CHAPTER 3

ADSORPTION STUDIES: EQUILIBRIUM AND KINETICS

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3.1 INTRODUCTION

The capacity of adsorbents is characterized by equilibrium isotherm. The mathematical relationship between the capacity of an adsorbent and the concentration of the pollutant at equilibrium at a certain temperature is termed as adsorption isotherm. The capacity and rate of removal of pollutant from the solution depend upon characteristics of adsorbent, adsorbate and operating parameters such as temperature and pH. The knowledge of adsorbent capacity and how this capacity is achieved with respect to time is essential for designing an efficient adsorption unit. For designing and operating the treatment processes, one should know the adsorption isotherms, effect of operating parameters, kinetics and thermodynamics of adsorption. Tables 2.1 and 2.2 in Chapter 2 list the different isotherm models that have been used to describe different adsorbent/phenolic systems. Fly ash and activated carbon have been used as adsorbents for the present study. In this chapter the procedure to generate equilibrium and kinetic data along with theoretical background of these critical aspects of adsorption is given. Results of these studies are correlated with different isotherm models. Kinetic mechanism and parameters have been determined. The degree of closeness of isotherm models fitting the data has statistically listed and the results obtained have been discussed.

3.2 THEORETICAL BACKGROUND

3.2.1 General Description

Adsorption is a surface related phenomenon and therefore involves surface forces for accumulation and concentration of adsorbate on the adsorbent. In the adsorption of an adsorbate on a solid surface from the aqueous solution, two factors namely hydrophobic character of the adsorbent and its affinity towards adsorbent play the most important role. In turn, both the factors are affected by different properties of adsorbent and adsorbate, and conditions of the solution such as temperature and pH. According to the most acceptable concepts of adsorption, specific affinity is the result of primarily one or more of the three types of interactions such as electrical, van der Walls (VDW) and chemical. In the first type of interaction, ions of the adsorbate are attracted to the charged sites at the surface of the adsorbent due to electrostatic attraction and this type of adsorption is called exchange adsorption and come under the scope of ion exchange. Adsorption due to weak VDW is termed as physical adsorption, an ideal adsorption. As the molecule is attached to the surface by weak forces, this is free to make transitional movement within the interface. In contrast, the adsorbate and molecules on the surface undergo chemical bonding in chemisorption. Essentially, different forces combine to cause adsorption of a particular adsorbate at the surface of the adsorbent. Therefore, it is generally not easy to differentiate among the types of adsorption, e.g. the adsorption of aromatic compounds with hydroxyl and nitro group substitution on activated carbon has been reported to take place through the formation of donor-acceptor complexes of organic molecules with surface carbonyl oxygen group and the adsorption was found to be continuing even after these sites were exhausted by complexation. This type of interaction has been documented as specific adsorption. This type of adsorption may exhibit large range of adsorption energies covering the full spectrum from physical adsorption at lower end and the chemical adsorption at higher end (Mattson et al. 1971, Weber 1972). However, Table 3.1 shows some of the salient features of the physical and chemical adsorptions so that a comparison can be made for practical purpose. Barring few cases of removal of trace impurity by chemical adsorption, most of the adsorptions in separation and purification processes come in the realm of physical adsorption.

Table 3.1. Parameters of physical adsorption and chemisorption (Ruthven 1984)

Parameter	Physical Adsorption	Chemisorption
Heat of adsorption	Low, <2 or 3 times the latent heat of evaporation	High, >2 or 3 times the latent heat of evaporation
Specificity	Nonspecific	Highly specific
Nature of adsorbed phase	Monolayer or multiplayer, no dissociation of adsorbed species	Monolayer only may involve dissociation
Temperature range	Only significant at relatively low temperatures	Possible over a wide range of temperature
Forces of adsorption	No electron transfer, although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface
Reversibility	Rapid, nonactivated, reversible	Activated, may be slow and irreversible

Both the rate and extent of adsorption are influenced by the properties of the adsorbate, adsorbent, and the system parameters such as mixing, temperature and pH of the solution. These include surface area, pore sizes and their distribution, size of the adsorbent, functional groups present on the surface of the adsorbent, etc. Besides, size of the adsorbate, nature of the adsorbate, type and position of functional group present on the parent molecule, all influence the adsorption. This study includes the effect of the above properties to explore the use of fly ash as an adsorbent to treat phenolic wastewater.

3.2.2 Adsorption Equilibrium Isotherm

Various isotherm models based on thermodynamic, kinetic, and adsorption potential approaches have been reported in the literature (Tien 1994) to represent the adsorption of gases on a porous adsorbent. Their applicability has been extended to liquid systems by replacing the pressure term with concentration and changing the units of the various parameters accordingly. Adsorption from liquid solution is comparatively a complex phenomena with some of the assumptions made in development of these models for gaseous systems not fully fulfilled in liquid systems. Therefore, the representation of isotherm data in liquid systems is more or less considered empirical rather than that based on theory. Freundlich, Langmuir, Toth and modified Langmuir are some of those models encountered in liquid systems (Tien 1994). Knaebal (1995) advocated the adsorption as an important separation process in environmental applications and compiled adsorption isotherms generally used in this field. Brief description about some of the isotherms is given in the following paragraphs:

Henry's law as applicable to solution of gases in liquids is the simplest representation of adsorption isotherm data, in which the amount adsorbed is directly proportional to the equilibrium concentration of adsorbate in solution. This isotherm is obtained at very low concentrations of adsorbate. Adsorption layer formed in such systems is incomplete and the amount adsorbed is only a fraction of the monolayer capacity. This is a one-parameter isotherm (Ruthven 1984).

The two-parameter isotherms are those of Langmuir, Freundlich and BET. Langmuir isotherm (1918) (Eq. 3.1) also called ideal localized monolayer model assumes that:

(i) The adsorption of adsorbate molecules takes place at well-defined localized sites.
(ii) All the adsorption sites are energetically similar and only one molecule is attached to each site
(iii) Adsorbed molecules do not interact with each other and they cannot migrate across the surface.

Langmuir isotherm: $$Q_e = \frac{QbC_e}{1+bC_e} \tag{3.1}$$

The monolayer capacity(Q_0) determined from the Langmuir isotherm defines the total capacity of the adsorbent for a particular adsorbate. At low concentrations, this reduces to Henry's law type isotherm. However, the assumption of homogeneous surface of adsorbent made in the derivation of this isotherm may not be valid in case of adsorbents having heterogeneous surface such as activated carbon and fly ash.

In order to extend the applicability of the Langmuir's isotherm to heterogeneous surfaces, these surfaces were considered to be composite of homogeneous patches, and the Langmuir's isotherm was written for each homogeneous patch. Assuming the distribution of energy to be continuous, the Langmuir equations for all the patches can be integrated over the entire surface. This results in an isotherm of type commonly referred to as Freundlich's isotherm (Freundlich 1926). Though Freundlich isotherm (Eq. 3.2) is the simplest for data representation, this has one flaw that this does not reduce to Henry's law at decreasing concentrations.

Freunlich isotherm: $$Q_e = K_f C_e^{1/n} \qquad (3.2)$$

Brunauer, Emmett and Teller (BET) developed an isotherm to represent the data of multilayer adsorption. This was obtained by generalization of Langmuir's idealized monolayer treatment. It was assumed that the adsorption takes place in multilayer even before monolayer coverage is complete. The layer beneath serves as a site for the layer above. The heat of adsorption of the second and subsequent layers is assumed to be equal to that of liquefaction of the bulk liquid and therefore this is different from the heat of adsorption of first layer. This is a two-parameter isotherm. Though this is seldom used for data correlation and representation, this is used in estimating the surface area of the adsorbents based on the assumption of monolayer coverage by the known size molecules of a gas. In some systems, a lacuna was felt in representing the experimental data with the above isotherms. This led to the development of three parameter isotherms. These are, in general, modifications of Langmuir isotherm to account for non-linearities and non-idealities of a particular adsorbate-adsorbent interaction. This class of isotherms includes those of Redlich-Peterson (Eq. 3.3), Toth (Eq.3.4) and Radke Praunitz (Eq. 3.5) equations. These three isotherms reduce to Henry's law at very low concentrations. Redlich-Peterson (1959) equation approaches Freundlich's equation at large concentrations. Radke and Prausnitz (1972) used this equation in a slightly different form. He transformed the Redlich-Peterson equation in such a way that the first term is similar to Henry's law and the second term resembles the Freundlich's isotherm. Therefore, this can be thought of as the combination of Henry's and Freundlich's isotherms. Toth started with Langmuir isotherm. Further, Toth found that typical experimental results on heterogeneous surfaces fall between the limits set by the Langmuir and Freundlich isotherms.

Redlich Peterson isotherm: $Q_e = \frac{K_1 C_e}{1 + K_2 C_e^{m}}$ (3.3)

Toth isotherm: $Q_e = \frac{T C_e}{\left(a + C_e^{th}\right)^{1/th}}$ (3.4)

Radke Prausnitz isotherm: $\frac{1}{Q_e} = \frac{1}{K C_e} + \frac{1}{k C_e^{1/p}}$ (3.5)

Fritz and Schlunder (1974) proposed a general empirical relationship for representing the bisolute data obtained in their research work on adsorption of p-nitrophenol and phenol on activated carbon. Fritz and Schlunder equation (Eq. 3.6) is general in sense that this reduces to well-known relationship, which can also be used for single solute data. For the single solute data adsorption relationship can be further modified to obtain Radke Prausnitz and Freundlich isotherms.

Fritz Schlunder isotherm: $Q_e = \frac{a_1 C_e^{b_1}}{1 + a_2 C_e^{b_2}}$ (3.6)

3.2.3 Adsorption Thermodynamics

Experimentally, the heat change resulting from adsorption can be determined in conjunction with the van't Hoff equation by carrying out adsorption measurements at different temperatures, where K= 1/b is the equilibrium constant for the adsorption process at a specified temperature.

$$\frac{d \ln K}{dT} = -\frac{\Delta H}{RT^2} \quad (3.7)$$

The change in surface free energy resulting from adsorption (ΔG) can be evaluated using:

$$\Delta G = -RT \ln K \quad (3.8)$$

Using a form of the equation (3.8) for the Gibbs free energy changes and its rearrangement leads to an estimation of the entropy change (ΔS) for the resulting adsorption process.

$$-\Delta S = \frac{\Delta H - \Delta G}{T} \tag{3.9}$$

3.2.4 Adsorption Kinetics

Adsorption is time-dependent process and the knowledge of the rate of uptake is essential for selecting and designing the process. Kinetic analysis (Yiacoumi and Tien 1995, Chen et al. 2001) not only allow estimation of sorption rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms. It must be stressed though that the problem of finding an appropriate conversion function with time is much simpler than establishing a real mechanism for process. A satisfactory rate equation does not always provide enough information to establish the reaction mechanism but fortunately this is not a requirement for process equipment design. So, the calculated kinetic parameters can be of a great practical value for technological applications since kinetic modeling successfully replaces time and material consuming experiments.

The main issue when searching for an appropriate sorption mechanism is to select a mathematical model that not only fits the data with satisfactory accuracy but also complies with a reasonable sorption mechanism. Thus, in order to identify the correct mechanism several models must be checked for suitability and consistency in a broad range of the system parameters. According to this, reaction based and diffusion-based tests available in literature applied to similar systems are required to be checked to increase the confidence in simulating our data.

It is found that most simple reactions have integer orders between zero and three (Lazaridis et al. 2003). For the sorption the values of order is customarily one or two (Ho and McKay 1998).

In literature it is found that Lagergren's pseudo-first order kinetic expression is applicable to sorption systems, it can be represented in the following linear form (Jadhav and Vanjara 2004):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3.10}$$

$$\ln(q_e - q_t) = \ln(\mathrm{q_e}) - k_1 t \tag{3.11}$$

where, the term k_1 refers to the pseudo-first order rate constant for the sorption process, q_e is the amount of phenols adsorbed at equilibrium and q_t is the amount of phenols adsorbed at time t.

The application of pseudo-second order kinetics given by Ho and Mckay (Eq. 3.12) to the overall rate of the sorption process can be used to assess the dependency of the process on the sorbed adsorbate concentration (Kelleher et al. 2002):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3.12}$$

where, k_2 is the overall rate constant for the sorption process, Integration of Eq.(3.12) leads to Eq. (3.13):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{3.13}$$

where, h is the initial sorption rate and is given by

$$h = k_2 q_e^2 \tag{3.14}$$

Identification of the individual steps in the adsorption process can assist in determining the factors that govern the overall rate of phenols uptake by adsorbent. Three main processes are thought to influence the kinetics of the adsorption process. (Seader and Henley 1998).

(i) Adsorbate transfer from the bulk liquid phase to the outer solid surface of the adsorbent.

(ii) Transport of adsorbate from the outer surface into the pores and to the surface of the adsorbent.

(iii) Adsorption on the porous surface

In case of chemisorptions, the third step may be slow and even controlling. However, for physical adsorption, third step is almost instantaneous as it depends only on collision frequency and orientation of the molecules with the porous surface. Therefore, first two steps determine the overall kinetics in case of physical adsorption. The above three steps are followed in reverse order during regeneration step. The first step is supposed to take place through the liquid film surrounding the particle. The transport inside the solid particle takes place either by pore diffusion, surface diffusion, or by both. According to the process conditions, the overall kinetics is governed by one of the steps. The knowledge of this step is very significant so that the process may be described in terms of appropriate rate expression and rate parameters. If sufficient turbulence is provided then due to vigorous shaking, the external liquid film will offer negligible mass transport resistance.

For transport inside the porous adsorbent, rate of mass transport is represented by Fickien diffusion and the diffusivity term in it. The diffusivity coefficient includes the effect of the tortuosity, pore size distribution and porosity on the mass transfer. No bulk flow is assumed inside the adsorbent. In writing the mass balance, the adsorbent particle is assumed to be spherical. A general description of intraparticle transport considers both the pore and surface diffusion to be operative and can be written in mathematical form as

$$\varepsilon_b \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left[D_p\, r^2 \frac{\partial c}{\partial r}\right] + \frac{\rho_P}{r_2}\frac{\partial}{\partial r}\left[D_s r^2 \frac{\partial q}{\partial r}\right] \qquad (3.15)$$

For solving Eq.(3.15), the knowledge of boundary conditions is desirable. Also, one more relationship between pore phase concentration and the adsorbate phase concentration, q is essential. This is given by appropriate isotherm equation of the form

$$q = f(c)$$

On differentiation, it becomes

$$dq = \mathrm{f}(\mathrm{c})\,\mathrm{dc} \qquad (3.16)$$

Substitution of Eq.(3.16) in Eq.(3.15), one gets after rearrangement

$$\varepsilon_b \frac{\partial c}{\partial t} + \rho_p \frac{\partial c}{\partial t} = \frac{\rho_\mathrm{p}}{\mathrm{r}^2}\frac{\partial}{\partial r}\left[D_p r^2 \frac{\partial q}{\partial r}\right] \qquad (3.17)$$

Where De is defined as

$$D_e = \frac{D_p}{f(c)}\frac{1}{\rho_p} + D_S \tag{3.18}$$

For process strictly controlled by pore diffusion, Eq.(3.17) reduces to Eq.(3.19) and when the surface diffusion defines the rate controlling step, the Eq.(3.17) becomes Eq. (3.20),

$$\varepsilon_b \frac{\partial c}{\partial t} + \rho_p \frac{\partial c}{\partial t} = \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left[D_p r^2 \frac{\partial q}{\partial r}\right] \tag{3.19}$$

$$\frac{\partial q}{\partial t} = \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial \mathrm{r}}\left[\mathrm{D}_s r^2 \frac{\partial q}{\partial r}\right] \tag{3.20}$$

In liquid adsorption systems, surface diffusion has been found to control the adsorption kinetics. Therefore, Eq.(3.20) is to be solved either numerically in order to determine the uptake of the adsorbate on the adsorbent. Appropriate initial and final boundary conditions for this equation are;

$$q(r,0) = q(t=0) \tag{3.21}$$

$$q(r,t) = q_s(t) \tag{3.22}$$

$$\frac{\partial q}{\partial r}_{r=0} = 0 \tag{3.23}$$

With both the above boundary conditions, the exact solution to the above Eq. (3.23) is as follows:

$$F = \frac{\bar{q} - q(t=0)}{q_0 - q(=0)} = 1 - \frac{6}{\pi}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_e t}{r_o^2}\right) \tag{3.24}$$

where, $\bar{q}$ is average solid phase concentration and can be obtained by the equation given below:

$$\bar{q} = \frac{3}{r_o^3}\int_0^{r_o} q r^2 \,\mathrm{dr} \tag{3.25}$$

Eq. (3.24) contains an infinite series, and hence requires much computation time memory. This equation is the design equation for the graphical method proposed by Boyd et al. (1949) for diffusion-controlled mechanism. In this method, equation is written as:

$$\mathrm{F} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\alpha}\frac{1}{n^2}\exp\left[-\mathrm{n}^2 Bt\right] \tag{3.26}$$

$$\mathrm{B} = \frac{\pi^2 Di}{r_0^2} = time\,\mathrm{constat} \tag{3.27}$$

Here, D_i, is the effective diffusion coefficient of the phenol in the adsorbent phase, r_0 is the adsorbent particle radius, assumed to be spherical, B is the slope of the Bt *versus* time plots, and n=1, 2, 3...are the integers defining the infinite series solution obtained by a fourier type of analysis. *Bt* values can be derived for each *F* value by the use of Reichenberg's table(1952). A plot of *Bt versus* time is employed to assess the contributions of film and particle diffusion on rates of adsorption. If a linear relationship is obtained and passes through the origin then it is total particle diffusion controlled process and if a linear relationship is observed but does not pass through the origin then it is film and particle diffusion controlled process. Where as if nonlinear relationship is observed then it is film diffusion controlled process.

Approximations to the Eq. (3.24) are available and are useful in determining the rate controlling step and effective diffusion coefficient. If fractional uptake is more than 0.7 then one may retain only the first term of Eq.(3.24) for calculations (Ruthven 1984)

$$F = 1 - \frac{6}{\pi^2}\exp\left(-\frac{\pi^2 D_e t}{r_o^2}\right) \tag{3.28}$$

An empirical approximation given by Vermeulen (1953) and Urano and Tachikawa (1991) applicable for entire range of fractional uptake can be considered. It is given as,

$$F = 1 - \frac{6}{\pi^2}\exp\left(-\frac{\pi^2 D_e t}{r_o^2}\right)^{0\ 5} \tag{3.29}$$

A linear form of representation is

$$\ln\left(\frac{1}{1-F^2}\right)=\mathrm{Kt} \tag{3.30}$$

$$where\ \mathrm{K}=\frac{\pi^2\mathrm{D_e}}{\mathrm{r_o}^2} \tag{3.31}$$

ln [1 / (1-F^2)] versus t plot will directly give the value of effective diffusion coefficient, De. However, for initial region, approach of plotting F versus $t^{0.5}$ is useful for identifying the rate controlling mechanism and has been used by Weber and Morris (1963) in their pioneering study.

$$F=\frac{6}{\sqrt{\pi}}\left(\frac{D_e t}{r_o^2}\right)^{0.5} \tag{3.32}$$

If particle diffusion is the absolute rate-controlling step at a certain concentration, this line will pass through the origin. Alternatively, film diffusion control will be rate limiting if graph of ln (1-*F*) *versus* time yields a straight line.

The activation energy (E_d), pre-exponential factor (D_0) and entropy of activation for diffusion controlled process can be calculated using following equations (Varghese 2003).

$$D_i=D_0\exp\left(\frac{\mathrm{-E}}{\mathrm{RT}}\right) \tag{3.33}$$

$$D_0=2.72d^2\frac{KT}{h}\exp\left(\frac{\Delta S^{\#}}{R}\right) \tag{3.34}$$

$$S^{\#}=8.314\ln\left(\frac{\mathrm{D_0}}{4.294x10^{-6}}\right) \tag{3.35}$$

3.3 EXPERIMENTAL

3.3.1 Material

Stock solution of 5,000 mg/l (5 g/l) of phenol, 3-aminophneol (Loba Chemie, Mumbai), catechol (National Chemicals, Baroda), resorcinol, hydroquinone (Qualigen fine chemicals, Mumbai) and 1000 mg/l of 2-aminophenol (National Chemicals, Baroda) were prepared by dissolving in distilled water. All the phenols were of AR grade and used as received.
Activated carbon (IC 810) obtained from Gujarat Industrial Carbon Ltd., Ankleshwer was used.

Fly ash was obtained from the four different thermal power plants using different types of fuels, (located in SOUTH GUJARAT region). The samples of fly ash were obtained from:

(i) Fly ash A: Lignite based fly ash from Gujarat Industrial Power Corporation Ltd., Nani-Naroli (Mangrol), Dist. Surat.
(ii) Fly ash B: Coal based fly ash from Gujarat Electricity Board, Ukai, Dist. Surat
(iii) Fly ash C: Coal based fly ash from Central Paper & Pulp Mill, Fort Songadh Dist. Surat.
(iv) Fly ash D: Bagasse based fly ash from Sayan Sugar Industries, Sayan , Dist. Surat.

Samples of about 5 kg of each type were collected by the coning and quartering method from cyclone separator or electrostatic precipitator. No pretreatment was given to fly ash A, B, D and activated carbons whereas samples of fly ash C were treated with dilute HCl to reduce the pH. These adsorbents were washed several times with distilled water to remove any leachable matter attached to these particles. Adsorbents were considered fit for use when the distilled water coming after the washing was visibly clear. After washing, adsorbents were dried in an oven at 105°C for 6 h. `HCl and NaOH, used to adjust the pH of the working solution, were of LR grade supplied by E. Merck, Mumbai, India.

3.3.2 Methods

3.3.2.1 Phenol Estimation

4- Amino antipyrine colorimetric method (5530 D APHA/ AWWA) has been used for phenol, catechol, resorcinol, 2-aminophenol and 3-aminophenol estimation using visible spectrophotometer (Systronic make VISIMAX-VISISCAN 167). Hydroquinone was estimated by direct photometric method (Ayranci and Duman 2005) using UV- VIS diode array spectrophotometer (HP 8452 A) at 288.5 nm. There are two absorption bands having significantly different λmax, 220.5 and 288.5 nm. Although the calibration data were derived at both λmax values for hydroquinone, only one of them at 288.5 nm was utilized since regression coefficient was found to be higher at this wavelength for calibration curve. Calibration curves for all phenols are given in Appendix A (Figs. A-1 to A-9).

pH measurements were done using a pH meter of Analab Instruments, Baroda. Sample shaking was done in a thermostatic water shaker bath of Nova Instruments Pvt. Ltd., Ahmedabad at 100 rpm for all the experiments.

3.3.2.2 Equilibrium Studies

Batch equilibrium studies were performed mainly for different adsorption isotherm calculations. The initial pH of the feed solution of a known concentration was adjusted by adding dilute HCl / NaOH and a known amount of adsorbent to 100 ml of the solution in a 250 ml stoppered conical flask. The flasks were shaken in a thermostatic shaker bath at 100 rpm at 30, 45 and 60°C. After equilibration the contents of the flask were filtered and the residual concentration of phenols was determined by spectrophotometric method described above. The average of initial and final pH was also observed. Percentage of phenol adsorbed was determined from the ratio of phenol adsorbed by the adsorbent and the initial concentration of phenols in the aqueous phase. The amount of compound adsorbed on sorbent was calculated as:

$$Qe = \frac{(Co - Ce) \times V}{M} \qquad (3.36)$$

Equilibrium studies were followed for 4 h and it has also been performed for finding the effect of parameters like dosage, pH, and presence of salt.

3.3.2.3 Kinetic Studies

In batch kinetic study of adsorption of phenols, 100 ml solution of desired concentration of phenol (25-500 ppm) was taken in stoppered conical flask and kept in a thermostatic shaker bath. After the temperature of the solutions reached the desired value (30-60°C), known amount of adsorbent was added to each flask. This time was taken as zero. All the experiments were performed after optimizing the amount of adsorbent required for each system. The optimum dosage of adsorbents was used for experiments. The flasks at pre-specified time interval (5 min- 240 min.) were taken out and filtered. The filtrate was used for the measurement of residual phenol concentration after dilution. The kinetics of the phenolic compounds was followed for 4 h. The ratio of amount of adsorbate adsorbed at any time (Qt) and the amount adsorbed at the time of equilibrium (Qe) is called fractional uptake (F).

$$Q_t = \frac{(C_o - C_t)\times V}{M} \tag{3.37}$$

$$F = \frac{Q_t}{Q_e} = \frac{C_o - C_t}{C_o - C_e} \tag{3.38}$$

3.4 RESULTS AND DISCUSSION

3.4.1 Sample Characterization

Detailed chemical analysis (Vogel, 1989, APHA/AWWA) of all the adsorbents is summarized in Table 3.2. Phase identification by X-ray diffraction was carried out at SICART. X -ray diffraction patterns of the different fly ash samples(Figs. A-10, A-11 A-12, and A-13 in Appendix A) provide d-spacing value, which reflect the presence of Mullite, Haematite, Quartz, and Alumina, TiO_2(Rutile), TiO_2 (Anatase) and MnO_2. Heavy metal elements were analysed with AA100 of Perkin Elmer make Atomic absorption spectrometer.

Analyses of physical properties of adsorbents are presented in Table 3.3. BET-N_2 surface area of all the adsorbents was got done at CSMCRI (Central Salt and Marine Chemicals Research Institute), Bhavnagar, using Micromeritics make BET surface area analyzer. Surface areas of these adsorbents, measured by BET apparatus, were found to be 0.75, 23.66, 3.26, 81.31 and 671.182 m^2/g for Fly ash A, B, C, D and commercial activated carbon respectively. All other parameters listed in Table 3.3 were measured as per IS-1350.

Table 3.4 shows different size analysis of the adsorbents, which has been done by laser particle size analyzer at SICART. The major fraction in fly ash A, B, C and D is in the range 90-140 μm.

Table 3.2. Chemical composition of different fly ash

Parameters	Fly Ash A	Fly Ash B	Fly Ash C	Fly Ash D
% SiO2	67.80	63.70	65.88	61.48
% Al_2O_3	23.44	24.60	23.60	5.96
% Fe_2O_3	5.26	7.20	6.21	17.05
% P_2O_5	0.01	0.18	0.15	0.30
% SO_3	0.25	0.20	0.55	0.58
% CaO	0.50	0.40	0.48	3.10
% MgO	0.20	0.14	0.22	1.68
% Na_2O	0.24	0.20	0.18	0.18
% K_2O	0.70	0.58	0.80	0.40
Heavy metal elements				
Cd, mg/kg	6.0	8.8	9.0	Nil
Cr, mg/kg	68	74	97	Nil
Cu, mg/kg	80	260	245	Nil
Ni, mg/kg	12	20	28	Nil
Pb, mg/kg	40	46	76	Nil
Zn, mg/kg	72	80	98	Nil
As, mg/kg	67	78	74	Nil
Mn, mg/kg	14	22	26	0.6

Table 3.3. Physical properties of adsorbents

Parameters	**Fly Ash A**	**Fly Ash B**	**Fly Ash C**	**Fly Ash D**	**Commercial Activated Carbon**
BET surface Area(m^2/g)	0.75	23.66	3.26	81.31	671.18
Iodine Number	419	404	117.6	443	483
Carbon content (g/kg)	3.56	108.8	19.88	> @5%	> @99 %
pH of 10 % solution	8.55	7.65	12.99	8.97	10.08
Bulk density (g/cc)	1.11	0.58	0.66	0.3560	0.5
% Moisture	0.11	0.69	1.42	6.85	8.9
% Ash	99.32	90.43	93.57	87.29	90.10
% Loss on ignition	0.68	9.57	6.43	12.71	9.9
Hardness	0.026	0.156	0.684	0.729	0.196

Table 3.4. Size analysis of the fly ash and activated carbon

Adsorbent/ Size fraction	**<10%**	**<50%**	**<90%**	**Volume mean diameter**
Fly ash A	1.98μm	10.28μm	92.16 μm	30.1μm
Fly ash B	3.30μm	24.92μm	99.36 μm	41.0μm
Fly ash C	4.57μm	33.01μm	109.25μm	46.6μm
Fly ash D	15.26μm	54.96μm	139.94μm	71.3μm
Commercial Activated carbon	-	-	-	4-8 mm

The composition of activated carbon and fly ash (Table 3.2) reveals that, the major constituents are silica and alumina. Silica contains oxygen bridges between silicon atoms. The central ion of silicates (Si^{4+}ion) has a very strong affinity for electrons; therefore, the oxygen atoms bound to silicon ion, have a very low basicity causing the silica surface to act as a very weak acid. The oxygen atoms on the silica surface are free to react with water, forming surface silanol groups. Silica content plays a vital role in the adsorption of cations. The anions are probably adsorbed on the alumina surface because of strong tendency for chemical bonding between the anionic group and alumina. Studies of Vasudevan and Stone (1998) indicate involvement of other metal oxides in adsorption of hydroxy and aminophenols. Being of clay origin and generated at high temperature (>1000°C), the fly ash was found to have the properties like porosity, high specific surface and chemical inertness to water and dilute acids, which make it suitable for adsorption in aqueous media.

`3.4.2 Effect of Initial Concentration and Contact Time

Effect of initial concentration on adsorption of all the phenols on fly ash A, B, D and activated carbon were studied by changing initial concentrations from 25 to 500 ppm at 30, 45 and 60°C. For fly ash C, initial concentration range of 25 to 100 ppm was studied for all the phenols. Optimum mass of adsorbent, neutral pH, stirring speed of 100 rpm and particle size range were kept constant for all the experiments. The representative plots of percentage removal of 3-aminophenol/fly ash A system versus time are given in Figs. 3.1 to 3.3 for all the three temperatures. Similar types of plots are obtained in case of adsorption of phenol, catechol, resorcinol, hydroquinone, 2-aminophenol and 3-aminophenol on fly ash A, B, C, D and commercial activated carbon. Percent removal with respect to initial concentration for all these systems is given in Table 3.5. From the plots, it can be seen that percentage removal increases with increase in time and after 80-100 minutes it becomes almost constant. It is also found that about 50% of adsorption of phenols on fly ash and activated carbon occurred within first 20-30 min. The percentage removal on fly ash A decreased from 50.3 % to 10.3 % with increasing phenol concentration. The adsorption rate slowed down with increase in initial phenol concentration from 25 to 500 ppm as a result equilibrium time increased from 80 to 240 min. Therefore, the kinetic studies were performed for 240 min in all the experiments.

The percentage adsorption of phenol decreased from 50 to 10% for fly ash A, 55 to 14% for fly ash B, 24 to 11% for fly ash C, 100 to 48% for fly ash D and 100 to 63% for activated carbon respectively at 30°C. Similar trend in other phenols studied (catechol, hydroquinone, resorcinol, 2-aminophenol and 3-aminophenol) was observed on all these adsorbents. The higher percentage removal at low concentration is attributed to the availability of greater surface area with active centers on the adsorbent for less amount of adsorbate. However, the amount of adsorbate adsorbed seems to increase with initial concentration, which is in agreement with the finding that the rate of uptake of adsorbate is found to increase nonlinearly with increasing concentration of solute. (Weber and Morris 1963)

Table 3.5. Effect of initial concentration on % removal of phenols
[Dose of adsorbent = optimum, contact time= 4 h, pH= 7.0]

System	Conc. (ppm)	Temp(°C) 30	45	60	System	Conc. (ppm)	Temp(°C) 30	45	60
Fly ash A systems									
Phenol / Fly ash A	25	50.3	49.1	48.4	**Resorcinol/ Fly ash A**	25	43.4	40.6	39.62
	50	37.7	36.8	36.5		50	36.0	33.6	29.9
	100	33.5	32.3	31.1		100	70.92	26.6	26.0
	200	21.5	20.1	19.3		200	20.1	17.2	16.6
	300	16.4	14.8	14.7		300	15.2	13.4	11.4
	400	13.2	12.6	11.4		400	12.7	10.9	8.9
	500	10.4	10.1	9.4		500	10.40	8.98	7.80
Catechol/ Fly ash A	25	70.0	67.5	65.0	**Hydroquinone/ Fly ash A †**	25	70.0	70.0	66.7
	50	62.5	61.3	55.0		50	57.6	59.32	57.63
	100	56.3	53.1	50.0		100	54.2	51.1	40.4
	200	49.2	45.3	44.5		200	47.87	46.8	40.4
	300	45.3	39.6	37.5		300	43.7	43.0	36.6
	400	40.6	33.6	29.7		400	38.3	37.23	34.0
	500	36.3	28.1	24.4		500	35.59	33.89	31.35
2-Aminophenol/ Fly ash A	25	42.2	40.6	40.6	**3-Aminophenol/ Fly ash A**	25	44.8	40.0	36.0
	50	35.2	34.4	32.8		50	40.1	36.4	26.4
	100	26.5	25.5	24.5		100	35.0	30.5	19.0
	200	19.5	17.6	17.1		200	30.2	22.7	12.7
	300	14.7	14.0	14.0		300	23.7	16.3	9.32
	400	12.2	11.2	11.2		400	17.7	12.5	7.2
	500	9.8	9.0	9.0		500	14.4	10.2	6.6
Fly ash B sytems									
Phenol/ Fly ash B	25	54.7	54.1	52.8	**Resorcinol/ Fly ash B**	25	48.1	44.2	42.5
	50	46.9	45.3	44.7		50	39.6	33.0	34.0
	100	39.0	36.2	35.8		100	34.9	26.0	24.9
	200	26.2	26.0	25.4		200	24.0	21.3	18.9
	300	21.4	20.6	18.0		300	17.3	15.9	13.8
	400	16.9	16.3	14.4		400	13.6	12.7	11.4
	500	13.7	13.5	11.7		500	11.3	9.9	9.2
Catechol/ Fly ash B	25	71.9	70.0	67.5	**Hydroquinone/ Fly ash B †**	25	66.1	62.7	62.7
	50	69.9	68.8	62.5		50	61.0	59.3	58.8
	100	60.9	56.3	51.6		100	55.1	50.0	49.2
	200	52.3	49.2	44.5		200	45.3	43.2	41.5
	300	43.8	40.1	36.5		300	35.0	31.1	28.5
	400	39.5	35.5	32.0		400	28.7	23.8	23.3
	500	33.8	29.4	27.5		500	25.4	18.6	18.6

Table 3.5. Effect of initial concentration on % removal of phenols
[Dose of adsorbent = optimum, contact time= 4 h, pH= 7.0] **(Continued)**

System	**Conc. (ppm)**	**Temp(°C)** 30	45	60	**System**	**Conc. (ppm)**	**Temp(°C)** 30	45	60
2-Aminophenol/ Fly ash B	25	45.3	44.5	41.4	**3-Aminophenol/ Fly ash B**	25	48.41	46.0	44.8
	50	41.4	40.2	38.3		50	41.2	39.0	38.0
	100	36.6	35.6	34.6		100	37.5	34.0	30.0
	200	31.7	30.2	24.9		200	31.9	28.5	26.2
	300	23.8	22.6	17.9		300	26.50	21.3	18.5
	400	19.5	18.3	16.3		400	20.0	16.2	15.0
	500	16.0	15.0	13.1		500	16.4	13.2	11.6
Fly ash C Systems									
Phenol	25	24.4	22.9	22.7	**Resorci- -nol**	25	21.2	19.6	18.0
	50	18.0	16.1	14.1		50	14.9	12.5	11.3
	75	13.9	12.0	10.3		75	11.7	10.2	8.6
	100	10.7	9.9	8.7		100	10.2	9.0	7.8
Catechol	25	17.5	16.6	15.0	**Hydro quinone †**	25	21.3	18.0	10.1
	50	12.5	11.3	9.4		50	14.4	13.4	9.3
	75	10.8	10.0	8.3		75	12.5	9.1	6.8
	100	9.4	8.1	7.5		100	11.0	10.2	6.8
2- Amino phenol	25	19.2	17.7	16.6	**3- Amino phenol**	25	25.4	23.0	22.7
	50	14.1	12.5	10.2		50	18.1	16.1	14.1
	75	11.5	10.4	9.4		75	14.8	12.1	9.4
	100	9.8	9.0	8.2		100	10.7	10.1	8.1
Fly ash D									
Phenol/ Fly ash D	25	100.0	100.0	100.0	**Resorcinol/ Fly ash D**	25	85.7	85.8	81.1
	50	100.0	100.0	100.0		50	79.6	76.4	76.4
	100	78.0	76.4	75.6		100	77.7	78.7	75.2
	200	68.5	60.6	58.7		200	63.6	61.5	52.7
	300	58.7	52.8	51.4		300	50.9	50.7	48.8
	400	50.8	48.8	46.9		400	46.2	45.3	37.9
	500	48.0	46.5	44.9		500	37.4	36.9	31.4
Catechol/ Fly ash D	25	100.0	100.0	100	**Hydroquinone / Fly ash D †**	25	100.0	100.0	100.0
	50	97.5	92.8	92.5		50	97.6	98.4	98.4
	100	91.9	91.6	91.3		100	90.2	89.5	89.8
	200	89.8	89.1	86.7		200	89.8	87.8	86.8
	300	87.0	81.3	87.0		300	86.3	85.3	84.7
	400	82.8	82.8	82.0		400	81.5	80.5	79.5
	500	78.13	77.5	76.3		500	77.7	68.4	68.0
2-Aminophenol/ Fly ash D	25	82.8	79.7	78.1	**3-Aminophenol/ Fly ash D**	25	84.0	82.4	81.6
	50	80.2	79.4	78.6		50	76.9	76.5	75.7
	100	75.8	75.0	74.2		100	76.0	76.0	75.8
	200	62.0	61.0	58.5		200	62.5	61.3	60.8
	300	47.9	44.6	43.0		300	50.0	48.4	46.7
	400	41.5	39.0	36.6		400	45.1	40.1	40.1
	500	33.6	32.8	31.6		500	36.1	35.1	34.1

Table 3.5. Effect of initial concentration on % removal of phenols

[Dose of adsorbent = optimum, contact time= 4 h, pH= 7.0] **(Continued)**

System	**Conc.**	**Temp(°C)**			**System**	**Conc.**	**Temp(°C)**		
	(ppm)	30	45	60		**(ppm)**	30	45	60
Activated Carbon systems									
Phenol/ Activated carbon	25	100.0	100.0	100.0	**Resorcinol/ Activated carbon**	25	92.5	81.1	76.4
	50	100.0	100.0	100.0		50	81.13	76.4	75.0
	100	96.2	95.4	95.1		100	69.3	67.4	66.0
	200	90.16	83.3	80.3		200	56.2	55.6	54.7
	300	82.9	75.1	60.6		300	50.8	46.9	45.9
	400	74.4	58.7	48.4		400	40.8	37.9	34.9
	500	62.7	48.0	39.4		500	34.8	31.4	29.1
Catechol/ Activated carbon	25	100.0	100.0	100.0	**Hydroquinone/ Activated carbon †**	25	100.0	100.0	100.0
	50	100.0	100.0	100.0		50	100.0	100.0	100.0
	100	95.6	95.6	95.0		100	95.8	95.8	95.8
	200	88.3	94.5	89.1		200	85.1	84.0	83.0
	300	87.0	92.2	87.0		300	80.3	78.9	78.2
	400	84.4	90.6	85.9		400	69.15	68.09	67.0
	500	81.3	88.8	84.4		500	58.5	55.9	67.0
2-Aminophenol/ Activated carbon	25	100.0	100.0	100.0	**3-Aminophenol/ Activated carbon**	25	92.8	92.0	93.6
	50	100.0	92.2	87.5		50	90.0	80.0	84.0
	100	88.3	87.9	87.9		100	90.0	80.0	78.0
	200	80.00	77.6	77.6		200	80.2	60.0	52.5
	300	65.47	64.17	64.17		300	74.5	43.3	38.3
	400	51.22	49.8	48.78		400	55.6	33.2	32.5
	500	41.4	40.6	39.5		500	46.1	28.0	26.0

† The experiments were performed at pH= 6.0.

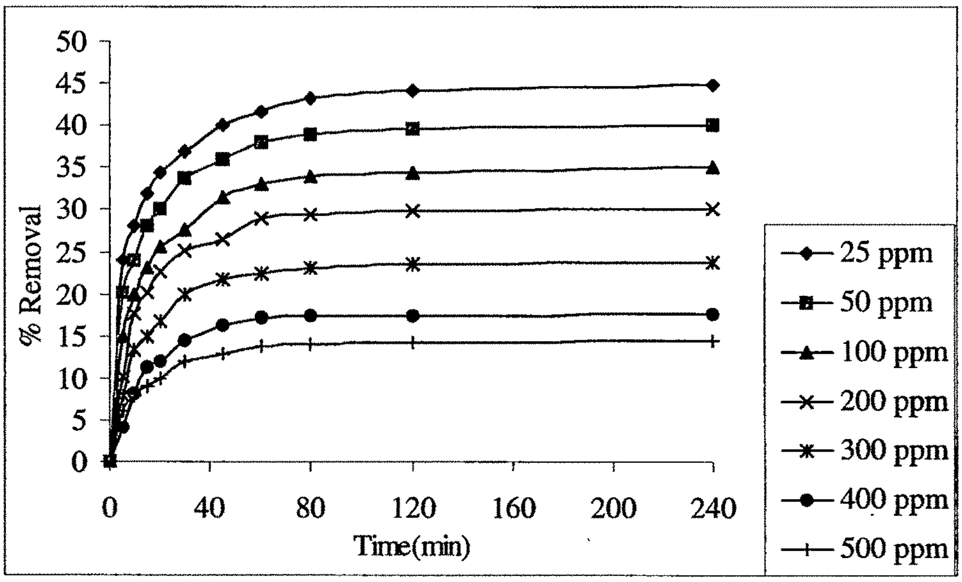

Figure 3.1. Effect of contact time and initial concentration on % removal of 3-aminophenol by adsorption on fly ash A

[Temp. = 30 ±1 °C, pH= 7.0, Adsorbent mass= 2.5 g/100 ml]

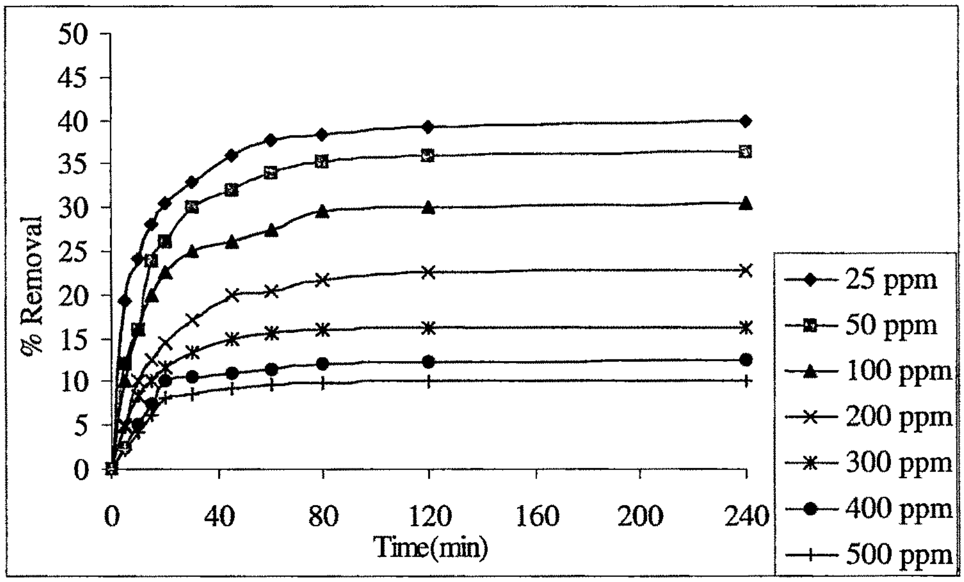

Figure 3.2. Effect of contact time and initial concentration on % removal of 3-aminophenol by adsorption on fly ash A

[Temp.= 45 ±1 °C, pH= 7.0, Adsorbent mass= 2.5 g/100 ml]

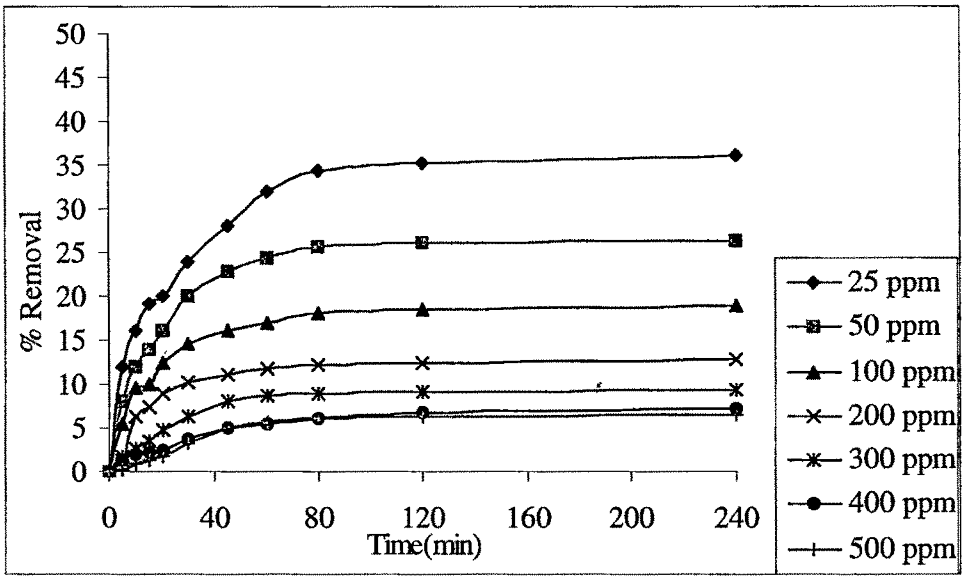

Figure 3.3. Effect of contact time and initial concentration on % removal of 3-aminophenol by adsorption on fly ash A

[Temp.= 60 ±1 °C, pH= 7.0, Adsorbent mass= 2.5 g/100 ml]

3.4.3 Effect of pH

The pH is the most important factor affecting the adsorption process. To study the influence of pH on the adsorption capacity of all types of fly ash and activated carbon, experiments were performed at initial pH ranging from 2 to11 for all the phenols except hydroquinone. For hydroquinone, the effect of pH on adsorption has been studied in the range of 2 to7. The initial concentration 100 ppm of phenols was used to study the effect of pH on fly ash A, B, C and D. Whereas initial concentration of 300 ppm of phenols was used for studies on activated carbon. The variation of percentage removal by each sorbent with initial pH for all the compounds is given in Table 3.6. It was observed that the adsorption process is dependent on pH of the solution and in general the uptake decreases as pH increases for all hydroxy phenols. However for amino substituted phenols mixed behavior was observed. Lower pH (2.0) and higher pH (11.0) have been found to be favorable for aminophenol adsorption on fly ash B, C and D. Incase of fly ash A, low pH(2.0) whereas in case of activated carbon high pH(11.0) has been found to be favorable for adsorption of aminophenols. This behavior may be due to presence of different ionic species in the solution and their corresponding interactions with the surface of adorbents.

Phenol and hyroxy phenols: It is a common observation that anions are favorably adsorbed on the surface of adsorbents at low pH because the presence of hydrogen ions activates the surface for adsorption. In general, the adsorption rate of industrial organic pollutants from wastewater increases with decreasing pH. A decrease in pH probably results in a reduction of the negative charges at the surface of fly ash and activated carbon, thus enhancing the sorption of the negatively charged ions. This may be explained on the basis of the formation of a positively charged surface in an acid medium and a negatively charged oxide surface in basic medium from hydroxylated oxide surface of fly ash, which can be represented as

$$MOH \overset{H^+}{\rightleftharpoons} M^+ + H_2O \qquad (3.39)$$

$$MOH \overset{OH^-}{\rightleftharpoons} MO^- + H_2O \qquad (3.40)$$

At lower pH values, the lone pair of electrons on the oxygen atom of the un-dissociated -OH group in phenol coordinates with the highly positively charged surface. But at higher pH, the phenoxide ion is repelled by the negatively charged oxide surface. Thus the removal capacity of different fly ash and activated carbon at different pH values decreases with increase in pH. The removal capacity of fly ash A, B, C, D and activated carbon in the order: resorcinol >hydroquinone > catechol >phenol. This may be due to difference in solubility of these phenols(Table B-1, Appendix B).

Aminophenols: The complex behavior observed in case of aminophenols may be attributed to different ionic equilibrium exist at different pH as shown below:

$$^{+}H_3NC_6H_4OH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} {}^{+}H_3NC_6H_4O^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_2NC_6H_4O^- \qquad (3.41)$$

For 3-aminophenol, pK_a= 4.2 and pK_b= 9.9. At low pH $^{+}H_3NC_6H_4OH$, at intermediate pH $^{+}H_3NC_6H_4O^-$(zwitter ion) while at high pH, $H_2NC_6H_4O^-$specie will be dominating. Thus interaction between pollutant and adsorbent will be highly dependent on the pH. This complex equilibrium is mainly responsible for the complex behavior for removal of aminophenols.

In case of fly ash, the larger sorption capacity at low pH may be the result of strong chemical bonding between the lone pair of electrons present on the –OH group in phenols and the central ion of silicates (Si^{4+}) as well as weakly acidic alumina surface at lower pH values. The negatively charged surface of activated carbons is a collection of organic functional group containing oxygen. Phenols are adsorbed at the carbonyl oxygen on the activated carbon surface according to donor acceptor complexion mechanism. At a low pH, there is a reasonably strong interaction between the negatively charged adsorbent and the polar resonance contributed phenol structure. In addition, hydrogen bonding by the phenolic protons with the oxygen present on the carbon surface is also quite probable. The adsorption decreased with increasing pH for all the hydroxy phenols is due to repulsive force between the negative surface charge of the activated carbon and the phenols. Similar results were obtained by Singh (1994), and Reddy (1989) who have studied the adsorption of phenol on fly ash and activated carbon respectively.

A neutral pH was chosen to run the adsorption of all the phenols except hydroquinone in a wide concentration range. The neutral pH is physiologically significant, as most of the reactions in living systems take place in neutral medium.

Hyroquinone has been studied at pH 6.0, since it may oxidize to 1,4-benzoquinone. Its stability depends on the pH of the solution. Oxidation occurs slowly in neutral, very slowly in acidic but very rapidly even in slightly alkaline solutions. Therefore, the solutions of hydroquinone in neutral or acidic solutions were freshly prepared prior to experiments for calibration or for adsorption. However, it could not be studied in alkaline solution due its rapid oxidation.

Table 3.6. Effect of pH on % removal of phenols by different adsorbents
[initial conc.= 100 mg/l, contact time= 4 h, temp.= 30 °C, dose= optimum]

pH	**Phenol**	**Catechol**	**Hydroquinone**	**Resorcinol**	**2-Aminophenol**	**3-Aminophenol**
% adsorption on Fly Ash A						
2	40.9	74.7	70.8	40.9	35.3	40.1
3	40.2	72.7	68.8	35.0	35.3	40.1
4	39.0	70.6	64.6	33.8	33.3	39.1
5	37.8	68.5	62.5	32.0	31.4	37.6
6	37.0	66.3	54.2	30.3	27.5	35.1
7	33.5	56.3	52.1	29.1	26.5	35.1
8	29.9	54.7	-	20.2	24.5	34.1
9	28.0	53.1	-	17.3	23.5	33.1
10	24.8	51.6	-	14.3	23.5	32.1
11	20.5	50.0	-	11.3	21.6	30.6
% adsorption on Fly Ash B						
2	40.9	76.6	74.2	48.6	46.8	47.1
3	40.2	75.0	71.2	48.0	45.3	45.6
4	39.0	73.4	68.2	47.4	45.3	45.1
5	37.8	71.9	66.1	46.8	43.8	42.6
6	37.4	68.8	55.1	43.9	39.5	40.6
7	39.0	60.9	55.1	35.0	36.5	37.6
8	33.1	57.8	-	29.1	40.4	38.1
9	29.1	54.7	-	23.2	40.9	38.6
10	27.2	53.1	-	17.3	39.9	38.6
11	25.2	50.0	-	14.3	39.9	40.1
% adsorption on Fly Ash C						
	Phenol	Catechol	Hydroquinone	Resorcinol	2-Aminophenol	3-Aminophenol
2	13.4	13.8	16.9	15.4	14.1	12.5
3	12.3	12.5	16.9	14.9	13.7	12.1
4	11.8	11.3	15.3	13.7	13.3	12.1
5	11.5	10.6	14.4	12.8	12.1	11.7
6	11.0	10.0	11.0	10.6	10.9	11.5
7	10.6	9.4	11.9	10.2	9.4	10.7
8	9.9	8.1	-	9.0	11.7	10.9
9	9.4	6.9	-	7.8	12.5	11.5
10	8.5	5.0	-	5.4	12.9	11.3
11	8.0	4.4	-	3.1	13.7	11.9

Table 3.6. Effect of pH on % removal of phenols by different adsorbents [initial conc.= 100 mg/l, contact time= 4 h, temp.= 30 °C, dose= optimum] **(Continued)**

pH	Phenol	Catechol	Hydroquinone	Resorcinol	2-Aminophenol	3-Aminophenol
			% adsorption on Fly Ash D			
2	82.8	95.0	94.9	82.2	80.9	84.0
3	82.5	95.0	94.5	82.2	80.5	83.0
4	80.9	94.4	94.1	82.0	80.5	82.0
5	80.2	93.8	93.4	81.5	80.1	81.6
6	79.8	93.1	90.2	81.3	79.3	81.2
7	78.0	91.3	89.8	77.7	75.8	76.0
8	77.2	90.6	-	76.8	77.0	78.2
9	76.4	90.0	-	76.1	78.1	78.8
10	76.2	89.4	-	75.6	78.9	79.2
11	76.1	88.8	-	75.4	79.3	79.6
			% adsorption on Activated Carbon*			
2	88.2	91.1	91.5	61.8	62.2	73.9
3	87.9	90.6	90.8	61.4	62.2	73.9
4	87.5	90.1	89.4	61.2	62.5	73.7
5	87.1	89.6	88.7	60.8	63.2	73.9
6	86.7	88.5	80.3	60.2	63.8	74.2
7	82.9	87.0	79.6	50.7	65.5	74.5
8	81.4	85.9	-	50.2	66.1	76.0
9	80.6	84.4	-	50.0	66.8	76.4
10	80.2	83.3	-	49.6	67.4	76.5
11	79.7	81.3	-	49.4	69.1	76.7

* For activated carbon initial conc. of phenols = 300 ppm

3.4.4 Effect of Mass of Adsorbent

The experiments on the optimization of adsorbent mass in adsorption studies have been carried out with the solution having the initial concentration of 100 ppm phenolic solution at pH 7.0 and 30°C for all the fly ashes. For activated carbon, phenolic solutions having initial concentration of 300 ppm have been used. Results for this are shown in Table 3.7 and Fig. 3.4 to 3.8. The results show that, the increase in amount of adsorbent mass increases the percentage removal and decreases the adsorption density. The decrease in adsorption density may be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process, where as the number of available adsorption sites increases by increasing the adsorbent dose that results in the increase of removal efficiency.

Table 3.7. Effect of mass of adsorbent on % removal of phenols
[Initial conc.= 100 mg/l, contact time= 4 h, temperature= 30 °C, pH= 7.0]

	g in 100 ml	Phenol	Catechol	Resorcinol	Hydro-quinone†	2-Amino phenol	3-Amino phenol
% removal by Fly Ash A	0.5	21.3	14.1	11.3	47.9	10.8	15.1
	1	29.1	21.9	16.1	52.1	17.6	25.1
	2.5	33.5	56.3	29.1	54.2	26.5	35.1
	5	34.3	59.4	32.0	58.3	29.4	37.6
	7.5	35.0	62.5	32.6	60.4	30.4	39.6
	10	35.8	64.1	33.8	62.5	31.4	40.1
	15	36.2	65.6	34.4	62.5	32.4	40.6
	20	36.6	65.5	35.0	64.6	32.4	41.1
% removal by Fly Ash B	0.5	17.3	21.9	11.3	16.1	12.1	20.1
	1	29.1	53.1	23.2	34.7	26.8	30.1
	2.5	39.0	60.9	35.0	55.1	36.5	37.6
	5	41.3	62.5	37.9	58.5	41.4	42.6
	7.5	43.3	64.1	39.7	59.7	43.8	43.1
	10	45.3	65.6	41.5	60.2	44.3	44.1
	15	45.7	67.2	42.1	61.0	44.8	44.1
	20	46.1	68.8	42.1	61.0	44.3	45.1
% removal by Fly Ash C	0.5	3.9	3.1	5.0	3.4	3.1	4.1
	1	8.0	6.3	7.6	6.8	6.3	8.1
	2.5	10.6	9.4	10.2	9.3	9.8	10.7
	5	12.0	11.3	10.9	10.2	10.2	12.1
	7.5	13.1	11.9	11.3	11.0	10.5	12.9
	10	13.4	12.5	11.6	11.9	10.9	13.3
	15	13.7	13.1	12.1	12.7	11.3	13.5
	25	13.9	13.8	12.1	14.4	11.7	13.7

Table 3.7. Effect of mass of adsorbent on % removal of phenols
[Initial conc.= 100 mg/l, contact time= 4 h, temperature= 30 °C, pH= 7.0] **(Continued)**

	g in 100 ml	**Phenol**	**Catechol**	**Resorcinol**	**Hydro-quinone†**	**2-Amino phenol**	**3-Amino phenol**
% removal by Fly Ash D	0.5	37.0	36.9	30.3	21.9	31.6	37.1
	1	68.5	64.4	61.1	56.3	62.1	63.0
	1.5	78.0	91.3	77.7	90.2	75.8	76.0
	3	78.3	92.5	78.2	91.8	77.3	78.4
	5	79.5	93.1	78.7	92.6	78.5	79.6
	7.5	80.3	93.8	78.9	93.4	78.9	82.0
	10	81.1	94.4	79.4	94.1	79.7	84.0
	15	81.9	95.0	79.6	94.5	80.1	84.0
% removal by Activated Carbon*	0.1	54.1	35.4	19.3	22.5	48.2	58.4
	0.25	73.8	67.7	37.0	52.1	59.9	68.7
	0.5	82.9	79.2	50.8	85.2	65.5	74.5
	2.5	85.3	86.5	56.5	87.3	69.4	76.4
	5.0	86.7	87.0	57.7	88.7	71.3	76.9
	10.0	87.8	87.5	58.7	90.1	73.0	77.9

***(For all the fly ash initial conc. of phenols = 100 ppm, for activated carbon initial conc. of phenols= 300 ppm) † The experiments were performed at pH= 6.0.**

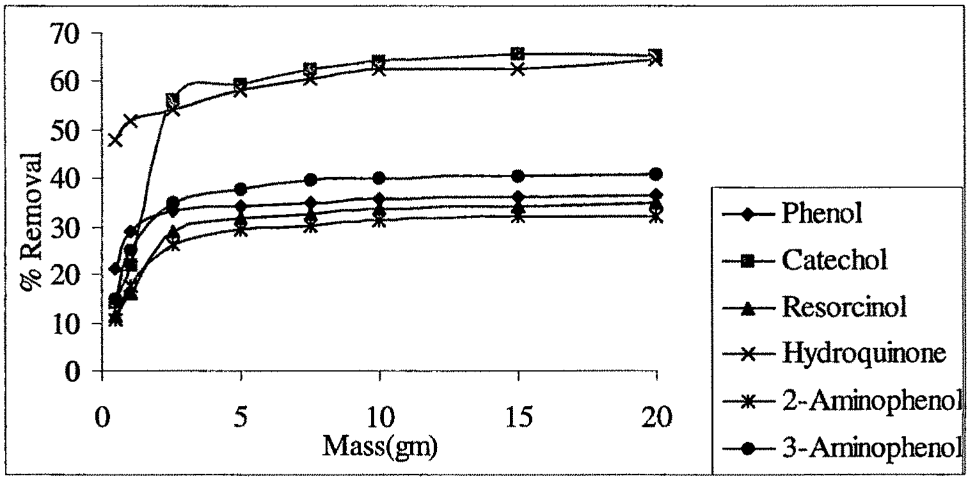

Figure 3.4. Effect of dose of FLY ASH A on the percentage removal of phenols
[Temp.= 30 ±1 °C, pH= 7.0, Initial phenol conc.= 100 mg/l, contact time= 4 h]

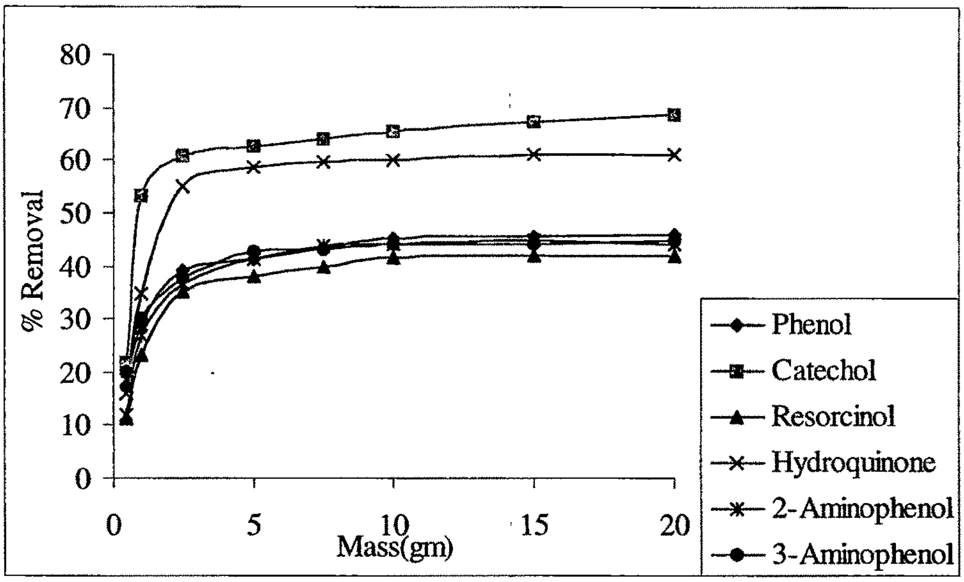

Figure 3.5. Effect of dose of FLY ASH B on the percentage removal of phenols

[Temp.= 30 ±1 °C, pH= 7.0, Initial phenol conc.= 100 mg/l, contact time= 4 h]

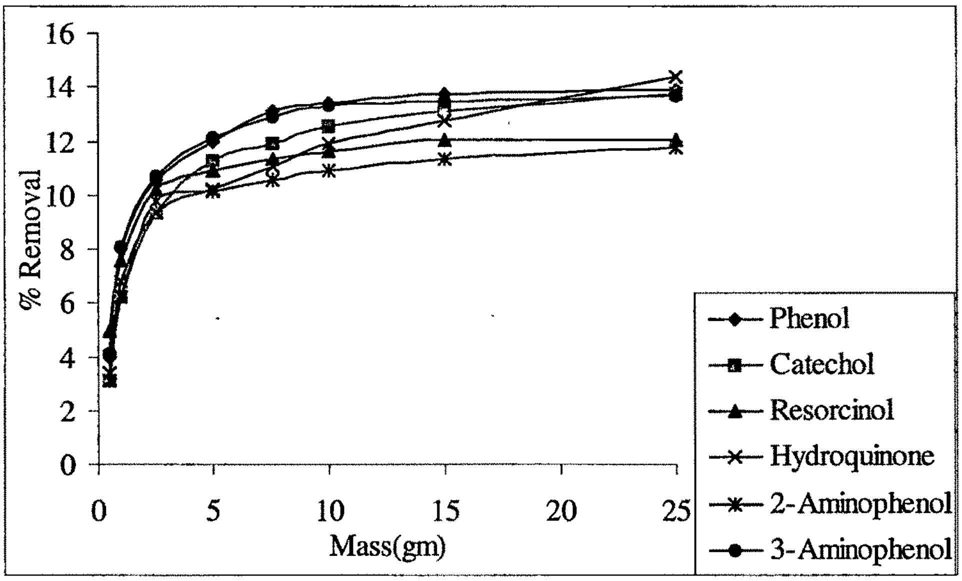

Figure 3.6. Effect of dose of FLY ASH C on the percentage removal of phenols

[Temp.= 30 ±1 °C, pH= 7.0, Initial phenol conc.= 100 mg/l, contact time= 4 h]

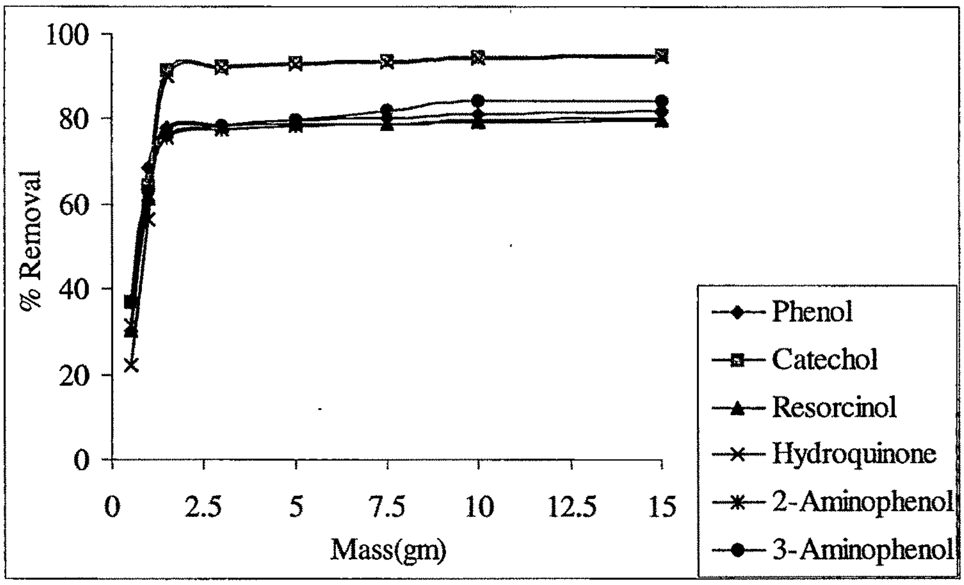

Figure 3.7. Effect of dose of FLY ASH D on the percentage removal of phenols
[Temp.= 30 ±1 °C, pH= 7.0, Initial phenol conc.= 100 mg/l, contact time= 4 h]

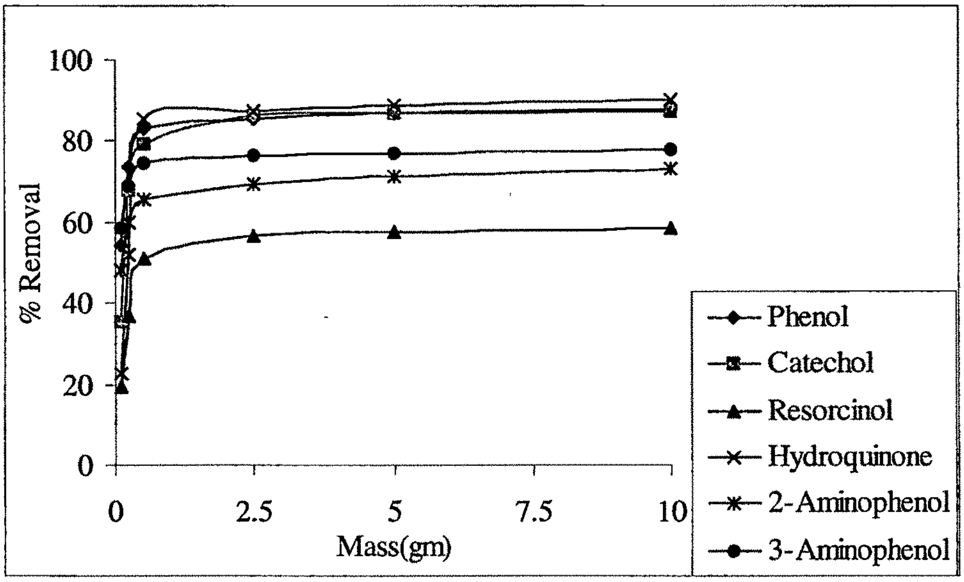

Figure 3.8. Effect of dose of ACTIVATED CARBON on the percentage removal of phenols
[Temp.= 30 ±1 °C, pH= 7.0, Initial phenol conc.= 300 mg/l, contact time= 4 h]

Another reason may be due to aggregation/agglomeration of adsorbent particles at higher concentration. Such aggregation would lead to decrease in surface area of adsorbent particles available to phenols for adsorption and an increase in diffusional path length. The particle interaction brought about by high sorbent concentration may also desorb some of the sorbate which is only loosely and reversibly bound to the adsorbent surface.

The optimum amount of adsorbent for the adsorption of phenols for 100 ml solution on; fly ash A 2.5, fly ash B 2.5, fly ash C 2.5, fly ash D 1.5 and activated carbon 0.5 g was found respectively. The low optimum mass of activated carbon, compared to that of fly ash, shows that activated carbon has greater adsorptive capacity than fly ashes. For initial step change in adsorbent dose, change in percentage removal is higher, but afterwards incremental change in percentage phenols removal with the change in adsorbent is very low. It is also clear from the figures 3.4 to 3.8 that to achieve more than 80-90 % of the total removal capacity, increase in dose has very little effect. It indicates that a single stage batch reactor is not a better option. Number of sites are greater at high doses of adsorbents, therefore, the adsorption becomes independent of the adsorbent dose. In a batch reactor, adsorbent is in contact with decreasing concentration, for this reason, the driving force for mass transfer is in decreasing order and, therefore, after a certain contact time, the adsorbate/adsorbent reaches a dynamic equilibrium. Also the adsorption desorption rate will be much slower; therefore, it will take much longer time to reach dynamic equilibrium. Hence additional dose will be practically useless. Thus, it may be suggested that multistage batch adsorption or column configuration may be used, where adsorbent is always in contact with approximately constant concentration of the compound.

3.4.5 Effect of Salt

The impact of the presence of other dissolved ionic substances can give insight into the dominant mechanism of sorption. This is also important in evaluating the effectiveness of the treatment. Commonly found salt/electrolytes in the effluent are NaCl and Na_2SO_4. The effect of these salts on the adsorption have been studied for solutions containing NaCl and Na_2SO_4 of 1M and 0.5 M concentration respectively with 100 ppm solution of phenols. Results shown in Table 3.8, clearly indicate that in presence of 1 M NaCl, 0.5 to 2 % increase in percentage removal of phenols on fly ashes, while in presence of 0.5 M Na_2SO_4, 1 to 3 % increase in percentage removal of phenols on fly ashes were observed. Hence presence of salt would increase the removal of phenolic compounds. This is due to decrease in solubility of phenols in water in the presence of NaCl and Na_2SO_4.

TABLE 3.8. Effect of salt on % removal of phenols
[Initial conc.= 100 mg/l, time= 4 h, temp.= 30 °C, pH= 7, dose= optimum]

Compound	**% Removal of Phenolic Compound (Co=100 ppm, T=30°C, pH=7,Optimum dosage, Speed =100 rpm)**			
	Adsorbent	**In Water**	**In 1.0 M NaCl**	**In 0.5 M Na_2SO_4**
Phenol	Activated Carbon	96.22	96.22	99.35
	Fly Ash A	33.50	34.13	34.80
	Fly Ash B	39.00	39.64	40.46
	Fly Ash C	26.00	26.24	27.02
	Fly Ash D	78.00	78.81	79.90
Catechol	Activated Carbon	90.60	92.17	93.62
	Fly Ash A	56.30	56.93	58.02
	Fly Ash B	60.94	61.61	62.10
	Fly Ash C	9.40	9.47	9.57
	Fly Ash D	91.3	92.16	93.99
Resorcinol	Activated Carbon	69.30	70.65	72.04
	Fly Ash A	29.10	29.37	30.01
	Fly Ash B	35.00	35.30	35.95
	Fly Ash C	10.20	10.37	10.52
	Fly Ash D	77.80	79.26	80.89
Hydroquinone†	Activated Carbon	99.15	99.15	99.15
	Fly Ash A	55.50	56.62	58.84
	Fly Ash B	55.10	55.75	56.96
	Fly Ash C	32.20	32.78	33.23
	Fly Ash D	89.80	91.00	91.72

† The experiments were performed at pH= 6.0.

TABLE 3.8. Effect of salt on % removal of phenols
[Initial conc.= 100 mg/l, time= 4 h, temp. = 30 °C, pH= 7, dose= optimum] **(Continued)**

Compound.	**% Removal of Phenolic Compound (Co=100 ppm, T=30°C,pH=7,Optimum dosage, Speed =100 rpm)**			
	Adsorbent	In Water	In 1.0 M NaCl	In 0.5 M Na_2SO_4
2-Aminophenol	Activated Carbon	88.28	89.43	91.55
	Fly Ash A	26.8	27.13	27.75
	Fly Ash B	36.5	37.07	37.66
	Fly Ash C	9.4	9.52	9.66
	Fly Ash D	75.8	76.92	78.05
3-Aminophenol	Activated carbon	90.01	91.81	92.89
	Fly Ash A	35.1	35.77	36.47
	Fly Ash B	37.56	37.9	38.93
	Fly Ash C	10.7	10.9	10.8
	Fly Ash D	76	76.94	78.08

3.4.6 Effect of Temperature

Effect of temperature on adsorption of phenols on fly ash and activated carbon was studied at three temperatures: 30°C, 45°C and 60°C. The effect of temperature on fly ash A and 3-aminophenol system at equilibrium is shown in Fig. 3.9. The nature of the curves shows that these isotherms can be classified as L type as per Gile's(1960) classification, which indicates favorable adsorption. Similar trends were obtained with other adsorbate/adsorbent systems.

From Table 3.5, it is observed that the adsorption of phenol decreases with increase in temperature. The percentage adsorption of phenol decreased from 33.5 to 31.1% for fly ash A, 39 to 35.8% for fly ash B, 10.7 to 8.7% for fly ash C, 78 to 75.6% for fly ash D and 96.2 to 95.1% for activated carbon respectively at initial concentration of 100 ppm on reducing the temperature from 60 to 30°C. Similar trend in other phenols studied (catechol, hydroquinone, resorcinol, 2-aminophenol and 3-aminophenol) was observed on all these adsorbents at different temperatures. Hence the lower temperature is more favorable for the adsorption of phenols on all the five adsorbents. The decrease in adsorption with increase in temperature is partly due to the weakening of attractive forces between the phenol and adsorbent, and partly due to the enhancement of thermal energy of adsorbate, thus making the force of attraction between adsorbent and phenol insufficient to retain the adsorbed molecules at the binding sites. Effect of temperature on kinetics is discussed later under kinetics part.

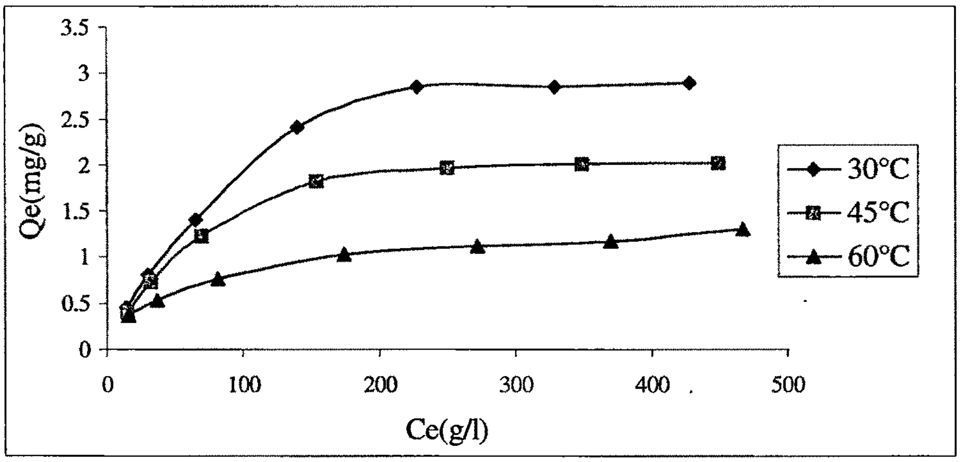

Figure 3.9. Effect of Temperature on equilibrium uptake capacity of adsorbent [Fly Ash A / 3-Aminophenol system]

3.4.7 Isotherms

In the present study, six isotherm models reported in literature on adsorption from aqueous solution have been tried to fit the experimental data.

The surface of all the adsorbents used in the present work is heterogeneous; therefore, extremely low equilibrium concentrations are required to attain the Henry's law region. For any adsorbent–adsorbate system, the linear isotherm cannot represent the data beyond a certain low concentration region. The concentration range studied in this work is very wide (25 to 500 mg/l), therefore, Henry's law model was not used, though Freundlich model does not reduce to Henry's law at low concentration, and the Langmuir's isotherm model is applicable for homogeneous surfaces only. These two models have found wide acceptance for representing the adsorption isotherm data in wastewater treatment. It has been given, in the literature review in Chapter 2, that these two models have been most widely used for correlating the data for phenolic solutions of different concentration ranges. The other four models have also been reported for correlation of data of phenol systems. The adsorption equilibrium data in present work has been correlated with these six adsorption isotherm models using Windows based statistical software, SPSS version 8.0. This software utilizes Marquardt-Levenberg optimization procedure. Any nonlinear regression technique such as Marquardt-Levenberg requires the correct estimation of initial values so that the convergence is achieved and the parameter values obtained are reasonable. The two parameter models, viz. Freundlich and Langmuir can be readily linearized and hence the parameter values can easily be obtained using linear regression. The parameter values obtained from these two linearized isotherms give rough estimates of the initial values for other models. For nonlinear regression, only those parameter values, which give the best statistical representation of data, were retained.

In this procedure, three criteria namely correlation coefficient(R^2), maximum percentage deviation and percentage standard deviation(σ) are met to get the parameter values. All the data points for each phenolic compound were used in estimating the parameter values. Subsequently, with these values, the percentage deviation and σ were calculated using Eq.(3.42) and Eq.(3.43) respectively.

$$\text{Percentage deviation} = \frac{Q_{\text{experimental}} - Q_{\text{predicted}}}{Q_{\text{experimental}}} \times 100 \qquad (3.42)$$

$$\text{Percentage standard deviation } (\sigma) = \left[\frac{1}{n} \sum \left\{ \frac{Q_{\text{experimental}} - Q_{\text{predicted}}}{Q_{\text{experimental}}} \right\}^2 \right]^{\frac{1}{2}} \qquad (3.43)$$

Table 3.9 enlists the values of the parameters along with the R^2, σ and maximum percentage deviation for all the 30 adsorbate-adsorbent systems at 30, 45 and 60°C for all the six isotherm models.

Further, in order to check the conformity of experimental methods and the results obtained in the present work, the earlier studies of different investigations were reviewed on the basis of the surface area of the adsorbent and equilibrium concentration range (Table 2.1 in Chapter 2). The adsorption is surface phenomenon; therefore, its surface area should have a considerable bearing on the adsorption capacity. In the study by Kumar et al. (1987), fly ash having surface area comparable with fly ash A, was used. The parameters Q^0 and b calculated for Langmuir equation in the concentration range of 50 to 600 ppm of phenol at 30°C and optimum adsorbent mass of 25 g/l were 2.35 mg/g and 0.017 l/mg respectively. In our work for adsorption of phenol on fly ash A at similar operating condition, the values obtained are 2.15 mg/g and 0.023 l/mg respectively. Slightly lower value of Q and higher value of b may be due to difference in surface area.

Figure 3.10 shows the comparisons of percentage deviation of predicted values of uptake by all the six isotherms studied for the six phenolic compounds on fly ash A. Amongst six isotherms used, Langmuir gave the poorest fit with correlation coefficient (R^2) of 0.85-0.99, average % standard deviation (σ) of 3.27% and maximum percentage deviation of 41%. All other isotherms correlate data very well. The R^2 values for rest of the models were more than 0.9. The σ values for Freundlich, Redlich Peterson, Toth, Radke Prausnitz and Fritz Schlunder were 2.84%, 2.23%, 2.63%, 2.23% and 2.28% respectively.

This indicates that amongst three parameter isotherms, Toth isotherm gave the poorest fit. There is remarkable similarity in the output of Redlich Peterson and Radke Prausniz models. This was expected as the two models are same with the difference only in the presentation of the equations. The only four parameter isotherm model studied is by Fritz Schlunder which represents data reasonably well.

Standard error of the estimates have also been calculated and presented (Table B-2 Appendix B). With the estimate and its standard error we can find confidence intervals of appropriate confidence level. Standard error also gives authenticity of estimates.

As is evident from the Table 3.5, the relative adsorbabilities of phenolic compounds are in the order for fly ash A,
Catechol > hydroquinone > 3-aminophenol > phenol ~ resorcinol > 2-aminophenol
whereas for fly ash B, fly ash D and activated carbon,
Catechol > hydroquinone > 3-aminophenol > 2-aminophenol >phenol > resorcinol,
Catechol > phenol > hydroquinone > 3-aminophenol>2-aminophenol > resorcinol,
Catechol >hydroquinone >phenol >resorcinol >3-aminophenol >2-aminophenol,
respectively.
For fly ash C, the capacity almost remains constant.

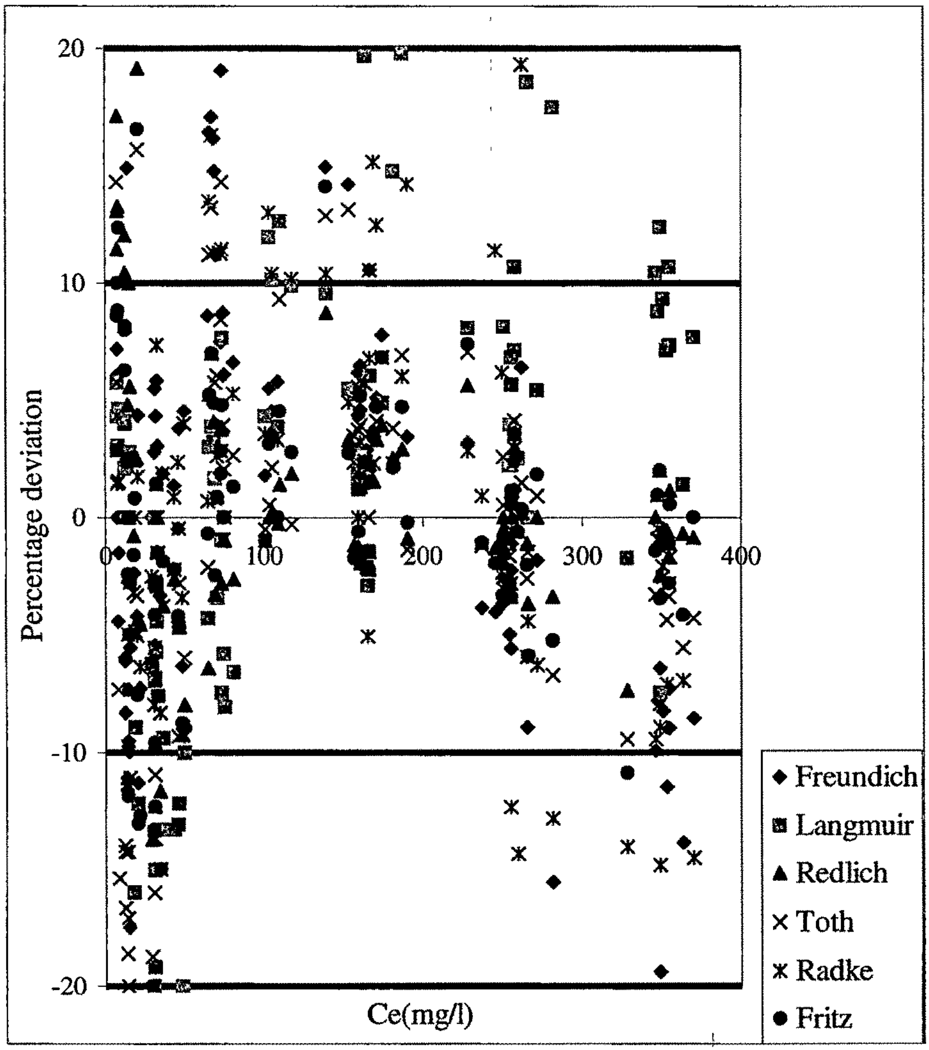

Figure 3.10. Comparison of experimental and predicted amount of phenol, catechol, resorcinol, hydroquinone, 2-aminophenol and 3-aminophenol adsorbed on fly ash A

The difference in adsorbability can be explained in terms of solubility, molecular weight and the presence and position of amino and hydroxyl group on the aromatic benzene ring of adsorbate. It was concluded by Mattson and Mark (1971) that the carboxyl oxygen group on the carbon surfaces interacted with aromatic ring of the phenols in a donor acceptor complex mechanism. In this reaction, the carbonyl group on the surface is electron donor and the aromatic ring of the adsorbate acts as the acceptor. Whereas Coughlin et al. (1968) reported that the dispersive force between π-electrons in the phenol and the π-electrons in the carbon contribute to such interactions. The electron density in the π-system of the aromatic ring is increased because of the amino group in the aminophenol in comparison to phenol itself. This hinders the possibility of the donor acceptor mechanism.

Catechol and hydroquinone have one more functional group (-OH) than the phenol. This increase in functional group imparts these compounds the ability to form more chemical bonding in the adsorption reaction. Thus, the higher adsorption capacity of the catechol can be explained through this factor. However, less adsorption capacity of resorcinol cannot be explained on these lines. Solubility of adsorbate and position of the functional group also play a role in adsorption and interactions. The solubility of the resorcinol is more as compared to that of phenol (Perry and Chilton 1973), thus resorcinol has more affinity towards water (i.e. hydrophilic), this may be one of the possible reasons for its less adsorbability.

It has also been observed that for the same functional group but at ortho position greatly enhances the adsorption energies of the compound. Whereas the substitution at the meta position, as in the case of resorcinol does not affect the adsorption capacity substantially. Since solubility of aminophenols is very less as compared to that of resorcinol and phenol, the adsorption is slightly higher in case of fly ash B and D. In case of activated carbon surface charge is very high so solubility effect is less. Similarly in case of fly ash C there is no surface charge hence no difference in adsorbabilities of the different compounds. Therefore the cumulative effect of additional functional groups and their position on the aromatic benzene ring and the solubility may be responsible for this order of adsorption capacity.

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated

r. o	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
	Fly Ash A	Phenol	K_f=0.172	Q=2.11	K_1=0.045	T=14.5	K=0.11	a_1=0.05
	(T= 30°C)		n=2.25	b=0.023	K_2=0.027	a=1.61	k=0.3	a_2=0.032
					m=0.93	th=0.2	p=2.8	b_1=0.93
								b_2=0.87
		Max. Dev.	16.42	20	-13.3	-16	13.43	-13.33
		Std. Dev.	3.65	4.11	3.12	4.08	3.11	2.76
		R^2	0.97	0.97	0.99	0.98	0.99	0.99
	Fly Ash A	Phenol	K_f=0.174	Q=1.98	K_1=0.05	T=34.28	K=-83.2	a_1=0.048
	(T= 45°C)		n=2.33	b=0.024	K_2=0.044	a=1.17	k=0.14	a_2=0.045
					m=0.88	th=0.144	p=2.13	b_1=1.02
								b_2=0.89
		Max. Dev.	17.05	-19.18	-12.33	-14.29	16.28	-12.33
		Std. Dev.	3.54	3.98	2.81	4.04	4.24	2.80
		R^2	0.97	0.97	0.99	0.97	0.98	.99
	Fly Ash A	Phenol	K_f=1.89	Q=1.89	K1=0.044	T=20.7	K=0.077	a_1=0.054
	(T= 60°C)		n=0.025	b=0.025	K2=0.027	a=1.13	k=0.47	a_2=0.026
					m=0.95	th=0.15	p=3.9	b_1=0.91
								b_2=0.9
		Max. Dev.	16.13	-15.07	10.42	-16.67	11.29	-9.59
		Std. Dev.	3.69	3.08	2.48	3.96	2.51	2.11
		R^2	0.98	0.98	0.99	0.97	0.99	0.99
	Fly Ash A	Catechol	K_f=0.186	Q=5.92	K1=0.12	T=249.3	K=0.37	a_1=0.13
	(T= 30°C)		n=1.524	b=0.017	K2=0.16	a=4.8	k=0.28	a2=0.082
					m=0.55	th=.23	p=1.71	b1=0.87
								b2=0.52
		Max. Dev.	-3.85	-16	11.4	5.71	5.7	8.57
		Std. Dev.	0.94	6.59	2.02	1.24	1.28	1.57
		R^2	0.99	0.98	0.99	0.99	0.99	0.99
	Fly Ash A	Catechol	K_f=0.199	Q=5.35	K_1=0.088	T=110.2	K=0.17	a_1=0.1
	(T= 45°C)		n=1.65	b=0.017	K_2=0.042	a=3.23	k=0.48	a_2=0.043
					m=0.78	th=0.22	p=2.14	b_1=0.93
								b_2=0.72
		Max. Dev.	19.46	14.7	13.2	-7.35	-5.95	8.82
		Std. Dev.	2.09	4.76	2.42	1.81	1.23	1.74
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
	Fly Ash A	Catechol	K_f=0.17	Q=4.71	K_1=0.058	T=95.59	K=0.31	a_1=0.07
	(T= 60°C)		n=1.63	b=0.017	K_2=0.004	a=2.79	k=0.25	a_2=0.02
					m=1.1	th=0.21	p=1.8	b_1=0.99
								b_2=0.85
		Max. Dev.	-15.58	-20.9	24.6	-21.82	-12.84	-12.73
		Std. Dev.	3.73	6.27	4.45	5.08	3.41	3.59
		R^2	0.99	0.97	0.99	0.97	0.99	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. o	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
.	Fly Ash A (T= 30°C)	Resorcinol	$K_f=0.133$ n=2.08	Q=2.17 b=0.017	$K_1=0.04$ $K_2=0.04$ m=0.85	T=25.34 a=1.7 th=0.18	K=0.046 k=0.72 p=4.95	$a_1=0.035$ $a_2=0.046$ $b_1=1.08$ $b_2=0.89$
		Max. Dev.	-11.63	-6.9	-2.88	-18.6	-3.31	-4.17
		Std. Dev.	3.3	2	.72	3.53	0.9	0.97
		R^2	0.98	0.99	0.99	0.99	0.99	0.99
	Fly Ash A (T= 45°C)	Resorcinol	$K_f=0.131$ n=2.19	Q=1.89 b=0.017	$K_1=0.04$ $K_2=0.05$ m=0.84	T=35.1 a=1.33 th=0.14	K= -2084.79 k=0.1 p=1.9	$a_1=0.017$ $a_2=0.042$ $b_1=1.4$ $b_2=1.15$
		Max. Dev.	13.08	7.3	-2.5	-20	-22.03	-2.94
		Std. Dev.	3.41	1.57	.89	3.68	5.06	.73
		R^2	0.98	0.99	0.99	0.99	0.98	0.99
	Fly Ash A (T= 60°C)	Resorcinol	$K_f=.14$ n=2.41	Q=1.61 b=0.021	$K_1=0.03$ $K_2=0.01$ m=1.08	T=16.46 a=1.04 th=0.15	K=0.041 k=0.68 p=6.48	$a_1=.041$ $a_2=.015$ $b_1=0.9$ $b_2=0.96$
		Max. Dev.	19.05	-13.3	-11.7	-22.5	11.23	-15
		Std. Dev.	4.75	2.79	2.74	5.48	2.98	2.93
		R^2	0.94	0.98	0.99	0.93	0.98	0.98
0.	Fly Ash A (T= 30C)	Hydroquinone	$K_f=.17$ n=1.52	Q=5.02 b=0.019	$K_1=0.07$ $K_2=0.02$ m=0.76	T=260.5 a=3.95 th=.21	K=0.288 k=0.329 p=1.9	$a_1=0.14$ $a_2=0.11$ $b_1=0.83$ $b_2=0.44$
		Max. Dev.	-11.3	32.4	13.04	-21.74	15.13	-13.04
		Std. Dev.	3.98	9.02	5.11	3.98	4.4	2.95
		R^2	0.99	0.95	0.99	0.99	0.99	0.99
1.	Fly Ash A (T= 45°C)	Hydroquinone	$K_f=.18$ n=1.56	Q=4.92 b=0.02	$K_1=0.08$ $K_2=0.05$ m=0.69	T=225.1 a=4.85 th=0.23	K=0.92 k=0.23 p=1.71	$a_1=0.21$ $a_2=0.21$ $b_1=0.61$ $b_2=-0.47$
		Max. Dev.	-6.34	31.2	17.1	14.29	12.45	-8.78
		Std. Dev.	2.04	8.51	4.84	3.02	3.1	2.28
		R^2	0.99	0.96	0.99	0.98	0.99	0.99
2.	Fly Ash A (T= 60 °C)	Hydroquinone	$K_f=.168$ n=1.628	Q=4.04 b=0.02	$K_1=0.12$ $K_2=0.56$ m=0.39	T=372.07 a=5.72 th=0.22	K=.32 k=.29 p=2.02	$a_1=0.127$ $a_2=1.09$ $b_1=19.84$ $b_2=19.15$
		Max. Dev.	-26.38	-41.1	30.3	27.27	-23.31	22.75
		Std. Dev.	4.75	10.49	6.87	6.72	5.84	5.79
		R^2	0.98	0.95	0.98	0.98	0.98	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
.	Fly Ash A (T= 30°C)	2-Amino phenol	K_f=.126 n=2.087	Q=2.049 b=0.017	K_1=0.04 K_2=0.05 m=0.83	T=39.7 a=1.57 th=0.16	K=0.048 k=0.55 p=4.2	a_1=0.11 a_2=0.049 b_1=0.61 b_2=0.52
		Max. Dev.	-9.52	9.3	4.8	-14.29	3.23	-11.9
		Std. Dev.	2.79	2.47	0.98	2.69	.66	2.25
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
.	Fly Ash A (T= 45°C)	2-Amino phenol	K_f=0.13 n=2.17	Q=1.9 b=0.018	K_1=0.04 K_2=0.06 m=0.81	T=41.74 a=1.39 th=0.14	K=0.04 k=0.72 p=5.71	a_1=0.06 a_2=0.03 b_1=0.78 b_2=0.75
		Max. Dev.	-9.76	7.3	3	-17.07	2.96	-2.44
		Std. Dev.	2.87	2.05	.65	3.05	0.6	.74
		R^2	0.98	0.99	0.99	0.99	0.99	0.99
.	Fly Ash A (T= 60°C)	2-Amino phenol	K_f=0.12 n=2.14	Q=1.82 b=0.019	K_1=0.05 K_2=0.1 m=0.75	T=35.18 a=1.6 th=0.16	K=0.056 k=0.36 p=3.45	a_1=0.06 a_2=0.13 b_1=0.93 b_2=0.67
		Max. Dev.	-7.32	10.7	3.6	-9.76	3.55	3.6
		Std. Dev.	2.11	3.15	087	1.88	0.79	0.87
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
.	Fly Ash A (T= 30°C)	3-Amino phenol	K_f=0.099 n=1.63	Q=3.83 b=0.009	K_1=0.05 K_2=0.03 m=0.84	T=65.19 a=2.38 th=0.19	K=0.042 k=0.93 p=3.83	a_1=-0.121 a_2=-0.68 b_1=4.05 b_2=3.56
		Max. Dev.	-21.05	9.5	-13.8	-35.56	-14.04	-44.44
		Std. Dev.	4.93	2.48	3.78	7.31	2.98	8.74
		R^2	0.97	0.99	0.97	0.95	0.99	0.94
.	Fly Ash A (T= 45°C)	3-Amino phenol	K_f=0.11 n=1.93	Q=2.68 b=0.011	K_1=0.03 K_2= 0.005 m=1.13	T=28.1 a=1.58 th=0.17	K=0.031 k=2.58 p=107.64	a_1=0.038 a_2=0.003 b_1=0.91 b_2=1.13
		Max. Dev.	-19.4	-7.5	-3.3	-40	-8.96	-5
		Std. Dev.	5.2	1.59	0.99	7.44	1.76	1.3
		R^2	0.95	0.99	0.99	0.95	0.99	0.99
.	Fly Ash A (T= 60°C)	3-Amino phenol	K_f=0.13 n=2.61	Q=1.19 b=0.02	K_1= 0.033 K_2= 0.048 m=.88	T=16.3 a=1.02 th=0.14	K=- 1403.68 k=0.11 p=2.42	a1=0.081 a2=0.059 b1=0.64 b2=0.6
		Max. Dev.	-8.55	-9.4	5.06	-11.11	-14.25	5.6
		Std. Dev.	2.44	2.65	1.37	2.41	2.94	1.37
		R^2	0.98	0.98	0.99	0.98	0.99	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
9.	Fly Ash B (T= 30 °C)	Phenol	K_f=0.194 n=2.11	Q=2.85 b=0.021	K_1=0.066 K_2=0.05 m=0.85	T=4.18 a=12.24 th=0.63	K=-92.7 k=0.15 p=1.86	a_1=0.06 a_2=0.049 b_1=0.99 b_2=0.84
		Max Dev.	8.1	13.46	-3.3	-3.35	-26.94	-3.35
		Std. Dev.	2.34	3.45	1.05	0.97	5.42	1.08
		R^2	0.99	0.98	0.99	0.99	0.99	0.99
0.	Fly Ash B (T= 45 °C)	Phenol	K_f=0.183 n=2.1	Q=2.68 b=0.021	K_1=0.058 K_2=0.04 m=0.86	T=4.03 a=14.05 th=0.65	K=0.087 k=0.57 p=3.48	a_1=0.08 a_2=0.025 b_1=0.82 b_2=0.81
		Max Dev.	10	-10.73	7.4	5.56	-5.75	3.7
		Std. Dev.	3.04	2.83	1.38	1.09	1.21	.82
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
1.	Fly Ash B (T= 60 °C)	Phenol	K_f=0.2 n=2.28	Q=2.49 b=0.022	K_1=0.049 K_2=0.016 m=1.01	T=2.66 a=53.11 th=1	K=0.06 k=1.05 p=6.23	a_1=0.069 a_2=0.023 b_1=0.89 b_2=0.9
		Max Dev.	-6.7	-13.48	9.4	7.55	5.91	-4.49
		Std. Dev.	1.8	4.13	1.77	1.52	1.51	1.13
		R^2	0.99	0.96	0.99	0.99	0.99	0.99
2.	Fly Ash B (T= 30 °C)	Catechol	K_f=0.26 n=1.67	Q=6.94 b=0.016	K_1=0.15 K_2=0.11 m=0.69	T=21.4 a=7.07 th=0.42	K=0.12 k=4.02 p=9.04	a_1=0.12 a_2=0.14 b_1=1.17 b_2=0.8
		Max Dev.	11.9	-13.39	-5.6	-8.33	-8.61	4.96
		Std. Dev.	2.84	3.52	1.43	1.76	1.95	1.35
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
3.	Fly Ash B (T= 45 °C)	Catechol	K_f=0.25 n=1.733	Q=6.135 b=0.017	K_1=0.13 K_2=0.098 m=0.71	T=16.6 a=7.47 th=0.44	K=0.11 k=3.64 p=9.64	a_1=0.16 a_2=0.05 b_1=0.85 b_2=0.67
		Max Dev.	-17.3	-14.29	8.7	8.7	-14.22	8.7
		Std. Dev.	3.68	3.72	2.22	2.27	2.89	2.38
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
4.	Fly Ash B (T= 60 °C)	Catechol	K_f=.22 n=1.74	Q=5.03 b=0.018	K_1=0.11 K_2=0.09 m=0.7	T=16.2 a=7.83 th=0.44	K=0.13 k=0.83 p=2.85	a_1=0.13 a_2=0.08 b_1=0.9 b_2=0.65
		Max Dev.	-16.5	-7.35	-7.3	-6.8	-5.83	-6.8
		Std. Dev.	4.57	2.38	1.69	1.52	1.31	1.49
		R^2	0.99	0.99	0.99	0.99	0.99	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
Fly Ash B (T= 30°C)	Resorcinol	K_f=0.16 n=2.13	Q=2.48 b=0.017	K_1=0.04 K_2=0.006 m =1.13	T=2.35 a=247.05 th=1.31	K=0.05 k=1.01 p=6.04	a_1=0.054 a_2=0.01 b_1=0.89 b_2=0.99
	Max Dev.	-10.1	-15.667	10.8	10.42	9.29	-10.13
	Std. Dev.	2.1	4.88	2.18	2.3	2.47	1.85
	R^2	0.99	0.95	0.99	0.99	0.99	0.99
Fly Ash B (T= 45°C)	Resorcinol	K_f=.117 n=1.98	Q=2 b=0.019	K_1=0.03 K_2=0.01 m=0.1	T=2.85 a=49.46 th=0.86	K=0.136 k=0.17 p=2.28	a_1=0.06 a_2=0.04 b_1=0.82 b_2=0.68
	Max Dev.	-18.2	12.28	-9.6	20.45	12.28	-9.09
	Std. Dev.	5.36	2.79	4.57	3.92	2.64	2.68
	R^2	0.96	0.99	0.99	0.99	0.99	0.98
Fly Ash B (T= 60°C)	Resorcinol	K_f=0.131 n=2.16	Q=1.86 b=0.019	K_1=0.037 K_2=0.041 m=0.85	T=2.85 a=13.55 th=0.63	K=0.05 k=0.37 p=3.43	a_1=0.049 a_2=0.052 b_1=0.92 b_2=0.77
	Max Dev.	-11	9.87	7.1	-6	7.24	5.26
	Std. Dev.	3.17	2.64	1.81	1.52	1.44	1.34
	R^2	0.99	0.99	0.99	0.99	0.99	0.98
Fly Ash B (T= 30°C)	Hydroquinone	K_f=.225 n=1.78	Q=5.32 b=0.016	K_1=0.077 K_2=0.01 m=1.04	T=5.53 a=113.89 th=1.1	K=-1083.03 k=0.16 p=1.51	a_1=0.07 a_2=0.01 b_1=1.02 b_2=1.03
	Max Dev.	-5.7	-15.73	9.1	9.09	-46.34	9.09
	Std. Dev.	1.82	4.74	1.64	1.65	9.03	1.67
	R^2	0.99	0.97	0.99	0.99	0.99	0.99
Fly Ash B (T= 45°C)	Hydroquinone	K_f=.228 n=1.89	Q=4.76 b=0.016	K_1=0.06 K_2=0.002 m=1.27	T=4.12 a=713.83 th=1.56	K=0.07 k=4.07 p=32.8	a_1=0.39 a_2=-0.0066 b_1=0.41 b_2=-0.003
	Max Dev.	10.7	-22.89	14.3	-12.5	10.98	-58.73
	Std. Dev.	2.26	6.16	3.26	3.05	2.33	10.8
	R^2	0.99	0.95	0.99	0.99	0.99	0.92
Fly Ash B (T= 60°C)	Hydroquinone	K_f=0.24 n=1.97	Q=4.42 b=0.017	K_1=0.06 K_2=0.005 m=1.18	T=3.99 a=298.92 th=1.38	K=0.08 k=3.81 p=35.71	a_1=0.074 a_2=0.01 b_1=0.99 b_2=1.065
	Max Dev.	9.9	-17.46	11.1	-10.66	9.94	-9.64
	Std. Dev.	2.05	5.76	2.84	2.78	2.12	2.24
	R^2	0.99	0.95	0.99	0.99	0.98	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. 'o	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
1.	Fly Ash B (T= 30°C)	2-Amino phenol	K_f=0.098 n=1.59	Q=4.29 b=0.0084	K_1=0.05 K_2= 0.044 m=0.78	T=3.63 a=805.99 th=1.41	K=-135.29 k=0.069 p=1.38	a_1=0.044 a_2=0.0006 b_1=0.88 b_2=1.34
		Max Dev.	8.9	-17.04	-17.8	-6.85	-43.41	5.53
		Std. Dev.	1.65	4.62	4.19	1.81	8.23	1.24
		R^2	0.99	0.97	0.98	0.99	0.98	0.99
2.	Fly Ash B (T= 45°C)	2-Amino phenol	K_f=0.1 n=1.64	Q=3.86 b=0.0093	K_1=0.05 K_2= 0.033 m=0.82	T=3.26 a=1728.53 th=1.58	K=0.04 k=1.25 p=4.79	a_1=0.038 a_2=0.02 b_1=1.03 b_2=0.91
		Max Dev.	9.1	15.35	-13.8	11.11	9.96	-11.25
		Std. Dev.	1.87	4.66	3.67	2.22	2.37	2.76
		R^2	0.99	0.97	0.98	0.99	0.99	0.99
3.	Fly Ash B (T= 60°C)	2-Amino phenol	K_f=0.1 n=1.76	Q=3.4 b=0.0094	K_1= 0.037 K2= 0.017 m=0.93	T=3.36 a=61.77 th=0.91	K=0.032 k=3.33 p=195.7	a_1=0.006 a_2=0.013 b_1=1.67 b_2=1.39
		Max Dev.	-10.2	18.84	-9.8	-7.32	-10.65	-6.02
		Std. Dev.	1.96	5.15	2.35	2.1	2.03	1.76
		R^2	0.99	0.96	0.99	0.99	0.99	0.99
4.	Fly Ash B (T= 30°C)	3-Amino phenol	K_f=0.1 n=1.59	Q=4.03 b=0.01	K_1=0.03 K_2= 0.001 m=1.29	T=3.94 a=769.2 th=1.38	K=0.072 k=0.27 p=2.04	a_1=-0.074 a_2=-0.45 b_1=1.738 b_2=1.21
		Max Dev.	12.9	-19.31	16.7	14.58	-20.25	-47.92
		Std. Dev.	3.28	4.3	3.06	2.98	3.82	9.38
		R^2	0.99	0.99	0.99	0.99	0.99	0.95
5.	Fly Ash B (T= 45°C)	3,Amino-phenol	K_f=0.11 n=1.75	Q=3.22 b=0.01	K_1=0.04 K_2=0.03 m=0.87	T=3.01 a=733.31 th=1.43	K=0.053 k=0.499 p=2.92	a_1=0.117 a_2=0.34 b_1=0.99 b_2=0.62
		Max Dev.	11.8	-19.16	-14.1	15.22	-15.71	-26.09
		Std. Dev.	2.96	4.76	3.28	3.12	3.46	6.02
		R^2	0.99	0.95	0.99	0.99	0.99	0.95
5.	Fly Ash B (T= 60°C)	3-Amino phenol	K_f=0.11 n=1.84	Q=2.69 b=0.014	K_1=0.03 K_2= 0.002 m=1.22	T=2.86 a=256.35 th=1.21	K=0.059 k=0.39 p=2.86	a_1=0.16 a_2=-0.06 b_1=0.46 b_2= -0.000026
		Max Dev.	13.7	17.54	22.2	15.56	14.69	-31.11
		Std. Dev.	3.64	3.96	4.4	3.62	3.02	6.36
		R^2	0.99	0.97	0.98	0.98	0.99	0.95

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
7.	Fly Ash C (T= 30°C)	Phenol	K_f=0.084 n=2.66	Q=0.56 b=0.04	K_1= 0.018 K_2=0.01 m=1.24	T=6.37 a=0.9 th=.14	K=0.02 k=0.56 p=9032.1	a_1=0.02 a_2=0.025 b_1=0.98 b_2=1.07
		Max Dev.	5.56	-4.2	-4.2	-8.33	-4.17	-4.17
		Std. Dev.	2.4	1.5	1.38	3.01	1.5	1.33
		R^2	0.99	0.99	0.99	0.94	0.99	0.99
8.	Fly Ash C (T= 45°C)	Phenol	K_f=0.1 n=3.35	Q=0.45 b=0.06	K_1=0.1 K_2=0.71 m=0.76	T=7.97 a=0.63 th=0.1	K=-1086.56 k=0.1 p=3.32	a_1=0.01 a_2=0.11 b_1=2 b_2=1.73
		Max Dev.	0	-3.1	0	0	0	0
		Std. Dev.	0	1.22	0	0	0	0
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
9.	Fly Ash C (T= 60°C)	Phenol	K_f=0.1 n=3.8	Q=0.36 b=0.08	K_1=0.36 K_2=3.49 m=0.73	T=16.1 a=0.5 th=0.07	K=0.038 k=0.25 p=12.7	a_1=0.028 a_2=0.29 b_1=2.5 b_2=2.22
		Max Dev.	4.35	8.6	4.3	4.35	5.71	4.35
		Std. Dev.	1.8	2.71	1.8	1.8	2.18	1.8
		R^2	0.98	0.92	0.97	0.97	0.94	0.98
0.	Fly Ash C (T= 30°C)	Catechol	K_f=0.036 n=1.91	Q=0.52 b=0.024	K_1= 0.047 K_2=0.92 m=0.53	T=2.41 a=3.48 th=0.29	K=18.03 k=0.036 p=1.93	a_1=0.039 a_2=0.124 b_1=0.52 b_2=0.004
		Max Dev.	-4	-8	-4	-4	-4	-4
		Std. Dev.	1.42	2.51	1.25	1.42	1.25	1.25
		R^2	0.99	0.98	0.99	0.99	0.99	0.99
1.	Fly Ash C (T= 45°C)	Catechol	K_f=0.04 n=2.14	Q=0.43 b=0.03	K_1=0.09 K_2=1.93 m=0.56	T=2.18 a=2.71 th=0.289	K=1048.4 k=0.04 p=2.16	a_1=-0.014 a_2=-0.41 b_1=1.69 b_2=1.191
		Max Dev.	5.88	6.1	5.9	5.88	6.67	6.67
		Std. Dev.	1.69	2.52	2.01	2.01	1.67	1.67
		R^2	0.99	0.97	0.97	0.97	0.99	0.99
2.	Fly Ash C (T= 60°C)	Catechol	K_f=0.034 n=2.13	Q=0.36 b=0.32	K_1=0.14 K_2=4.46 m=0.5	T=2.97 a=3.02 th=0.27	K=-1.38 k=0.04 p=2.41	a_1=0.023 a_2=-0.41 b_1=0.547 b_2=-0.45
		Max Dev.	-10	-10.5	6.7	6.67	3.11	-10.53
		Std. Dev.	3.22	3.63	2.28	2.28	-10.53	3.11
		R^2	0.96	0.9	0.96	0.95	0.95	0.97

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
3.	Fly Ash C (T= 30°C)	Resorcinol	K_f=0.059 n=2.35	Q=0.51 b=0.035	K_1=0.08 K_2=1.01 m=0.62	T=25.84 a=1.17 th=0.12	K=0.02 k=0.29 p=8.53	a_1=0.06 a_2=-0.004 b_1=0.41 b_2=0.43
		Max Dev.	3.33	4.9	-2.9	-2.86	-3.33	3.33
		Std. Dev.	1.1	1.64	0.94	0.94	1.26	1.1
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
4.	Fly Ash C (T= 45°C)	Resorcinol	K_f=0.058 n=2.53	Q=0.415 b=0.043	K_1=0.17 K_2=2.85 m=0.6	T=24.13 a=1.03 th=0.11	K=0.02 k=0.27 p=11.63	a_1=0.03 a_2=0.56 b_1=7.62 b_2=7.21
		Max Dev.	-4	8.3	5	5	-8	5
		Std. Dev.	1.74	3.15	1.74	1.74	2.741	1.74
		R^2	0.99	0.95	0.98	0.98	0.96	0.99
5.	Fly Ash C (T= 60°C)	Resorcinol	K_f=0.061 n=2.87	Q=0.35 b=0.051	K_1=0.26 K_2=4.34 m=0.64	T=18.59 a=0.82 th=0.101	K=0.02 k=0.22 p=11.65	a_1=0.11 a_2=-0.008 b_1=0.1 b_2=0.85
		Max Dev.	-3.85	9.7	5.6	5.56	6.45	4.35
		Std. Dev.	1.25	2.82	1.87	1.87	2.17	1.09
		R^2	0.97	0.94	0.96	0.96	0.95	0.99
5.	Fly Ash C (T= 30°C)	Hydroquinone	K_f=0.344 n=1.96	Q=0.59 b=0.026	K_1= 0.036 K_2=0.44 m=0.59	T=42.92 a=1.87 th=0.14	K= 1589.12 k=0.047 p=2.01	a_1=0.04 a_2=-0.11 b_1=0.38 b_2=0.27
		Max Dev.	-3.45	-10.3	-6.9	-6.9	5.13	-3.45
		Std. Dev.	1.07	2.9	2.19	2.19	1.54	1.22
		R^2	0.99	0.97	0.98	0.98	0.99	0.98
7.	Fly Ash C (T= 45°C)	Hydroquinone	K_f=.037 n=1.96	Q=0.48 b=0.027	K_1=0.15 K_2=4.75 m=0.45	T=39.2 a=1.76 th=0.14	K=0.032 k=0.07 p=2.76	a_1=0.112 a_2=-0.01 b_1=0.09 b_2=0.86
		Max Dev.	-10.34	14.6	-13.8	-13.79	12.2	8
		Std. Dev.	3.69	4.91	4.14	4.03	4.12	2.26
		R^2	0.94	0.94	0.91	0.90	0.96	0.98
3.	Fly Ash C (T= 60°C)	Hydroquinone	K_f=0.036 n=2.09	Q=0.39 b=0.031	K1=0.14 K2=4.45 m=0.49	T=32.013 a=1.49 th=.13	K=-0.56 k=0.04 p=2.25	a_1=0.03 a_2=0.2 b_1=0.52 b_2=0.0001
		Max Dev.	-10	-15	11.8	-15	-10	11.76
		Std. Dev.	3	4.71	3.93	4.1	3.06	3.93
		R^2	0.93	.87	0.95	0.93	0.92	0.95

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
9.	Fly Ash C (T= 30°C)	2-Amino phenol	K_f=0.046 n=2.09	Q=0.53 b=0.027	K_1= 0.027 K_2=0.24 m=0.69	T=37.13 a=1.4 th=.13	K=0.017 k=0.29 p=8.02	a_1=0.032 a_2=0.032 b_1=0.65 b_2=0.65
		Max Dev.	-2.56	-3.6	0	0	0	0
		Std. Dev.	0.64	1.1	0	0	0	0
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
0	Fly Ash C (T= 45°C)	2-Amino phenol	K_f=0.043 n=2.14	Q=0.468 b=0.029	K_1=0.09 K_2=1.81 m=0.56	T=38.23 a=1.46 th=.12	K=0.01 k=0.27 p=9.06	a_1=0.04 a_2=-0.06 b_1=0.47 b_2=-0.29
		Max Dev.	0	5.6	0	0	-4	0
		Std. Dev.	0	1.71	0	0	1.22	0
		R^2	0.99	0.98	0.99	0.99	0.98	0.99
1.	Fly Ash C (T= 60°C)	2-Amino phenol	K_f=0.041 n=2.21	Q=0.37 b=0.036	K_1=0.19 K_2=5.43 m=0.5	T=36.5 a=1.58 th=0.13	K=0.02 k=0.18 p=6.67	a_1=0.038 a_2=0.16 b_1=0.5 b_2=-0.019
		Max Dev.	-15	-20	-15	-15	-15	-15
		Std. Dev.	4.4	6.09	4.83	4.83	4.71	4.83
		R^2	0.92	.85	0.94	0.93	.87	0.94
2.	Fly Ash C (T= 30°C)	3-Amino phenol	K_f=0.091 n=2.77	Q=0.56 b=0.044	K_1= 0.017 K_2= 0.006 m=1.33	T=0.47 a=343.72 th=1.75	K=-36.18 k=0.08 p=2.6	a_1=-0.019 a_2=-0.24 b_1=1.67 b_2=1.29
		Max Dev.	-6.98	-4.7	-5.6	4.55	-9.3	11.36
		Std. Dev.	2.73	1.63	1.61	1.45	3.13	3.71
		R^2	0.93	0.98	0.96	0.96	0.95	0.81
3.	Fly Ash C (T= 45°C)	3-Amino phenol	K_f=0.081 n=2.8	Q=0.48 b=0.046	K_1=0.03 K_2=0.12 m=0.86	T=9.52 a=0.51 th=0.09	K=0.02 k=0.3 p=10.1	a_1=0.024 a_2=0.12 b_1=1.16 b_2=0.98
		Max Dev.	3.13	-2.8	-2.8	-13.04	-2.78	0
		Std. Dev.	1	0.93	.69	3.32	.69	0
		R^2	0.99	0.99	0.99	0.94	0.99	0.99
4.	Fly Ash C (T= 60°C)	3-Amino phenol	K_f=0.12 n=4.78	Q=0.34 b=0.1	K_1=0.15 K_2=1.01 m=0.82	T=5.09 a=0.35 th=0.07	K=-93.16 k=0.12 p=4.75	a_1=0.02 a_2=0.13 b_1=1.74 b_2=1.57
		Max Dev.	-7.14	-7.1	-7.1	-7.14	-7.14	-7.14
		Std. Dev.	2	1.95	2	2	2	2
		R^2	0.93	0.94	0.92	0.92	0.94	0.92

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

:. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
.	Fly Ash D (T= 30°C)	Phenol	K_f=1.37 n=2.26	Q=17.33 b=0.019	K_1=0.7 K_2=0.22 m=0.69	T=154.1 a=1.85 th=0.2	K=0.48 k=0.51 p=4.51	a_1=0.01 a_2=0.006 b_1=2.58 b_2=2.2
		Max Dev.	6.13	9.8	-4.2	-4.06	4.06	-4.2
		Std. Dev.	1.72	2.29	1.18	1.35	1.16	1.18
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
.	Fly Ash D (T= 45°C)	Phenol	K_f=1.18 n=2.22	Q=15.06 b=0.02	K_1=0.85 K_2=0.57 m=0.57	T=260.7 a=2.3 th=0.19	K=18.5 k=1.32 p=2.35	a_1=0.62 a_2=0.64 b_1=8.85 b_2=8.36
		Max Dev.	5.23	17.5	12.4	11.98	7.94	10.02
		Std. Dev.	1.76	5.1	2.97	2.91	1.99	2.33
		R^2	0.99	0.95	0.98	0.98	0.99	0.99
.	Fly Ash D (T= 60°C)	Phenol	K_f=1.18 n=2.27	Q=14.36 b=0.02	K_1=0.87 K_2=0.61 m=0.57	T=279 a=2.22 th=0.19	K=35.48 k=1.32 p=2.4	a_1=0.63 a_2=0.65 b_1=13.6 b_2=13.12
		Max Dev.	-6.01	17.9	13.1	13.89	8.62	10.91
		Std. Dev.	1.96	5.25	3.13	3.19	2.16	2.52
		R^2	0.99	0.94	0.98	0.98	0.99	0.99
.	Fly Ash D (T= 30°C)	Catechol	K_f=1.94 n=1.74	Q=37.15 b=0.022	K_1=0.88 K_2= 0.027 m=0.98	T=242.1 a=1.87 th=0.22	K=0.83 k=37.13 p=21108	a_1=0.44 a_2=0.05 b_1=1.44 b_2=1.19
		Max Dev.	-10.86	2.7	-3.5	-33.72	2.67	0.17
		Std. Dev.	3.86	.76	0.79	6.83	0.76	0.06
		R^2	0.97	0.99	0.99	0.98	0.99	0.99
.	Fly Ash D (T= 45°C)	Catechol	K_f=2.06 n=1.79	Q=33.46 b=0.027	K_1=0.84 K_2=0.02 m=1.03	T=217.3 a=2.33 th=0.25	K=1 k=17.86 p=7.16	a_1=0.86 a_2=0.018 b_1=0.98 b_2=1.04
		Max Dev.	11.54	-5.4	4.4	-18.6	5.03	4.57
		Std. Dev.	3.57	1.36	1.36	4.15	1.29	1.36
		R^2	0.97	0.99	0.99	0.98	0.99	0.99
.	Fly Ash D (T= 60°C)	Catechol	K_f=1.93 n=1.73	Q=30.71 b=0.028	K_1=0.71 K_2= 0.012 m=1.08	T=258.5 a=2.14 th=0.23	K=1.57 k=4.80 p=2.51	a_1=0.71 a_2=0.019 b_1=1.02 b_2=1.03
		Max Dev.	13.74	-15.3	13.1	-19.02	11.21	-12.8
		Std. Dev.	3.7	3.72	3.77	5.22	3.16	3.65
		R^2	0.97	0.98	0.99	0.97	0.99	0.98

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

:. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
	Fly Ash D (T= 30°C)	Resorcinol	K_f=1.85 n=2.91	Q=13.32 b=0.28	K_1=0.54 K_2=0.1 m=0.83	T=40.88 a=1.53 th=0.25	K=0.61 k=4.72 p=5.39	a_1=1.77 a_2=-0.14 b_1=0.31 b_2= 0.00004
		Max Dev.	-6.67	7.2	5.4	5.84	5.6	-8.09
		Std. Dev.	2.1	2.26	1.41	1.59	1.4	2.36
		R^2	0.98	0.99	0.98	0.98	0.99	0.97
	Fly Ash D (T= 45°C)	Resorcinol	K_f=1.94 n=3.03	Q=12.7 b=0.032	K_1=0.83 K_2=0.22 m=0.77	T=74.95 a=1.05 th=0.17	K=1.51 k=2.7 p=3.63	a_1=2.95 a_2=1.1 b_1=0.26 b_2=-0.49
		Max Dev.	-5.45	-10.4	5.1	5.29	5.13	5.87
		Std. Dev.	1.53	2.96	1.34	1.27	1.33	1.38
		R^2	0.99	0.97	0.98	0.98	0.99	0.98
	Fly Ash D (T= 60°C)	Resorcinol	K_f=1.92 n=3.33	Q=10.82 b=0.033	K_1=0.61 K_2=0.15 m=0.82	T=27.9 a=1.4 th=0.26	K=14.87 k=1.93 p=3.34	a_1=2.59 a2=0.98 b1=0.25 b2=-0.59
		Max Dev.	10.96	-17.1	-11.4	-9.96	10.96	10.35
		Std. Dev.	2.82	3.95	2.96	2.8	2.82	2.82
		R^2	0.98	0.93	0.94	0.94	0.97	0.99
	Fly Ash D (T= 30°C)	Hydroquinone	K_f=1.18 n=1.72	Q=40 b=0.018	K_1=0.86 K_2=0.03 m=0.94	T=37.2 a=33.29 th=0.92	K=0.74 k=40 p= 29228.24	a_1=0.02 a_2=0.005 b_1=2.88 b_2=2.48
		Max Dev.	-13.46	8	-10	-9.3	8.02	0.98
		Std. Dev.	4.41	2.25	2.3	2.21	2.25	0.30
		R^2	0.91	0.99	0.99	0.99	0.99	0.99
	Fly Ash D (T= 45°C)	Hydroquinone	K_f=2.14 n=1.98	Q=34.18 b=0.02	K_1=0.59 K_2= 0.002 m=1.39	T=29.76 a=22.2 th=0.91	K=0.69 k=34.18 p=16307.8	a_1=0.65 a_2=0.015 b_1=1.06 b_2=1.14
		Max Dev.	-17.95	-14.4	2	-22.48	-14.4	-9.4
		Std. Dev.	6.84	3.2	0.43	4.95	3.2	2.33
		R^2	0.91	0.99	0.99	0.97	0.99	0.9
	Fly Ash D (T= 60°C)	Hydroquinone	K_f=2.14 n=2	Q=30.78 b=0.023	K_1=0.63 K_2= 0.006 m=1.22	T=29.7 a=20.67 th=0.89	K=0.73 k=30.76 p=6062.7	a_1=1.78 a_2=0.007 b_1=0.62 b_2=0.93
		Max Dev.	-19.11	-7.6	-5.8	-17.03	-7.63	-19.7
		Std. Dev.	5.92	2.06	1.44	4.21	2.06	4.64
		R^2	0.93	0.99	0.99	0.98	0.99	0.96

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

r. o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
7.	Fly Ash D (T= 30°C)	2-Amino phenol	$K_f=1.98$ n=3.23	Q=12.15 b=0.029	$K_1=0.42$ $K_2=0.05$ m=0.91	T=14.37 a=8.5 th=0.67	K=0.41 k=7.97 p=13.35	$a_1=0.8$ $a_2=0.024$ $b_1=0.65$ $b_2=0.77$
		Max Dev.	8.11	-4.1	3.2	-3.13	3.17	-3.55
		Std. Dev.	2.46	1.21	0.93	0.96	0.91	0.99
		R^2	0.97	0.99	0.99	0.99	0.99	0.99
8.	Fly Ash D (T= 45°C)	2-Amino phenol	$K_f=2.036$ n=3.38	Q=11.46 b=0.031	$K_1=0.53$ $K_2=0.1$ m=0.86	T=220.5 a=1.63 th=0.31	K=0.42 k=7.38 p=12.88	$a_1=1.19$ $a_2=0.01$ $b_1=0.48$ $b_2=0.75$
		Max Dev.	-5.2	-7.4	-5.6	6.27	-6.38	-6.16
		Std. Dev.	2.36	1.81	1.52	1.82	1.49	1.7
		R^2	0.96	0.99	0.98	0.98	0.99	0.97
9.	Fly Ash D (T= 60°C)	2-Amino phenol	$K_f=2.05$ n=3.53	Q=10.79 b=0.032	$K_1=0.64$ $K_2=0.15$ m=0.84	T=23.83 a=2.35 th=0.28	K=0.47 k=5.84 p=9.3	$a_1=1.46$ $a_2=0.02$ $b_1=0.42$ $b_2=0.58$
		Max Dev.	8.08	-6.3	-4.2	5.26	-4.9	-4.3
		Std. Dev.	1.88	1.79	1.26	1.45	1.25	1.47
		R^2	0.97	0.99	0.98	0.98	0.99	0.98
0.	Fly Ash D (T= 30°C)	3-Amino phenol	$K_f=1.76$ n=2.89	Q=13.21 b=0.0256	$K_1=0.41$ $K_2=0.06$ m=0.88	T=28.1 a=2.19 th=0.33	K=0.46 k=5.86 p=6.92	$a_1=1$ $a_2=0.002$ $b_1=0.52$ $b_2=0.97$
		Max Dev.	-7.82	6.7	5.4	5.82	5.57	-4.5
		Std. Dev.	2.38	1.9	1.39	1.69	1.38	1.33
		R^2	0.97	0.99	0.98	0.98	0.99	0.98
1.	Fly Ash D (T= 45°C)	3-Amino phenol	$K_f=1.94$ n=3.17	Q=12.14 b=0.029	$K_1=0.57$ $K_2=0.11$ m=0.84	T= 25.59 a=1.82 th=0.31	K=0.5 k=5.75 p=7.56	$a_1=1.29$ $a_2=0.008$ $b_1=0.46$ $b_2=0.73$
		Max Dev.	6.61	5.9	1.6	3.06	1.71	2.67
		Std. Dev.	1.74	1.5	0.51	0.9	0.52	0.82
		R^2	0.98	0.99	0.99	0.99	0.99	0.99
2.	Fly Ash D (T= 60°C)	3-Amino phenol	$K_f=1.97$ n=3.25	Q=11.82 b=0.03	$K_1=0.6$ $K_2=0.12$ m=0.83	T=24.21 a=1.81 th=0.32	K=0.51 k=5.55 p=7.48	$a_1=1.32$ $a_2=0.01$ $b_1=0.45$ $b_2=0.69$
		Max Dev.	7.03	5.3	-3	3.45	-3.43	3.33
		Std. Dev.	1.73	1.66	0.8	1.01	0.8	1
		R^2	0.98	0.99	0.99	0.99	0.99	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

o.	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
.	Activated carbon (T= 30°C)	Phenol	K_f=13.46 n=3.184	Q=58.44 b=0.1276	K_1=6.45 K_2=0.15 m=0.91	T=120.3 a=1.22 th=0.32	K=14.1 k=22.81 p=4.81	a_1=6.39 a_2=0.27 b_1=1.27 b_2=1.27
		Max Dev.	-10.64	-15.9	16.6	4.05	-5.26	3.44
		Std. Dev.	3.09	4.22	3.62	1.33	1.47	2.11
		R^2	0.97	0.98	0.98	0.99	0.99	0.99
.	Activated carbon (T= 45°C)	Phenol	K_f=14.01 n=4.18	Q=46.33 b=0.15	K_1=8.84 K_2=.3 m=0.9	T=59.23 a=1.79 th=0.51	K=12.4 k=23.09 p=6.99	a_1=6.8 a_2=0.26 b_1=1.22 b_2=1.11
		Max Dev.	12.74	-16.2	-8.7	-7.9	9.15	-8.77
		Std. Dev.	3.49	3.76	2.41	2.2	2.29	2.59
		R^2	0.95	0.97	0.97	0.97	0.99	0.96
.	Activated carbon (T= 60°C)	Phenol	K_f=15.13 n=5.62	Q=50 b=0.154	K_1=10.5 K_2=0.38 m=0.93	T=44.4 a=1.28 th=0.52	K=10.5 k=27.02 p=14.4	a_1=8.17 a_2=0.32 b_1=1.22 b_2=1.15
		Max Dev.	9.37	-6	1	-0.88	0.96	1.19
		Std. Dev.	2.59	1.61	0.23	0.25	0.24	0.28
		R^2	0.95	0.99	0.99	0.99	0.99	0.99
.	Activated carbon (T= 30°C)	Catechol	K_f=8.17 n=1.51	Q=125.61 b=0.0178	K_1=2.12 K_2= 0.016 m=0.98	T=624.6 a=4.19 th=0.32	K=2.66 k=35.25 p=3.58	a_1=1.93 a_2=0.026 b_1=1.06 b_2=0.96
		Max Dev.	6.88	-4.9	4.2	-21.01	3.28	4.8
		Std. Dev.	2.17	1.26	1.08	4.77	0.95	1.2
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
.	Activated carbon (T= 45°C)	Catechol	K_f=8.41 n=1.68	Q=113.32 b=0.046	K_1=0.98 K_2= -0.97 m=-0.19	T=641.9 a=3.48 th=0.33	K=5.93 k=56.03 p=5.54	a_1=0.97 a_2=0.088 b_1=3.15 b_2=2.63
		Max Dev.	7.86	7.8	25	-4.65	-4.54	-1.75
		Std. Dev.	2.14	2.04	6.78	1.32	1.17	.49
		R^2	0.99	0.99	0.9	0.99	0.99	0.99
.	Activated carbon (T= 60°C)	Catechol	K_f=7.5 n=1.85	Q=77.16 b=0.064	K_1=3.63 K_2=0.18 m=0.588	T=791.2 a=4.08 th=0.31	K=1288 k=8.4 p=1.99	a_1=2.86 a_2=0.51 b_1=7.97 b_2=7.34
		Max Dev.	-11.82	-26	35.1	21.16	11.72	20.63
		Std.Dev.	3.09	7.57	7.16	5.09	3.55	4.38
		R^2	0.99	0.95	0.97	0.97	0.99	0.99

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
	Activated carbon (T= 30°C)	Resorcinol	K_f=3.66 n=2.48	Q=40.73 b=0.016	K_1=1.81 K_2=0.21 m=0.73	T=143.7 a=1.93 th=0.25	K=0.83 k=18.73 p=7.36	a_1=0.11 a_2=0.01 b_1=1.64 b_2=1.44
		Max Dev.	10.44	-7.1	-8.7	-8.7	6.67	-6.89
		Std. Dev.	2.81	1.77	2.6	2.51	1.64	1.93
		R^2	0.97	0.99	0.97	0.97	0.99	0.98
	Activated carbon (T= 45°C)	Resorcinol	K_f=3.99 n=2.72	Q=37.29 b=0.017	K_1=0.62 K_2=0.01 m=1.02	T=130.8 a=1.41 th=0.228	K=0.64 k=36.64 p=302.1	a_1=0.078 a_2=0.006 b_1=1.76 b_2=1.58
		Max Dev.	-8.84	2.5	-2.1	-10.91	2.46	3.06
		Std. Dev.	3.05	0.66	0.62	2.84	0.66	1.02
		R^2	0.95	0.99	0.99	0.96	0.99	0.99
	Activated carbon (T= 60°C)	Resorcinol	K_f=4.34 n=2.94	Q=34.93 b=0.018	K_1=0.51 K_2=0.005 m=1.17	T=75.87 a=1.62 th=0.287	K=0.62 k=34.89 p=4287	a_1=4.74 a_2=0.53 b_1=0.78 b_2=0.55
		Max Dev.	10.99	5.3	2.7	-14.33	5.31	-16.83
		Std. Dev.	3.88	1.46	0.88	3.63	1.46	4.11
		R^2	0.91	0.99	0.99	0.93	0.99	0.91
	Activated carbon (T= 30°C)	Hydroquinone	K_f=12.65 n=3.32	Q=52.99 b=0.13	K_1=5.54 K_2=0.16 m=0.88	T=113.1 a=1.28 th=0.324	K=44.7 k=14.18 p=3.56	a_1=17.8 a_2=0.73 b_1=0.23 b_2=-0.71
		Max Dev.	9.97	-23.7	22.4	-10.18	8.91	-8.25
		Std. Dev.	2.74	5.75	5.35	2.61	2.58	2.59
		R^2	0.98	0.95	0.95	0.98	0.99	0.97
	Activated carbon (T= 45°C)	Hydroquinone	K_f=12.87 n=3.46	Q=51.25 b=0.14	K_1=7.43 K_2=0.26 m=0.85	T=102.75 a=1.25 th=0.33	K=57.2 k=13.97 p=3.64	a_1=16.76 a_2=0.544 b_1=0.233 b_2=-0.82
		Max Dev.	9.71	-24.1	-14.4	-11.12	-9.12	-8.29
		Std. Dev.	2.97	5.8	4.25	2.89	2.86	2.98
		R^2	0.97	0.95	0.96	0.97	0.99	0.96
	Activated carbon (T= 60°C)	Hydroquinone	K_f=13.66 n=3.81	Q=48.87 b=0.15	K_1=8.45 K_2=0.27 m=0.89	T=66.3 a=1.99 th=0.51	K=19.9 k=18.36 p=4.87	a_1=17.31 a_2=0.47 b_1=0.21 b_2=-0.9
		Max Dev.	-16.14	-22.9	-15.8	-14.72	-12.7	-11.3
		Std. Dev.	4.59	5.51	4.29	4.02	4.05	4.43
		R^2	0.93	0.95	0.91	0.92	0.97	0.88

Table 3.9. List of parameter values of the six adsorption isotherms for different systems investigated **(Continued)**

:. o	Adsorbent	Comp.	Freundlich	Langmuir	Redlich-Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
5.	Activated carbon (T= 30°C)	2-Amino phenol	K_f=10.51 n=3.83	Q=45.37 b=0.054	K_1=2.22 K_2= 0.035 m=1.06	T=12.8 a=45.75 th=1.26	K=2.48 k=45.36 p=18658.8	a_1=1.63 a_2=0.034 b_1=1.15 b_2=1.17
		Max Dev.	13.85	-3.1	0.4	1.09	-3.14	1.53
		Std. Dev.	4.96	0.94	0.12	0.3	0.94	0.42
		R^2	0.88	0.99	0.99	0.99	0.99	0.99
5.	Activated carbon (T= 45°C)	2-Amino phenol	K_f=10.15 n=3.82	Q=43.71 b=0.055	K_1=2.23 K_2=0.04 m=1.03	T=42.6 a=28.3 th=1.12	K=2.43 k=43.5 p=1056.28	a_1=1.41 a_2=0.038 b_1=1.23 b_2=1.21
		Max Dev.	11.41	2.8	-2	2.31	2.8	2.91
		Std. Dev.	4.38	0.66	0.63	0.65	0.67	0.91
		R^2	0.99	0.99	0.99	0.99	0.99	0.99
7.	Activated carbon (T= 60°C)	2-Amino phenol	K_f=105 n=3.98	Q=42.91 b=0.057	K_1=2.13 K_2= 0.035 m=1.06	T=40.94 a=44.25 th=1.25	K=2.46 k=42.9 p=7345	a_1=1.07 a_2=.029 b_1=1.34 b_2=1.32
		Max Dev.	11.9	4.1	-2.5	3.25	4.1	4.13
		Std. Dev.	4.76	1.05	0.81	0.89	1.05	1.22
		R^2	0.88	0.99	0.99	0.99	0.99	0.99
3.	Activated carbon (T= 30°C)	3-Amino phenol	K_f=10.42 n=3.47	Q=49.7 B=0.056	K_1=2.26 K_2= 0.029 m=1.07	T=48.34 a=34.83 th=1.18	K=2.85 k=47.11 p=95.6	a_1=2.25 a_2=0.024 b_1=0.968 b_2=1.079
		Max Dev.	18.92	9.8	-9.3	-9.78	10.06	9.67
		Std. Dev.	5.44	2.43	2.74	2.59	2.44	2.95
		R^2	0.88	0.99	0.96	0.96	0.99	0.96
).	Activated carbon (T= 45°C)	3-Amino phenol	K_f=9.56 n=5.29	Q=28.68 b=0.063	K_1=1.94 K_2=0.07 m=0.98	T=29.1 a=11.35 th=0.91	K=1.87 k=27.13 p=100.5	a_1=-5.66 a_2=-0.54 b_1=5.8 b_2=5.64
		Max Dev.	8.78	2.1	-1.8	3.4	-1.8	-8.94
		Std. Dev.	2.36	0.56	0.54	0.56	0.54	2.54
		R^2	0.93	0.99	0.99	0.99	0.99	0.92
).	Activated carbon (T= 60°C)	3-Amino phenol	K_f=8.78 n=5.32	Q=25.92 b=0.067	K_1=4.28 K_2=0.35 m=0.86	T=58.63 a=0.56 th=0.2	K=8.55 k=10.37 p=6.25	a_1=6.6 a_2=0.63 b_1=1.07 b_2=0.91
		Max Dev.	3.34	-6.6	3.4	3.61	3.53	3.53
		Std. Dev.	0.97	2.13	0.98	0.92	0.9	0.9
		R^2	0.98	0.96	0.98	0.98	0.98	0.98

It is also evident from the Table 3.5 that the relative adsorbabilities of phenolic compounds for different adsorbents are in the order;

Activated carbon > fly ash D > fly ash B> fly ash A> fly ash C

It may be explained on the basis that as surface area increases the capacity of the adsorbent increases. On comparing the fly ash composition, we find that the carbon content of;

Fly ash D > fly ash B> fly ash A> fly ash C

Hence carbon content also plays very important role in adsorption capacity.

3.4.8 Thermodynamics

The calculated values of standard free energy (ΔG), standard enthalpy changes (Δ*H*) and standard entropy changes (ΔS) are summarized in Table 3.10. Equilibrium constant for free energy determination, van't Hoff plot as shown in Fig. 3.11 has been used. The negative values of ΔG indicate the feasibility of the process and the spontaneous nature of the adsorption. The positive value of ΔS shows the increase in entropy caused by randomness of displaced water molecules from the surface of adsorbent and the negative entropy change (ΔS) reflects an affinity of the adsorbing ash for the phenolic adsorbate. The enthalpy values of the order -25 kJ/mole indicate physical adsorption (Farooqui 2004), however this criteria is not applicable strictly. The negative value for enthalpy change (Δ*H*) indicates the adsorption to be an exothermic process.

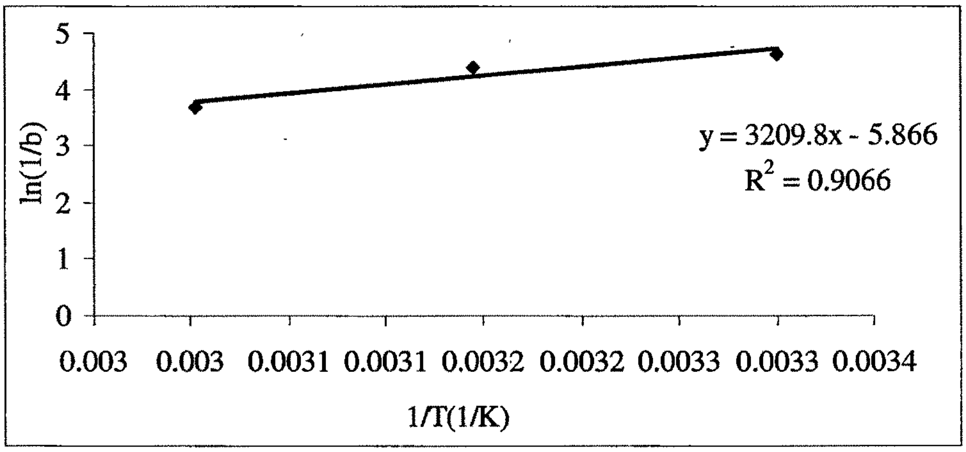

Figure 3.11. van't Hoff plot to calculate equilibrium constant
[Fly Ash A / 3-Aminophenol system]

Table 3.10. Determination of Thermodynamic parameters

System	Temp(°C)	K	ΔG (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)
		Fly ash A			
Phenol	30	42.94	-9.47	25.37	-1.80
	45	42.095	-9.89		
	60	40.252	-10.23		
Catechol	30	63.931	-10.47	28.88	-1.71
	45	60.985	-10.87		
	60	60.162	-11.34		
Resorcinol	30	59.982	-10.31	16.09	-5.48
	45	56.917	-10.69		
	60	49.229	-10.79		
Hydroquinone	30	56.715	-10.17	25.25	-2.53
	45	54.721	-10.58		
	60	51.788	-10.93		
2- Aminophenol	30	58.252	-10.24	28.82	-1.51
	45	56.909	-10.69		
	60	55.178	-11.10		
3-Aminophenol	30	103.876	-11.70	-48.77	-26.69
	45	81.823	-11.65		
	60	39.666	-10.19		
		Fly ash B			
Phenol	30	50.070	-9.86	23.53	-2.74
	45	48.182	-10.24		
	60	45.376	-10.56		
Catechol	30	63.263	-10.45	24.94	-2.89
	45	59.457	-10.80		
	60	57.074	-11.20		
Resorcinol	30	56.196	-10.15	26.23	-2.20
	45	53.855	-10.54		
	60	51.946	-10.94		
Hydroquinone	30	62.538	-10.419	24.03	-3.148
	45	59.620	-10.808		
	60	55.860	-11.138		
2- Aminophenol	30	114.089	-11.93	29.62	-2.95
	45	106.66	-12.35		
	60	102.715	-12.82		
3- Aminophenol	30	98.847	-11.57	8.09	-9.13
	45	83.968	-11.71		
	60	71.303	-11.81		

Table 3.10. Determination of Thermodynamic parameters **(Continued)**

System	Temp(°C)	K	ΔG (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)
			Fly ash C		
Phenol	30	24.906	-8.10	-38.04	-19.56
	45	15.843	-7.30		
	60	12.410	-6.97		
Catechol	30	41.804	-9.40	3.97	-8.16
	45	34.101	-9.33		
	60	31.274	-9.53		
Resorcinol	30	28.290	-8.42	-7.09	-10.57
	45	23.349	-8.33		
	60	19.378	-8.21		
Hydroquinone	30	37.303	-9.12	16.67	-4.10
	45	36.121	-9.48		
	60	32.166	-9.61		
2- Aminophenol	30	35.879	-9.02	4.57	-7.70
	45	33.533	-9.29		
	60	27.179	-9.14		
3- Aminophenol	30	22.784	-7.88	-50.87	-23.38
	45	16.432	-7.40		
	60	9.841	-6.33		
			Fly ash D		
Phenol	30	52.083	-9.96	22.80	-3.03
	45	47.791	-10.22		
	60	46.786	-10.65		
Catechol	30	44.439	-9.56	8.01	-7.08
	45	36.538	-9.51		
	60	34.568	-9.81		
Resorcinol	30	35.409	-8.99	13.08	-4.99
	45	30.962	-9.08		
	60	29.660	-9.38		
Hydroquinone	30	53.971	-10.05	10.44	-6.92
	45	49.310	-10.31		
	60	42.092	-10.35		
2- Aminophenol	30	34.254	-8.90	19.23	-3.08
	45	32.456	-9.20		
	60	30.680	-9.48		
3- Aminophenol	30	38.901	-9.22	14.21	-4.88
	45	33.861	-9.31		
	60	32.722	-9.66		

Table 3.10. Determination of Thermodynamic parameters **(Continued)**

System	Temp(°C)	K	ΔG (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)
		Activated carbon			
Phenol	30	7.848	-5.19	-23.78	-12.44
	45	6.606	-4.99		
	60	5.019	-4.47		
Catechol	30	55.775	-10.13	-85.37	-35.77
	45	21.693	-8.14		
	60	15.654	-7.62		
Resorcinol	30	60.256	-10.32	26.77	-2.21
	45	57.784	-10.73		
	60	55.671	-11.13		
Hydroquinone	30	7.619	-5.12	4.68	-3.71
	45	7.236	-5.23		
	60	6.668	-5.25		
2- Aminophenol	30	18.295	-7.32	19.65	-1.38
	45	17.978	-7.64		
	60	17.412	-7.91		
3- Aminophenol	30	17.716	-7.24	7.49	-4.94
	45	15.553	-7.26		
	60	14.865	-7.47		

3.4.9 Kinetics

For identification of rate controlling step, plots of F versus (time) $^{0.5}$, ln (1-F) versus time (Lagergren plot), and ln (1-F^2) versus time have been drawn(Figs. 3.12 to 3.21). Film diffusion control is rate limiting if a graph of ln (1-F) versus time yields a straight line. Alternatively, particle diffusion controls the overall adsorption rate if a plot of F against t$^{0.5}$ produces a straight line. If particle diffusion is the absolute rate controlling mechanism at a certain concentration this line will pass through the origin. ln (1-F) versus time yields a straight line in all the cases, however data doesnot fit well. Representative plots Figs. 3.12, 3.15 and 3.18 show that plot F versus t$^{0.5}$ is not passing through origin, however the plot can be divided into three parts showing fast, medium and slow rates . The initial fast rate indicates intra particle diffusion control; medium rate shows that both intra particle and film diffusion control whereas slow rate indicates film control is the controlling step. Hence the intra particle diffusion is not the only rate-limiting step, film diffusion also contributes resistance to the overall rate.

It is evident from the discussion in the preceding section that the rates of adsorption of all the phenols on all the adsorbents are controlled by diffusion mechanism. Hence, as given in theoretical section, the rate of transport in this regime may be characterized by effective diffusion coefficients.

The effective diffusion coefficients were determined by Vermeulen (1953) and Urano and Tachikawa (1991) approximation. Representative plot for calculations are shown by Figs. 3.15, 3.18 and 3.20, and value obtained all the cases are tabulated in Table 3.11. This method has also been used by Kumar et al. (2003) to calculate the diffusivity of phenolic compounds on activated carbon in batch reactor. The diffusion coefficients in all present cases lie in the range of 10^{-12}-10^{-14} m^2/s for fly ash and 10^{-8} m^2/s in case of activated carbon. This supports the particle diffusion control.

The relatively short duration of the present experiments (4 h) is a first indication that sorption of phenols is a kinetic process. Following Jadhav and Vanjara (2004), Lagergren's pseudo first order kinetics has been used for kinetic determination. On simplification, Lagergren's equation is converted to linear relationship of ln(1-F) and time, hence ln(1-F) versus time plot and Lagergren's plot are same. Figures 3.13, 3.16 and 3.19 outlines the first order kinetic plots for the sorption of varying initial concentration of 3-aminophenol on fly ash A. The constants associated with process are outlined in Table 3.11 for all the systems. The correlation coefficients are found to be in the range of 0.7-0.98 for all the systems.

The application of pseudo second order kinetics given by Ho and Mckay (1998), to the overall rate of the sorption process has also been used to assess the dependency of the process on the sorbed phenol concentration. Figs. 3.21 to 3.23 show the appropriate second order plots for 3-aminophenol adsorption of fly ash A at different temperatures. The plots and data have very high correlation coefficients (R^2) of greater than 0.99 and good compliance with the pseudo second order equation. The initial sorption rates (h) increase with the increase in initial concentration of phenols. This may be due to increase in bulk concentration, which increases driving force for mass transfer. Sometimes after certain increase in concentration, sorption rate reduces also, due to which any firm conclusion cannot be drawn only based on h values. The values of the overall sorption rate constants, k_2, were found to decrease with increasing initial phenol concentrations. The similar results were obtained by Kellher et al.(2002) for adsorption of chromium on fly ash.

The rate constants for 1st, 2nd and diffusion controlled adsorption of the all the systems are listed in Table 3.11. The correlation coefficients (R^2) are significantly lower for first order than corresponding second order coefficient. This gives a clear indication that the sorption of phenols by fly ash is more accurately represented as a pseudo second order process.

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon

	Co ppm	Temperature 30°C				Temperature 45°C				Temperature 60°C			
		k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}
Phenol/ Fly Ash A	25	0.043	0.237	0.065	7.98	0.038	0.130	0.036	6.91	0.039	0.143	0.038	7.02
	50	0.044	0.130	0.082	8.08	0.042	0.120	0.072	7.66	0.042	0.132	0.077	7.77
	100	0.045	0.102	0.196	7.02	0.039	0.059	0.112	7.20	0.040	0.070	0.121	7.20
	200	0.047	0.043	0.146	8.83	0.040	0.057	0.162	7.32	0.042	0.072	0.187	7.66
	300	0.041	0.024	0.116	7.55	0.041	0.056	0.194	7.52	0.040	0.064	0.215	7.32
	400	0.039	0.026	0.138	7.18	0.037	0.039	0.179	6.61	0.039	0.035	0.138	7.04
	500	0.042	0.038	0.187	7.64	0.039	0.049	0.219	6.91	0.038	0.039	0.158	6.8
Catechol/ Fly Ash A	25	0.046	0.131	0.072	7.89	0.044	0.095	0.051	7.48	0.049	0.107	0.053	8.5
	50	0.039	0.054	0.097	6.93	0.033	0.041	0.075	7.36	0.055	0.081	0.111	9.88
	100	0.034	0.013	0.092	5.83	0.379	0.025	0.133	5.8	0.034	0.040	0.180	5.80
	200	0.049	0.005	0.118	9.38	0.04	0.009	0.159	7.2	0.39	0.014	0.214	7.02
	300	0.035	0.002	0.117	6.19	0.042	0.005	0.165	7.8	0.04	0.007	0.193	7.43
	400	0.036	0.001	0.131	6.40	0.035	0.006	0.217	6.33	0.36	0.014	0.364	6.31
	500	0.044	0.002	0.170	8.42	0.033	0.005	0.224	5.76	0.034	0.007	0.215	5.98
Resorcinol / Fly Ash A	25	0.038	0.231	0.047	6.70	0.036	0.242	0.043	6.35	0.923	0.204	0.035	5.51
	50	0.042	0.117	0.069	7.69	0.038	0.063	0.036	6.86	0.958	0.048	0.024	5.64
	100	0.038	0.054	0.085	6.40	0.036	0.074	0.095	6.40	0.976	0.020	0.032	4.63
	200	0.038	0.046	0.138	6.81	0.037	0.027	0.067	6.12	0.906	0.023	0.055	4.68
	300	0.041	0.048	0.177	7.39	0.034	0.023	0.076	6.08	0.954	0.007	0.028	5.73
	400	0.037	0.036	0.171	6.51	0.034	0.036	0.129	6.03	0.988	0.010	0.036	5.24
	500	0.037	0.015	0.071	6.58	0.034	0.013	0.060	5.90	0.978	0.016	0.056	5.69
Hydroquinone/ Fly Ash A	25	0.058	0.122	0.066	11.38	0.027	0.040	0.026	4.47	0.040	0.166	0.078	6.53
	50	0.056	0.064	0.098	10.96	0.041	0.044	0.074	6.86	0.037	0.089	0.130	6.68
	100	0.055	0.022	0.122	10.85	0.032	0.009	0.062	5.64	0.039	0.042	0.129	6.45
	200	0.045	0.023	0.375	7.82	0.061	0.053	0.088	12.13	0.033	0.012	0.163	5.57
	300	0.049	0.010	0.324	8.63	0.058	0.004	0.151	11.52	0.035	0.011	0.256	6.15
	400	0.046	0.005	0.251	7.94	0.034	0.130	0.170	5.41	0.305	0.008	0.294	5.12
	500	0.035	0.008	0.474	6.23	0.030	0.114	0.170	5.25	0.033	0.003	0.204	5.69

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon

(Continued)

		Temperature 30°C				Temperature 45°C				Temperature 60°C			
	Co ppm	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}
2-Aminophenol/ Fly Ash A	25	0.033	0.344	0.064	5.667	0.031	0.230	0.041	5.28	0.032	0.288	0.050	5.391
	50	0.039	0.293	0.150	7.021	0.031	0.131	0.068	6.49	0.037	0.213	0.097	6.539
	100	0.33	0.126	0.152	5.552	0.033	0.117	0.132	5.55	0.032	0.120	0.125	5.437
	200	0.036	0.069	0.182	6.309	0.031	0.078	0.162	5.05	0.035	0.083	0.164	5.988
	300	0.035	0.056	0.190	6.057	0.038	0.076	0.231	6.74	0.033	0.070	0.213	5.988
	400	0.027	0.026	0.112	4.382	0.030	0.043	0.152	4.98	0.031	0.046	0.162	5.093
	500	0.028	0.019	0.092	4.772		0.049	0.181	8.47	0.031	0.042	0.150	5.116
3-Aminophenol/ Fly Ash A	25	0.039	0.349	0.074	7.066	0.039	0.369	0.063	6.97	0.035	0.182	0.027	6.034
	50	0.044	0.193	0.132	8.011	0.042	0.142	0.083	4.59	0.039	0.149	0.047	7.089
	100	0.042	0.032	0.090	6.951	0.039	0.088	0.143	6.95	0.035	0.106	0.069	6.034
	200	0.045	0.052	0.328	8.305	0.039	0.039	0.150	7.09	0.038	0.054	0.068	6.769
	300	0.046	0.043	0.377	8.420	0.044	0.054	0.233	8.19	0.037	0.038	0.058	6.676
	400	0.045	0.033	0.298	8.420	0.038	0.041	0.188	6.86	0.023	0.022	0.041	3.533
	500	0.043	0.044	0.396	7.777	0.039	0.043	0.195	7.07	0.029	0.023	0.027	4.889
Phenol / Fly Ash B	25	0.04	0.137	0.047	13.30	0.042	0.025	0.008	14.2	0.038	0.162	0.051	12.6
	50	0.042	0.080	0.080	14.6	0.037	0.075	0.071	12.3	0.039	0.072	0.067	13.1
	100	0.039	0.058	0.157	10.9	0.034	0.031	0.079	12.3	0.037	0.034	0.086	12.3
	200	0.036	0.040	0.195	11.9	0.038	0.025	0.128	12.8	0.038	0.022	0.113	12.5
	300	0.038	0.038	0.275	12.3	0.037	0.021	0.154	12.4	0.042	0.022	0.128	14.5
	400	0.036	0.025	0.214	11.8	0.036	0.019	0.157	11.9	0.032	0.022	0.139	9.92
	500	0.035	0.024	0.204	11.4	0.024	0.017	0.147	7.02	0.034	0.022	0.144	10.9
Catechol/ Fly Ash B	25	0.026	0.035	0.025	7.79	0.051	0.141	0.077	16.34	0.03	0.056	0.032	9.32
	50	0.022	0.011	0.034	6.13	0.035	0.031	0.073	11.45	0.029	0.025	0.051	9.15
	100	0.023	0.006	0.060	7.92	0.026	0.014	0.093	9.57	0.030	0.013	0.075	9.57
	200	0.023	0.004	0.104	6.77	0.035	0.008	0.158	1.13	0.033	0.001	0.050	10.7
	300	0.029	0.003	0.121	9.20	0.040	0.007	0.220	13.49	0.035	0.004	0.123	11.3
	400	0.024	0.002	0.119	7.02	0.035	0.004	0.194	11.3	0.029	0.004	0.145	9.10
	500	0.027	0.001	0.118	8.39	0.031	0.001	0.093	9.19	0.030	0.003	0.147	9.49

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon

(Continued)

		Temperature 30°C				Temperature 45°C				Temperature 60°C			
	Co ppm	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}
Resorcinol / Fly Ash B	25	0.04	0.307	0.075	13.3	0.030	0.177	0.038	9.28	0.032	0.206	0.040	10.1
	50	0.040	0.127	0.087	13.4	0.043	0.211	0.098	14.6	0.039	0.160	0.079	12.7
	100	0.037	0.045	0.102	12.3	0.037	0.085	0.103	12.2	0.037	0.090	0.100	12.2
	200	0.042	0.052	0.212	14.0	0.039	0.052	0.170	12.8	0.040	0.036	0.099	13.6
	300	0.040	0.058	0.267	13.4	0.041	0.054	0.214	13.6	0.028	0.026	0.086	8.51
	400	0.042	0.046	0.238	14.3	0.041	0.059	0.262	13.6	0.027	0.020	0.082	8.09
	500	0.038	0.038	0.218	12.6	0.038	0.066	0.277	12.3	0.033	0.007	0.042	10.7
Hydroquinone/ Fly Ash B	25	0.052	0.273	0.126	16.85	0.054	0.186	0.080	16.73	0.050	0.193	0.083	16.05
	50	0.035	0.077	0.125	11.06	0.035	0.065	0.102	11.45	0.039	0.075	0.117	11.66
	100	0.056	0.066	0.344	15.07	0.044	0.032	0.149	15.49	0.048	0.046	0.200	15.49
	200	0.039	0.012	0.194	15.02	0.044	0.022	0.302	15.07	0.04	0.024	0.302	12.09
	300	0.029	0.011	0.227	9.02	0.035	0.018	0.289	11.28	0.048	0.019	0.259	15.70
	400	0.029	0.009	0.238	9.15	0.043	0.014	0.236	13.62	0.038	0.016	0.254	12.64
	500	0.032	0.006	0.202	9.19	0.025	0.009	0.160	10.84	0.040	0.011	0.189	12.13
2-Aminophenol/ Fly Ash B	25	0.041	0.257	0.057	13.84	0.041	0.286	0.061	13.5	0.038	0.150	0.030	12.7
	50	0.047	0.112	0.086	16.51	0.048	0.121	0.088	16.5	0.039	0.044	0.034	13.2
	100	0.043	0.049	0.121	14.86	0.044	0.047	0.112	10.3	0.032	0.020	0.052	10.4
	200	0.042	0.017	0.140	14.05	0.047	0.019	0.137	16.2	0.029	0.008	0.050	9.19
	300	0.048	0.022	0.217	16.94	0.047	0.018	0.164	14.8	0.034	0.014	0.086	10.8
	400	0.042	0.016	0.191	14.17	0.044	0.018	0.185	16.2	0.030	0.004	0.053	9.53
	500	0.041	0.012	0.161	13.92	0.040	0.018	0.195	13.3	0.037	0.010	0.094	12.1
3-Aminophenol/ Fly Ash B	25	0.054	0.184	0.048	17.9	0.044	0.238	0.055	15.23	0.039	0.115	0.028	13.11
	50	0.044	0.086	0.068	15.0	0.047	0.106	0.073	16.26	0.043	0.050	0.038	14.79
	100	0.041	0.032	0.090	14.5	0.043	0.038	0.086	12.77	0.038	0.030	0.057	12.77
	200	0.035	0.010	0.092	11.5	0.046	0.012	0.090	15.83	0.044	0.013	0.081	14.98
	300	0.046	0.010	0.135	15.8	0.04	0.009	0.090	13.41	0.031	0.009	0.065	9.748
	400	0.036	0.009	0.128	11.9	0.041	0.009	0.091	14.13	0.025	0.017	0.117	7.407
	500	0.037	0.006	0.099	12.2	0.038	0.009	0.096	12.73	0.041	0.011	0.089	13.66

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon

(Continued)

		Temperature 30°C				**Temperature 45°C**				**Temperature 60°C**			
	Co ppm	**k_1‡**	**k_2†**	**h**	**D_i* x10^{13}**	**k_1‡**	**k_2†**	**h**	**D_i* x10^{13}**	**k_1‡**	**k_2†**	**h**	**D_i* x10^{13}**
Phenol / Fly Ash C	25	0.017	0.065	0.005	7.14	0.016	0.029	0.005	6.98	0.017	0.153	0.009	7.42
	50	0.017	0.059	0.010	7.75	0.015	0.020	0.001	6.21	0.017	0.102	0.011	7.93
	75	0.021	0.034	0.009	5.82	0.012	0.020	0.000	4.89	0.015	0.169	0.013	6.16
	100	0.015	0.077	0.016	6.10	0.014	0.007	0.000	5.94	0.021	0.088	0.012	9.95
Catechol/ Fly Ash C	25	0.016	0.187	0.007	6.48	0.014	0.136	0.005	5.39	0.031	0.340	0.009	1.56
	50	0.015	0.042	0.004	5.72	0.011	0.066	0.004	4.12	0.014	0.169	0.007	5.39
	75	0.013	0.068	0.009	4.84	0.008	0.029	0.004	3.19	0.014	0.112	0.008	8.63
	100	0.014	0.066	0.011	5.33	0.009	0.022	0.004	3.29	0.012	0.036	0.005	4.56
Resorcinol / Fly Ash C	25	0.015	0.026	0.002	6.32	0.013	0.048	0.003	5.55	0.016	0.149	0.006	7.97
	50	0.015	0.042	0.006	6.32	0.014	0.017	0.003	6.05	0.019	0.438	0.024	8.91
	75	0.013	0.025	0.005	5.11	0.014	0.032	0.005	6.10	0.017	0.245	0.018	7.69
	100	0.014	0.028	0.007	5.77	0.013	0.013	0.002	5.66	0.023	0.055	0.008	1.09
Hydro quinone / Fly Ash C	25	0.015	0.145	0.007	5.94	0.01	0.051	0.002	3.79	0.017	0.129	0.002	6.32
	50	0.010	0.088	0.008	4.01	0.009	0.045	0.004	3.74	0.018	0.078	0.004	9.73
	75	0.009	0.062	0.010	3.35	0.023	0.077	0.008	8.14	0.017	0.129	0.008	6.54
	100	0.009	0.038	0.009	3.35	0.012	0.056	0.011	4.56	0.019	0.051	0.005	5.61
2- Amino phenol /Fly Ash C	25	0.014	0.227	0.009	5.99	0.013	0.016	0.076	5.33	0.013	0.288	0.009	5.5
	50	0.013	0.106	0.010	5.39	0.012	0.016	0.043	4.95	0.017	0.133	0.006	7.42
	75	0.012	0.117	0.015	4.67	0.011	0.014	0.057	4.12	0.013	0.087	0.008	5.55
	100	0.010	0.057	0.010	3.74	0.011	0.014	0.051	4.45	0.020	0.046	0.007	9.35
3- Amino phenol /Fly ash C	25	0.072	0.006	0.003	7.15	0.016	0.033	0.003	7.20	0.017	0.194	0.011	7.37
	50	0.060	0.010	0.004	7.75	0.016	0.038	0.006	6.93	0.018	0.166	0.015	8.14
	75	0.033	0.009	0.007	5.83	0.014	0.028	0.006	5.83	0.015	0.149	0.013	6.65
	100	0.078	0.016	0.008	6.10	0.014	0.007	0.003	6.10	0.024	0.148	0.017	1.09

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon

(Continued)

		Temperature 30°C				Temperature 45°C				Temperature 60°C			
	Co ppm	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}
Phenol/Fly Ash D	100	0.086	0.077	2.14	58.2	0.062	0.029	0.81	68.9	0.082	0.030	0.84	88.7
	200	0.057	0.025	2.22	61.3	0.053	0.011	0.89	56.4	0.073	0.016	1.06	81.9
	300	0.058	0.022	3.12	62.9	0.057	0.009	1.18	61.1	0.078	0.009	1.12	88.7
	400	0.062	0.028	5.31	67.4	0.050	0.003	0.59	53.3	0.060	0.005	0.96	61.3
	500	0.060	0.019	5.00	74.8	0.073	0.001	0.43	82.5	0.076	0.004	0.98	86.2
Catechol/Fly Ash D	100	0.051	0.038	1.47	54.1	0.051	0.041	1.61	53	0.035	0.037	1.44	48.6
	200	0.048	0.016	2.46	50.1	0.049	0.016	2.38	51.3	0.047	0.017	2.41	50.2
	300	0.054	0.009	2.89	57	0.053	0.010	3.37	56.3	0.048	0.011	3.56	74.1
	400	0.050	0.005	2.82	70.2	0.047	0.004	2.50	48.9	0.047	0.010	4.94	49.2
	500	0.068	0.003	2.47	52	0.048	0.004	3.10	50.5	0.069	0.009	6.42	72
Resorcinol / Fly Ash D	100	0.057	0.042	1.18	65.5	0.036	0.022	0.65	35.4	0.067	0.029	0.80	69.3
	200	0.060	0.028	2.09	61.1	0.051	0.018	1.30	53.9	0.064	0.016	0.85	66.4
	300	0.56	0.022	2.43	59.6	0.054	0.016	1.71	57.9	0.05	0.014	1.42	56
	400	0.053	0.019	2.99	56.6	0.051	0.020	3.00	54.1	0.04	0.006	0.77	46.5
	500	0.053	0.007	1.43	56.4	0.050	0.007	1.26	52.4	0.038	0.005	0.61	38.4
Hydroquinone/ Fly Ash D	100	0.056	0.046	1.71	60.4	0.055	0.025	0.95	58.6	0.056	0.039	1.47	59.1
	200	0.054	0.021	3.22	57.9	0.049	0.006	0.99	51.4	0.050	0.015	2.19	51.7
	300	0.058	0.018	5.53	63.1	0.048	0.004	1.42	50.2	0.052	0.010	2.96	54.6
	400	0.052	0.012	6.07	54.5	0.039	0.002	1.22	38.7	0.047	0.006	3.04	48.8
	500	0.051	0.008	5.31	54	0.047	0.002	1.30	49.1	0.048	0.006	3.37	49.9
2-Amino Phenol/ Fly Asjh D	100	0.054	0.043	1.15	56.9	0.086	0.048	1.26	97.8	0.079	0.051	1.30	89.5
	200	0.051	0.003	0.33	53.3	0.44	0.003	0.29	44.8	0.050	0.003	0.30	51.9
	300	0.049	0.003	0.44	51.6	0.047	0.004	0.43	48.8	0.051	0.005	0.45	53.4
	400	0.042	0.002	0.42	42.3	0.044	0.003	0.44	44.5	0.039	0.003	0.42	38.2
	500	0.038	0.007	0.94	37.3	0.040	0.007	1.00	39.9	0.042	0.009	1.09	43

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon

(Continued)

		Temperature 30°C				Temperature 45°C				Temperature 60°C			
	Co ppm	k₁‡	k₂†	h	D_i* x10^{13}	k₁‡	k₂†	h	D_i* x10^{13}	k₁‡	k₂†	h	D_i* x10^{13}
3-Amino Phenol/ Fly Ash D	100	0.059	0.041	1.10	63.9	0.054	0.026	0.73	58.1	0.039	0.016	0.47	38.2
	200	0.057	0.027	1.99	61.4	0.054	0.011	0.82	57.2	0.072	0.030	2.06	81
	300	0.052	0.016	1.74	54.8	0.054	0.007	0.80	57.2	0.054	0.008	0.84	57.8
	400	0.053	0.011	1.71	55.9	0.044	0.006	0.76	44.8	0.044	0.006	0.78	45.1
	500	0.047	0.010	1.61	49.2	0.043	0.002	0.46	43.9	0.044	0.005	0.83	45.7
Phenol/ Activated carbon	100	0.068	0.017	6.68	5.37	0.069	0.019	7.24	5.30	0.049	0.003	1.41	3.66
	200	0.055	0.005	6.69	4.14	0.059	0.003	4.25	4.57	0.038	0.002	2.25	2.68
	300	0.056	0.004	11.55	4.28	0.052	0.001	2.55	3.87	0.036	0.002	3.23	2.45
	400	0.055	0.003	10.05	4.13	0.043	0.001	1.85	3.11	0.031	0.0002	0.91	2.07
	500	0.060	0.003	13.05	4.66	0.051	0.001	2.79	3.82	0.035	0.001	1.28	2.38
Catechol/ Activated carbon	100	0.041	0.008	2.93	2.9	0.052	0.013	4.85	3.86	0.060	0.007	2.61	4.27
	200	0.037	0.003	3.71	2.5	0.049	0.005	8.07	3.57	0.046	0.003	4.78	3.40
	300	0.034	0.001	4.21	2.3	0.053	0.004	11.66	3.93	0.049	0.002	5.43	3.62
	400	0.034	0.001	5.42	2.3	0.048	0.002	11.49	3.52	0.042	0.001	5.57	3.03
	500	0.037	0.001	3.68	2.6	0.049	0.002	12.97	3.64	0.042	0.001	5.36	3.04
Resorcinol / Activated carbon	100	0.047	0.009	1.95	3.48	0.043	0.006	1.21	3.14	0.058	0.009	1.69	4.43
	200	0.054	0.008	4.53	4.06	0.046	0.002	1.41	3.34	0.049	0.003	1.54	3.62
	300	0.044	0.004	4.32	3.18	0.048	0.001	1.23	3.56	0.050	0.002	1.93	3.71
	400	0.041	0.004	4.66	2.93	0.046	0.001	0.99	3.43	0.042	0.002	1.59	3.41
	500	0.049	0.004	4.61	3.62	0.047	0.001	1.33	3.49	0.035	0.002	1.63	3.05

Table 3.11. Rate constants for 1st and 2nd order and diffusion controlled adsorption of phenols on to fly ash A, B, C, D & activated carbon **(Continued)**

	Co ppm	Temperature 30°C				Temperature 45°C				Temperature 60°C			
		k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}	k_1‡	k_2†	h	D_i* x10^{13}
Hydro-quinone/ Activated carbon	100	0.05	0.004	1.77	3.43	0.045	0.004	1.62	3.33	0.032	0.002	1.09	2.10
	200	0.068	0.003	4.11	5.40	0.044	0.002	2.48	3.17	0.041	0.002	2.47	2.92
	300	0.047	0.001	3.26	3.43	0.047	0.001	3.22	3.47	0.043	0.001	3.22	3.12
	400	0.059	0.002	6.07	3.13	0.04	0.001	2.79	2.84	0.04	0.001	3.32	2.87
	500	0.039	0.001	4.44	2.76	0.041	0.001	3.55	2.94	0.046	0.001	2.78	3.10
2-Amino Phenol/ Activated carbon	100	0.055	0.011	3.70	4.14	0.056	0.012	3.79	4.21	0.055	0.012	3.77	4.17
	200	0.054	0.009	9.36	4.07	0.052	0.009	8.69	3.87	0.052	0.007	7.20	3.91
	300	0.048	0.002	3.80	3.53	0.049	0.002	3.95	3.71	0.044	0.002	3.86	3.191
	400	0047	0.003	5.10	3.45	0.046	0.003	4.75	3.37	0.047	0.003	4.58	3.42
	500	0.067	0.003	6.08	5.31	0.067	0.004	6.85	5.30	0.046	0.002	3.29	3.35
3-Amino Phenol/ Activated carbon	100	0.026	0.002	0.71	1.7	0.023	0.002	0.66	1.367	0.029	0.002	0.58	1.92
	200	0.243	0.001	1.06	3.19	0.026	0.001	0.85	1	0.022	0.002	1.07	1.30
	300	0.491	0.0005	1.49	3.71	0.044	0.002	1.31	3.19	0.027	0.002	1.21	1.76
	400	0.404	0.001	1.65	2.92	0.033	0.002	1.58	2.22	0.023	0.001	1.07	1.43
	500	0.034	0.0004	1.36	2.34	0.034	0.001	1.16	2.32	0.025	0.001	1.00	1.58

† R^2 = >0.99

‡ R^2 = 0.70-0.99

*** R^2 = 0.90-0.99**

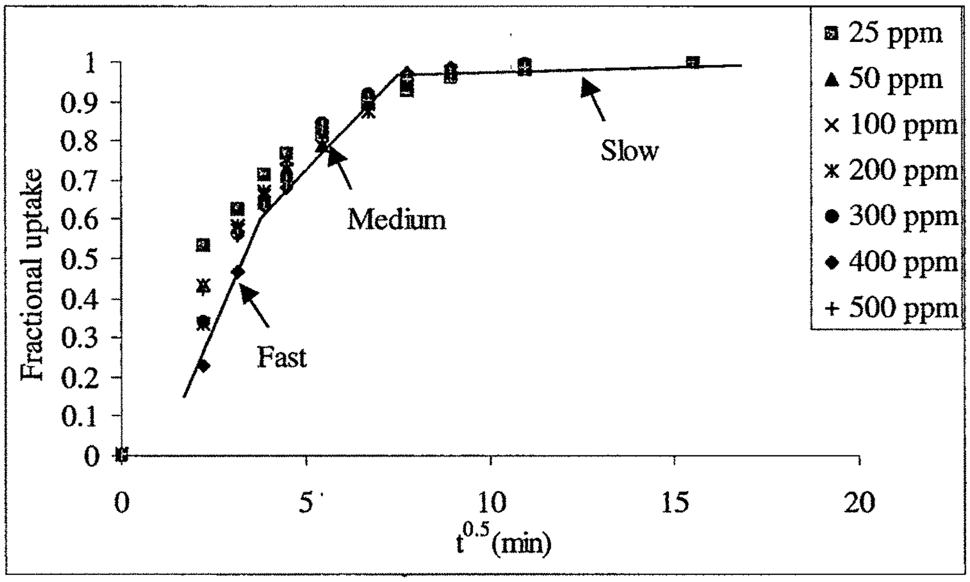

Figure 3.12. Typical Fractional up take curve (Weber-Morris plot) for 3-aminophenol adsorption on fly ash A at 30 °C using different initial concentration

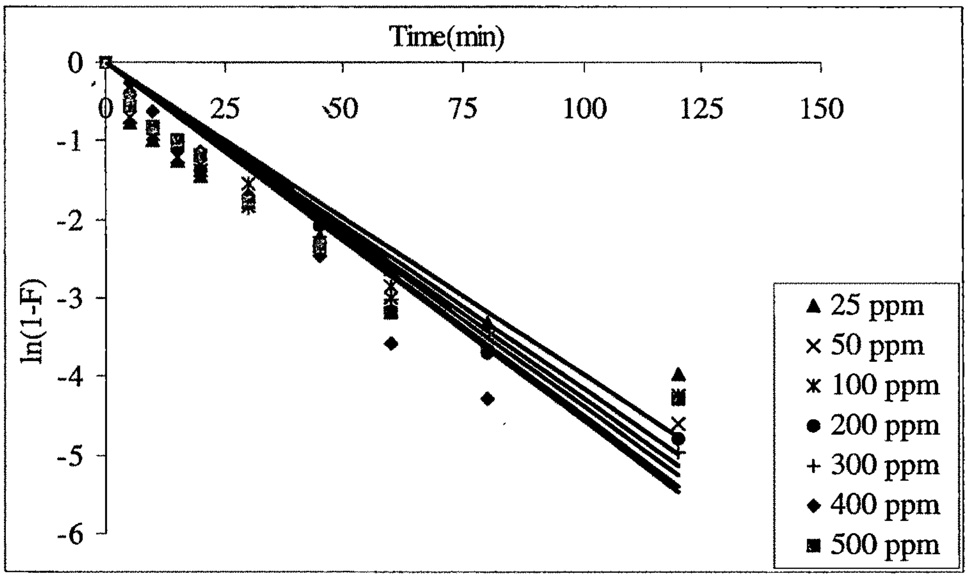

Figure 3.13. Plot to determine first order kinetics (Lagergren equation) for adsorption of 3-aminophenol on fly ash A at 30 °C

Trendline equation and correlation coefficient values of Fig. 3.13							
	25 ppm	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
y=	-0.0396x	-0.0438x	-0.0416x	-0.045x	-0.0456x	-0.0455x	-0.0428x
R^2=	0.795	0.8911	0.8948	0.931	0.9473	0.8727	0.8872

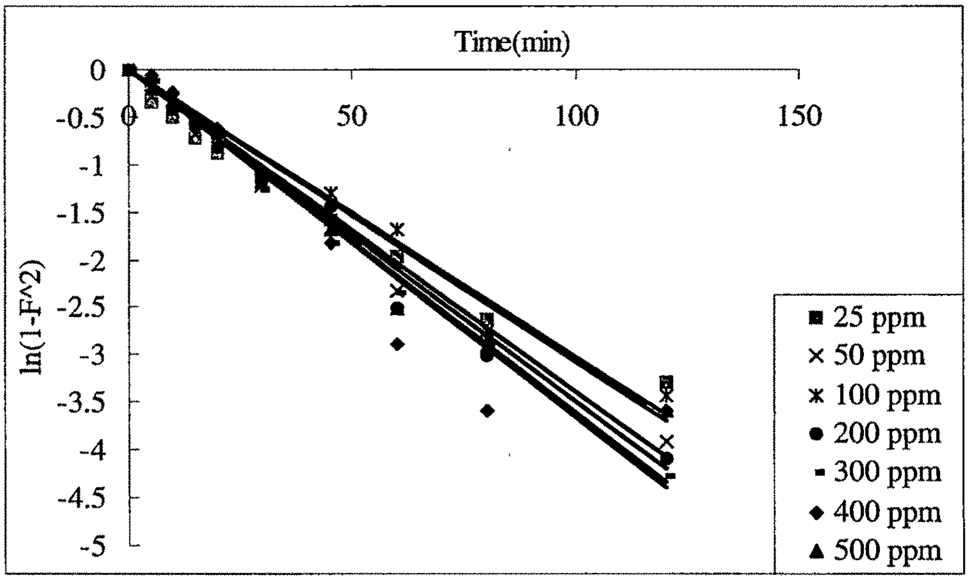

Figure 3.14. Plot to calculate effective Diffusion coefficient at 30 °C using Vermeulen or Urano approximations [Fly Ash A / 3-Aminophenol system]

Trendline equation and correlation coefficient values for Fig. 3.14							
	25 ppm	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
y=	-0.0308x	-0.0349x	-0.0303x	-0.0362x	-0.0367x	-0.0367x	-0.0339x
R^2=	0.9507	0.9837	0.9776	0.9852	0.9942	0.9109	0.9614

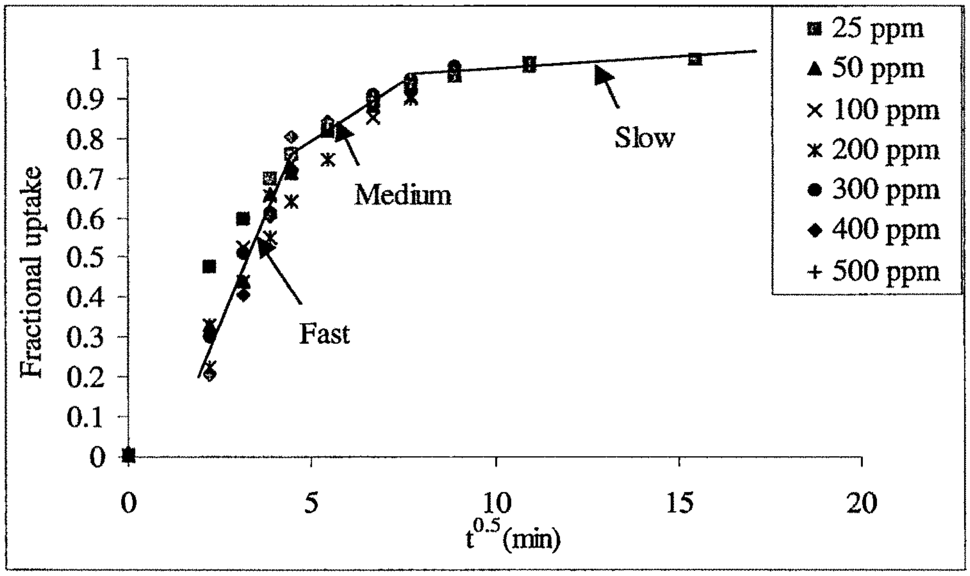

Figure 3.15. Typical Fractional up take curve (Weber-Morris plot) for 3-aminophenol adsorption on fly ash A at 45 °C using different initial concentration

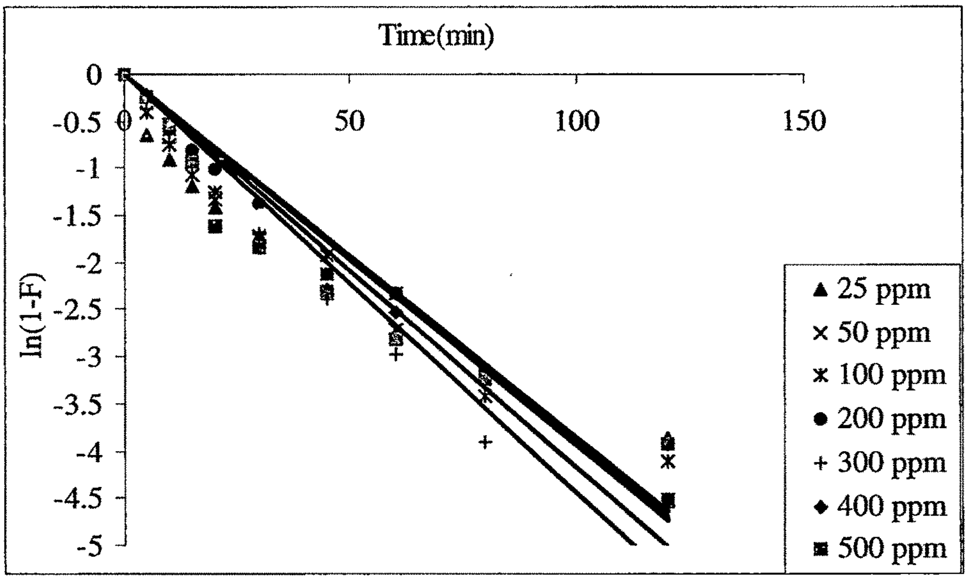

Figure 3.16. Plot to determine first order kinetics (Lagergren equation) for adsorption of 3-aminophenol on fly ash A at 45°C

Trendline equation and correlation coefficient values for Fig. 3.16

	25 ppm	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
y=	-0.0392x	-0.0418x	-0.0391x	-0.0394x	-0.0445x	-0.0386x	-0.0395x
R^2=	0.7928	0.9435	0.9044	0.981	0.936	0.8653	0.849

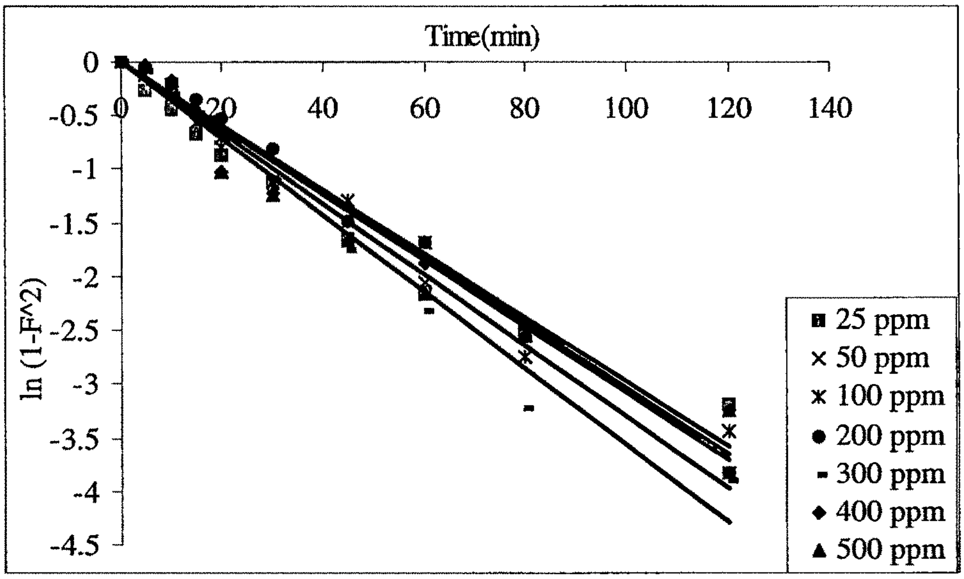

Figure 3.17. Plot to calculate effective Diffusion coefficient at 30 °C using Vermeulen or Urano approximations [Fly Ash A / 3-Aminophenol system]

Trendline equation and correlation coefficient values for Fig. 3.17

	25 ppm	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
y=	-0.0304x	-0.0331x	-0.0303x	-0.0309x	-0.0357x	-0.0299x	-0.0308x
R^2=	0.941	0.9943	0.9776	0.9924	0.9799	0.9541	0.94

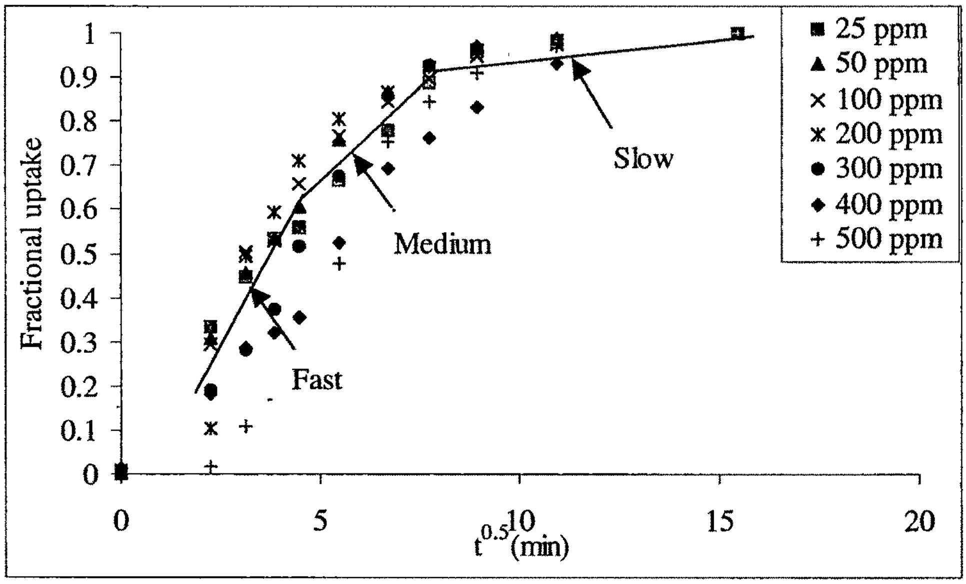

Figure 3.18. Typical Fractional up take curve (Weber-Morris plot) for 3-aminophenol adsorption on fly ash A at 60 °C using different initial concentration

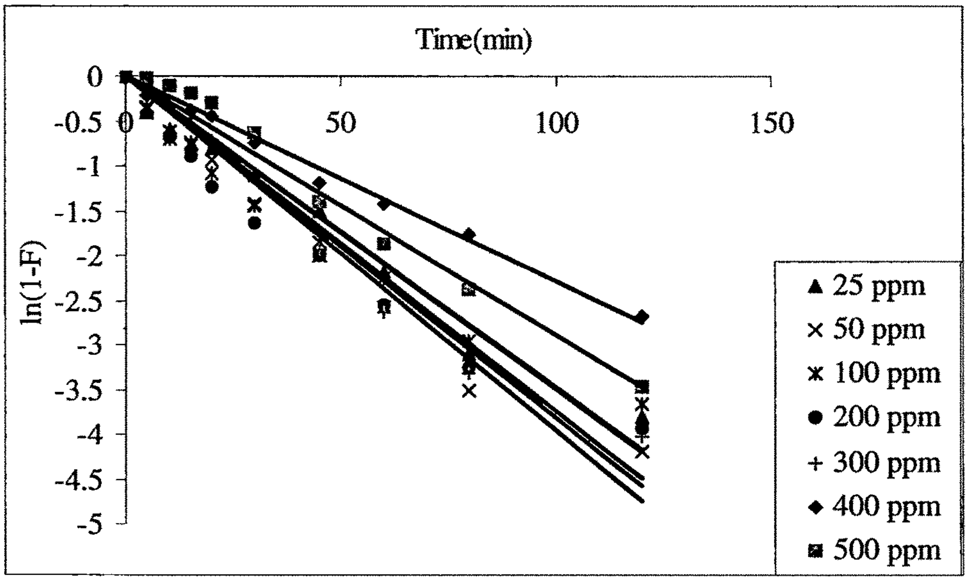

Figure 3.19 Plot to determine first order kinetics (Lagergren equation) for adsorption of 3-aminophenol on fly ash A at 60°C

Trendline equation and correlation coefficient values for Fig. 3.19

	25 ppm	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
y=	-0.0347x	-0.0395x	-0.0349x	-0.0381x	-0.0375x	-0.023x	-0.0289x
R^2=	0.9674	0.9612	0.9252	0.9189	0.9691	0.9907	0.9795

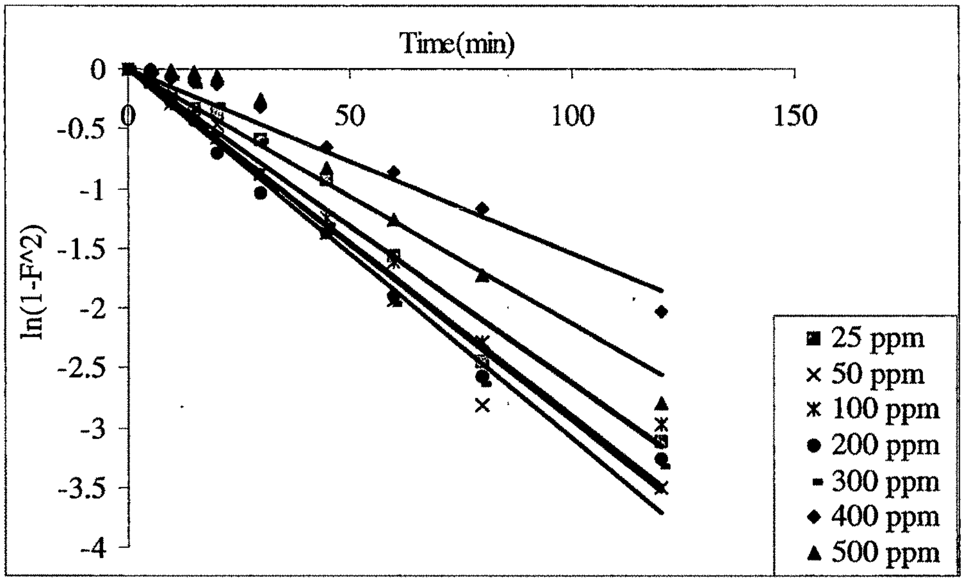

Figure 3.20. Plot to calculate effective Diffusion coefficient at 60 °C using Vermeulen or Urano approximations [Fly Ash A / 3-Aminophenol system]

Trendline equation and correlation coefficient values for Fig. 3.20

	25 ppm	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
y=	-0.0263x	-0.0309x	-0.0263x	-0.0295x	-0.0291x	-0.0154x	-0.0213x
R^2=	0.9758	0.9834	0.9901	0.982	0.9651	0.9709	0.942

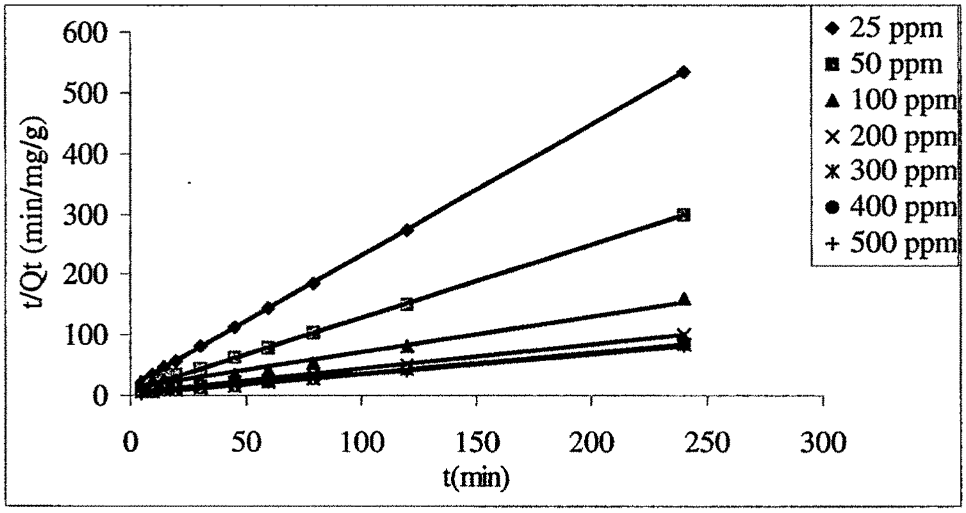

Figure 3.21. Plot to determine pseudo second order kinetics for adsorption of 3-aminophenol on fly ash A at 30 °C

Trendline equation and correlation coefficient values for Fig. 3.21

Co	25 ppm	50 ppm	100 ppm	200 ppm
y=	2.17x + 13.509	1.2109x + 7.5882	0.6x + 11.157	0.3997x + 3.0446
R^2=	0.9999	0.9998	0.9872	0.9994
Co	300 ppm	400 ppm	500 ppm	
y=	0.3367x + 2.652	0.3313x + 3.3576	0.3322x + 2.5261	
R^2=	0.9993	0.997	0.9994	

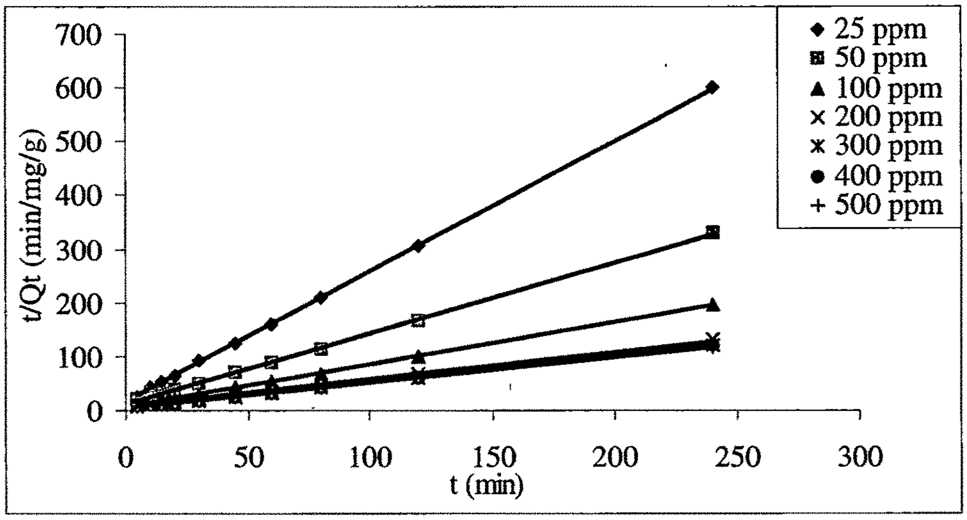

Figure 3.22. Plot to determine pseudo second order kinetics for adsorption of 3-aminophenol on fly ash A at 45 °C

Trendline equation and correlation coefficient values for Fig. 3.22

Co	25 ppm	50 ppm	100 ppm	200 ppm
y=	2.4244x + 15.941	1.3079x + 12.083	0.7839x + 6.9957	0.5119x + 6.6811
R^2=	0.9999	0.999	0.9996	0.9981
Co	300 ppm	400 ppm	500 ppm	
y=	0.4841x + 4.3002	0.4682x + 5.3182	0.4677x + 5.1404	
R^2=	0.9989	0.9962	0.996	

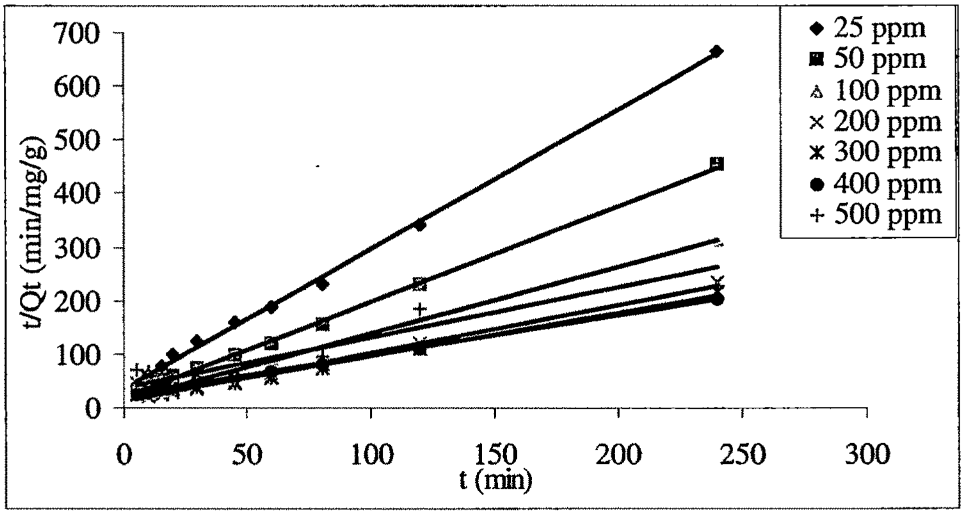

Figure 3.23. Plot to determine pseudo second order kinetics for adsorption of 3.-aminophenol on fly ash A at 60 °C

Trendline equation and correlation coefficient values for Fig. 3.23

Co	25 ppm	50 ppm	100 ppm	200 ppm
y=	2.5928x + 37.032	1.7772x + 21.173	1.2403x + 14.581	0.89x + 14.625
R^2=	0.998	0.9986	0.9994	0.9758
Co	300 ppm	400 ppm	500 ppm	
y=	0.8034x + 17.121	0.7389x + 24.613	0.9345x + 37.318	
R^2=	0.9904	0.9937	0.6868	

For diffusion-controlled process, Arrhenius type equation has been used. Representative plot is shown in Fig. 3.24 and calculated parameters are tabulated in Table 3.12. The Fig.3.24 indicates inconsistency in the results; this is because the experiments were performed at only three temperatures. The negative values of E_d suggest that the rise in solution temperature does not favor the adsorption. The negative values of $\Delta S^{\#}$ indicate a greater order of reaction for the sorption. The electrostatic attraction enhances the adsorption forces on the adsorbent surface and, thus association, fixation and immobilization of phenol molecules on the surface reduces the freedom of the phenol molecules. The results also indicate that no significant change occurs in the internal structure of adsorbent during the adsorption of phenols.

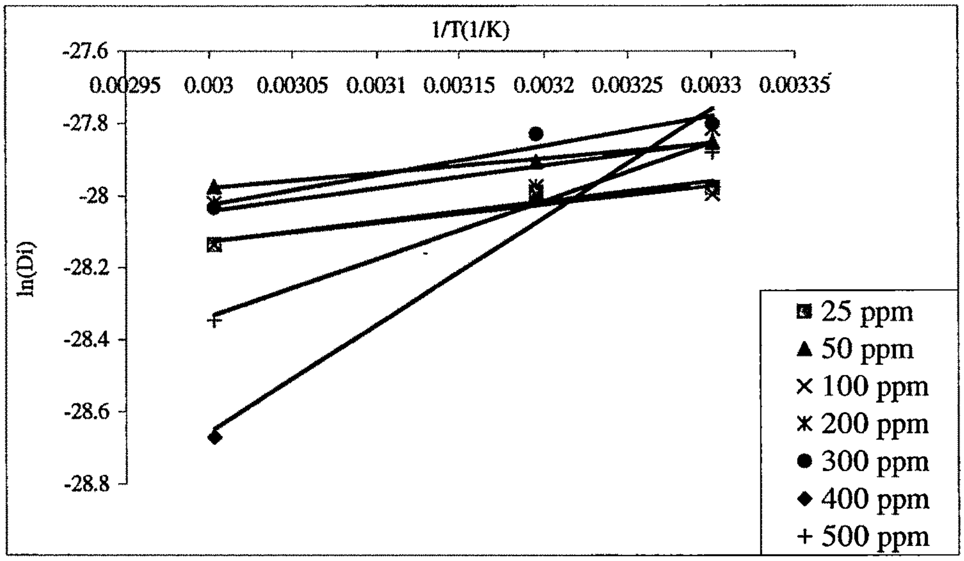

Figure. 3.24. Do and Ed determination using Arrhenius equation for diffusion controlled adsorption of 3-aminophenol on fly ash A

Trendline equation and correlation coefficient values for Fig. 3.24				
Co	25 ppm	50 ppm	100 ppm	200 ppm
Y=	558.44x - 29.803	403.21x - 29.188	508.01x - 29.65	634.01x - 29.945
R^2=	0.9222	0.9917	0.8777	0.7931
Co	300 ppm	400 ppm	500 ppm	
Y=	815.07x - 30.47	2986.1x - 37.615	1606.6x - 33.156	
R^2=	0.9397	0.9833	0.9744	

Table 3.12. Initial diffusion co-efficient, Entropy of activation and Activation energy for diffusion controlled adsorption

Co ppm	D_o (m^2/s)	E_d (J/mol)	$\Delta S^{\#}$ (J/mol k)	$D_o(m^2/s)$	E_d (J/mol)	$\Delta S^{\#}$ (J/mol K)	D_o (m^2/s)	E_d (J/mol)	$\Delta S^{\#}$ (J/mol K)
	Phenol / Fly Ash A			**Catechol/ Fly Ash A**			**Resorcinol/ Fly Ash A**		
25	2.2x 10^{-13}	-3072.1	-139.3	2.1x 10^{-12}	2617.7	-120.6	7.38x 10^{-14}	-5572.46	-148.6
50	5.6x 10^{-13}	-845.9	-131.7	4.0x 10^{-11}	10289.4	-96.3	2.51x 10^{-14}	-8612.47	-157.6
100	9.0x 10^{-13}	633.9	-127.8	3.5x 10^{-13}	-117.7	-131.8	1.46x 10^{-14}	-9634.26	-162.1
200	2.2x 10^{-13}	-3247.9	-139.2	4.9x 10^{-14}	-7261.8	-152.0	8.63x 10^{-15}	-11134.11	-166.5
300	5.2x 10^{-13}	-904.7	-132.3	3.5x 10^{-12}	4223.8	-116.4	5.31x 10^{-14}	-6523.16	-151.4
400	6.5x 10^{-13}	-138.6	-130.4	5.5x 10^{-13}	-373.8	-131.9	5.99x 10^{-14}	-6016.43	-150.4
500	2.3x 10^{-13}	-2880.5	-138.9	2.9x 10^{-14}	-8165.3	-156.3	1.44x 10^{-13}	-3775.05	-143.1
	Hydroquinone / Fly Ash A			**2-Aminophenol/ Fly Ash A**			**3-Aminophenol/ Fly Ash A**		
25	8.34x 10^{-15}	-11608.0	-166.8	3.56x 10^{-13}	-1109.8	-135.5	1.13x 10^{-13}	-4642.87	-145.0
50	7.25x 10^{-15}	-12332.1	-167.9	3.48x 10^{-13}	-1709.0	-135.7	2.02x 10^{-13}	-3352.29	-139.9
100	7.35x 10^{-15}	-12088.6	-167.8	4.34x 10^{-13}	-622.8	-133.9	1.33x 10^{-13}	-4223.60	-143.7
200	7.13x 10^{-15}	-12421.9	-168.1	4.97x 10^{-13}	-382.5	-132.8	9.88x 10^{-14}	-5271.16	-146.2
300	1.01x 10^{-14}	-11624.6	-165.1	2.01x 10^{-13}	-2917.5	-140.3	5.85x 10^{-14}	-6776.49	-150.5
400	8.85x 10^{-15}	-11087.5	-166.3	2.05x 10^{-12}	3814.0	-120.9	4.61x 10^{-17}	-24826.44	-209.9
500	2.92x 10^{-13}	-1758.16	-137.2	4.13x 10^{-13}	-944.5	-134.3	3.98x 10^{-15}	-13357.27	-172.9
	Phenol / Fly Ash B			**Catechol/ Fly Ash B**			**Resorcinol/ Fly Ash B**		
25	7.5x 10^{-13}	-1508.7	-129.4	1.8 x 10^{-12}	1450.5	-121.9	1.0x 10^{-13}	-6107.80	-145.7
50	5.7x 10^{-13}	-2192.4	-131.6	2.3 x 10^{-11}	8663.2	-100.8	6.1x 10^{-13}	-2088.56	-131.0
100	4.9x 10^{-12}	3775.7	-113.7	5.3 x 10^{-12}	4675.2	-113.1	1.1x 10^{-12}	-255.40	-126.1
200	1.8x 10^{-12}	1031.5	-121.9	6.5 x 10^{-11}	11124.1	-92.3	1.1x 10^{-12}	-469.43	-125.9
300	6.6x 10^{-12}	-4280.0	-111.3	5.9 x 10^{-12}	4301.2	-112.2	6.3x 10^{-15}	-13695.6	-169.1
400	1.5x 10^{-13}	-5305.3	-142.8	6.6 x 10^{-12}	-5239.9	-111.3	2.0x 10^{-15}	-16603.0	-178.3
500	5.5x 10^{-13}	-1686.1	-132.7	2.8 x 10^{-12}	3212.9	-118.5	1.9x 10^{-13}	-4811.48	-140.8

Table 3.12. Initial diffusion co-efficient, Entropy of activation and Activation energy for diffusion controlled adsorption(**Continued**)

Co ppm	D_o (m^2/s)	E_d (J/mol)	$\Delta S^\#$ (J/mol K)	D_o (m^2/s)	E_d (J/mol)	$\Delta S^\#$ (J/mol K)	D_o (m^2/s)	E_d (J/mol)	$\Delta S^\#$ (J/mol K)
	Hydroquinone / Fly Ash B			**2-Aminophenol/ Fly Ash B**			**3-Aminophenol/ Fly Ash B**		
25	9.6×10^{-13}	-1426.68	-127.3	5.2×10^{-13}	-2489.13	-132.4	9.25×10^{-12}	-8277.83	-77.6
50	1.9×10^{-12}	1385.11	-121.5	1.2×10^{-13}	-6612.71	-144.3	1.89×10^{-11}	-1192.48	-55.0
100	2×10^{-12}	684.18	-121.2	4.1×10^{-14}	-8790.39	-153.5	6.68×10^{-2}	-3552.24	-63.6
200	6.4×10^{-13}	-1923.94	-130.6	7.7×10^{-15}	-13414.64	-167.4	4.77×10^{-10}	7575.47	-28.2
300	4.1×10^{-10}	15438.2	-77.1	1.2×10^{-14}	-12573.26	-164.0	1.57×10^{-13}	-13336.49	-94.9
400	3.8×10^{-11}	9235.19	-96.6	$1.1\times$ 1.2 10^{-14}	-12538.34	-164.5	6.63×10^{-14}	-15089.91	-102.0
500	2.0×10^{-11}	7755.88	-102.1	4.3×10^{-13}	-2926.03	-133.9	8.14×10^{-11}	3124.00	-42.9
	Phenol / Fly Ash C			**Catechol/ Fly Ash C**			**Resorcinol/ Fly Ash C**		
25	1.16×10^{-12}	1248.93	-125.8	2.55×10^{-8}	27180.12	-42.6	1.18×10^{-11}	7599.33	-106.4
50	1.44×10^{-12}	1794.99	-123.9	4.71×10^{-22}	-56602.5	-305.5	3.75×10^{-11}	10456.52	-96.9
75	1.48×10^{-12}	2563.95	-123.7	8.47×10^{-10}	19467.23	-70.9	4.54×10^{-11}	11269.63	-95.2
100	1.94×10^{-10}	14731.58	-83.2	1.93×10^{-13}	-2117.74	-140.7	1.12×10^{-09}	19323.40	-68.6
	Hydroquinone / Fly Ash C			**2-Aminophenol/Fly Ash C**			**3-Aminophenol/ Fly Ash C**		
25	2.62×10^{-12}	4235.15	-118.9	2.66×10^{-13}	-1956.0	-137.9	1.01×10^{-12}	863.66	-126.9
50	1.42×10^{-8}	26796.02	-47.5	2.63×10^{-11}	10004.2	-99.8	1.65×10^{-12}	2038.34	-122.8
75	1.88×10^{-10}	15262.84	-83.4	4.33×10^{-12}	5804.8	-114.8	2.74×10^{-12}	3948.32	-118.6
100	7.06×10^{-11}	13314.04	-91.6	1.26×10^{-08}	26412.7	-48.5	5.63×10^{-10}	17415.34	-74.3
	Phenol / Fly Ash D			**Catechol/ Fly Ash D**			**Resorcinol/ Fly Ash D**		
100	6.06×10^{-10}	11741.8	-73.7	1.58×10^{-12}	-3037.60	-123.18	3.5×10^{-11}	4898.36	-97.4
200	1.31×10^{-10}	7896.55	-86.5	4.95×10^{-12}	-57.21	-113.68	2.00×10^{-11}	3182.85	-101.9
300	2.46×10^{-10}	9402.30	-81.2	1.1×10^{-10}	-7904.12	-88	3.00×10^{-12}	-1710.85	-117.8
400	2.05×10^{-12}	-2849.29	-121.0	2.0×10^{-13}	-8700.60	-140.31	6.10×10^{-13}	-5658.43	-131.1
500	3.07×10^{-11}	4006.18	-96.9	2.5×10^{-10}	9886.18	-81.14	7.10×10^{-14}	-11101.68	-149.0

Table 3.12. Initial diffusion co-efficient, Entropy of activation and Activation energy for diffusion controlled adsorption(**Continued**)

Co ppm	**D_o (m^2/s)**	**E_d (J/mol)**	**$\Delta S^\#$ (J/mol K)**	**D_o (m^2/s)**	**E_d (J/mol)**	**$\Delta S^\#$ (J/mol K)**	**D_o (m^2/s)**	**E_d (J/mol)**	**$\Delta S^\#$ (J/mol K)**
	Hydroquinone/ Fly Ash D			**2-Aminophenol/ Fly Ash D**			**3-Aminophenol/ Fly Ash D**		
100	4.94x 10^{-12}	-483.20	-113.7	4.56x 10^{-10}	10645.2	-76.1	4.56x 10^{-14}	-14798.09	-160.1
200	1.89x 10^{-12}	-2730.82	-121.7	5.20x 10^{-12}	112.07	-113.3	5.20x 10^{-10}	8629.93	-83.9
300	1.70x 10^{-12}	-3112.60	-122.5	1.70x 10^{-10}	1321.18	-84.3	1.70x 10^{-12}	1350.53	-108.3
400	2.66x 10^{-12}	-1482.97	-118.8	1.17x 10^{-12}	-3318.12	-125.6	1.17x 10^{-13}	-5253.03	-130.5
500	2.52x 10^{-12}	-1850.45	-119.3	1.74x 10^{-11}	3862.52	-103.2	1.74x 10^{-12}	-1588.31	-119.2
	Phenol / Activated Carbon			**Catechol / Activated Carbon**			**Resorcinol/ Activated Carbon**		
100	6.13x 10^{-10}	-11397	-73.6	1.64x 10^{-06}	10010.06	-7.9	6.93x 10^{-07}	7735.43	-15.1
200	2.18x 10^{-10}	-13482	-82.2	6.51x 10^{-10}	8284.57	-73.1	1.48x 10^{-08}	-2389.11	-47.1
300	7.58x 10^{-11}	-16065	-90.9	3.61x 10^{-09}	12747.02	-58.9	1.59x 10^{-07}	3987.39	-27.4
400	2.06x 10^{-11}	-19115	-101.8	5.55x 10^{-10}	8070.07	-74.4	2.39x 10^{-09}	-6552.76	-62.3
500	2.52x 10^{-11}	-18996	-100.2	1.61x 10^{-10}	4658.92	-84.7	5.28x 10^{-09}	-4876.41	-55.7
	Hydroquinone / Activated Carbon			**2-Aminophenol/ Activated Carbon**			**3-Aminophenol/ Activated Carbon**		
100	1.15x 10^{-10}	-14506.27	-87.5	4.45 x 10^{-8}	169.61	-37.9	1.12x 10^{-07}	5037.12	-30.3
200	9.87x 10^{-11}	-15551.34	-88.8	2.74 x 10^{-8}	-960.10	-42.0	2.62x 10^{-12}	-23369.82	-118.9
300	1.11 x 10^{-8}	-2897.01	-49.5	1.00 x 10^{-8}	-3263.49	-50.4	7.76x 10^{-12}	-21462.59	-109.9
400	1.36 x 10^{-8}	-2024.13	-47.8	3.18 x 10^{-8}	-189.83	-40.8	9.63x 10^{-12}	-20173.92	-108.1
500	9.55 x 10^{-8}	3100.04	-31.6	2.49 x10^{-10}	-13674.87	-81.1	2.48 x10^{-10}	-11593.87	-81.1

3.5 Concluding Remarks

Adsorption isotherm and kinetic studies along with the effect of various parameters for six phenolic compounds on different fly ashes have been studied. Fly ash obtained from different industrial sources is an effective adsorbent for the removal of phenols from aqueous solution and its use in phenolic wastewater treatment can be economically and ecologically feasible. Capacity of fly ash to remove phenol depends not only on surface area but also on carbon content and source of fly ash. Bagasse based fly ash D is found to be most effective and having highest surface area where as coal based fly ash C is found to be least effective and also has a minimum surface area.

The effect of parameter pH: with decrease in pH, removal was found to be more for hydroxyl phenols where as for amino phenols mixed behavior was observed. Lower pH (2.0) and higher pH (11.0) have been found to be favorable for aminophenol adsorption on fly ash B, C and D. Incase of fly ash A, low pH(2.0) whereas in case of activated carbon high pH(11.0) has been found to be favorable for adsorption of aminophenols. The complex behavior is due to existence of different ionic equilibrium in aqueous solution for aminophenols. With the presence of salts like NaCl and Na_2SO_4 capacity of adsorbent increases slightly. The percentage removal of phenols decreases with the increasing initial concentration; however the uptake decreases with increase in initial concentration. This implies that at low concentration, the capacity of adsorbent cannot be utilized fully in batch contactors.

Six isotherm models were tested using statistical analysis. Amongst them, Langmuir gave the poorest fit with correlation coefficient (R^2) of 0.85-0.99, average % standard deviation (σ) of 3.27% and maximum percentage deviation of 41%. All other isotherms correlate data very well. The R^2 values for rest of the models were more than 0.9. The σ values for Freundlich, Redlich Peterson, Toth, Radke Prausnitz and Fritz Schlunder were 2.84%, 2.23%, 2.63%, 2.23% and 2.28% respectively. Fitting of Langmuir is poorest; because heterogeneous nature of all the fly ashes.

Standard error of the estimates have also been calculated and presented. Amongst the six phenols investigated presently, catechol and hydroquinone have the maximum adsorption capacity. The adsorption capacity of the adsorbent was found to depend upon the type of functional groups, their position and solubility of phenols.

The adsorption of all the phenols on all the adsorbents studied was found to be exothermic. Both film and intraparticle diffusion steps are found to be rate controlling mechanism in all the cases. Pseudo second order kinetics given by Ho and Mckay is followed by all the systems studied for adsorption.

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