

# MODELING OF ADSORPTION STUDIES OF PHENOL AND SALICYLIC ACID ON DUOLITE RESIN

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 the dissertation entitled **“MODELING OF ADSORPTION STUDIES OF PHENOL AND SALICYLIC ACID ON DUOLITE RESIN”**, in partial fulfillment of the requirement for the award of the degree of Master of Technology in Chemical Engineering with specialization in **“COMPUTER AIDED PROCESS PLANT DESIGN”**, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during the period from July 2005 to August 2005 and January 2007 to June 2007, under the guidance of **Dr.(Mrs.) SHASHI**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

The matter embodied in this project work has not been submitted for the award of any other degree.

Date: 8<sup>th</sup> June, 2007

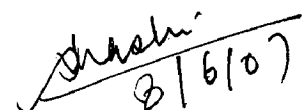
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## **CERTIFICATE**

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

  
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Assistant Professor,  
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## ACKNOWLEDGEMENT

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*Mohangarge*  
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## ABSTRACT

Phenolic compounds are undesirable pollutants in the environment, specifically in aquatic media. Salicylic acid is a phenolic compound, and together with phenol, which is its precursor, it is present in wastewaters from different industries. Adsorption being one of the most common ways for these wastewater treatment, a mathematical model to describe the adsorption phenomenon is developed. Langmuir Isotherm is taken as the basis to predict the equilibrium concentrations of the adsorbed and the solute phases. For modeling the adsorption kinetics, a linear driving force (LDF) approximation was used. The LDF rate constant accounting for macropore diffusion and adsorption and the film mass transfer resistance were grouped in an overall mass transfer coefficient. The model developed is solved by the PDEPE TOOLBOX of MATLAB 7.1.0. and the adsorption of phenol and salicylic acid onto Duolite resin is compared. The adsorptive capacity of the Duolite is more for phenol (96.13 mg/g) than that of salicylic acid (43.01 mg/g). The model well predicts this phenomenon, as the adsorption of phenol is more than that of the salicylic acid on the considered Duolite resin for the different runs carried out.

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## NOMENCLATURE

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$A$	Sub index for the solute
$B$	Sub index for the solvent
$C$	Concentration in the bulk fluid phase (mg /L)
$C_0$	Initial liquid-phase concentration of phenol (mg /L)
$d_p$	Diameter of the particle of the adsorbent (cm)
$D_{ax}$	Axial dispersion ( $m^2/s$ )
$D_{pe}$	Effective pore diffusivity ( $m^2/s$ )
$D_m$	Molecular diffusivity ( $m^2/s$ )
$f_h$	Humidity factor (g dry adsorbent/g adsorbent)
$\Delta H_L$	Adsorption enthalpy ( $J\ mol^{-1}$ )
$k_{LDF}$	Linear driving force (LDF) kinetic rate constant ( $s^{-1}$ )
$k_f$	External film mass transfer coefficient ( $m\ s^{-1}$ )
$k_s$	Overall mass transfer coefficient ( $s^{-1}$ )
$K_L$	Parameter in the Langmuir isotherm model ( $m^3\ g^{-1}$ )
$k_L^\infty$	Equilibrium constant corresponding to the Langmuir model ( $m^3\ g^{-1}$ )
$L$	Total bed length (m)
LUB	Length of unused bed (m)
$L_t$	Length of the transference zone (m)
MW	Molecular weight ( $gmol^{-1}$ )
$M_B$	Molecular weight of solvent B ( $gmol^{-1}$ )
$Pe$	Peclet number
$q$	Solute adsorbed per dry mass of adsorbent at a certain time (mg/g)
$q^*$	Solute adsorbed per dry mass of adsorbent in equilibrium with the phenol concentration in solution (mg/g)
$Q$	Constant in the Langmuir isotherm model (mg/g) related to the adsorptive capacity
$R_p$	Radius of the particle of the adsorbent (m)
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$t$	Time (s)
$t_{bp}$	Breakthrough time at 2% outlet concentration (s)
$t_{st}$	Stoichiometric time (s)
$T$	Absolute temperature (K)
$u_o$	Superficial velocity (m/s)
$u_i =$	$(u_o/\epsilon)$ interstitial velocity (m/s)
$U$	Feed flow rate ( $m^3/s$ )
$V$	Volume of the solution (L)

$V_A$	Molar volume of solute a at its normal boiling temperature ( $\text{cm}^3 \text{g-mol}^{-1}$ )
$W$	Dry weight (g) of the corresponding adsorbent
$Z$	Aaxial coordinate in the bed (m)

*Greek letters*

$E$	Bed porosity
$\epsilon_p$	Porosity of the adsorbent
$\varphi$	Dimensionless association factor of solvent B
$\eta$	Viscosity of the solution (Pa.s)
$\eta_B$	Viscosity of solvent B (cp)
$\rho_p$	Density of the adsorbent ( $\text{kg/m}^3$ )
$\rho_f$	Density of the solution ( $\text{kg/m}^3$ )
$\tau$	Tortuosity of the adsorbent



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# CHAPTER 1: INTRODUCTION

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## 1.1 INTRODUCTION:

Waste water is the effluent coming out of chemical, fertilizer, petrochemical, electrochemical etc. industries and also municipal waste. Increased number 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 wastewater consisting of physical adsorption processes employing modeling concept is discussed.

Advanced wastewater treatment encompasses several individual unit operations, used separately or in combination with other processes, to achieve very high overall treatment efficiencies. These processes employ physical, chemical, and biological treatment methods. The objective of advanced wastewater treatment is to improve the removal of suspended solids, organic matter, dissolved solids and nutrients.

Phenol-containing wastewater presents a serious environmental problem since biological degradation of phenol occurs too slowly or does not occur at all. Such organic contaminants from industrial waste streams that seriously threaten the human health and the environment, has been recognized as an issue of growing importance in recent years. It is now widely recognized that sorption processes provide a feasible method for the removal of pollutants from wastewaters.

So, adsorptive processes are widely used in the purification of such polluted streams and diluted wastewaters. For some target solutes, it is also interesting fact that sorption operations are able to concentrate solutes, especially when these solutes are valuable compounds. Phenols are probably the most extensively studied compounds in the field of wastewater treatment as they are persistent pollutants with high toxicity that are released

in the wastewaters of a considerable number of industries. Different techniques are used for the removal of phenol and phenolic compounds from wastewater.

Adsorption of phenolic compounds onto different polymeric adsorbents has been studied by various groups. Salicylic acid is a drug compound that nowadays is usually produced from phenol. The manufacture of acetylsalicylic acid (ASA) is accompanied by the production of phenolic wastewaters containing salicylic acid. Acetylsalicylic acid (ASA), the salicylate ester of acetic acid, is rapidly hydrolyzed to give salicylic acid, which is its active form. The manufacturing of ASA is not the only use of salicylic acid; other applications of salicylic acid are cosmetics, wart-removing medicines, to externally treat fungus infections, as an acne topic treatment and to increase the cell turnover as a component of skin creams. This compound is also employed as food preservative and in plants protection against insects and pathogens and it is present in wastewaters of different industries. Salicylic acid has also been shown to be present in the so-called grey wastewaters, which are those from households, schools, hotels, business complexes as well as some types of industries where no contributions from toilets, bidets or heavily polluted process water are included.

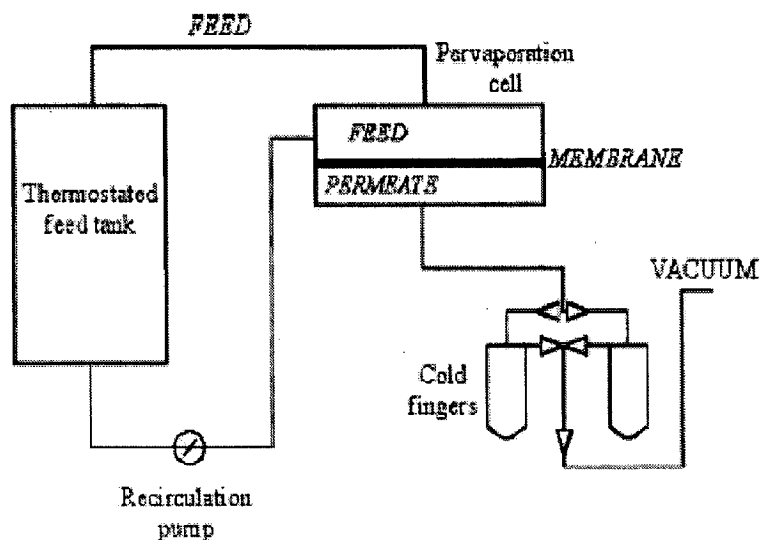
The performance of any adsorption-based process greatly depends on the effectiveness of design and operating conditions. Therefore, rigorous approaches to the design and operation of the adsorption system must be used to ensure efficient applications. In order to get this, the mechanism and dynamics of adsorption must be understood, as well as major variables that affect the adsorptive process.

## **1.2 Different methods used for removal of phenol and phenolic compounds:**

### **1.2.1 Pervaporation:**

In this method, an alternative hybrid process (distillation–pervaporation–adsorption) for the treatment of effluents from the cumene oxidation process to remove phenol is considered. Pervaporation is an energy saving membrane technique used to

separate liquid mixtures. This technique would allow removal of a considerable part of the organic pollutants, whereas adsorption, the classical separation technique, would lower the phenol concentration of the treated effluent to the level acceptable by wastewater treatment plant.



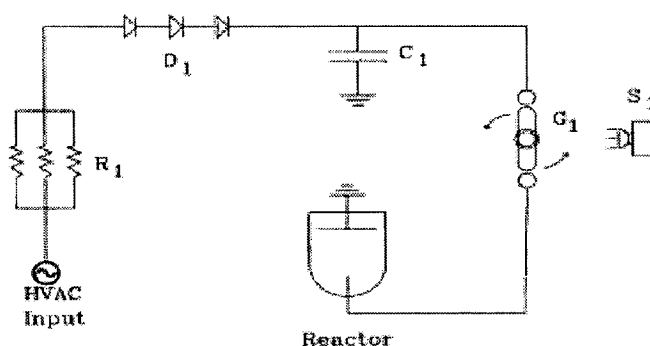
Scheme of the laboratory scale pervaporation setup.

### 1.2.2 Novel two-step method:

Treatment of high-strength phenolic wastewater by a novel two-step method was investigated in this method. The two-step treatment method consisted of chemical coagulation of the wastewater by metal chloride followed by further phenol reduction by resin adsorption. The present combined treatment was found to be highly efficient in removing the phenol concentration from the aqueous solution and was proved capable of lowering the initial phenol concentration from over 10,000 mg/l to below direct discharge level (1mg/l). In the experimental tests, appropriate conditions were identified for optimum treatment operation. Theoretical investigations were also performed for batch equilibrium adsorption and column adsorption of phenol by macroreticular resin. The empirical Freundlich isotherm was found to represent well the equilibrium phenol adsorption. The column model with appropriately identified model parameters could accurately predict the breakthrough times.

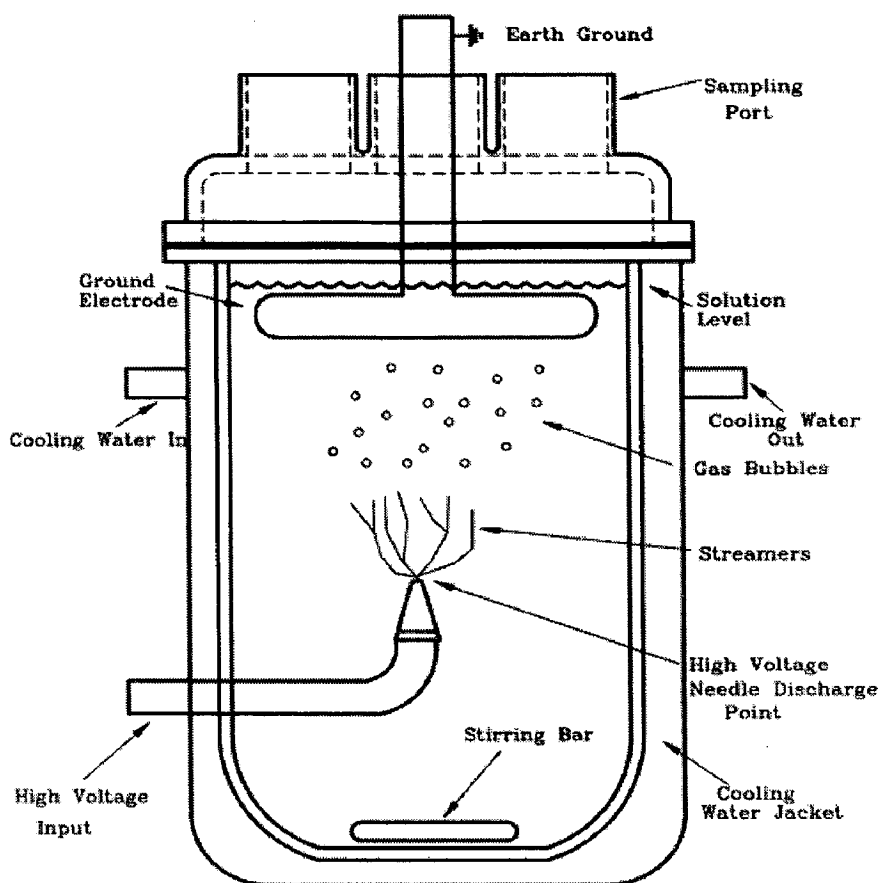
### 1.2.3 Aqueous-phase pulsed streamer corona reactor using suspended activated carbon particles for phenol oxidation:

A pulsed high-voltage electrical discharge that produces streamers, or regions of non-thermal plasma, has been shown to be useful for degrading small organic species in synthetic wastewater in a bench-scale experimental system. This process is an example of an advanced oxidation technology that leads to the formation of hydroxyl radicals, hydrogen peroxide, and aqueous electrons, which in turn lead to organic contaminant removal through direct chemical reactions. Experimental results show that with activated carbon particles present, the removal of organic contaminants is increased due to the combination of direct oxidation of the organic species in the bulk fluid by pulsed corona and adsorption of the organic species to the surface of the activated carbon.



Pulsed power circuit diagram

The specifications of the above pulsed power reactor. HVAC = 0-100 kV, 0-28 mA,  $R_1 = 333 \text{ k}\Omega$ ,  $D_1 = 60 \text{ kV}$ , 12 A Max,  $C_1 = 2900 \text{ pF}$ ,  $G_1 =$  rotating spark gap, 1800 RPM, 60 discharges per sec,  $S_1 =$  Strobe lamp.



Liquid-phase reactor

There exists also the possibility of reactions occurring on the surface of the activated carbon-induced by the electrical discharge, thus continually regenerating the activated carbon.

#### 1.2.4 Fixed bed adsorption:

Fixed-bed adsorption process has been widely used to remove many organic pollutants including phenolic compounds from industrial wastewater, and the relevant breakthrough curves for a specific adsorption process are essential when determining the operating parameters such as feed flow rate and aspect ratio. Among the environmentally concerned substances, phenols, which are considered highly toxic, are the most common pollutants. Adsorptive processes are widely used in the purification of polluted streams and diluted wastewaters. An interesting aspect of sorption operations is their ability to

concentrate solutes. Conventional fixed bed processes involve a saturation, adsorption or loading step, followed by desorption, elution or regeneration steps. On the whole, wastewater purification by means of conventional fixed bed 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.

### **1.3 Adsorption principles;**

#### **1.3.1 Definition of adsorption terms:**

- (i) Adsorption: The process where a substance is accumulated on an interface between phases
- (ii) Adsorbent: The phase that collects the substance to be removed on its surface.
- (iii) Adsorbate: The substance to be adsorbed (to be removed from the fluid phase).
- (iv) Isotherm: A relation between the equilibrium amount of a substance adsorbed per weight of sorbent and its concentration in the fluid phase at constant temperature.

#### **1.3.2 Physical Vs Chemical Adsorption:**

Physical adsorption occurs due to van der Waals or electrostatic forces. The attraction depends upon the polar nature of the fluid component being adsorbed as well as that of the adsorbent. Van der Waals forces are directly related to the polarizability. An estimate of the relative strength of interaction is based on the sorbate size and polarizability. Electrostatic forces include polarization forces and field-dipole interactions. These forces arise when the surface is polar. In case of a polar solvent like water with non-polar organic impurities, the organic molecules will prefer to stick to a non-polar adsorbent such as activated carbon or organic polymeric resins, considered in this work. Physical adsorption is reversible. Physical adsorption is sensitive to temperatures, relatively non-specific regarding sorbates, relatively fast



kinetically and has low heat of adsorption. Multiple sorbate layers can form on the sorbent surface.

Chemical adsorption (chemisorption) occurs when the attraction between the adsorbent and the adsorbate can form a covalent bond, or when a chemical reaction occurs between the adsorbate and adsorbent. Usually chemical reaction will only allow a single layer of molecules (monolayer) to accumulate on the surface of the adsorbent. Chemisorption is usually irreversible. Chemisorption is typically more specific, kinetically slower and has a large heat of adsorption.

## CHAPTER 2: LITERATURE REVIEW

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### 2.1 PROBLEM STATEMENT:

Wastewater consists of many polluting chemicals. Of these, phenol and salicylic acid are the most important pollutants to be removed from wastewater before they can be discharged. Since, biodegradation of phenolic compounds is very difficult, these can be removed using the adsorption process. In this work, modeling studies are done to study the adsorption of phenolic compounds on fixed bed Duolite resin. A mathematical model is required which can predict the performance and extent of adsorption of the system. Further this model can be utilized to study adsorption process on different resins.

### 2.2 OBJECTIVES:

1. To describe the process of adsorption of phenol and salicylic acid onto polymeric resin Duolite with the help of mathematical model.
2. To validate this model with the available literature data [1]
3. To compare adsorption of phenol and salicylic acid on to this resin with the help of the validated model.

## 2.3 LITERATURE REVIEW:

The review of literature on assigned dissertation topic is the pinnacle of every dissertation work. As our dissertation topic is related to modeling studies of fixed bed physical adsorption system, enormous literature is available on its various aspects. In this chapter, we will discuss briefly different literature available on adsorption system.

### **B.C. PAN (2005) ET AL:**

Fixed-bed adsorption process has been widely used to remove many organic pollutants including phenolic compounds from industrial wastewater, and the relevant breakthrough curves for a specific adsorption process are essential when determining the operating parameters such as feed flow rate and aspect ratio. Although many models were developed to predict the breakthrough curve, most of them are sophisticated and need many parameters determined by serial independent batch kinetic tests or estimated by suitable correlations. Hence, a model without tedious tests or mathematical calculations is needed to predict the breakthrough curve. In the present study, an effective method based on combining the constant-pattern wave approach theory and the Freundlich model was used to determine the breakthrough curve of a fixed-bed adsorption system. Amacrorreticular polymeric resin adsorbent NDA-100 was selected as adsorbent for its wide use in theoretical study and field application, and phenol and *p*-nitrophenol were selected as adsorbate due to their frequent appearance in industrial wastewater.

The adsorption isotherms of both phenolic compounds onto resin NDA-100 were obtained to help to develop the model. Column experimental results obtained at different test conditions proved the validity of the model well. A model based on the constant-pattern wave approach theory and the Freundlich model was used to predict the breakthrough curves of phenol and *p*-nitrophenol adsorption onto resin NDA-100 at different test conditions. Batch column runs indicate it would predict the breakthrough curves satisfactorily.

## MARTA OTERO (2005) ET AL:

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. A package for the simulation of this cyclic operation was used to predict model results, which were satisfactorily compared to those experimentally obtained. Adsorption of phenol onto polymeric resins (Sephabeads SP206 and SP207) and activated carbon (Filtrisorb F400) was studied. Batch tests were carried out in order to make a screening of adsorbents related to the effect of temperature on the adsorptive behaviour.

On the basis of the separation parameter  $b$ , Sephabeads SP206 showed the higher separation potential in function of temperature for the adsorption of phenol. Dynamic studies were also done for the adsorption of phenol onto the polymeric resins and onto the activated carbon to ascertain the applicability of the LDF model in fixed bed. The effect of temperature on the fixed bed adsorption of phenol was also more noticeable for the polymeric resins, especially for Sephabeads SP206, rather than for the Filtrisorb F400. Pilot scale fixed bed using Sephabeads SP206 as adsorbent was studied before operating the parametric pumping unit. Model equations including intraparticle mass

transfer described by the LDF model satisfactorily predicted the breakthrough curves at pilot scale (in an 800mm×90mm bed) carried out both at 293 and 333 K.

#### **S. BEKKOUCHE (2004) ET AL:**

The adsorption of the phenol on  $\text{TiO}_2$  was done in a Pyrex vessel with a double envelope with a capacity of 500 ml. To maintain the temperature constant, water was recirculated through the double envelop from a Lauda RC6 thermostated bath, provided for a pump. Mixing was done with a magnetic stirrer. All studies were made at a temperature of 25°C. The samples were taken at regular intervals by syringes on which filters of 0.2  $\mu\text{m}$  were adapted to eliminate particles of  $\text{TiO}_2$ . Their absorbance was then measured and transformed in concentration (C) by a standardization sorbance concentration previously made.

The phenol was weakly adsorbed on  $\text{TiO}_2$ . This adsorption is a chemisorption, and it is represented well by the Langmuir model in the studied concentration domain. The aggregation effect of  $\text{TiO}_2$  in aqueous solution had an optimal concentration of the catalyst for a concentration of phenol. The adsorption was optimal for a pH between 5 and 6 in the neighborhood of the iso-electric point of  $\text{TiO}_2$ .

#### **SHENG H LIN (2002) ET AL:**

Traditionally, activated sludge process has been the most widely used method to deal with phenolic wastewater because of its simplicity and relatively low cost [2]. However, the microorganisms in an activated sludge system, even well acclimated, can only deal with chemical wastewater containing relatively low concentration of phenolic compounds, usually less than 100 mg/l due to low biodegradability and inhibitory effects of these compounds. Unfortunately, the chemical wastewaters from many heavy chemical and petrochemical industries contain phenolic compounds exceeding this concentration

level. Hence, treatment of high concentration phenolic wastewaters by chemical or physical alternatives is crucial in these industries.

The objective of this work is to present a new two-step method for dealing with phenolic wastewater containing phenol over tens of thousands mg/l. The present method consists of first step chemical precipitation of phenol by metal chloride. In this step, the metal chloride converts phenol under alkaline conditions to metal phenolate that precipitates out of the aqueous solution due to its very low solubility and the phenolate is thus recovered for reuse. The efficiency of this chemical precipitation, when properly operated and with the right kind of metal chloride, can far exceed 90%. The remaining wastewater containing considerably reduced amount of phenol is then treated using adsorption resin which is able to further lower the phenol concentration to below the discharge level of 1 mg/l. The previous investigations of the phenol adsorption by resin focused primarily on the practical aspects only. In the present work, several theoretical aspects of resin adsorption of phenol were examined using the observed data. Again, the phenol is recovered in this adsorption step when the adsorption resin is regenerated.

The present two-step method was found to be highly efficient, as would be elaborated later, enabling essentially total phenol recovery from the wastewater for reuse. The high-strength phenol wastewater was treated by a novel two-step process in the present study. The two-step method consists of chemical precipitation of the high-strength phenolic wastewater by metal chloride followed by phenol adsorption using macroporous resin. The two-step treatment method offers an excellent means for dealing with the high-strength phenolic wastewater. Based on the results obtained from tests of individual step, the optimum operating conditions were identified.

**Nilsun H Ince (2000) et al:**

A more commonly employed advanced treatment technique is adsorption on activated carbon; a process based on the concentration and immobilization of a contaminant on the surfaces of granular or powdered activated carbon. The technique is

well known as an "interface phenomenon", encompassing a state of dynamic equilibrium between the solute in the aqueous phase and that adsorbed on the carbon surface. When equilibrium is reached, adsorption parameters can be simply established by using an appropriate isotherm equation. As a whole, adsorption is a simple-to-operate process and relatively cost-effective, due to low (or no) energy requirements and the possibility of reclaiming and reusing the spent carbon via regeneration.

However, surface phenomena involving the accumulation of undesired contaminants on the solid surface end up in large quantities of "spent adsorbent" and/or "regeneration solutions", both of which have to be handled as "hazardous wastes". Accordingly, tertiary treatment by adsorption alone is not an environmentally complete system, unless the destruction of immobilized contaminants on the spent or wasted carbon surface is heeded as well. Furthermore, the incomplete system is incomparable to treatment by advanced oxidation, where there is neither any accumulation, nor transport of the contaminant from one medium to another.

A recently proposed advanced method to cope with the above problem was called "phase-transfer oxidation", which involved two consecutive operational steps characterized by fixed-bed adsorption for effluent treatment and advanced oxidation for destructive regeneration of the adsorbent. The strategy was reported to provide a significant advantage as "onsite regeneration" to minimize adsorbent inventory and eliminate unloading, transportation and repacking of the adsorbent.

The purpose of this study was to investigate a modified version of "phase-transfer oxidation", in which effluent treatment or the first-step operation was carried out by the simultaneous operation of activated carbon adsorption and advanced oxidation in the same reactor. The second consecutive step similarly involved destructive regeneration of the spent adsorbent by advanced oxidation. The advantages expected from this modification were: (i) delayed exhaustion of the adsorbent  $\pm$  less frequent regeneration/disposal and fresh supply of activated carbon; (ii) increased cost-effectiveness due to lowered energy and oxidant consumption during the destructive

regeneration of the spent carbon. This expectancy is based on the fact that the so called "regeneration solution" to be treated by advanced oxidation in the second-stage will be made of partly degraded by-products of the parent compound as a consequence of its oxidative degradation in the first stage.

•  
**SANG-MO KOH (2001) ET AL:**

This study is focused on developing effective and economic organo-modified minerals available for the removal of NOCs such as benzene, phenol, and toluene, which are the major components of the wastewater from petroleum refineries. The adsorption capacity of phenol, benzene, and toluene on organo-minerals is estimated and the application of these organo-minerals for the removal of NOCs from contaminated wastewater is evaluated.



## CHAPTER 3: MODEL DEVELOPMENT

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### 3.1 Assumptions:

- 1) Isothermal adsorption process is considered.
- 2) Monolayer adsorption is assumed to take place.
- 3) Langmuir isotherm is assumed.
- 4) It is assumed that adsorption occurs onto specific sites of uniform energetic surface.
- 5) The adsorption isotherm is used to describe the diffusional mass transfer inside adsorbent particles.
- 6) Kinetics are assumed to follow the Linear Driving Force (LDF) model.

### 3.2 Adsorption isotherms

The amount of salicylic acid or phenol adsorbed onto the two different adsorbents,  $q_e$  (mg.g<sup>-1</sup>), was calculated by a mass balance relationship (Eq. (1)).

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where  $C_0$  (mg L<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) are the initial and equilibrium liquid-phase concentrations, respectively,  $V$  the volume of the solution (L) and  $W$  is the dry weight (g) of the corresponding polymeric resin. The adsorption equilibrium isotherms for phenol and salicylic acid onto each adsorbent at various temperatures,  $q^*$  (mg g<sup>-1</sup>) versus the adsorbate liquid concentration at equilibrium,  $C$  (mg g<sup>-1</sup>) were fitted with the Langmuir model. The following Langmuir equation (Eq. (2)) is based on a theoretical 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.

$$q^* = \frac{QK_L C}{1 + K_L C} \quad (2)$$

where  $Q$  is the maximum adsorptive capacity and  $K_L$  is a parameter which relates to the adsorption energy [3].

$$K_L = K_L^\infty \exp\left(-\frac{\Delta H_L}{RT}\right) \quad (3)$$

From the equilibrium results, it may be found the separation to be expected as a function of temperature for each of the systems phenol-adsorbent. The adsorption enthalpy in the Langmuir constant is generally a net value that includes the solvent desorption and the solute adsorption.

### 3.3 Fixed bed adsorption modeling:

The model used to predict the fixed bed adsorption of these phenolic compounds comprises a mass balance, the adsorption equilibrium isotherm at the liquid/solid interface and a linear driving force (LDF) rate equation was used to describe the diffusional mass transfer inside adsorbent particles.

#### 3.3.1 Species mass balance:

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_p f_h \frac{\partial q(z,t)}{\partial t} \quad (4)$$

where  $D_{ax}$  is the axial dispersion coefficient,  $u_i$  the interstitial velocity,  $\varepsilon$  the bed porosity,  $z$  the axial position,  $t$  the time,  $\rho_p$  the adsorbent particle density,  $f_h$  the humidity factor of the corresponding adsorbent,  $q$  the average concentration in the adsorbent particle and  $C$  is the concentration in the bulk fluid phase. The boundary conditions are the Danckwerts boundary conditions:

$$z = 0, \quad D_{ax} \frac{\partial C(z,t)}{\partial z} \Big|_{z=0} = u_i (C(0,t) - C_0) \quad (5)$$

$$z = L, \quad \left. \frac{\partial C(z,t)}{\partial z} \right|_{z=L} = 0 \quad (6)$$

Initial conditions are:

$$C(z,0) = 0 \quad (7)$$

$$q(z,0) = 0 \quad (8)$$

The axial dispersion coefficient,  $D_{ax}$  to be included in the mass balance above was obtained from the following expression [3].

$$\frac{u_0 d_p}{D_{ax}} = 0.2 + 0.11 \text{Re}^{0.48} \quad (9)$$

The Reynolds number and the peclet number are evaluated using the following expressions:

$$\text{Re} = \frac{u_0 \rho_f d_p}{\eta}$$

$$\text{Pe} = \frac{u_0 L}{\varepsilon D_{ax}}$$

### 3.3.2 Adsorption equilibrium isotherm:

The adsorption equilibrium isotherm is described by the Langmuir equation shown above (Eqs. (2) and (3)).

### 3.3.3 Adsorption kinetics:

The adsorption rate can be represented by a linear driving force approximation expressed as follows:

$$\frac{\partial q(z,t)}{\partial t} = k_s [q^*(z,t) - q(z,t)] \quad (10)$$

where  $k_s$  is an overall mass transfer coefficient,  $q^*$  the adsorbed phase concentration in equilibrium with the bulk concentration  $C$  and  $q$  is the average adsorbed phase concentration in the adsorbent particle (described as homogeneous). As expressed by this model, the rate of adsorption into the particle is essentially proportional to the driving

force (difference between adsorbed phase concentration in equilibrium with the bulk fluid concentration and the average adsorbed concentration in the particle) still required to reach equilibrium [6].

The effective mass transfer coefficient ( $k_s$ ) was estimated from the following correlation [7–10];

$$\begin{aligned} \frac{1}{k_s} &= \frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} + \frac{r_p^2}{15d_{pe}} \rho_p f_h \frac{dq^*}{dC} \\ &= \frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} + \frac{1}{k_{LDF}} \end{aligned} \quad (11)$$

which considers macropore and film resistances to the mass transfer and where  $k_s$  is the overall mass transfer coefficient,  $D_{pe}$  the effective pore diffusivity,  $r_p$  the radius of the particle of the adsorbent,  $k_{LDF}$  the coefficient accounting for macropore diffusion and adsorption and  $k_f$  is the external film mass transfer coefficient and where the derivative  $\left(\frac{dq^*}{dC}\right)$  represents the average slope of the Langmuir isotherm corresponding to the concentration range of the experiment. The second term of the right hand side of Eq. (11) corresponds to  $1/k_{LDF}$ .  $k_{LDF}$  is represented [6] as:

$$\frac{1}{k_{LDF}} = \frac{r_p^2}{15d_{pe}} \rho_p f_h \frac{dq^*}{dC}$$

The  $D_{pe}$  ( $m^2/s$ ) was calculated as [31]:

$$D_{pe} = \frac{D_m \epsilon_p}{\tau} \quad (12)$$

where  $D_m$  is the molecular diffusivity of salicylic acid in water,  $\tau$  the tortuosity of the adsorbent and  $\epsilon_p$  its porosity. The molecular diffusivity of salicylic acid in water  $D_m$  ( $m^2/s$ ) was estimated, after the corresponding unit transformations, according to the Wilke–Chang [12] method, which assigns for the  $D_m$  ( $cm^2/s$ ):

$$D_m = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2} T}{\eta_B V_A^{0.6}} \quad (13)$$

where  $\Phi$  is the non-dimensional association factor corresponding to the solvent,  $M_B$  the molecular weight of the solvent,  $T$  the corresponding temperature,  $\eta_B$  viscosity of the solvent and  $V_A$  is the volume of the solute. In this study, the solvent was water and the solutes, phenol and salicylic acid. Wilke and Chang recommended that  $\Phi$  be chosen 2.6 if the solvent is water. The values of  $V_A$  were estimated by the Le Bas additive method [13], in the case of phenol  $V_A = 108 \text{ cm}^3 \text{ g-mol}^{-1}$  and  $V_A = 146.8 \text{ cm}^3 \text{ g-mol}^{-1}$  for salicylic acid.

Many correlations have been published for the estimation of  $k_f$ , most of which are modified versions [14,15] of the well-known Ranz–Marshall equation [36]. These empirical correlations have been used for different systems and may predict quite different values of the film mass transfer [17, 18]. Mass transfer data in packed beds have been correlated by the Ranz–Marshall equation [16]:

$$\begin{aligned} Sh = \frac{k_f d_p}{D_m} &= 2.0 + 0.6 \left( \frac{\eta}{\rho_f D_m} \right)^{1/3} \left( \frac{u_0 \rho_s d_p}{\eta} \right)^{1/2} \\ &= 2.0 + 0.6 Sc^{1/3} Re^{1/2} \end{aligned} \quad (14)$$

where  $Sh$ ,  $Sc$  and  $Re$  stand for the Sherwood, Schmidt and Reynolds numbers, respectively. Table 6 shows the values of the  $k_f$  coefficients predicted by the Ranz–Marshall correlation for the systems adsorbent–solute studied here. In the specific case of phenol adsorption from liquid phase, a correlation for the estimation of the film mass transfer coefficient  $k_f$  was developed [19].

In the specific case of phenol adsorption from liquid phase, a correlation for the estimation of the film mass transfer coefficient  $k_f$  was developed in laboratory [19]:

$$j_D = 7.32 Re^{1-0.569} \quad (15)$$

where the Chilton–Colburn factor  $j_D$  and the  $Re'$  are given as:

$$j_D = \frac{Sh}{Re Sc^{1/3}}; \quad Re' = \frac{Re}{(1-\epsilon)}$$

### 3.4 Model parameters:

The properties of the Duolite resin are given as below in Table 1:

Table 1

Resin Properties	Description
Matrix	Aromatic porous resin with hydrophobic substituents
Chemistry	Polystyrene DVB
Physical form	White beads
Humidity factor	0.28
Density (kg/m <sup>3</sup> )	1020
Particle size (10 <sup>-4</sup> m)	5.6
Porosity	0.72

The experimental column is having diameter of 0.01m and 0.3m long. The adsorption experiments are carried out at various temperatures; viz 293K, 310K and 333K. The flow rates are maintained at 5.5 ml/min and 10 ml/min at the above said temperatures. The model developed is simulated at these conditions.

### 3.5 Simulation Parameters:

The model is developed taking into consideration the Langmuir Isotherm. The parameters corresponding to the equilibrium data of the adsorption of salicylic acid and phenol onto the resin Duolite used are given as follows Table 2 and Table 3:

**For phenol:** Table 2

Parameter	Value
Q (mg/mole)	96.13
$k_L^\infty$ (m <sup>3</sup> /g)	1.22 x 10 <sup>-5</sup>
$\Delta H_L$ (J/mole)	-12.93 x 10 <sup>3</sup>

**For Salicylic Acid:**

Table 3

Parameter	Value
Q (mg/mole)	43.01
$k_L^\infty$ (m <sup>3</sup> /g)	$3.18 \times 10^{-6}$
$\Delta H_L$ (J/mole)	$-23.57 \times 10^3$

The parameters that are taken in simulation of the model are given for adsorption of phenol onto Duolite at 293K and flow rate of 5.5 ml/min are given in Table 4 below. The parameters for rest of cases are similarly calculated and used in simulation of the same.

Table 4

Parameter	Value
$D_{pc}$ (m <sup>2</sup> /s)	$3.2 \times 10^{-10}$
$D_m$ (m <sup>2</sup> /s)	$8.9 \times 10^{-10}$
$K_f$ (m/s)	$8.3 \times 10^{-5}$
$k_s$ (s <sup>-1</sup> )	0.0185
$D_{ax}$ (m <sup>2</sup> /s)	$2.63 \times 10^{-6}$

The partial differential equations thus, developed for the modeling of the fixed bed adsorption were solved using the PDEPE TOOLBOX of MATLAB 7.1.0.

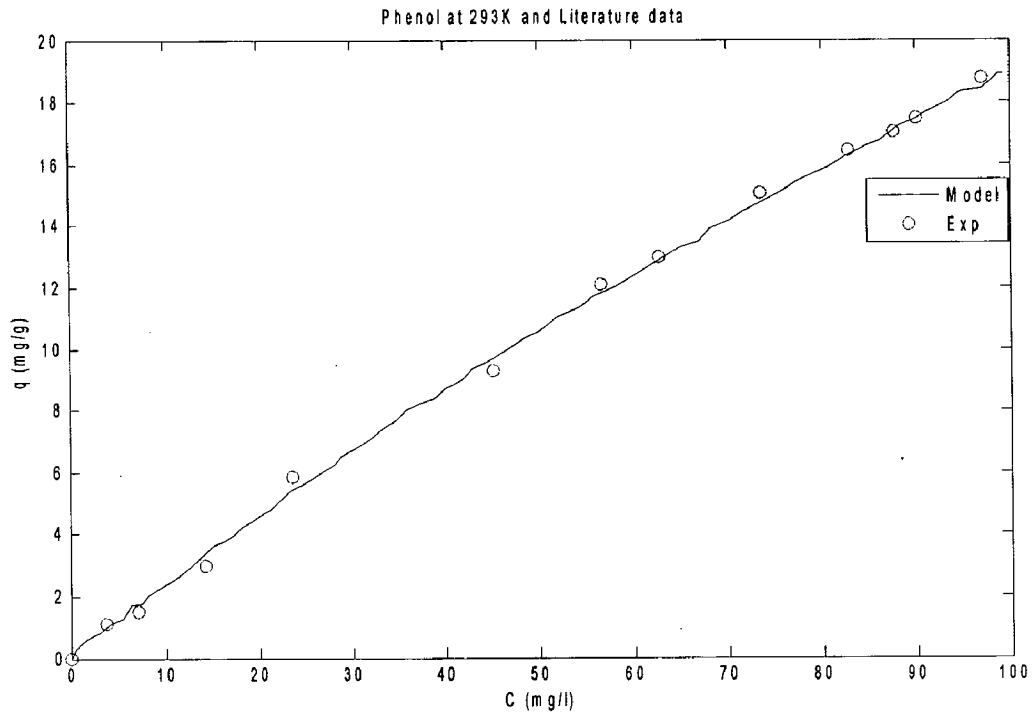


Fig. 1 Langmuir Isotherm of Phenol on Duolite at 293K showing comparison between experimental values and the model curve



Phenol on Duolite at 293K 5.5

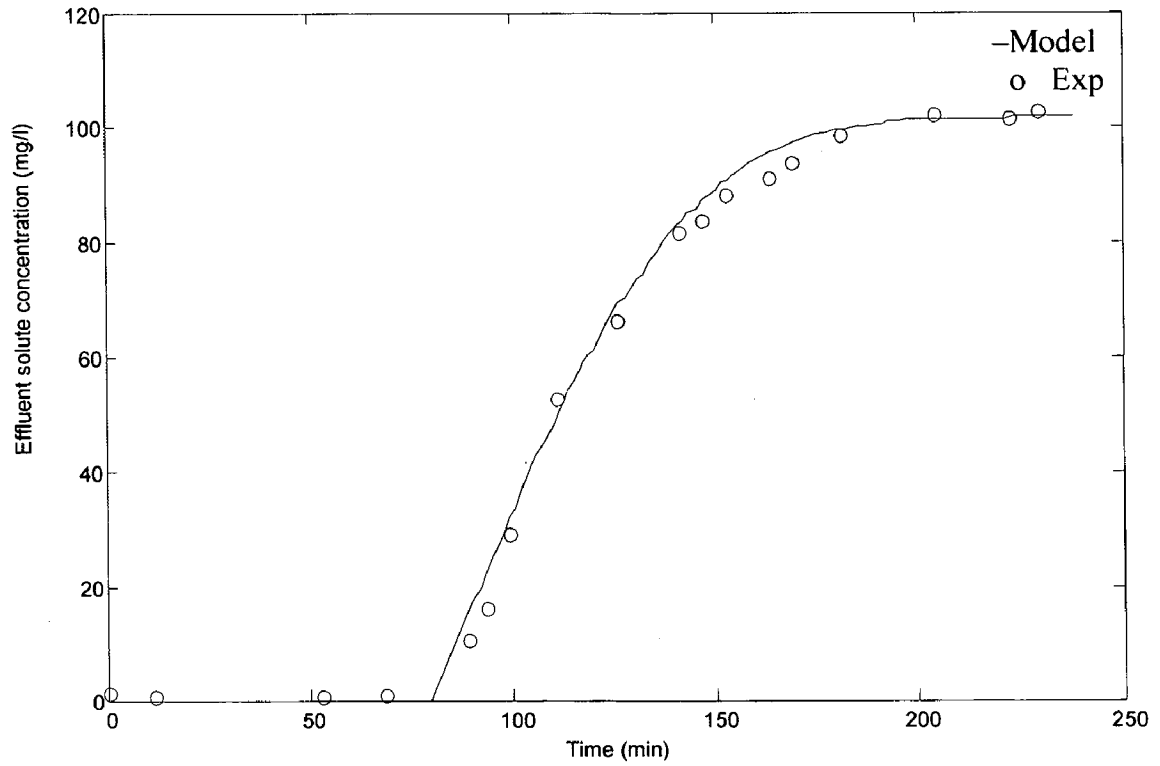


Fig. 2 Phenol on Duolite at 293 K with a flow rate of 5.5 ml/min.

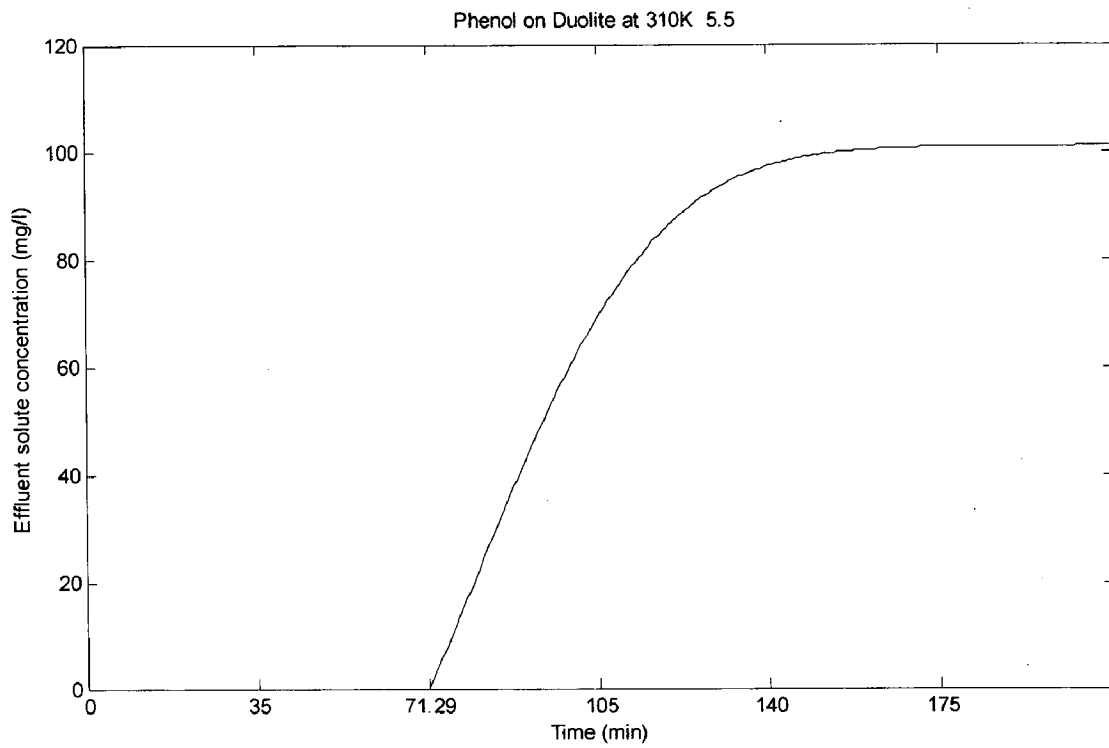


Fig. 3 Phenol on Duolite at 310 K with a flow rate of 5.5 ml/min.

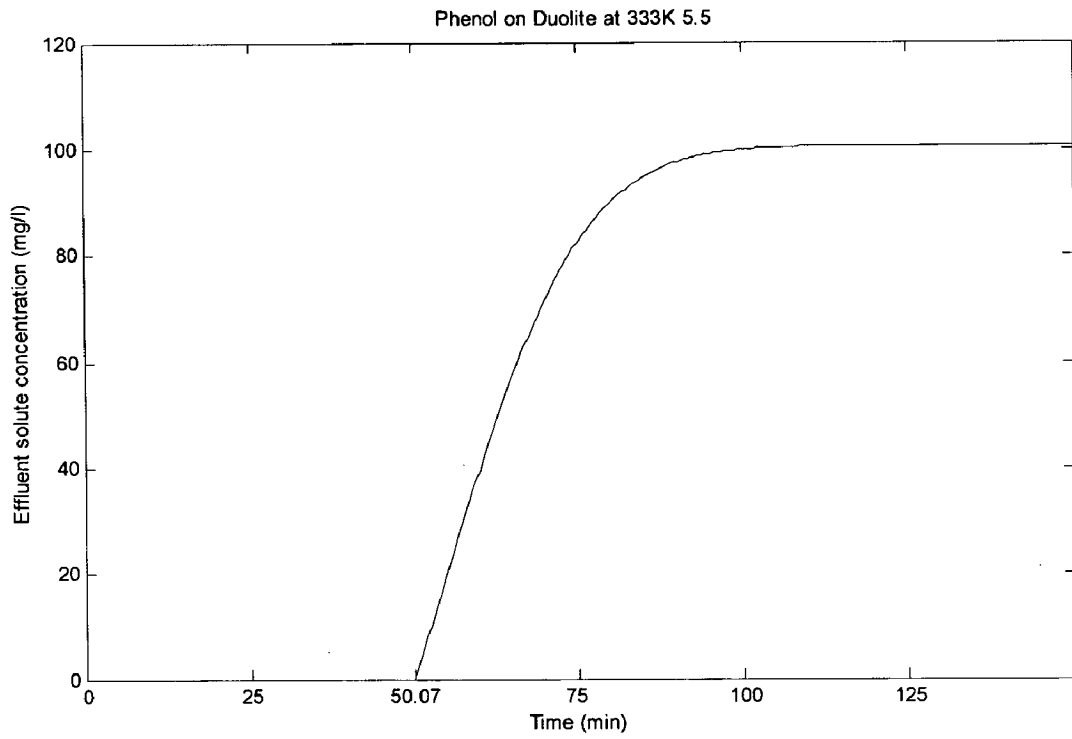


Fig. 4 Phenol on Duolite at 333 K with a flow rate of 5.5 ml/min

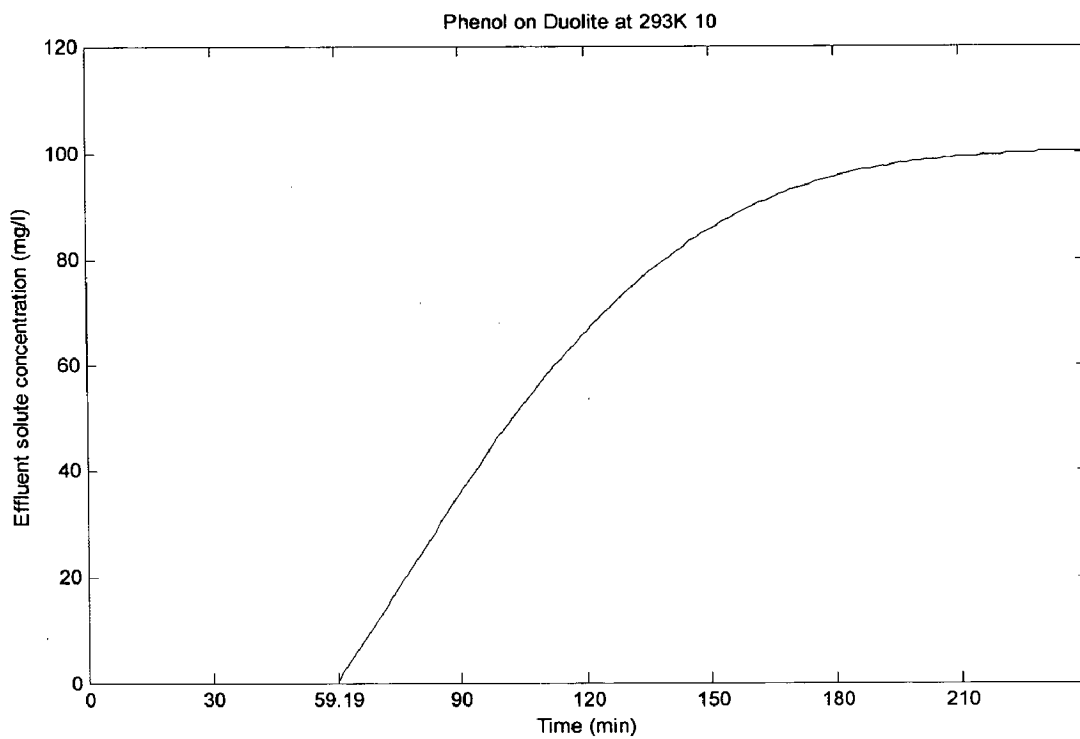


Fig. 5 Phenol on Duolite at 293 K with a flow rate of 10 ml/min

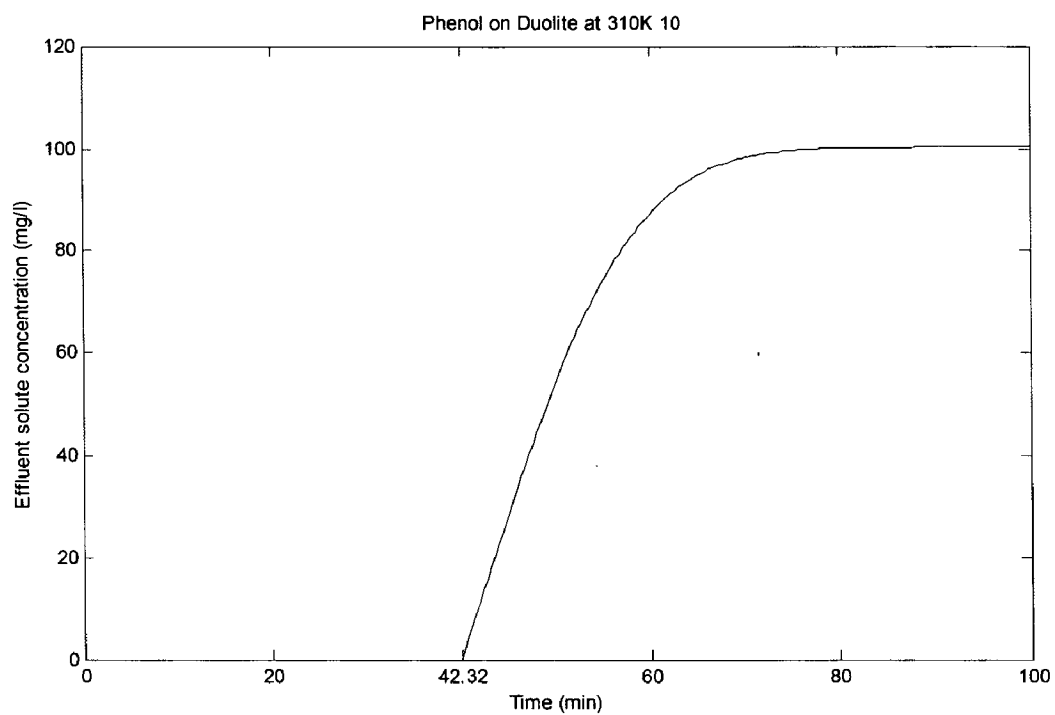


Fig. 6 Phenol on Duolite at 310 K with a flow rate of 10 ml/min

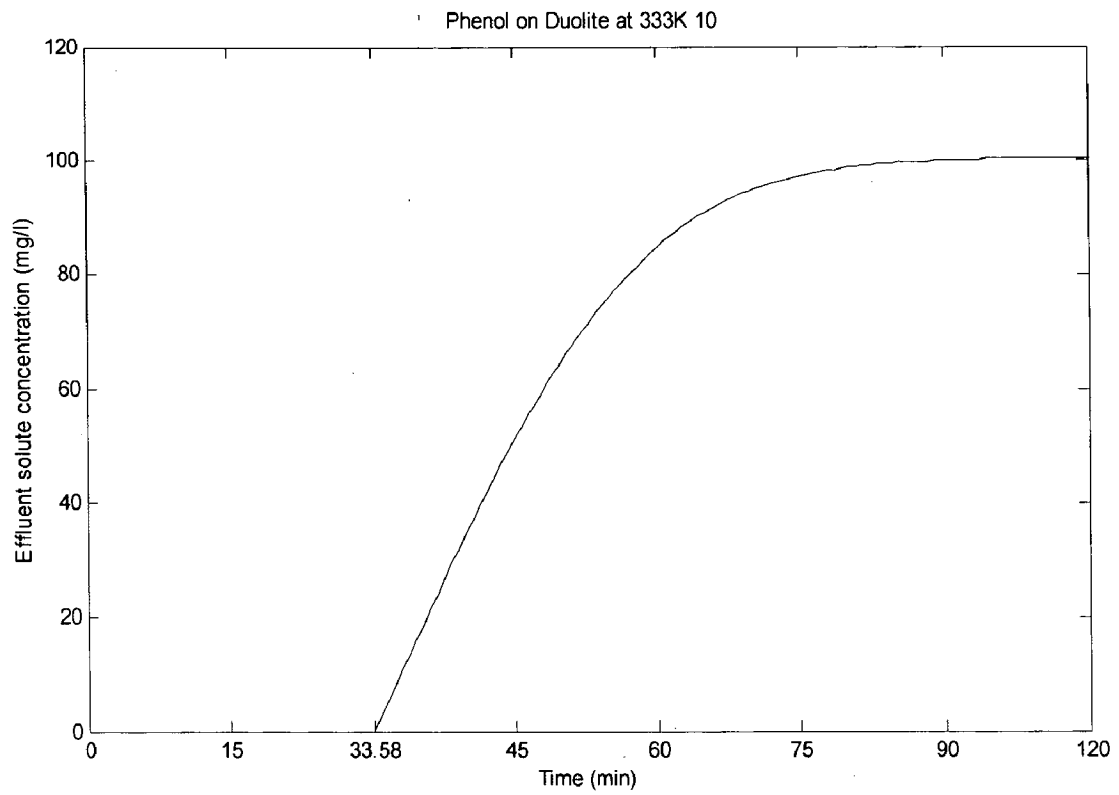


Fig. 7 Phenol on Duolite at 333 K with a flow rate of 10 ml/min

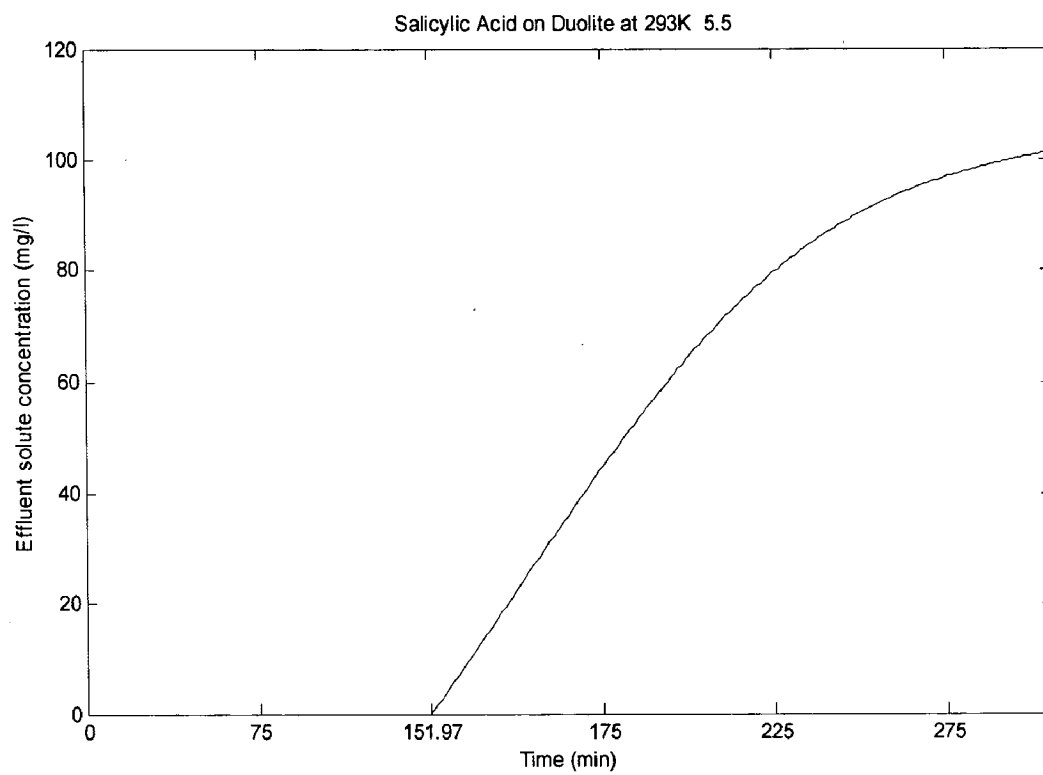


Fig. 8 Salicylic Acid on Duolite at 293 K with a flow rate of 5.5 ml/min

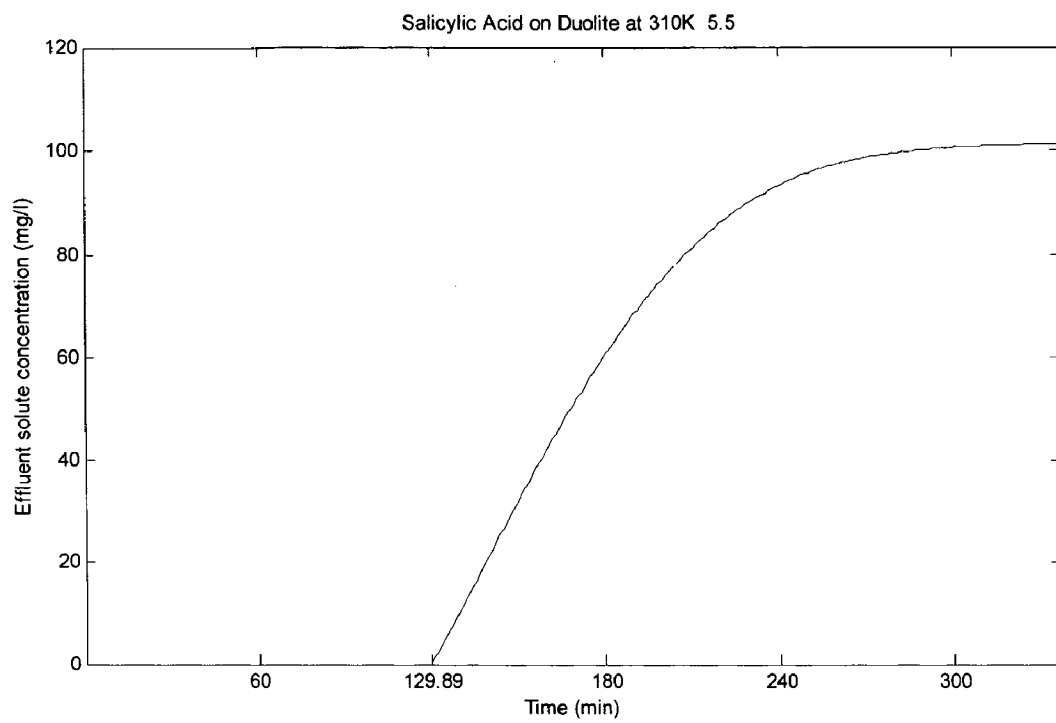


Fig. 9 Salicylic Acid on Duolite at 310 K with a flow rate of 5.5 ml/min



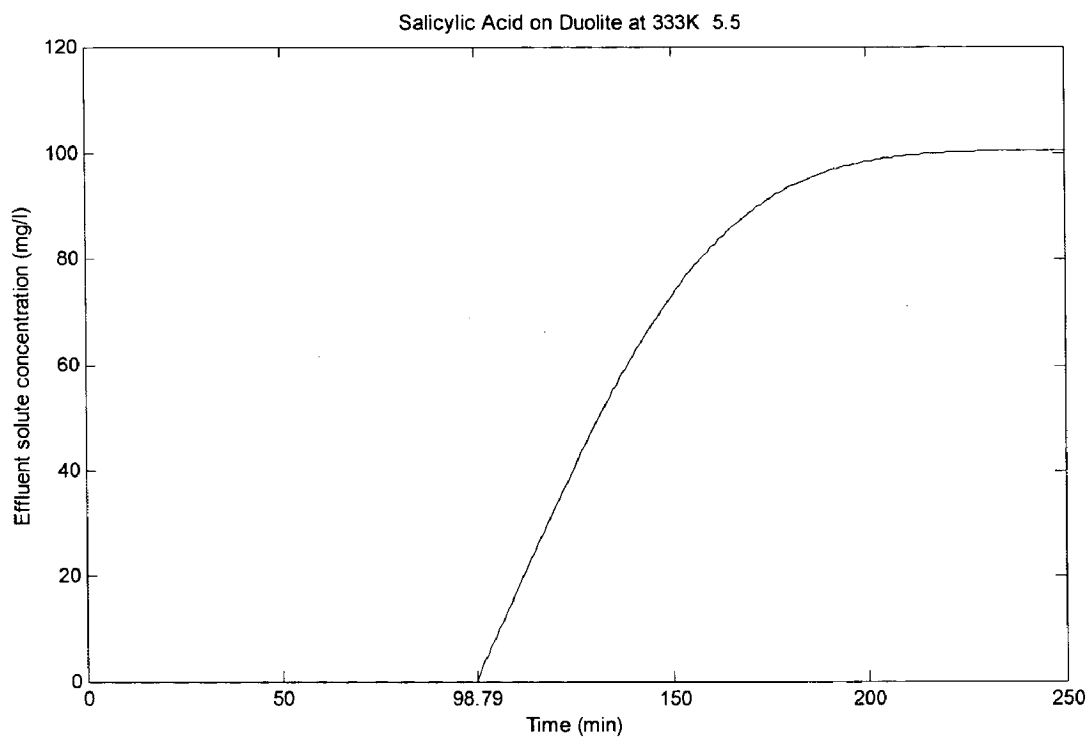


Fig. 10 Salicylic Acid on Duolite at 333 K with a flow rate of 5.5 ml/min

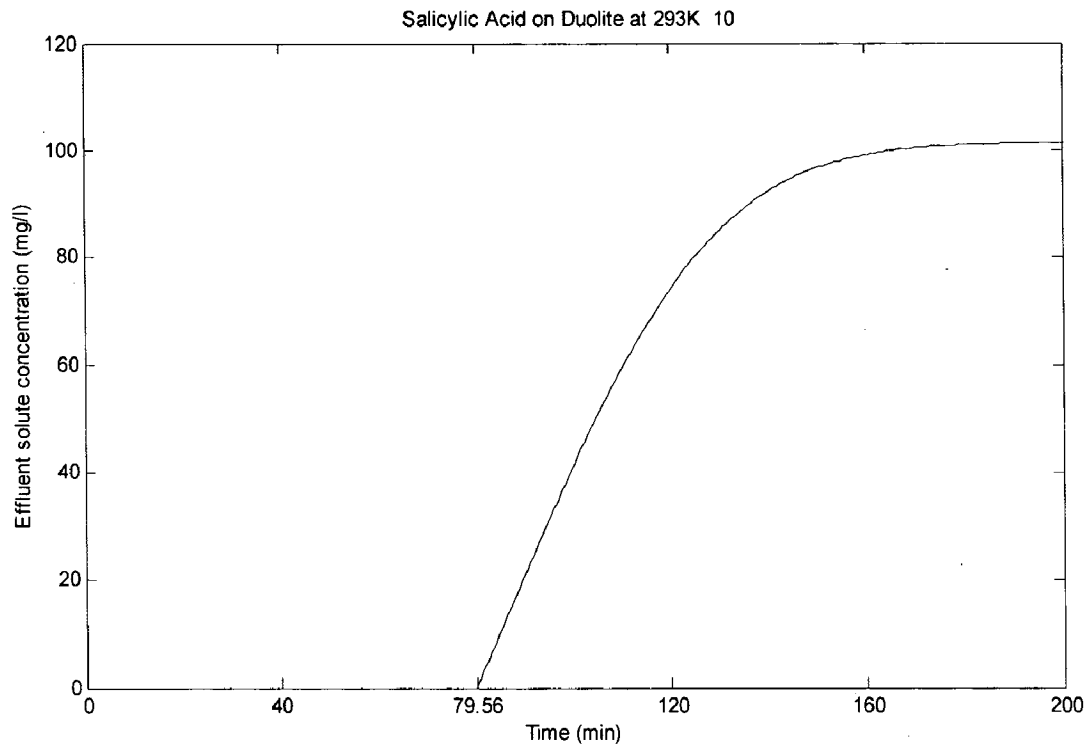


Fig. 11 Salicylic Acid on Duolite at 293 K with a flow rate of 10 ml/min

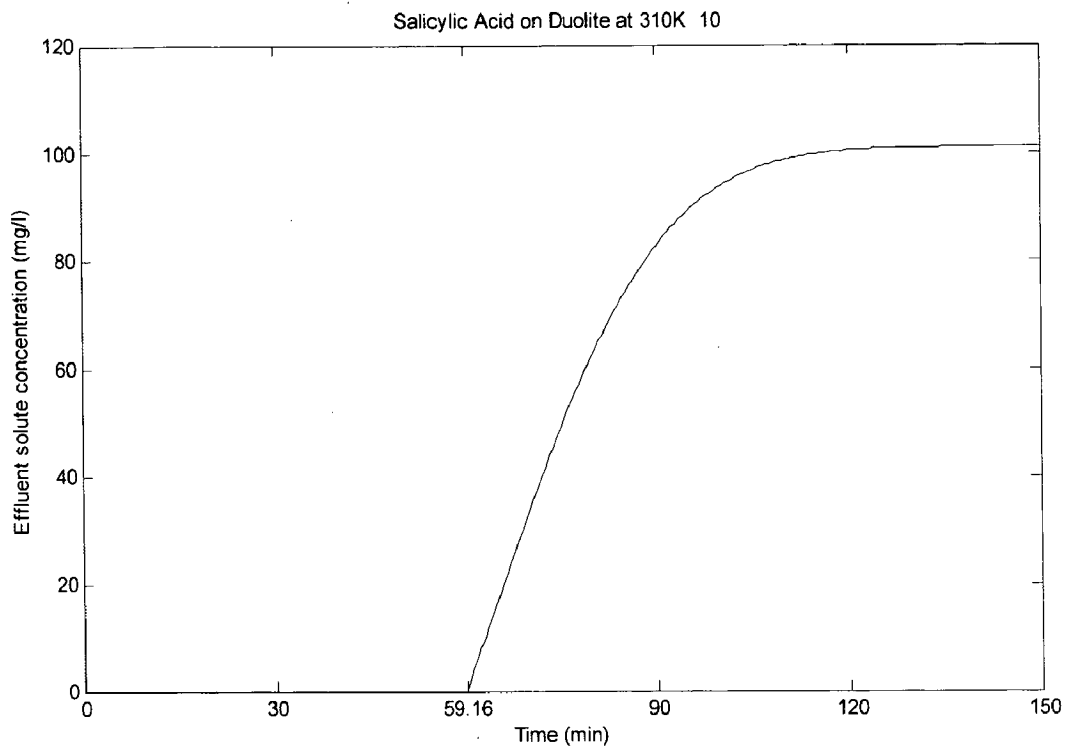


Fig. 12 Salicylic Acid on Duolite at 310 K with a flow rate of 10 ml/min

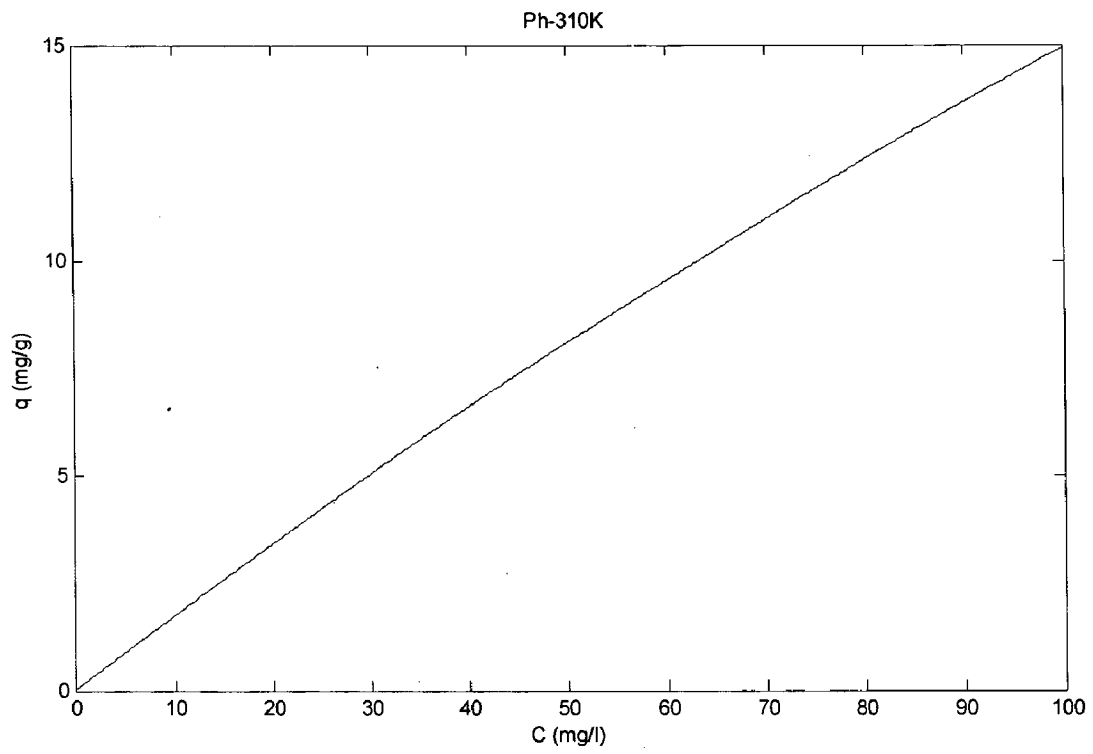


Fig.14 Langmuir Isotherm for Phenol at 310K

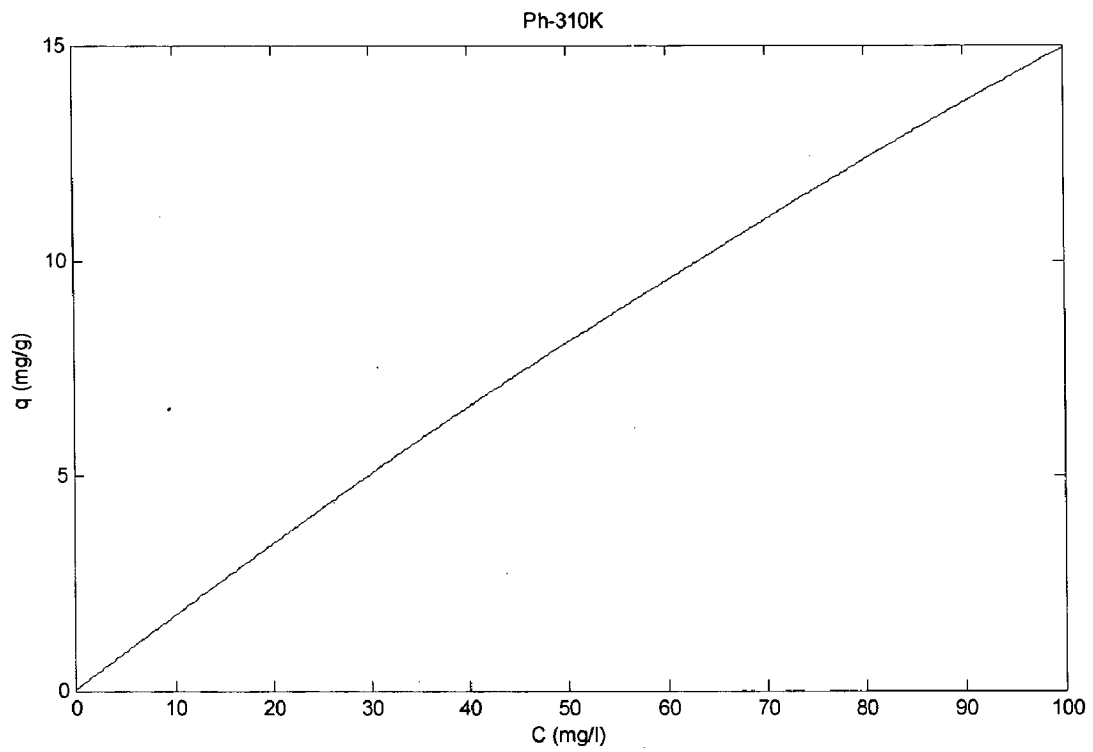


Fig.13 Langmuir Isotherm for Phenol at 310K

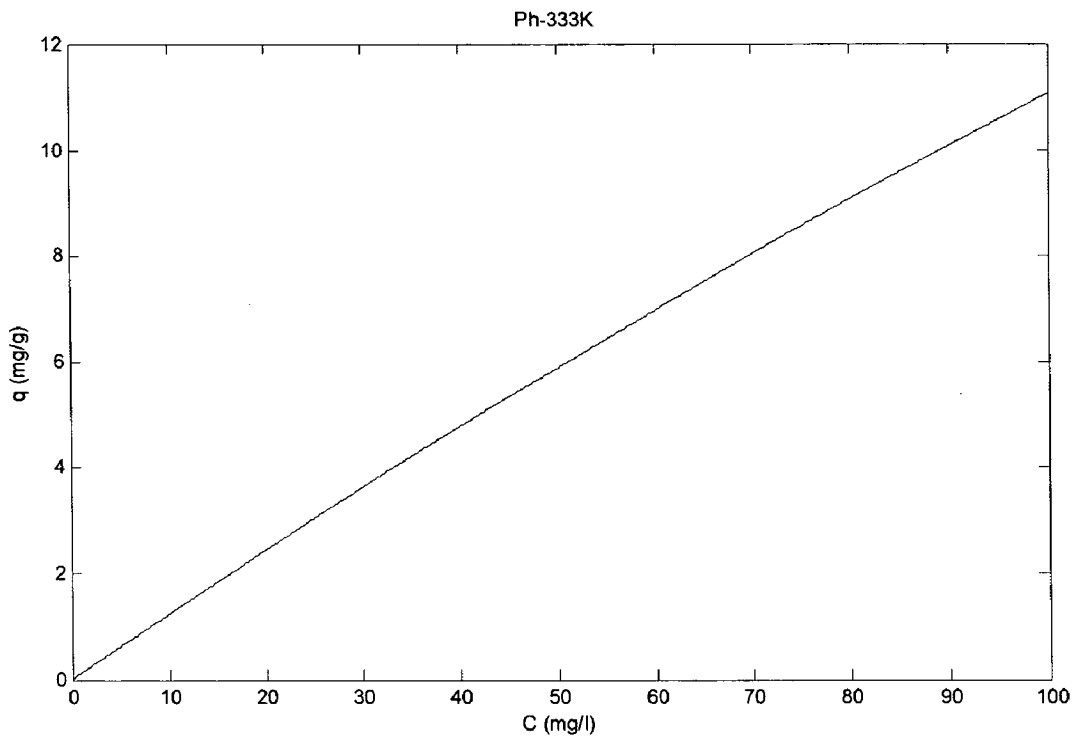


Fig.15 Langmuir Isotherm for Phenol at 333K

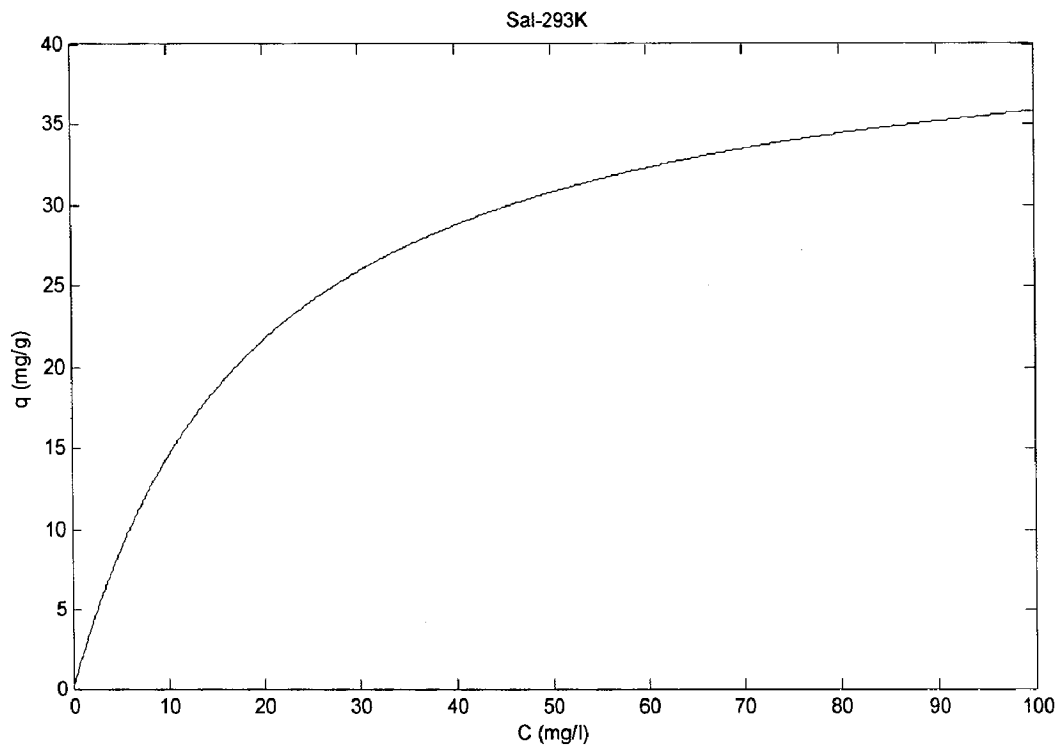


Fig.16 Langmuir Isotherm for Salicylic Acid at 293K

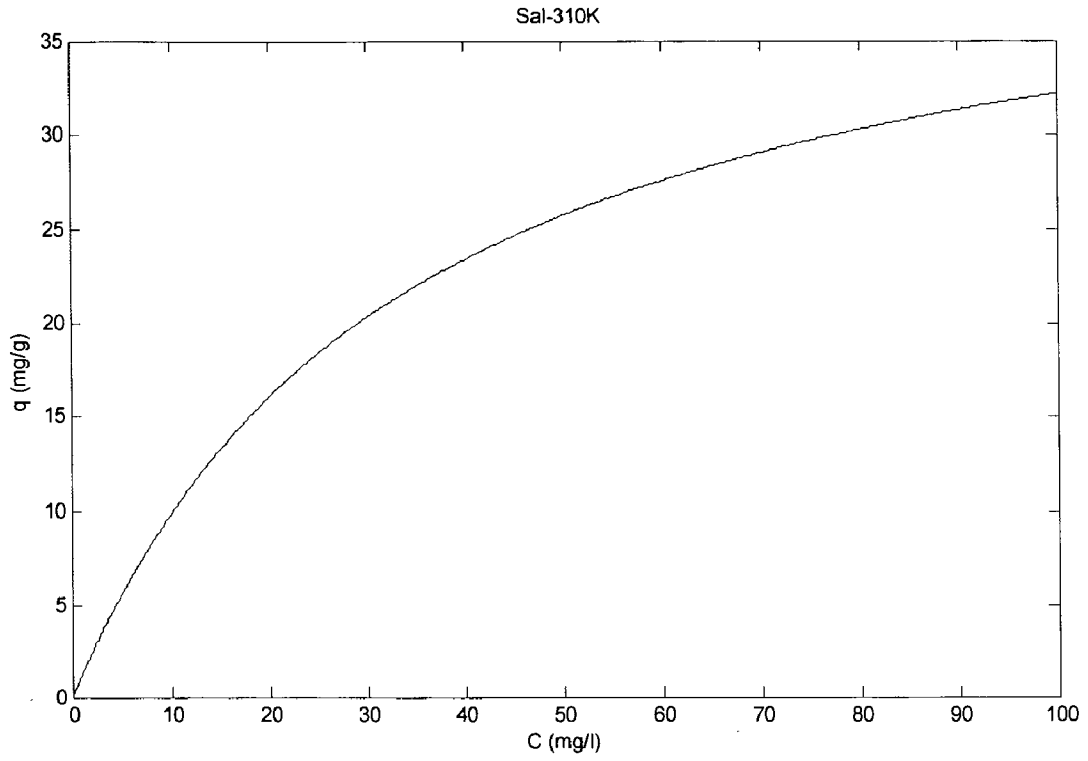


Fig.17 Langmuir Isotherm for Salicylic Acid at 310K



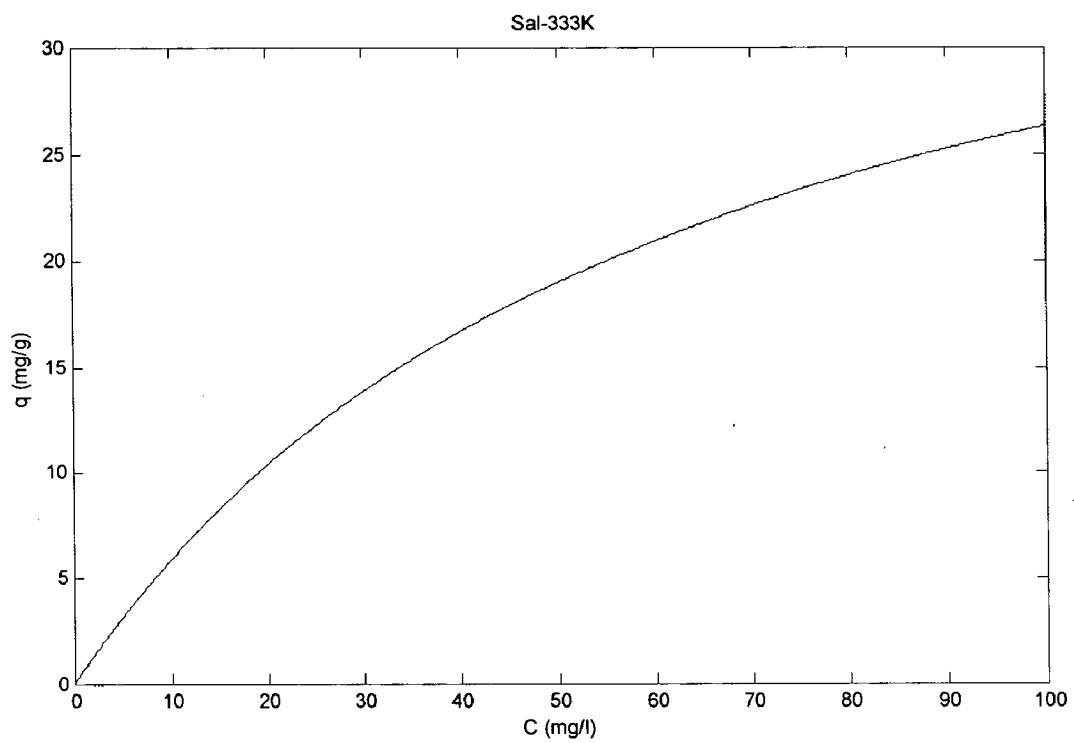


Fig.17 Langmuir Isotherm for Salicylic Acid at 333K

## CHAPTER 4: RESULTS AND DISCUSSIONS

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### 4.1 Model validation:

#### 4.1.1 Adsorption Isotherms:

As can be seen from fig.1 that the simulation results considering Langmuir Isotherm is in good agreement with the experimental ones. This confirms that the assumed Langmuir adsorption isotherm is verified.

#### 4.1.2 Fixed bed adsorption:

Fixed bed adsorption of phenol on Duolite is plotted at 293K with flow of 5.5 ml/min the literature data is also plotted in fig. 2 on the same plot. The simulated plot almost matches with that of literature profile. The ratio (LUB/L) from simulation and experiments are 0.51 and 0.46 respectively, which are in close agreement with each other. The simulated results seem to be in conservative nature.

### 4.2 Results and discussions:

#### 4.2.1 Adsorption Isotherms:

The experimental adsorbed concentrations as a function of liquid phase concentration corresponding to the phenol and salicylic acid adsorption onto each of the adsorbents at each of the temperatures considered are shown in Fig.2 respectively. The obtained fittings to the Langmuir model are shown together with the experimental points. As it may be seen, the Langmuir model well describes the equilibrium of phenol and salicylic acid onto the adsorbents used in this work. The characteristic parameters of the Langmuir model that were obtained for the adsorption of salicylic and phenol onto Duolite S861

The influence of temperature on the performance of each of these two adsorbents is reflected by these parameters. The value of  $\Delta H$  indicates that the adsorption of salicylic acid is more exothermic than that of phenol. Considering that non-specific interactions dominate in the adsorption systems, it can be seen from the fact that the net adsorption enthalpy of salicylic acid is higher than the one of phenol may be attributed to its higher molecular weight

#### 4.2.2 Fixed bed adsorption:

The fixed bed adsorption capacity increases when the temperature of operation decreases and the higher the temperature, the shorter it takes for the saturation of the bed for both the polymeric resins. It may be observed that lowering the flow-rate of the feeding leads to later breakthrough times. However, for the temperatures considered, for both the flow-rates and both the adsorbents, the beds have reached a constant-pattern. Fixed bed saturation of salicylic acid takes longer than that of phenol for both the resins employed. On the other hand, the breakthrough profiles corresponding to the adsorption of salicylic acid are more disperse than those corresponding to phenol, which is described by the model and the parameters used. In order to further compare the obtained results, the length of unused bed (LUB), which is a measure of the fixed bed performance, was obtained for all cases.

The following table gives the approximate equal values of the ratio (LUB/L) as the results obtained by the model with the available literature data. The simulated model shows sharp increase in the solute concentration after near zero values, which clearly depicts the start of the breakthrough curve. The results so obtained by the simulation are shown by the actual value of the time at which the breakthrough point is reached. The length of unused bed LUB can be calculated by the simple formula given as below:

$$\frac{LUB}{L} = \left(1 - \frac{t_{bp}}{t_s}\right)$$

where,  $L$  is the bed length (m)  $t_{bp}$  is breakthrough time (min) and  $t_s$  is the stoichiometric time (min) which can be determined from a single experimental breakthrough curve [23].

The comparison of literature data with that of model data are tabulated in tabular form in Table 5 and Table 6 as below.

**System: Phenol-Duolite**

Table 5

Flow (ml/min)	Temperature (K)	(LUB/L) <sub>simulation</sub>	(LUB/L) <sub>literature</sub>
5.5	293	0.51	0.46
5.5	310	0.44	0.4
5.5	333	0.38	0.34
10	293	0.680	0.61
10	310	0.554	0.59
10	333	0.52	0.49

**System: Salicylic Acid-Duolite**

Table 6

Flow (ml/min)	Temperature (K)	(LUB/L) <sub>simulation</sub>	(LUB/L) <sub>literature</sub>
5.5	293	0.367	0.32
5.5	310	0.466	0.41
5.5	333	0.48	0.46
10	293	0.532	0.57
10	310	0.562	0.58
10	333	0.627	0.61

#### **4.2.2.1 Effect of flow rate:**

The plots reflect the behavior of the adsorption system considered for varying solution flow rates. As can be seen from these figures that as the flow rate is increased, the adsorption extent is reducing. This can be confirmed by calculating the ratio (LUB/L) (LUB: Length of Unused Bed). The above table shows that for phenol, (LUB/L) at flow of 5.5 ml/min is 0.51 and that for flow of 10 ml/min is 0.68, keeping the temperature constant. This depicts that adsorption extent is reducing as flow is increased. Similar behavior can also be seen for salicylic acid at varied flow rates. For salicylic acid, the ratio (LUB/L) at flow of 5.5 ml/min and 10 ml/min are 0.52 and 0.532. The plots also compare the simulated data with that in the available literature. So, flow for the fixed bed adsorption is to be kept as low as possible to achieve the better utilization of the adsorber bed.

#### **4.2.2.2 Effect of temperature:**

The graphs provide the idea of behavior of the concerned adsorption system for varying temperatures. As the temperature is increased, the breakthrough point is shifted towards left. This can be easily seen with the help of the above table showing the ratio (LUB/L). For adsorption of salicylic acid at constant flow of 5.5 ml/min, the LUB/L is 0.367, 0.465 and 0.48 at a temperature of 293, 310, and 333K respectively. Similar behavior can be seen at flow of 10 ml/min; LUB/L is 0.532, 0.562 and 0.627 at a temperature of 293, 310, and 333K respectively. So, it can be concluded that the operating temperatures are chosen to be coldest temperatures for effective adsorption.

#### **4.2.2.3 Comparison of adsorption of phenol and salicylic acid:**

Fixed bed saturation of salicylic acid takes lesser time than that of phenol for both the resins employed. On the other hand, the breakthrough profiles corresponding to the adsorption of salicylic acid are more disperse than those corresponding to phenol, which is described by the model and the parameters used. Phenol being the precursor of

salicylic acid, the adsorption of both compounds onto polymeric resin Duolite S861 was compared. The equilibrium of adsorption of phenol and salicylic acid was described by the Langmuir isotherm model. From the equilibrium results, it may be seen that the capacity of Duolite S861 for phenol adsorption ( $Q = 96.13 \text{ mg g}^{-1}$ ) is nearly double than that of Duolite S861 ( $Q = 43.01 \text{ mg g}^{-1}$ ). This clearly indicates that adsorption extent of phenol on Duolite than that of Salicylic Acid is more, which is governed by the Langmuir isotherm.

## **CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS**

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### **5.1 CONCLUSION:**

The model to study the adsorption of phenol and salicylic acid onto polymeric resin Duolite is developed. The simulation results are in close agreement with that of the available literature data. The Langmuir adsorption isotherm which is assumed is also validated with the literature data. The performance of the adsorption mechanism is studied and the extent of the adsorption is calculated as the Length of Unused Bed (LUB). The effect of temperature as well as that of flow rate on the adsorption phenomenon is studied.

### **5.2 RECOMMENDATIONS:**

- Flow for the fixed bed adsorption is to be kept as low as possible to achieve the better utilization of the adsorber bed.
- From the above conclusions, it is recommended that the operating temperatures are chosen to be coldest temperatures for effective adsorption.

## REFERENCES

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- [1] **Marta Otero, Miriam Zabkova, Alirio E. Rodrigues,**  
*Separation and Purification Technology*, 45( 2), (2005), 86-95
- [2] **R.R. Davesac, L.T. Pinto, F.A. da Silva, L.M. Ferreira, A.E. Rodrigues,**  
*Chemical Engineering Journal*, 76 (2000) 115–125.
- [3] **G. Guiochon, S.G. Shirazi, A.M. Katti,**  
*Fundamentals of Preparative and Nonlinear Chromatography*, Academic Press,  
Boston, 1994.
- [4] **C.H. Giles, D. Smith, A. Huitson,**  
*Journal of Colloid Interface Science*, 47 (3) (1974) 755–765.
- [5] **R. Pigford, B. Baker, D. Blun,**  
*Industrial Engineering Chemistry Fundamentals* 12 (1973) 406–412, Press,  
London (1998).
- [6] **E. Glueckauf, J. Coates,**  
*Journal of Chemical Society* (1955) 1315–1321.
- [7] **S. Farooq, D.M. Ruthven,**  
*Industrial Engineering Chemistry Fundamentals* 29 (1990) 1084–1090.
- [8] **J.A. Silva, A.E. Rodrigues,**  
*Industrial Engineering Chemistry Fundamentals* 36 (1997) 3769–3777.
- [9] **A. Gorbach, M. Stegmaier, G. Eingenberger,**  
*Adsorption* 10 (2004) 29–46.
- [10] **D.C. Silva,**  
*Separation/reaction in simulated moving bed, application to the production of  
industrial sugars, Ph.D. thesis, Laboratory of Separation and Reaction  
Engineering, School of Engineering, University of Porto, Portugal, 2001.*
- [11] **R.C. Reid, J.M. Prausnitz, B.E. Poling,**  
*The Properties of Gases and Liquids*, McGraw-Hill International Editions, New  
York, 1988.
- [12] **C.R. Wilke, P. Chang,**  
*American Institute of Chemical Engineers Journal* 1 (1955) 264–273.



- [13] **G. Le Bas,**  
*The Molecular Volumes of Liquid Chemical Compounds, Longmans, New York, (1915).*
- [14] **G. Rexwinkel, A.B.M. Heesink, W.P.M. Van Swaij,**  
*Chemical Engineering Science 52 (1997) 3995–4003.*
- [15] **R.T. Yang,**  
*Gas Separation by Adsorption Processes, Butterworth Publishers, Stoneham, USA, 1987, p. 106.*
- [16] **W.E. Ranz, W.R. Marshall,**  
*Chemical Engineering Progress 48 (1952) 141–146.*
- [17] **C.K.D. Ko, J.F. Porter, G. McKay,**  
*Water Resources 35 (2001) 3876–3886.*
- [18] **R.H. Wijffels, M. Verheul, W.A. Beverloo, J. Tramper,**  
*Journal of Chemical Technology and Biotechnology 71 (1998) 147–154.*
- [19] **C. Costa, A.E. Rodrigues,**  
*American Institute of Chemical Engineers Journal 31 (1985) 1645–1654.*
- [20] **S. Diez, A. Leitao, L.M. Ferreira, A.E. Rodrigues,**  
*Sep. Purif. Technol. 13 (1998) 25–35*
- [21] **R.E. Treybal,**  
*Mass Transfer Operations, McGraw Hill, New York.*
- [22] **Richard D. Noble and Patricia A. Terry**  
*Principles of Chemical Separations with Environmental Applications, Cambridge University Press, 2004*
- [23] **D.M. Ruthven,**  
*Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984.*

