^{\circ}\text{C}$ , It is weak acid dissociating slightly in aqueous solution (known as carboic acid) [29].



## CHAPTER 3

### LITERATURE REVIEW.

The review of literature on assigned thesis topic is the pinnacle of every thesis work. As our thesis topic is related to modeling of physical adsorption in waste water systems enormous literature is available in various aspects. In this chapter we will discuss briefly different literature available on adsorption system.

This chapter is divided into two sections: The first section includes research papers related to experimental work in adsorption systems. The second section deals with mathematical modeling of adsorption systems.

#### 3.1 Experimental Studies on Adsorption

Table.5 Experimental studies on adsorption literature review

Adsorbent	Kinetics, isotherms	Name of pollutant	Type of system	Results
Granular activated carbon	Diffusion controlled with diffusion coefficient of $10^{-13} \text{ m}^2/\text{s}$ . Resorcinol: Freundlich isotherm Catechol: Redlich-peterson, Radke-Prausnitz, Toth, Fritz-Schlunder	Resorcinol and catechol	Batch	Catechol is adsorbed to great extent than Resorcinol

Author	Adsorbent	Kinetics, isotherm	Name of pollutant	Type of system	Results
C. Brasquet et.al (1999)[2]	Activated carbon cloths	Langmuir , Freundlich isotherms	Phenolic compounds	Batch	good kinetic and hydrodynamic performance of fibers enables us to imagine and propose new and smaller reactors.
S. Rengaraj et.al (2002)	Activated carbon from rubber seed coat	first order reversible kinetics, Linear Freundlich isotherms	Phenol	Batch and column	RSCC is 2.25 times more efficient compared to CAC based on column adsorption study.
Wojciech Kujawski et al(2003)	Amberlite resins XAD-4, XAD-7	Freundlich isotherms	phenol	Batch and column	Best sorption properties were found in the case of the Amberlite XAD-4.
Murat Akarsu et.al(2002)	Sol-Gel derived Zirconium oxide	Freundlich isotherms	Phenol and chlorophenol	Batch	the adsorption of phenol is more favorable than p-chlorophenol adsorption.
Anna Wolborska et.al (1996)	Granulated activated carbon AG5	Langmuir , Redlich-Peterson, Freundlich isotherms	Phenol, p-nitro phenol, benzoic acid	Fixed bed adsorption column	Break through time is estimated.
N. Abu.Zied et.al(1994)	Granular activated carbon	Freundlich isotherms	Phenol, cresol, nitrophenol	Batch	No significant effect on adsorptive capacity of GAC for aliphatics due to dissolved oxygen existence in the test environment.
M. Ghiaci et.al(2004)	Organo Zeolites	Langmuir , Redlich-Peterson, Freundlich, linear equation isotherms	Non ionic organic contaminants	Batch	MCM-41 much greater than natural clinoptilolite and ZMS-5 Zeolites

### **3.2 Modeling Studies**

#### **C.A.V Costa , A.E.Rodrigues, Georges Grevillot, Daniel Tondeur (1982)**

In this a new process for purification of phenolic waste water by parametric pumping is presented. An equilibrium (linear) model for nonmixed dead volumes thermal dierst mode parametric pumping is developed and the influence of bottom and top dead volume magnitudes on tranisent seperation is analyzed. It tells us that for each bottom dead volume magnitude there is a minimum top dead volume that should be maintained in order to get an improved transient seperation, relatively to the mixed case where inexistence of the top dead volume gives a better seperation. Analytical solutions for batch, continous and semicontinuous operations are presented. Experimental studies on the system phenol/water-Duolite ES861 include equilibrium isotherms at 20<sup>0</sup>c and 60<sup>0</sup>c and parapump runs for the cases mentioned above.

#### **M.F. Can and M. Can (2005)**

In this a model is proposed to predict the distribution of the concentration of the target solute along a fixed bed column reactor. It depends on two laws. The first law is the conservation of the amount of adsorbent in a column compartment. The second law is on the adsorption rate and is obtained experimentally through bottle tests. As an example, zeolite (clinoptilolite) is taken as adsorber and a quaternary amine, hexadecyl trimethyl ammonium bromide (HTAB) is used as the adsorbent. To adapt the model for other adsorber-adsorbent couples one needs only a set of bottle tests for the new couple. The breakthrough curves for the modification process obtained through our model are seen to be confirmed by the fixed bed reactor experiments.

Prediction of distribution of concentration along the length of column is of considerable importance for design of chemical reactors. Fluid mixing in a continuous flow system, fluid dispersion, volume efficiency together with the adsorbent and adsorbate characteristics dictates the optimum modification parameters. The prediction of break through point is very complex, because it consists of hydrodynamic parameters, nature of adsorption equilibrium, kinetics and mechanisms of the system.

**Marta Otero, Miriam Zabkova, Al'irio E. Rodrigues(2005)**

Phenol is a target pollutant to be removed from wastewaters from different industries. Adsorption of phenol from aqueous solutions onto two polymeric resins (Sephabeads SP206 and SP207) and onto activated carbon (Filtrisorb F400) was studied. Batch equilibrium experiments were carried out at three different temperatures (293, 310 and 333 K) for each of the adsorbents. In order to ascertain the fixed bed performance of the adsorbents considered, adsorption runs were carried out at laboratory scale at 293, 310 and 333 K. Equilibrium and fixed bed experimental results were compared to the simulated ones. Equilibrium data were well fitted by the Langmuir isotherm and the breakthrough curves simulation was based on this equilibrium isotherm together with a mass transfer description based on the Linear Driving Force (LDF) model. After the adsorbents screening and mass transfer parameters determination, Sephabeads SP206 was used to purify a phenolic solution by parametric pumping at pilot scale using hot and cold temperatures of 293 and 333 K, respectively. The adsorbent Sephabeads SP206 is the one which adsorption performance is affected by temperature in a higher degree. A package for the simulation of this cyclic operation was used to predict model results, which were satisfactorily compared to those experimentally obtained.

**B.C. Pan , F.W. Meng, X.Q. Chen, B.J. Pan, X.T. Li, W.M. Zhang, X. Zhang ,J.L. Chen, Q.X. Zhang, Y. Sun (2005)**

Removal of many organic pollutants including phenolic compounds from industrial wastewater can always be achieved by fixed-bed adsorption onto the polymeric resin adsorbent, and the relevant breakthrough curves would provide much valuable information to help to design a fixed-bed adsorption process in field application. In the present study, The adsorption rate can be described by the linear driving force model in terms of the overall liquid-phase mass-transfer coefficient , a model developed based on the constant-pattern wave approach theory and the Freundlich model was adopted to describe the breakthrough curves of phenol and *p*-nitrophenol adsorption onto a macro reticular resin adsorbent NDA-100 from aqueous solution.

High hydrophobicity (*p*-nitro phenol) was found favorable to the adsorption of organic compounds onto non-polar and moderate polar polymeric adsorbents from aqueous

## DEVELOPMENT OF MATHEMATICAL MODEL FOR FIXED BED ADSORPTION COLUMN

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### 4.0 Introduction

In this chapter, mathematical models have been developed for fixed bed adsorption columns. The macroscopic conservation equation is obtained by applying the control volume concept. A control volume is one which encloses certain material entities to which mass balance is applied.

### 4.1 Mathematical model for fixed bed adsorption column

The principle of mass conservation of adsorbate is simply

$$\left\{ \begin{array}{l} \text{Rate of accumulation} \\ \text{of adsorbate} \\ \text{mass within control volume} \end{array} \right\} = \left\{ \begin{array}{l} \text{Rate of net adsorbate} \\ \text{input into the control} \\ \text{volume associated} \\ \text{with bulk flow} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of net adsorbate} \\ \text{input into the control} \\ \text{volume associated} \\ \text{with bulk flow} \end{array} \right\} \quad (29)$$

#### 4.1.1 Assumptions

The assumptions employed in derivation of mathematical model are:

- The system operates under isothermal conditions
- The equilibrium of adsorption is described by Langmuir isotherm, a nonlinear isotherm.
- Intra particle mass transport is due to Fickian's diffusion, and it is characterized by the effective pore diffusion coefficient,  $D_{pe}$ .
- Mass transfer across the boundary layer surrounding the solid particle is characterized by the external mass transfer coefficient,  $k_f$ .

solutions. Column experiments were performed at different conditions to verify the model and the results proved that the model would describe the breakthrough curves well. Effect of the operation parameters on breakthrough curves was also discussed to get helpful information in choosing the adsorption process.  $t_{1/2}$  decreases and  $K_{La}$  increase with increasing feed flow rate, which is consistent with conclusion that  $K_{La}$  varied linearly with the feed flow rate.

The  $t_{1/2}$  values decrease with increasing  $C_F$ , on the other hand,  $K_{La}$  increases slightly with increasing  $C_F$ . This means the breakthrough curve is steeper at higher  $C_F$ .  $t_{1/2}$  value is roughly proportional to the bed height at a given  $U_0$ . On the otherhand; increasing bed height has little effect on the  $K_{La}$ . The values of  $t_{1/2}$  and  $K_{La}$  decrease with increasing temperature because the adsorption of phenols onto resin NDA-100 can be considered as physical adsorption, Different aspect ratios at given amount of resin adsorbent have little effect on the breakthrough curves ,a too large value of aspect ratio is not essential when designing adsorption process in field application.

### **3.3 OBJECTIVE OF THESIS**

On basis of reviewed literature as mentioned above, the following objectives have been planned.

- a) To develop the mathematical model for a fixed bed adsorption system for the removal of phenol in waste water.
- b) To solve the mathematical model equations by using suitable numerical technique or by using equation solver like MATLAB etc.
- c) To validate the proposed model with available industrial or experimental data.
- d) To study the effect of various operating and design parameters on its performance.

- The velocity of the fluid is regarded as constant along the length of column because the adsorbate concentration in the influent stream is small and the removal of adsorbate from the fluid stream by adsorption does not significantly affect the velocity.
- The macro porous adsorbent particles are spherical and homogenous in size and density.
- The liquid density is assumed to be constant.

#### 4.1.2 Derivation of Mathematical Model

In fixed bed adsorption columns we may take the control volume to be a small element of fixed bed bounded by an upper and lower surface with a distance of  $dz$  between them. If the flow is assumed to be one-dimensional (along the direction of the bed's axis), based on a unit cross sectional area, then the various terms in mass balance equation becomes

Rate of accumulation of adsorbate mass :  $(\Delta z)(\epsilon)(\Delta C / \Delta t)$

Rate of net adsorbate input associated with mass flow:  $(u_0 C)_z - (u_0 C)_{z+\Delta z}$

Rate of adsorbate efflux:

(a) Due to axial dispersion :  $-\left(D_{ax}\epsilon \frac{\partial C}{\partial z}\right)_{z+\Delta z} + \left(D_{ax}\epsilon \frac{\partial C}{\partial z}\right)_z$

(b) Due to uptake by pellet:  $(\Delta z)(1 - \epsilon)(\Delta q / \Delta t)\rho_f$

For the limiting case  $\Delta z \rightarrow 0$ , the macroscopic conservation equation becomes

$$D_{ax}\epsilon \frac{\partial^2 C(z,t)}{\partial z^2} - \frac{\partial u_0 C(z,t)}{\partial z} = \frac{\partial \epsilon C(z,t)}{\partial t} + (1 - \epsilon)\rho_f \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad (30)$$

The mass balance in a bed volume element is:



$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_f \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad (31)$$

where  $u_i$  is interstitial velocity given by  $u_i = u_0/\varepsilon$ ,  $D_{ax}$  is the axial dispersion,  $\varepsilon$  the bed porosity,  $z$  the axial position,  $C$  the concentration of phenol in the bulk fluid phase and  $\langle q \rangle$  is the average adsorbed phase concentration in the adsorbent particles.

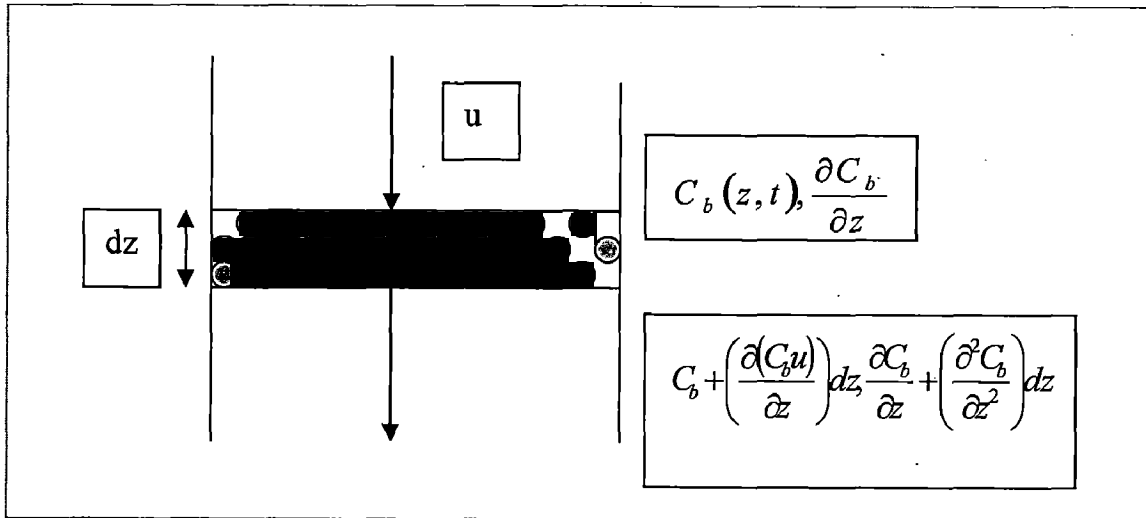


Fig. 4.1 Mass balance in element of fixed bed.

### 4.1.3 Constitutive Relationships and Parameters Employed

#### 4.1.3.1 Adsorption equilibrium isotherm

The amount of phenol adsorbed onto adsorbent ( $q_e$ ) is calculated by mass relationship

$$q_e = (C_0 - C_e)V/w \quad (32)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium liquid phase concentrations respectively,  $V$  is the volume of solution (L), and  $w$  is the dry weight (g) of the adsorbent. The adsorption equilibrium isotherms for phenol  $q^*$  ( $\text{mgg}^{-1}$ ) versus the adsorbate liquid concentration at equilibrium were fitted with Langmuir model, which assumes that adsorption occurs onto specific sites of a uniform energetic surface, without interactions between adsorbed molecules and adsorption is confined to monolayer coverage.

The adsorption equilibrium is described by the Langmuir isotherm:

$$q^*(z,t) = \frac{QK_L C(z,t)}{1 + K_L C(z,t)} \quad (33)$$

where Q is the maximum adsorptive capacity and  $K_L$  is a parameter which relates to the adsorption energy given by

$$K_L = K_L^\infty \exp\left(-\frac{\Delta H_L}{RT}\right) \quad (34)$$

$\Delta H_L$  is the adsorption enthalpy in Langmuir constant is generally a net value that includes the solvent desorption and the solute adsorption.

#### 4.1.3.2 Adsorption kinetics

To simplify calculations, the so-called lumped parameter model has been used. In essence, it is postulated that the uptake rate of adsorbate by pellet is linearly proportional to a driving force, defined as the difference between the surface concentration and the average adsorbed-phase concentration. can be written as The Linear Driving Force approximation is used to describe intra particle mass transfer:

$$\frac{\partial \langle q(z,t) \rangle}{\partial t} = k_s [q^*(z,t) - \langle q(z,t) \rangle] \quad (35)$$

where  $k_s$  is the Linear Driving Force kinetic constant and  $q^*(z, t)$  is the adsorbed phase concentration in equilibrium with the bulk concentration  $C(z, t)$ .

The effective mass transfer coefficient ( $k_s$ ) was estimated from the following correlation:

$$\frac{1}{k_s} = \frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} + \frac{r_p^2}{15D_{pe}} \rho_p f_h \frac{dq^*}{dC} \quad (36)$$

$$\frac{1}{k_s} = \frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} + \frac{1}{k_{LDF}} \quad (37)$$

which considers macro pore and film resistances to the mass transfer and where  $k_s$  is the overall mass transfer coefficient.. The  $k_{LDF}$  used in the models were estimated by the

following expression, based on the equivalence of LDF models for homogeneous and porous particles:

$$k_{LDF} = \frac{\Omega D_{pe}}{\rho f_h r_p^2 \frac{dq^*}{dc}} \quad (38)$$

where  $D_{pe}$  ( $\text{m}^2 \text{min}^{-1}$ ) is the effective pore diffusivity,  $r_p$  (m) the radius of the particle of the adsorbent,  $\Omega$  the LDF factor, which is equal to 15 for spherical particles,  $\rho$  the density of the adsorbent,  $f_h$  humidity factor and  $\left(\frac{dq^*}{dc}\right)$  is the slope of the equilibrium data.

#### 4.1.3.3 Evaluation of axial dispersion coefficient

The axial dispersion was obtained from the following expression:

$$\frac{u_0 d_p}{D_{ax}} = (0.2 + 0.011 \text{Re}^{0.48}) \quad (39)$$

With 
$$\text{Re} = \frac{u_i \rho_s \varepsilon d_p}{\eta} \quad (40)$$

The Reynolds, Peclet number and the axial dispersion  $D_{ax}$  are calculated.

#### 4.1.3.4 Evaluation of effective pore diffusion coefficient and film mass transfer coefficient

The LDF approximation is valid for cyclic processes with long cycle times as is the case of parametric pumping; in fact the half-cycle time is higher than  $1.5/k_{LDF}$ .

The  $D_{pe}$  ( $\text{m}^2 \text{min}^{-1}$ ) was calculated as: 
$$D_{pe} = \frac{\varepsilon_p D_m}{\tau} \quad (19)$$

Where  $D_m$  ( $\text{m}^2 \text{min}^{-1}$ ) is the molecular diffusivity of phenol in water,  $\tau$  the tortuosity of the adsorbent and  $\varepsilon_p$  is its porosity.

The molecular diffusivity of phenol in water  $D_m$  was estimated, after the corresponding unit transformations, according to the Wilke–Chang method:

$$D_m = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2}}{\eta_B V_A^{0.6}} \quad (41)$$

where  $V_A$  is the molar volume of the solute, the value of  $V_A = 108 \text{ cm}^3 \text{ g mol}^{-1}$  for phenol was estimated by the Le Bas additive method. Wilke and Chang recommended that  $\phi$  be

#### 4.1.4 Summary of Model equations to be solved

The following equations have been developed for the fixed bed adsorption column and are to be solved simultaneously.

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_f \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad (31)$$

$$\frac{\partial \langle q(z,t) \rangle}{\partial t} = k_s [q^*(z,t) - \langle q(z,t) \rangle] \quad (35)$$

#### 4.1.5 Initial and Boundary Conditions

The initial and boundary conditions are:

$$C(z, 0) = 0 \quad (43)$$

$$q(z, 0) = 0 \quad (44)$$

$$z=0, \quad t \geq 0 \quad D_{ax} \left. \frac{\partial C(z,t)}{\partial z} \right|_{z=0} = u_i (C(0,t) - C_0) \quad (45)$$

$$z=L, \quad t \geq 0 \quad \left. \frac{\partial C(z,t)}{\partial z} \right|_{z=L} = 0 \quad (46)$$

The independent variables  $z$  and  $t$  are the axial distances (measured along the direction of fluid flow) and time.  $t$  is measured from the instant fluid enters the bed. The boundary conditions are the so-called Danckwert's conditions.

chosen 2.6 if the solvent is water and the viscosity of water  $\eta_B$  at the corresponding temperature was used.

The estimation of film mass transfer coefficient ( $k_f$ ) for the adsorption of phenol from liquid phase is based on the correlation developed by Costa and Rodrigues:

$$j_D = 7.32 \text{Re}^{-0.569} \quad (42)$$

where Chilton-Colburn factor  $j_D = \frac{Sh}{\text{Re}Sc^{1/3}}$

$$\text{and } \text{Re}' = \text{Re}/(1-\epsilon)$$

#### 4.1.3.5 Parameters

**Physical properties of adsorbent Amberlite resin as follows:**

- Physical form: It is an aromatic porous resin with hydrophobic substituents in white translucent form.
- Humidity factor ( $f_h$ ) 0.34 (gram dry adsorbent/gram adsorbent)
- Density of adsorbent ( $\rho$ ): 1020 kg/m<sup>3</sup>
- Particles size ( $d_p$ ):  $5.6 \times 10^{-4}$  m
- Porosity ( $\epsilon_p$ ) 0.55
- tortuosity ( $\tau$ ) 2

**Fixed bed adsorption column:**

- Length (L): 0.3m
- Diameter (d): 0.01m
- Porosity ( $\epsilon$ ): 0.4

**Adsorption equilibrium isotherm fittings to Langmuir model:**

Parameters:

- Maximum adsorptive capacity (Q): 81.68 mg g<sup>-1</sup>.
- Adsorption enthalpy ( $\Delta H_L$ ) =  $-16.65 \times 10^3$  J mol<sup>-1</sup>
- $K_L^\infty = 7.02 \times 10^{-6}$  (m<sup>3</sup>g<sup>-1</sup>).

### Adsorption kinetic constants:

Table 6 Linear driving force constants

Temperature(K)	$D_m (\times 10^{-10} \text{m}^2 \text{s}^{-1})$	$D_{pe} (\times 10^{-10} \text{m}^2 \text{s}^{-1})$	$k_{LDF} (\times 10^{-4} \text{s}^{-1})$
293	8.9	2.45	6.83
333	2.2	6.05	23.67

Table 7 External film mass transfer coefficient and axial dispersion coefficients

T(K)	Flowrate (mL min <sup>-1</sup> )	Sc	Sh	Re	$j_D$	$K_f (\times 10^{-5} \text{ms}^{-1})$	$D_{ax} (\times 10^{-5} \text{m}^2 \text{s}^{-1})$
293	5.5	1149.2	7.0	0.633	7.1	7.52	1.188
293	10	1149.2	8.8	1.17	5.0	9.72	0.562
333	5.5	215.7	6.2	1.35	4.6	14.80	0.308
333	10	215.7	7.7	2.57	3.2	19.15	0.548

Table 8 Overall mass transfer coefficient

T(K)	Flowrate (mL min <sup>-1</sup> )	$1/k_{LDF} (\times 10^2 \text{s})$	$\frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} (\text{s})$	$1/k_s (\text{s})$
293	5.5	14.51	84.4	1536.00
293	10	14.51	65.3	1516.9
333	5.5	4.22	30.84	453.0
333	10	4.22	23.82	446.2

#### **4.1.6 Simulation Technique:**

Since nonlinear adsorption equilibrium is considered, the preceding set of partial differential equations are solved along with initial and boundary conditions by a computer program in MATLAB (v.7.3) (Math Works Inc.) was developed.

The main inputs to the computer program are:

1. Axial dispersion coefficient.
2. Interstitial velocity.
3. Overall mass transfer coefficient.
4. Adsorption equilibrium Langmuir constants.
5. Initial concentration.

The main outputs of computer program are:

1. Adsorption equilibrium data fittings to Langmuir isotherm model.
2. Concentration profile with time which is the break through curve for adsorption column.

## RESULTS AND DISCUSSION

The model used as describe above, determines the outlet adsorbate concentration at the different times based on operating conditions.

### 5.1 Adsorption equilibrium isotherm fittings to Langmuir model

Fig shows that experimental adsorption equilibrium data for the adsorption of phenol onto resin is well fitted to Langmuir isotherm model and the characteristic parameters are given. The influence of temperature on the performance of adsorbent is reflected by these parameters. The value of adsorption enthalpy ( $\Delta H$ ) indicates that the adsorption of phenol onto Amberlite XAD16 is an exothermic process; it is related to the structural characteristics of adsorbent and the interactions between the phenol and resin.

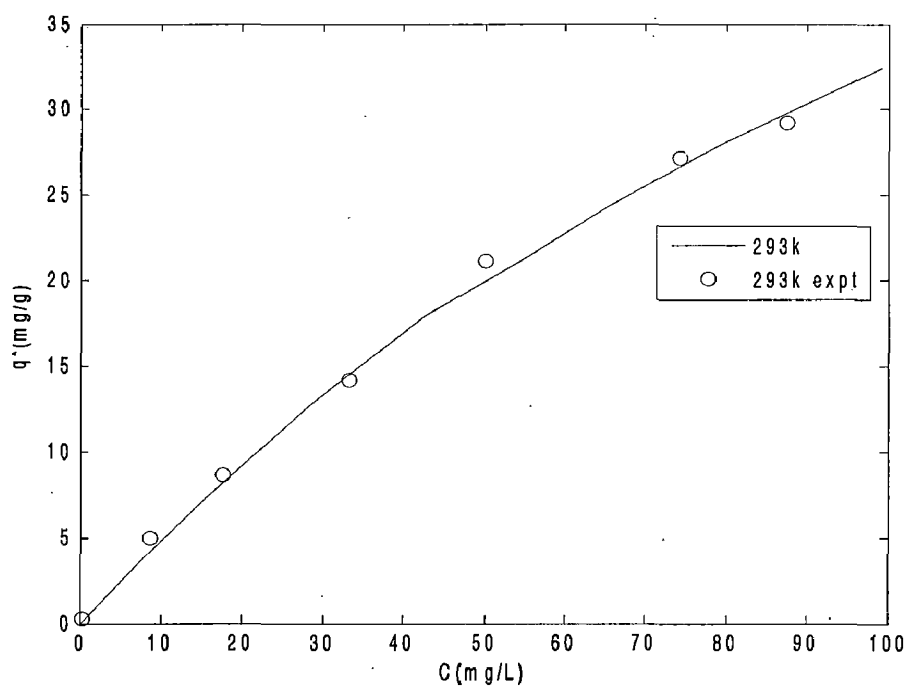


Fig.5.1 Experimental Adsorption equilibrium data  $q^*$  vs  $C$  at temperature  $T=293k$  and fitting to Langmuir isotherm model.



### Langmuir model Characteristic parameters:

- Maximum adsorptive capacity (Q) :  $81.68 \text{ mg g}^{-1}$ .
- Adsorption enthalpy( $\Delta H_L$ )=  $-16.65 \times 10^3 \text{ J mol}^{-1}$
- $K_L^\infty = 7.02 \times 10^{-6} \text{ (m}^3 \text{g}^{-1}\text{)}$ .

The adsorption equilibrium  $q^*$  vs C at different temperatures (T=293k, T=333k) fittings of Langmuir isotherm model for the adsorption of phenol onto Amberlite resin XAD16 are shown in Fig.5.2

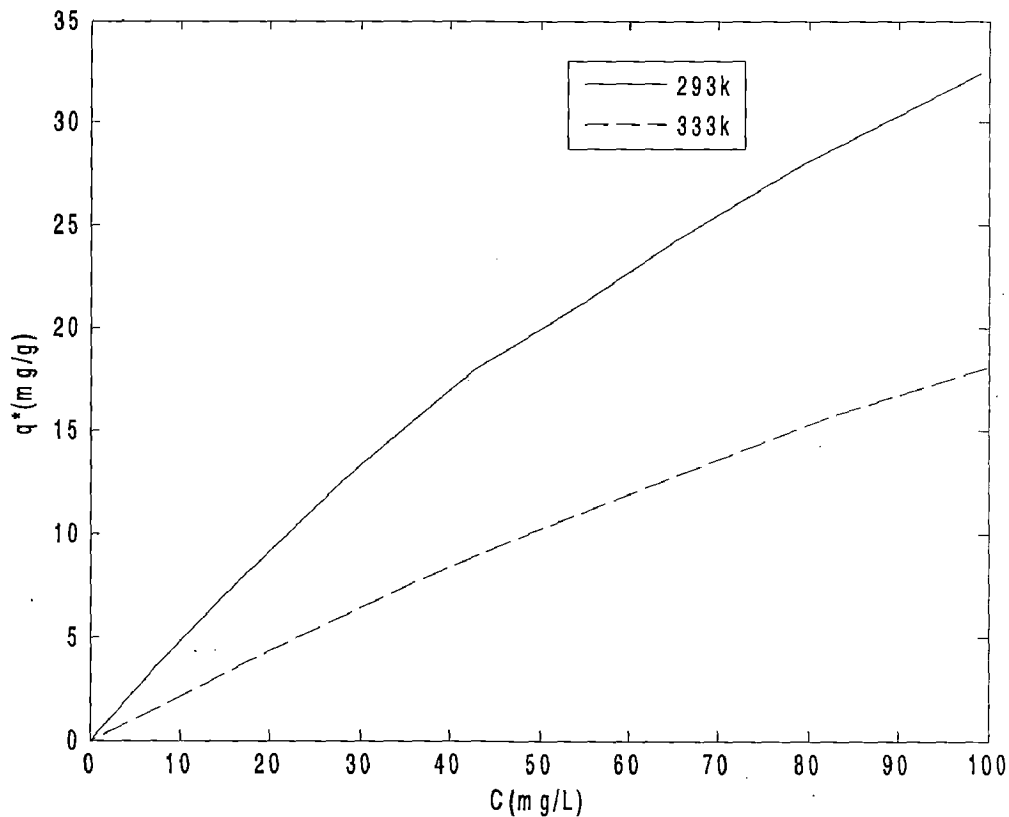


Fig.5.2 Adsorption equilibrium  $q^*$  vs C at different temperatures fittings of Langmuir isotherm model.

### 5.2 Effect of flow rate

The results for different feed solution flow rates are plotted for a bed height of 0.3m and an inlet adsorbate concentration of 100 mg/l. The flow rates considered are 5.5 and 10ml/ min. Fig.5.3 reveals that for the temperature T=293k as the flow rate increases from 5.5 to 10ml/min, the break through curve becomes steeper. The break point decreases from

125 minutes to 35 minutes. Fig.5.4 shows that for the temperature  $T=333\text{k}$  as the flow rate increase from 5.5 to 10 ml/min the break through curve becomes steeper and break through time decreases from 100 minutes to 35 minutes. This is because of residence time of phenol in the column, which is not long enough for adsorption equilibrium to be reached at high flow rates. So at high flow rate the adsorbate solution leaves the column before equilibrium occurs. Furthermore, a fixed saturation capacity of bed based on the same driving force gives rise to a shorter time for saturation at high flow rate.

### 5.3 Effect of temperature

The results for different feed solution temperatures are plotted for a bed height of 0.3m and an inlet adsorbate concentration of 100 mg/l. The temperatures considered are 293k and 333k. Fig.5.5 reveals that for the flow rate 5.5 ml/min as the temperature increases from 293 to 333k, the break through curve becomes steeper. The break point decreases from 145 minutes to 99 minutes. Fig.5.6 shows that for the flowrate 10ml/min as the temperature increases from 293k to 333k the break through curve becomes steeper and break through time decreases from 45 minutes to 35 minutes. This is because the adsorption of phenol onto resin is physical adsorption, an exothermic process and the adsorption capacity decreases as temperature increases.

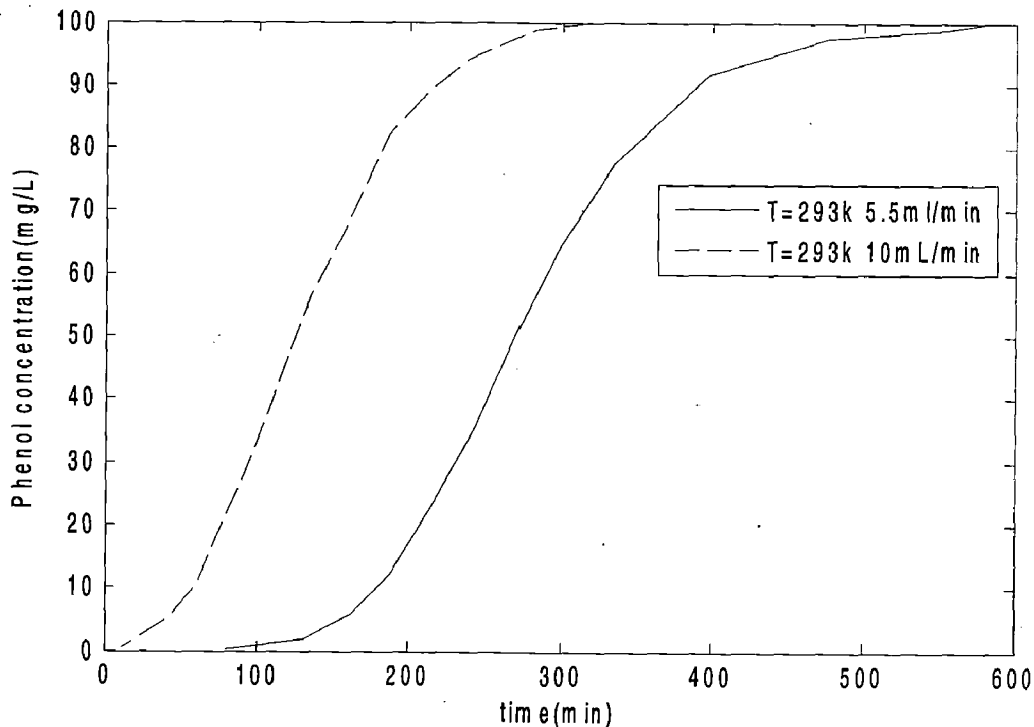


Fig.5.3 Effect of flow rate on break through curve at temperature  $T=293\text{k}$ .

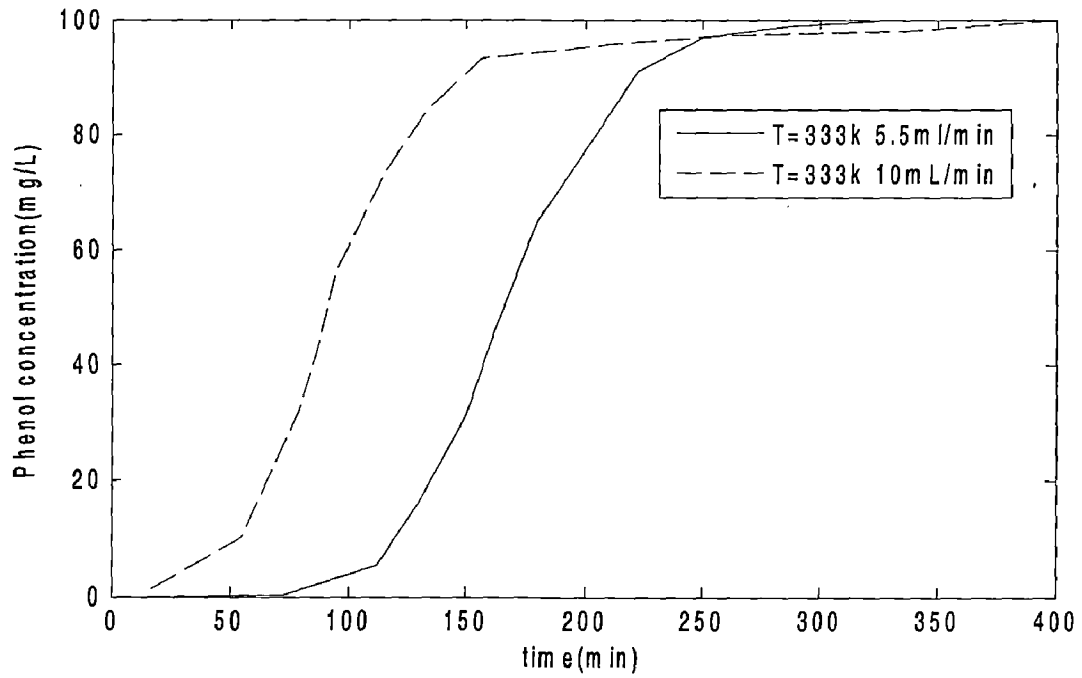


Fig.5.4 Effect of flow rate on break through curve at temperature T=333k.

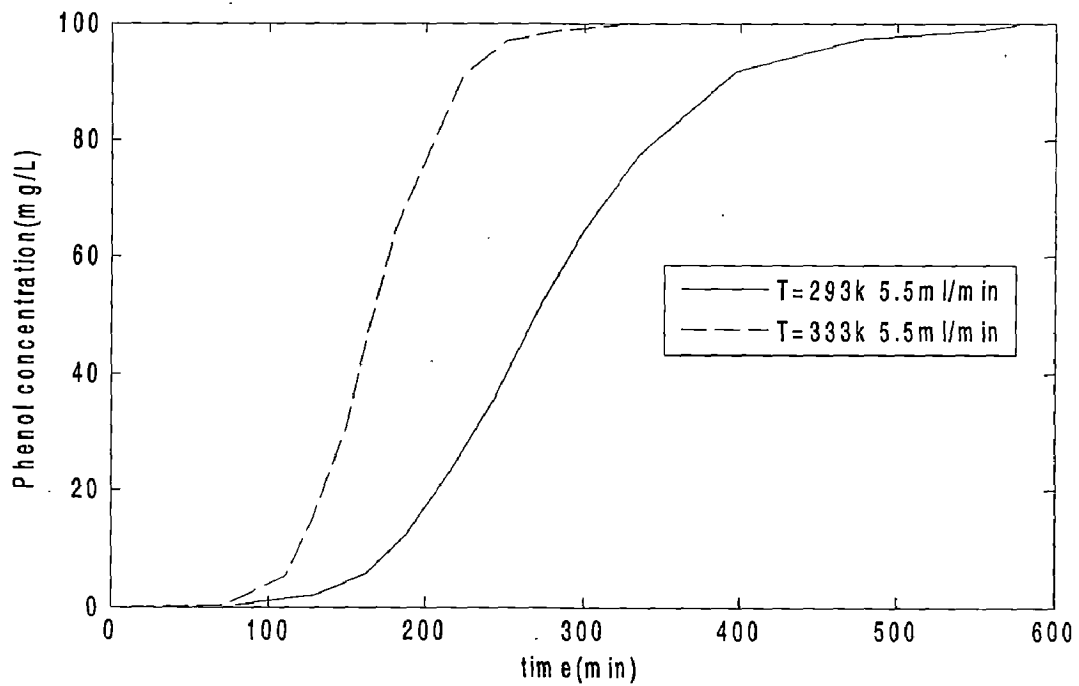


Fig. 5.5 Effect of temperature on break through curve for feed flow rate 5.5ml/min.

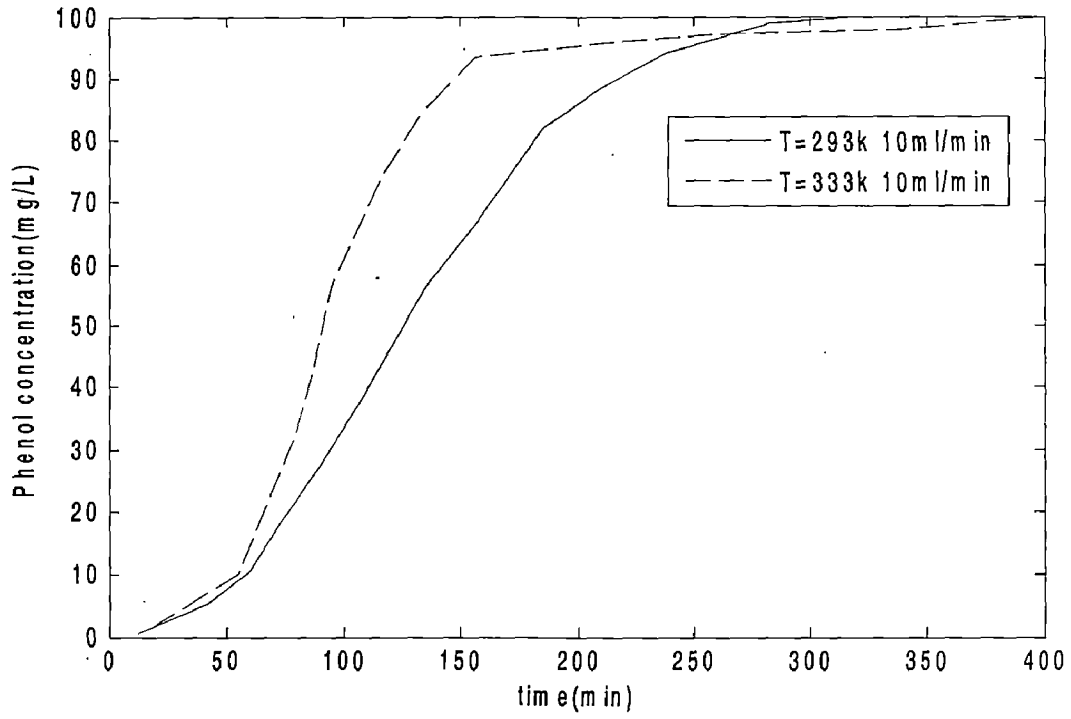
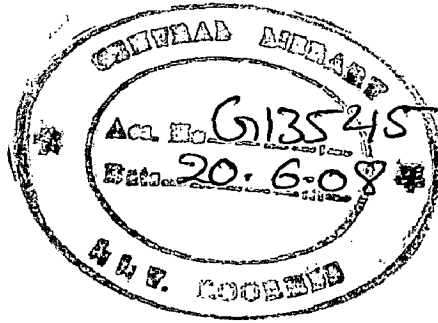


Fig.5.6 Effect of temperature on break through curve for feed flow rate 10 ml/min.

## 5.4 Validation of the Mathematical Model

The mathematical model is validated against the experimental data of Allirio E.Rodrigues et.al. They conducted dynamic column experiments by packing the adsorbents in lab scale columns and feeding these with phenol solution. Fig.5.7 shows the comparison of concentration profile from mathematical model with experimental values at temperature 293k for feed flow rate of 5.5 ml/min.

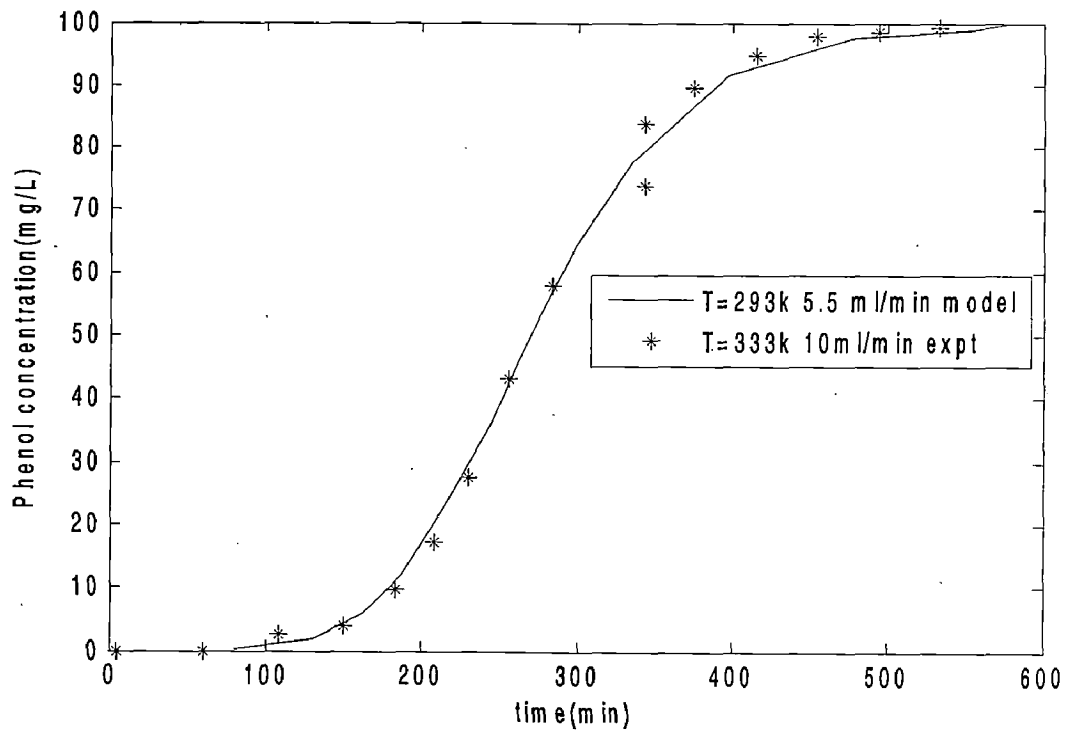


Fig .5.7 Validation of linear driving force model with data of Allirio E.Rodrigues et.al at temperature  $T=293\text{k}$  for feed flow rate of  $5.5\text{ml/min}$ .

## CONCLUSIONS AND RECOMMENDATIONS

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### **6.1 Conclusions**

The Linear driving force model which incorporates film mass transfer and pore diffusion resistances with constant velocity through out the fixed bed has been formulated and solved with the computer program. Following conclusions are drawn from the above discussed results:

1. Adsorption equilibrium data is fitted to Langmuir isotherm model.
2. As the flow rate is increased, the break through curve becomes steeper and the break through time decreases.
3. As the temperature is increased, the break through curve becomes steeper and the break through time decrease. This is because of physical adsorption and exothermic process.
4. The Linear Driving Force model seems to well describe the fixed bed adsorption of phenol onto the Amberlite XAD16 resin.

### **6.2 Recommendations For Future work**

The research work in the present work could be extended further by the following

1. By taking the velocity variation of fluid along the length of column.
2. To study the effects of various parameters like initial concentration, particle size, height and porosity of bed.
3. To predict the non isothermal behavior of fixed bed adsorption column.
4. We can also compare by taking different adsorbents.
5. We can study the adsorption equilibrium data fittings to other isotherm models.
6. To study various model to describe the fixed bed adsorption of phenol.

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