Effect of pH on Adsorption and Desorption Equilibria and Kinetics of 2-Nitrophenol and Phenol onto Two Activated Carbons

by

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ABSTRACT

Granular activated carbon (GAC) adsorption has become an important unit process for the removal of organic pollutants from waters and wastewaters. The application of activated carbon is limited by the high cost of GAC and its regeneration. To improve and reduce the cost of current regeneration process, electrochemical regeneration is currently being researched. As this type of regeneration appears to be dependent on desorption at extreme pHs it is of interest to quantify it.

The objective of this thesis was to investigate the impact of pH on the adsorption equilibria, adsorption kinetics, desorption equilibria and desorption kinetics. A study was conducted by using 2-nitrophenol (2NP) and phenol as organic pollutants and F-400 and WV-B carbons as adsorbents.

The batch adsorption isotherms study showed that at pHs less than pK_a (undissociated form of compounds), 2NP and phenol adsorption was markedly higher than at pHs greater than pK_a (dissociated form of compounds). Both carbons were similarly impacted by pH in the adsorption process and they had almost the same adsorption capacity in adsorbing phenol while F-400 showed more adsorption capacity in adsorbing 2NP.

Adsorption-desorption experiments showed that the adsorption of 2NP by F-400 carbon is fully reversible. The presence of 1% NaCl solution did not affect the extent of reversibility. Accordingly, experiments showed both carbons were similarly impacted by

pH in the desorption process. For both compounds, the extent of desorption was much greater for the pHs greater than the pK_a, i.e. when the adsorbate is in its dissociated form. For 2NP, as the extent of desorption at various pHs was predicted using the adsorption isotherm for the same pH, the adsorption of these compounds was fully reversible at the pHs tested. Much greater desorption at high pHs suggests that in an electrochemical regeneration process there is a higher probability of regeneration through enhanced desorption at the cathode, because it has a high localized pH.

The initial adsorption and desorption rates were significantly affected by pH. Adsorption kinetics of 2NP onto both carbons were described by the homogeneous surface diffusion model and it was not necessary to utilize separate terms for slow and rapid adsorption mechanisms. Also, it was found that the surface diffusion coefficient, D_s, within the HSSD model was essentially the same at all pHs.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The presence of hazardous chemicals in the environment continues to be an important concern. The demand for more stringent control and protection of our water resources from pollution has mounted steadily in recent decades. Activated carbon (AC) adsorption has become an important unit process for the removal of hazardous organic chemicals from both waters and wastewaters. Many applications particulary the removal of toxic chemicals, use of granular activated carbon (GAC) columns. It is being used in upgrading wastewater and water treatment plants, in treating contaminated groundwater and leachate from toxic waste dumps, and in home water treatment units. Characteristics of the contaminant(s), the AC and the water must be considered and evaluated if the most efficient utilization of activated carbon is to be obtained.

1.2 Statement of the Problem

The main drawback of GAC adsorbers is the high cost of GAC and its regeneration. Although, thermal, chemical, and biological methods of regeneration have been researched, in practice, thermal regeneration is used almost exclusively. The main disadvantages of this technology are its high cost and destruction of 5 to 15% of the GAC in each regeneration cycle. Narbaitz and Cen (1994) investigated the feasibility of electrochemical regeneration as a new technology for GAC regeneration. Their research showed nearly complete regeneration of GAC loaded with phenol with no apparent loss

of GAC mass. Thus, this technology has the potential of becoming a commercial product and merits further research. Narbaitz and Cen (1994) hypothesized that the regeneration was the result of enhanced desorption at the electrodes (due to the extreme local pHs) and oxidation at the anode. To confirm Narbaitz and Cen's hypothesis it is necessary to quantify the maximum extent of desorption (equilibrium), the rates at which it occurs, and the rates of destruction at both electrodes.

1.3 Objective

The objective of this study is to investigate the impact of pH on the adsorption equilibria, adsorption kinetics, desorption equilibria and desorption kinetics of two phenolic compounds using two different activated carbons.

1.4 Scope of Work

This thesis investigates the impact of pH on the adsorption/desorption of two organics: 2-nitrophenol and phenol. 2-nitrophenol is moderately soluble in water and has a pK_a=7.23. Phenol (pK_a=9.99) is highly soluble in water and a common contaminant. Since the properties of AC depend on the raw material and the method of activation, this study tested two adsorbates: Filtrasorb 400 (F-400), which is made from bituminous coal, and Westvaco (WV-B), which is made from wood. Moreover, phenol and F-400 were studied because they are the adsorption system investigated by Narbaitz and Cen (1994). They suspected that less than perfect regeneration of phenol-loaded F-400 was related to the fact that this phenol adsorbs partially irreversibly on this GAC. Thus, it is of interest to study the regeneration of sorbate/sorbent systems involving fully reversible adsorption. The sorbate/sorbent combinations of phenol/WV-B, 2-nitrophenol/WV-B, and

2-nitrophenol/F-400 were chosen because Vidic et al. (1993) showed that they exhibit fully reversible adsorption. Unfortunately, time limitations did not permit an investigation of the electrochemical regeneration of these GAC/contaminant systems.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Adsorption is a surface phenomenon in which matter is extracted from one phase and concentrated at the surface of another. The contaminant extracted is called the adsorbate and the surface the adsorbent. Due to its extremely large internal surface area activated carbon (AC) can adsorb large quantities of a very wide variety of organics, as well as inorganic compounds. Thus, activated carbon adsorption has become an important unit process for the removal of toxic organic chemicals from both waters and wastewaters. Because activated carbon has been in use for many years, there is a great deal of literature on this topic. This survey of literature is limited to very specific subjects related to the goal of this research: The effect of pH on adsorption and desorption of phenolics on activated carbons. The topics surveyed include general information about activated carbon, adsorption, factors affecting adsorption, desorption, kinetics characteristics, kinetics modelling, and the impact of pH.

2.2 Activated Carbon

Activated carbon removes organic contaminants from water by the process of adsorption. In general, high surface area and pore structure are the prime considerations in the adsorption of organics from water. While, the chemical nature of the carbon surface is of lesser importance. Granular activated carbon (GAC) typically has a surface area of 500-1400 m^2/g. Most of the surface area available for adsorption in GAC particles is found in the internal pores of molecular dimensions created during the activation process. A

molecule will be excluded from pores smaller than a certain critical diameter.

Activated carbons can be made from a variety of carbonaceous materials including wood, coal, peat, lignin, nut shells, sawdust, lignite, bone, and petroleum residues (Faust and Aly, 1987). The quality of the resulting activated carbon is influenced by the starting material as well as the activation process (Sontheimer et al., 1988).

Activated carbon is manufactured by a process consisting of material dehydration and carbonization followed by activation. The starting material is dehydrated and carbonized by slowly heating it in the absence of air, sometimes using a dehydrating agent, such as zinc chloride or phosphoric acid (Sontheimer et al., 1988). Excess water, including structural water, must be driven from the organic material. Carbonization converts this organic material to primary carbon, which is a mixture of ash (inert inorganics), tars, amorphous carbon, and crystalline carbon. Non-carbon elements (such as H and O) are removed as gases and the freed elementary carbon atoms are grouped into oxidized crystallographic formations (Weber, 1972). During carbonization, some decomposition products or tars will be deposited in the pores, but they will be removed in the activation step. Activation is essentially a two phase process requiring burn-off of amorphous decomposition products (tars), plus enlargement of pores in the carbonized material. Burn-off frees the pore openings, increasing the number of pores, and activation enlarges these pore openings.

2.3 Adsorption

2.3.1 Basics of Adsorption

Adsorption from aqueous solutions onto activated carbon can occur as a result of: (a) low solubility of a particular solute in the solution; (b) a high affinity of a particular solute in the aqueous solution for the activated carbon; or (c) a combination of the two. This second surface phenomenon may be due to electrical attraction of the solute to the carbon, Van der Waals attraction, or have a chemical nature.

Adsorption from aqueous solution involves concentration of the solute on the solid surface. After a period of contact time, some of the sorbed solute desorbs into the solution. Finally, the amount and the rate of the adsorption and desorption will be the same, i.e. adsorption equilibrium is reached. Adsorption equilibrium experiments are generally conducted at constant temperature so they are called isotherms. The most common experimental isotherm technique is the bottle-point method, so called because each bottle in the test generates a point in the equilibrium curve. These experiments are conducted by contacting the solution of interest in a set of bottles with different doses of activated carbon until equilibrium is reached. Then the solutions are separated from the carbon and are analyzed for the solute concentration. The experiments yield the equilibrium liquid phase concentration as a function of carbon dosage. The equilibrium solid phase concentration, which is also called equilibrium capacity, equilibrium loading or loading, can be calculated by using a mass balance.

$$q = \frac{V(C_o - C)}{m} \qquad (2\text{-}1)$$

where q is the equilibrium contaminant solid phase concentration (g of contaminant/g of

AC); C is the equilibrium contaminant liquid phase concentration (g of contaminant/m^3); C_0 is the initial contaminant liquid phase concentration (g of contaminant/m^3); m is the weight of AC (g); and V is the vessel volume (m^3).

The adsorption equilibria is generally presented as a graph of the amount of solute adsorbed per unit mass of adsorbent, q, as a function of equilibrium concentration in the bulk solution, C_e. This graph is also called the adsorption isotherm. Many factors associated with the adsorbate, adsorbent, and the experimental system influence the efficiency of activated carbon in removing contaminants from solution. They will be discussed later in this chapter.

2.3.2 Single Component Isotherm Models

Different isotherm equations have been proposed either based on empirical data or on physico-chemical or thermodynamic models. The models that have been most suitable for describing aqueous solutions are discussed by Sontheimer et al. (1988). Adsorption equilibria for most aqueous systems can be modelled by the Langmuir model and/or the Freundlich model. The Langmuir model, which is also called the ideal localized monolayer model, is based on the following basic assumptions: first, the molecules are adsorbed on definite sites on the surface of the adsorbent. Second, each site can accommodate only one molecule (monolayer). Third, the area of each site is a fixed quantity determined solely by the geometry of the surface. Fourth, adsorption energy is the same at all sites. Finally, the adsorbed molecules can not migrate across the surface or interact with neighbouring molecules.

The Langmuir isotherm originally was derived from kinetic analysis and later on by thermodynamic considerations (Adamson, 1982). For adsorption from solution by solid adsorbents, the Langmuir adsorption isotherm is expressed as:

$$q = \frac{q_m b C}{(1+bC)} \qquad (2-2)$$

where q_m is the amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface (g/g of AC); and b is a constant related to the heat of adsorption. The Langmuir isotherm model has been shown to fit some aqueous systems over limited concentration ranges (Singer and Yen, 1978; Razzaghi, 1976).

The Freundlich adsorption equation is the most widely used mathematical expression for the adsorption from dilute aqueous solutions. The Freundlich equation is an empirical expression that was later found to correspond to adsorption on a heterogenous surface with adsorption sites whose adsorption energies follow an exponential distribution (Young and Crowell ,1962). The heterogeneous surface of activated carbon probably makes it the most compatible isotherm model. It is expressed as:

$$q = KC^{1/n} \qquad (2-3)$$

where k and 1/n are constant characteristics of the system. For linearization, the Freundlich equation can be written in the following logarithmic form:

$$\log(q) = \log(K) + \frac{1}{n}\log(C) \qquad (2-4)$$

If the data fit this model, plotting log(q) versus log(C) yields a straight line with a slope

of 1/n and log(K) is the intercept of log(q) at C=1 (log C=0). The value of 1/n for the adsorption of most organic compounds by activated carbon is < 1. When 1/n is close to 1 (steep slopes), it indicates a high adsorptive capacity at high equilibrium liquid phase concentrations and rapidly diminishing capacities at lower equilibrium concentrations. When 1/n << 1 (flat slopes) it indicates that the adsorptive capacity is only slightly reduced at the lower equilibrium concentrations. As can be deduced from equation 2-3, higher capacities are obtained at higher equilibrium concentrations.

The amount of activated carbon required to reduce any initial concentration to a predetermined final concentration can be calculated from the Freundlich equation by substituting $V(C_0 - C)/m$ (eq. 2-1) instead of q in eq. (2-3).

2.4 Factors Affecting Adsorption

Several factors such as the nature of the activated carbon and the nature of the solution can influence adsorption by activated carbon.

2.4.1 Factors Associated with the Adsorbent

The adsorptive characteristics of an AC surface depend upon the source material of carbon as well as on the activation technique (Sontheimer et al., 1988). Size of carbon particles, pore structure and carbon surface area, and the amount of chemisorbed oxygen are the most important factors associated with the adsorbent.

2.4.1.1 Carbon Particle Size

Activated carbons are classified according to their form: powdered or granular. Granular

activated carbons (GAC) are those whose particles are larger than approximately U.S. sieve series #50, while powdered activated carbons (PAC) are those which are smaller. Figure 2.1 shows there is no influence of particle size on the adsorption of 2,4-DCP and 2,4-DNP on GAC Columbia LCK (Zogorski and Faust, 1978). Similar results have been reported by many investigators (i.e. Najm et al., 1990; Faust and Aly, 1987; Peel and Benedek, 1980-a; and Martin and Al-Bahrani, 1978). This is not surprising since the majority of the surface area is within the internal pores of the GAC particles. However, exceptions have been observed in studies with detergents (Leyva-Ramos, 1989; and Morris and Weber, 1964). One reason for this could be insufficient contact time for the entire particle to reach equilibrium, in this case small particles will have higher adsorptive capacities. Randtke and Snoeyink (1983) have reported that GAC exhibited almost no difference in activity with particle size for a low-molecular-weight adsorbates, such as 4-nitrophenol (4NP). Whereas it exhibited some difference for high-molecular-weight adsorbates, such as fulvic acid, because of differences in pore size distribution. Grinding to produce smaller particle sizes can destroy the number of large size pores necessary for the removal of large molecular size adsorbates. Uneven activation of the GAC followed by grinding can also yield AC particles whose adsorption differs with particle size (Randtke and Snoeyink 1983, and Narbatiz, 1985). However, in general adsorption capacity is independent of the adsorbents's particle size.

Fig 2.2 shows that small particles adsorbs contaminant more quickly and reach equilibrium much faster than large ones (Najm et al., 1990). Similar results are reported by Mathews and Zayas, (1989). Adsorption on the particles is often a diffusion limited process and the rate of adsorption is inversely proportional to the square of the

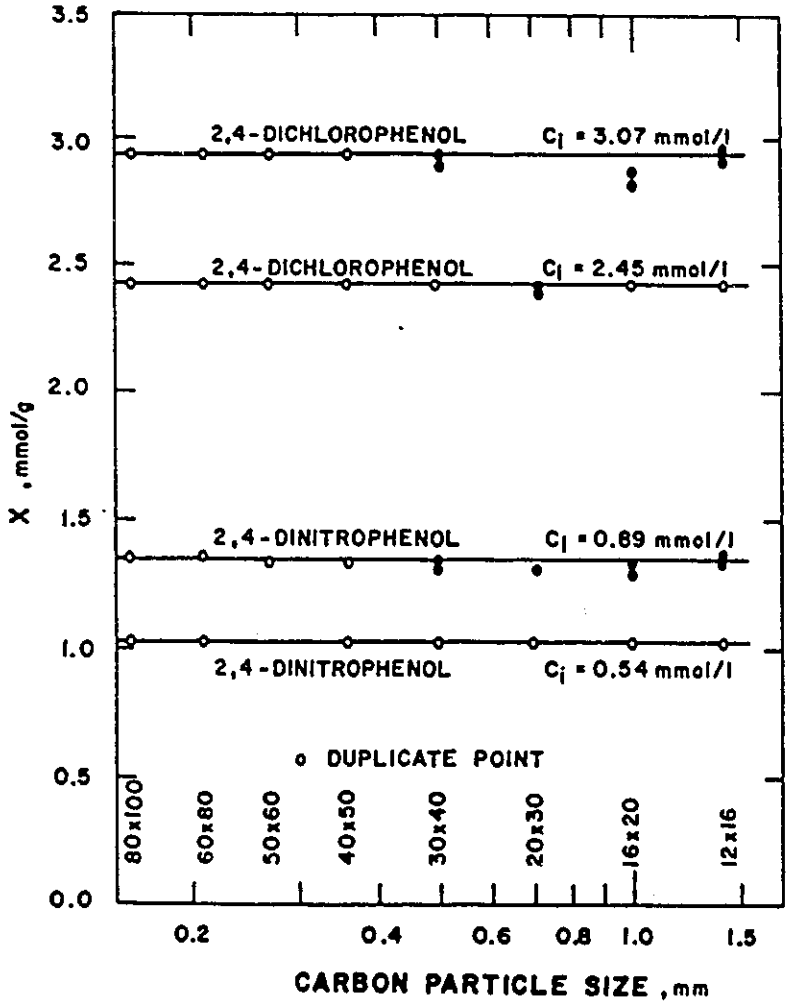


Fig. 2.1 Influence of carbon particle size on the adsorption of 2,4-dinitrophenol and 2,4-dichlorophenol at 20 °C.

(source: Zogorski and Faust, 1978)

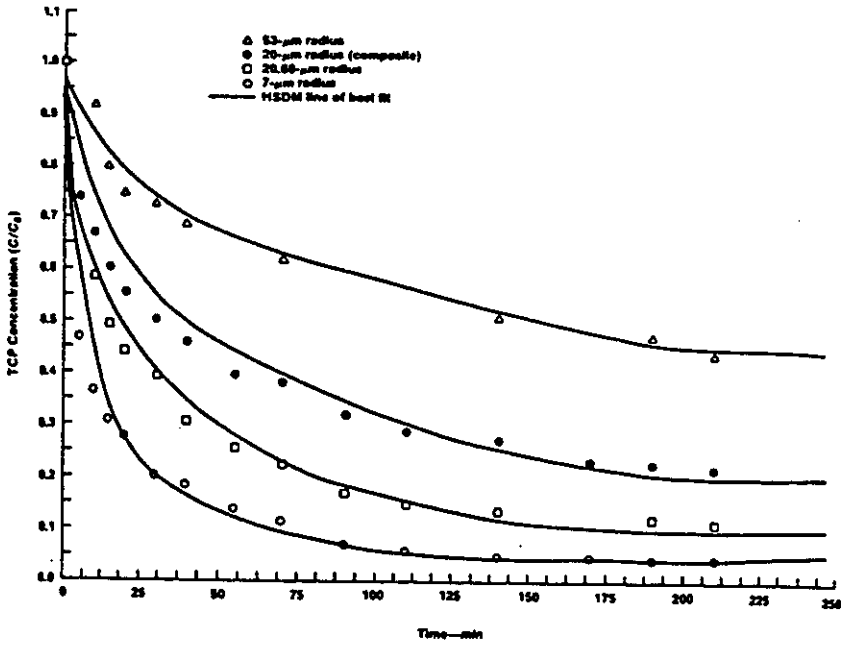


Fig. 2.2 Effect of particle size on the rate of adsorption of trichlorophenol on PAC in batch tests.

(source: Najm et al. 1990)

particle diameter (Faust and Aly, 1987; Zogorski and Faust, 1976-b; Weber and Morris,1963).

2.4.1.2 Pore Structure and Carbon Surface Area

The pores in activated carbon have been divided into macropores, transitional pores and micropores (Dubinin, 1966). Macropores are pores greater than 1000-2000 A° radius with the specific volumes from 0.2 to 0.8 cm^3/gram and specific surface area vary from 0.5 to 2 m^2/g (Peel, 1980). The macropores play a negligible role in physically adsorbing material because of the low area, but they provide rapid access to the interior of the carbon particle. Transitional pores are 15 to 1500 A° in size. Their specific surface area ranges from 20-70 m^2/g and the specific volume from 0.2 to 0.1 cm^3/g (Peel, 1980). However, these number may change from adsorbent to adsorbent. Micropores are pores with radii less than 15 A° and are of a comparable size to many adsorbing molecules. Micropores often contribute as much as 90 to 95 percent of the total surface area within the carbon (Ying, 1978) and they have specific volumes of 0.2 to 0.6 cm^3/g.

Both the rate of adsorption and the adsorptive capacity can be influenced by the pore structure. If the size of the adsorbate is greater than the largest pore opening, adsorption is limited to the external surface of the carbon particles. Usually the adsorbate is smaller than the macropore openings. In this case the amount of adsorption which results will greatly depend upon the fraction of the total measured surface area which is accessible to the adsorbate. Graham (1955) found that cationic dye adsorption was pore-size limited. Similar results are reported for different humic substances (Summers, 1986; Summers and Roberts 1988a,b). Kuhl et al. (1986) examined over 30 carbons and reported linear

correlations between the adsorption capacity for p-chlorophenol and the micropore volume of pores with radii less than 3 A°.

When adsorption results from physical attraction forces (i.e. van der Waal) between adsorbate and adsorbent, increasing the total surface area generally enhances the removal capacity of activated carbon. For example, Oda et al. (1981) found that the adsorption capacity of benzoic acid was surface area limited. But there is no direct way of predicting adsorption capacity based on surface area measurements. And a carbon with higher surface area than another, which is made of a different raw material or via a different manufacturing process, may or may not yield a higher adsorption capacity.

When adsorption occurs via specific chemical interactions between the adsorbate and certain functional groups on the carbon surface, the adsorption depends on the number of suitable functional groups present on the carbon surface and not on the surface area.

2.4.1.3 Chemisorbed Oxygen

Activated carbon is usually composed of 5 to 20 percent oxygen by weight and 80-95 percent carbon (Sontheimer et al., 1988; and Zogorski,1975). The characteristics and amount of the oxygen chemically sorbed onto the surface of the activated carbon depends on the raw material and the activation technique (Sontheimer et al, 1988). Based on the temperature at which activation was performed, the activated carbon can exhibit acidic or basic characteristics. Under most manufacturing and treatment conditions, the oxygen chemisorbed on the carbon surface is in the form of acidic surface oxides.

Graham (1955) observed that acidic oxygen groups on the carbon surface reduce the adsorption capacity of metanil yellow from water, while there was no effect on the adsorption of methylene blue . Graham attributed this to a repulsive interaction between the anionic form of mentanil yellow and the oxygen sites. Graham noted that, this kind of interaction might be expected for all anionic adsorbates. Coughline et al. (1970) showed the amount of adsorption of phenol, nitrobenzene, sodium benzenesulfonate and dextrose were reduced in the presence of acidic surface oxides. Similar results has been documented in numerous studies (i.e. Sontheimer et al., 1988; Youssef et al., 1982; Matsumura et al., 1985; Oda et al. 1981). The rates of adsorption were also reduced by the presence of surface oxygen oxides (Coughlin et al., 1970).

2.4.2 Factors Associated with the Experimental System

Temperature, salt concentration, presence of molecular oxygen, contact time, and hydronium ion concentration are the most important experimental system factors affecting adsorption. These will be discussed below, except for the later which will be discussed separately later in this chapter.

2.4.2.1 Temperature

The dependence of the rate of adsorption and adsorption capacity on the temperature has been studied by many researchers. Usually, the adsorption process is a combination of chemisorption (most frequently irreversible adsorption) and physical adsorption (most probably reversible adsorption). The latter, normally predominates because of the lower energy requirement. Physical adsorption capacity decreases with increasing temperature of the system due to breaking of weak bonds. Since the adsorption rate is a diffusion

limited process, the rate of adsorption of the organic from solution increases as the temperature of the system increase. Snoeyink (1968) studied the temperature dependence with phenol and 4-nitrophenol. These studies indicated that the rate of adsorption increases as the temperature of the system increases, however, the adsorption capacity decreases. Zogorski and Faust (1978) developed the isotherms for phenol and 2,4-DCP at temperatures of 8, 20, and 29 °C (Fig 2.3), the quantity adsorbed decreased with increasing temperature. However, when the phenol concentration was greater than 200 μmol/l, temperature had a lesser influence on the adsorption process. They also observed an increase of removal rate as the temperature of the system was increased. Raising the temperature from 10 to 30 °C increased the removal rate of phenol by 21% and of 2,4-DCP by 28%.

2.4.2.2 Salt Concentration

The increase of adsorption by salt addition has been reported by several researchers. Snoeyink et al. (1969) added 1 M NaCl to a solution of 4-nitrophenol (4NP) (pK_a=7.1) and found that the presence of NaCl had no effect on activated carbon adsorption at pH 2. However, at pH 10, where the PNP is highly ionized, the NaCl markedly increased PNP adsorption. Couglin and Tan (1968) studied the effect of adding 0.002 M and 0.004 M $CaCl_2$ to solutions of sodium benzenesulfonate (SBS) prior to adsorption onto activated carbon. The adsorption of SBS, which was strongly ionized in the solutions, increased by a factor of 1.15 to 3 by the addition of $CaCl_2$. Cooney and Wijaya (1987) reported similar results for benzoic acid. They proposed that adjacently adsorbed benzoate ions will strongly repel each other, as both have the same charge. The only way to counteract the repulsion of adjacently adsorbed SBS ions is to add positive ions to the solution. As more

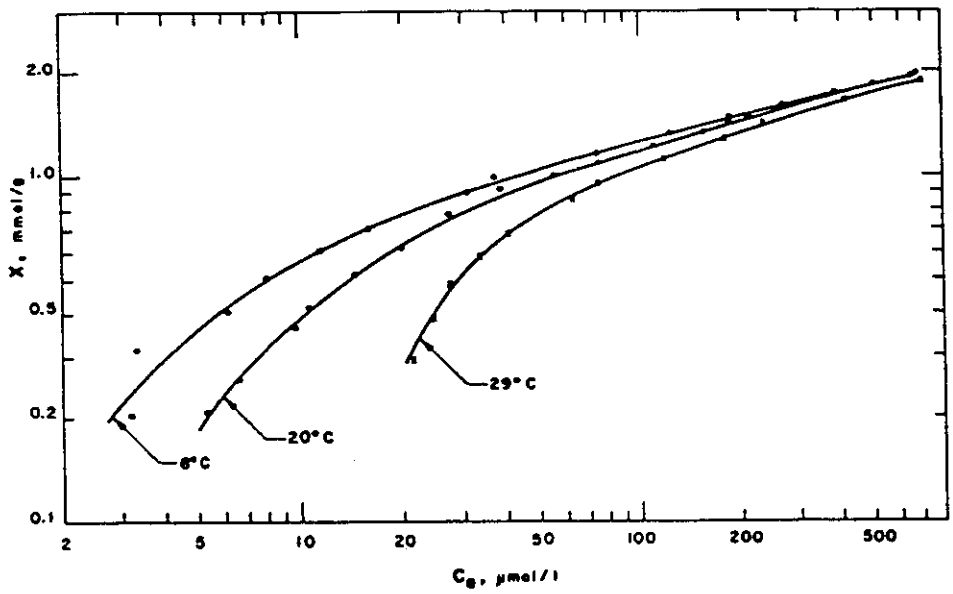


Fig. 2.3 Influence of temperature on the adsorption of phenol at pH 6.3.

(source: Zogorski and Faust, 1978)

and more positive ions are placed in the solution (by the addition of a salt), there will be more intrusion of these positive ions between the negative benzoate ions, nullifying, to some degree the repulsive forces between adjacent benzoate ions. The net result will be that the benzoate ions can adsorb much more densely on the carbon surface.

Jawaid and Weber (1979) investigated the effect of several salts on SBS adsorption by activated carbon. These salts were zinc chloride, calcium chloride, or potassium carbonate in the amount of 1 part salt per 100 parts charcoal. They found increases in adsorption of 19, 24, and 11% respectively, for these three salts.

Phosphate buffer at 0.05 M exhibited no discernable effect on the rate of adsorption and adsorption capacity of undissociated 2,4-dichlorophenol (2,4-DCP) and 2.4-dinitrophenol (2,4-DNP) (Zogorski and Faust, 1976-a). However, the amount of adsorption of the dissociated compounds was increased around 10% for 2,4-DCP and around 25% for 2,4-DNP in the presence of the phosphate buffer.

Randtke and Jepsen (1982) found that the presence of salts increased the activated carbon's adsorption capacity of different humic and fulvic acids. The anions had no detectable effect, Na had a slight gradual increase in capacity, while Ca and Mg produced very sharp increases in loading at concentrations of less than 1 mmole/l. In conclusion, salt addition significantly increases the adsorption capacity of GAC in adsorbing ionized form of organic compounds.

2.4.2.3 Molecular Oxygen

Different applications of activated carbon can cause the adsorption process to occur in the presence or the absence of molecular oxygen. Prober et al. (1975) showed that dissolved oxygen adsorbs on GAC in the range of 10 to 40 mg/g. This adsorption of oxygen increases the concentration of acidic oxide groups on the carbon surface which increases the base sorption capacity. Magne and Walker (1986) showed changes in the GAC adsorptive capacity for nitrobenzene and phenol as a result of chemisorption of oxygen. Vidic et al. (1990) indicated that the presence of molecular oxygen has a major effect on the adsorption capacity of GAC for several phenolic compounds : phenol, o-cresol and 3-ethylphenol. In some instances, the adsorption capacity in the presence of molecular oxygen was up to three times the capacity that was measured in the absence of molecular oxygen. They hypothesized that the presence of molecular oxygen promotes polymerization of the compound on the surface of the carbon which lead to the increased removals. However, Vidic et al. (1993) observed that the presence of molecular oxygen had very little influence on the adsorptive capacity of F-400 GAC in adsorbing nitrophenols (2-nitrophenol,3-nitrophenol, and 4-nitrophenol).

2.4.2.4 Contact Time

Contact time duration influences the efficiency of activated carbon in adsorbing solutes from solution (Summers, 1986; Peel and Benedek 1980-a; Randtke and Snoeyink, 1983). Many previously reported adsorption isotherms yielded low adsorption capacities because the equilibrium time was too short. Equilibrium time depends on the ratio of equilibrium to initial liquid-phase concentration, C/C_o, temperature, particle size, and the liquid-phase and intraparticle mass transfer rates (Sontheimer et al., 1988).

For example, Peel and Benedek (1980-a) observed a period of a month or longer was required to achieve equilibrium for o-chlorophenol in contact with GAC. However, PAC, which adsorbs faster due to the smaller particle size, required a week to reach equilibrium. Previous researchers reported a shorter period of time for both cases. Peel and Benedek, concluded that isotherm duration is the main reason for large differences reported in the literature for phenol isotherms using Calgon's F-400. So, sufficient contact time is necessary in all works involving carbon adsorption and 14 days should be adequate in most cases. However, humic acids adsorb much slower than synthetic compounds, so 14 days for humics may not be sufficient. For example Summers (1986) observed that in adsorption of humic substances, GACs gained 50% more adsorption capacity after 50 days comparing to the first 5 days.

2.5 Desorption

Desorption isotherms are used to determine the extent of irreversibility. The extent of irreversibility is a function of the strength of the sorbent-sorbate bond.

2.5.1 Desorption Experimental Procedures

Most research relating to desorption has been conducted on single-solute systems by using batch desorption procedures. Single cycle or multiple cycles of the bottle-point type technique can be used for desorption experiments. In some cases, a single GAC dose is tested; in others the tests are conducted for many doses (Narbaitz and Cen, 1994), yet in others large batch reactors are used (Snoeyink et al. 1969).

The first step is always loading the GAC with adsorbate using a batch loading procedure, such as the bottle-point technique. Following equilibration, the liquid and the AC are separated by filtration or by sedimentation. In the case of filtration, the GAC retained on the filters is rinsed back into a clean glass bottle with sorbate-free solution (Narbaitz, 1985). In the case of GAC separation by sedimentation a large fraction of the solution is decanted and replaced with sorbate-free solution (Snoeyink et al., 1969). The bottles are then agitated until a new equilibrium is reached. The liquid phase concentration is then determined and the solid phase loading on the GAC is calculated from:

$$q_d = q_{ad} - \frac{V(C_d - C_{od})}{m} \qquad (2\text{-}5)$$

where q_d is the solid phase concentration after the desorption step (g/g of AC); q_{ad} is the solid phase concentration after adsorption equilibrium (g/g of AC); C_d is the liquid phase concentration after the desorption step (g/l); V is the volume of the desorption solution (l); m is the mass of activated carbon in each bottle (g); and C_{0d} is the initial liquid phase concentration of desorption solution (g/l). In the case of multiple desorption cycles this process is repeated until the resultant liquid phase sorbate concentration is less than the analytical detection limit. The solid phase loading on the GAC is calculated after each desorption step by using

$$(q_d)_i = q_{ad} - \sum_{i=1}^{N} \frac{(C_{d_i} - C_{od_i})\, V_i}{m} \qquad (2\text{-}6)$$

where $(q_d)_i$ is the equilibrium solid phase loading at the end of desorption step i (g/g of AC); m is the mass of GAC in the desorption bottle (g); q_{ad} is the equilibrium solid phase concentration after the initial adsorption loading step (g/g of AC); C_{0di} is the liquid phase concentration at the start of desorption step i (g/l); and C_{di} is the equilibrium liquid phase

concentration after desorption cycle i and V_i is the volume of the desorption solution of step i.

2.5.2 Reversibility

Generally, the type of adsorption can be divided into three groups: completely reversible, completely irreversible, and partially irreversible.

Identical adsorption and desorption isotherms represent completely reversible adsorption. The desorption isotherm overlaps the adsorption isotherm and C_d and q_d from the desorption isotherms can also be described by the adsorption isotherm.

Irreversible adsorption is caused by chemisorption or hysteresis effects. For completely irreversible adsorption, C_d equals C_{od} and the contaminant liquid phase and solid phase concentration remain unchanged regardless of the initial liquid phase concentration of the desorption solution. So, the solid phase concentration is only a function of the loading attained during the adsorption cycle, and the desorption isotherms are horizontal constant loading lines connecting the adsorption loading with the ordinate.

Partially irreversible adsorption is similar to that of the fully irreversible case. These isotherms have higher loadings than the adsorption isotherm and they are slightly sloped. Figure 2.4 represent the phenol desorption isotherm for two masses of Columbia LC carbon, which is an example of partially irreversible adsorption (Snoeyink et al. 1969). These desorption isotherms were obtained from multiple desorption cycles and the solid triangles and circles represent the conditions at the end of a cycle. Narbaitz and Cen

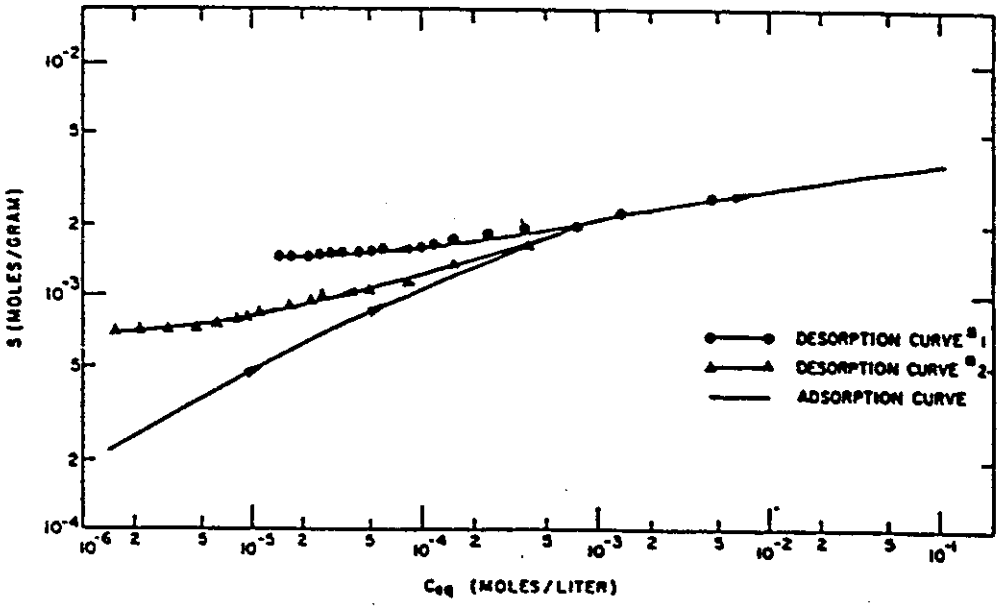


Fig. 2.4 Adsorption and desorption isotherms of phenol.

(source: Snoeyink et al., 1969)

(1994) used a single desorption cycle of different doses F-400 GAC to obtain a phenol desorption isotherm. As Fig. 2.5 shows, phenol adsorption on F-400 is also partially irreversible.

Chemisorption is the most logical explanation for irreversible adsorption (Yonge et al., 1985). Depending on the type of surface functional group and the type of adsorbent, a relatively strong bond that resists desorption can be formed. Therefore, the number of strong bonds will determine the degree of irreversibility. Physical adsorption which is primarily caused by Van der Waals Forces, which creates weaker bonds, should be reversible. Snoeyink (1968) have shown that only 50% of the adsorbed phenol was desorbed from a Columbia LC GAC. In contrast, Schultz (1982) obtained 100% adsorption reversibility for phenol adsorbed on a powdered coconut-shell based activated carbon. Pirbazari and Weber (1981-a and 1981-b) indicated that benzene exhibits complete reversibility while, polychlorinated biphenyls behaved completely irreversible in the batch and continuous-flow column studies on GAC. Leyva-Ramos (1989) observed that the adsorption of anionic detergent sodium dodecyl benzene sulfonate (SDBS) onto a wood based activated carbon from aqueous solutions was irreversible and the order of magnitude of the heat of adsorption indicates that SDBS is chemisorbed on activated carbon. Thus, these results prove that the occurrence of irreversible adsorption is a function of both adsorbate and adsorbent type.

Yonge et al. (1985) tested the desorption of 2-ethylphenol (2-EP), O-cresol (O-C), O-methoxy phenol (O-M), 4-isopropyl phenol (4-IPP), and phenol (Ph) from F-400 carbon. These experiments showed a high degree of irreversibility associated with the adsorption

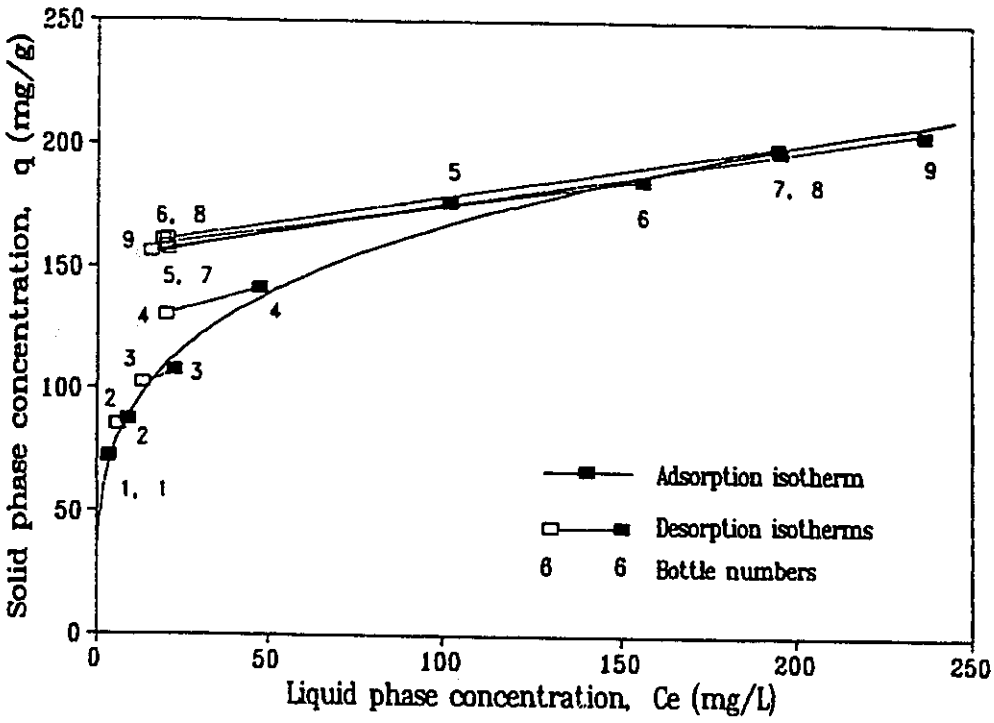


Fig. 2.5 Phenol adsorption and desorption isotherms. Desorption tests were conducted in 1% NaCl solution.

(source: Narbaitz and Cen, 1994)

of each of the sorbates. They hypothesized that the dominant adsorption mechanism is high-energy bonding to specific functional groups on the activated carbon surfaces. They also found that phenol and 4-IPP had the lowest degree of irreversible adsorption while 2-EP, O-C and O-M were the most irreversible. They suggested that the addition of the methyl, ethyl and methoxy groups in the ortha position of the phenol molecule intensifies the binding energy to the activated carbon surface functional group. This can result in an inductive effect that is stronger than that exhibited by the same group in the para position. They hypothesised that this more intense inductive effect could result in a stronger sorbate-sorbent bond and therefore, a higher degree of irreversibility as observed for the ortho-substituted phenols.

Vidic et al. (1990, 1993) observed that the adsorption of phenol, o-cresol, and 3-ethyphenol on F-400 carbon was irreversible in the presence of oxygen due to their reaction with the AC to form polymeric species on the carbon surface. However, Vidic et al. (1993), reported that experiments with three nitrophenols (2-nitrophenol, 3-nitrophenol, 4-nitrophenol) showed almost 100% reversibility in the presence and absence of oxygen from loaded F-400 carbon. It shows that not all phenolics adsorb irreversibly even on the same carbon.

2.6 KINETICS

2.6.1 Adsorption Kinetics

Adsorption kinetics is one of the two major types of information required to design and model absorbers, the other being adsorption isotherms. Kinetic information can be obtained from a wide variety of experiments that monitor the changes in solute

concentration with time caused by a given mass of adsorbent. The mass transfer of adsorbate from the bulk liquid to an adsorption site on the surface of adsorbent controls the rate of achievement of equilibrium. This mass transfer takes place via three main steps. First, transfer across the external liquid film that surrounds the adsorbent particle. Second, transfer from the liquid phase to the solid phase (adsorption step). Third, intraparticle diffusion either by surface diffusion in the adsorbed site along the walls of the pores or pore diffusion in the liquid within the pores. Generally the adsorption step itself is very fast and is not the rate-limiting step in the adsorption of organic compounds (Sontheimer et al., 1988; Weber, 1972 and Smith, 1968). Thus, the two remaining steps in the overall transport determine the rate limiting step. Degree of mixing, concentration of adsorbate, carbon particle size, diffusivity of the adsorbate, and affinity of the adsorbate for the adsorbent are of importance in determining which mechanism is the rate-limiting step. Transfer across the external liquid film could be rate limiting step in systems that have poor mixing, small particle size of carbon, dilute concentrations and high affinity of adsorbate for adsorbent (Zogorski, 1975). Intraparticle resistances control the overall transfer in the systems that have good mixing, high concentration of adsorbate, large particle size of carbon, low affinity of adsorbate for adsorbent (Zogorski, 1975).

2.6.2 Kinetic Modelling

Modelling the adsorption rate is a subject that has received considerable attention over the last decades. Early models made many simplifying assumptions such as negligible intraparticle mass transfer resistance, in order to solve the model analytically. For example, Fritz et al. (1981) found that in modelling a column receiving a 1 mmol/l phenol solution, intraparticle resistance was not required to obtain good predictions, the film

resistance sufficed. Due to the shortcomings of the simplified models, recent models reduced the number of assumptions.

Present models assume that the rate of adsorption is not the rate limiting step, and the adsorption is controlled by either the liquid film or the intraparticle diffusion. Two different mechanism can be assumed for intraparticle diffusion: pore diffusion and surface diffusion. In the pore diffusion model it is assumed that a molecule can not move once adsorbed. So, the adsorption step occurs at the final place of adsorption. In the surface diffusion model, adsorption of adsorbate occurs at the outer surface of adsorbent particle and diffuses to its final adsorption site along the pore walls. The concentration gradient in the liquid phase is the driving force for transport in the pore diffusion model. While, the driving force in the surface diffusion model is the concentration gradient in the solid phase. If adsorption is strongly favoured and a relatively dilute solution are used, surface transport will normally be the dominant mechanism (Peel, 1980). In contrast, when the attraction between the adsorbate and adsorbent is relatively weak, or when liquid phase concentration is high, pore diffusion will play a significant role (Peel, 1980). Many researchers have used either pore diffusion model or surface diffusion model or combination of two (i.e. Fritz et al., 1981; Dedrick and Beckmann, 1967; Brecher et al, 1967). For more detailed reviews, refer to Sontheimer et al., (1988); Faust and Aly (1987); Mathews and Weber (1984); Peel, (1980); and, Narbaitz, (1985).

A recurrent problem experienced when the single-diffusion models are used to simulate rate data for phenolics, is that the fit between the data and the model prediction becomes increasingly inaccurate as the system approaches equilibrium. The models require a large

diffusion coefficient to fit the data during the initial stages of batch kinetic experiments, but this diffusivity overestimates the fractional uptake of the solute during the latter stages. By decreasing the diffusion coefficient, the latter stages can be approximated, but only by sacrificing the accuracy during the initial stages. Several modifications to the modelling of activated carbon intraparticle diffusion have been proposed, which address this discrepancy (i.e. Weber and Liang, 1983; Famularo et al. 1980; and Peel and Benedek, 1980-b). In these models the adsorbent particle is divided into two diffusion domains and typically, three or four parameters are evaluated by fitting the model to the data. A problem with all of these two-domain models is the lack of independent methods of evaluating the transport and macro- and micro-domain equilibrium partitioning parameters (Sontheimer et al., 1988).

Famularo et al. (1980) were unsuccessful in modelling their batch kinetic data using the surface diffusion model even when they included a concentration dependent diffusivity. The data were successfully described by a model that included film diffusion and two intraparticle mass transfer resistances in series. Famularo et al. (1980) divided the carbon particles into uniform-state regions: a macroshell surrounding a microcore. These regions are modeled with linear solid-phase concentration driving forces.

Peel (1980) tried to analyze the o-chlorophenol and phenol batch kinetic data with previous models. He observed that neither single intraparticle rate models, combined pore and surface diffusion models, or concentration dependent diffusion coefficient models could explain the observed initial rapid uptake followed by a slow approach to equilibrium. Peel (1980) during batch kinetic studies, observed that adsorption mechanism

occur in two different rates. One part of adsorption was fairly fast while, the other part was much slower. The slow part of adsorption, which he called the slow adsorption phenomenon, was hypothesized to be caused by chemical or pore size limitation. The fraction of the slow adsorption in a adsorption process was found to be proportional to the molecular size of adsorbate. He mentioned that a longer term kinetic tests are needed to observe both slow and rapid adsorption. Based on this hypothesis two dual rate models were developed. The proposed model by Peel (1980) divides the particle into two homogeneously distributed regions: macropore and micropore. Fig 2.6 shows the physical structure of the activated carbon particle as assumed by Peel. The macropores and micropores, however, are not necessarily related to the conventional definition of these terms with respect to pore size. Macropores are those pores in which the pore radii are several times greater than the radii of the diffusing species, as low as 50 A° or less. In these pores it has been assumed that transport occurs by either pore or surface diffusion. These larger pores have been assumed to be homogeneously distributed through the particle and provide access channels to the interior part of the AC particles. It is assumed that the rapid initial uptake of substrate takes place within this region. Micropores (or slow adsorbing pores) are those pores that have radii of comparable size to the diffusing species and include all the remaining pores available for adsorption. It is assumed that within these pores transport rates are strongly hindered, either by the proximity of the walls or by the restraining effect of the sorbate-sorbent interactive forces. It is in these small pores that the slow adsorption, that follows the initial rapid uptake occurs. Diffusion in the macropores is described by a surface diffusion mechanism and in the micropore by a linear driving force equation between the local macro- and micropore solid phase concentrations.

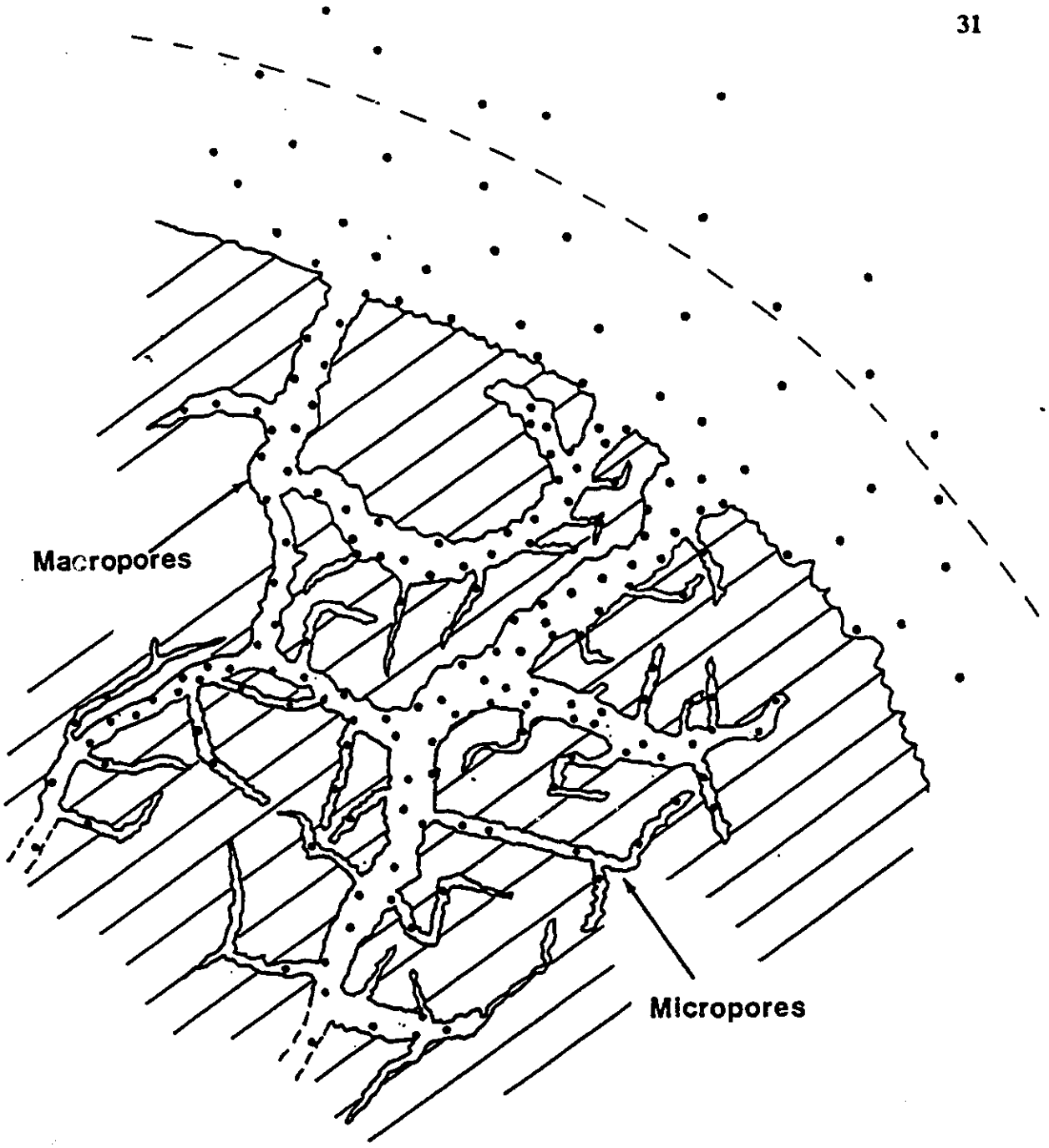


Fig. 2.6 Idealized activated carbon pore structure.

(source: Peel, 1980)

Narbaitz (1985) analyzed the data of 1,1,2-Trichloroethane batch kinetics tests using both the Peel (1980) dual rate model and the homogeneous solid surface diffusion (HSSD) model. He concluded that both models behaved similarly and the branch pore transfer resistance was not required.

Summarizing, the pore and surface diffusion models and their combination are widely used. In some cases, particularly with phenolics, it has been shown that an additional intraparticle resistance is required to model the observed data.

2.6.3 Mathematical Form of Peel's Dual Rate Model

Figure 2.7 presents a schematic of Peel's model. The model assumptions include: a) a liquid film resistance; b) an adsorption step onto the exterior surface of the AC particle; c) entrance to the particle via the macropores; d) transport towards the interior of the particle within the macropores via surface diffusion; e) simultaneous transport from the macropores onto the micropores or branch pores; f) the AC particle is spherical. Referencing Fig. 2.6 the following mass balances were written.

Macropore Mass Balance

$$f\frac{\partial q_m}{\partial t} = \frac{fD_s}{r^2}\frac{\partial}{\partial r}r^2\frac{q_m}{\partial r} - R_b \qquad (2-7)$$

where, f is the fraction of the total particle capacity in the macropores; q_m is the solid phase concentration in the macropores (g/g of AC); D_s is the surface diffusivity coefficient in the macropores (cm^2/s); r is the particle radial variable (cm); R_b is the local rate of transfer from the macro to micropores (g/g/t). Note that q_m is a function of

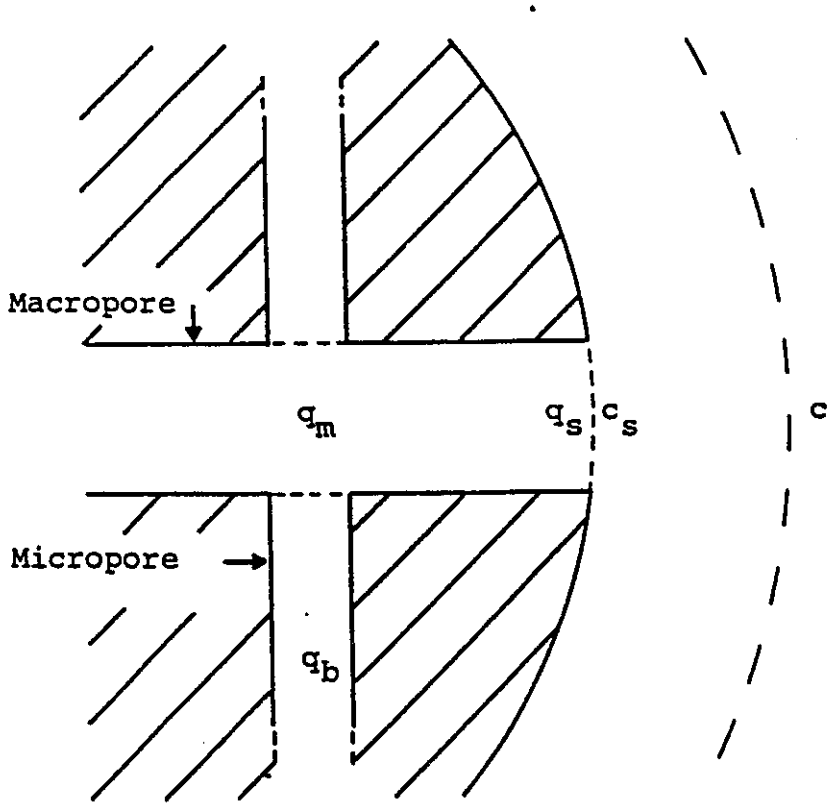


Fig. 2.7 Conceptual diagram of proposed branched pore model.

(source: Peel, 1980)

time and radial position within the particle.

Micropore Mass Balance

$$(1-f)\frac{\partial q_b}{\partial t} = K_b(q_m - q_b) = R_b \qquad (2\text{-}8)$$

where q_b is the solid phase concentration in the branch pores, (g/g of AC); K_b is the pseudo mass transfer coefficient for transport to the branch pores.

Liquid Phase Balance in the Batch Reactor

$$\frac{dc}{dt} = \frac{-(1-\varepsilon)}{\varepsilon}\frac{3K_f}{R_p}(C - C_s) \qquad (2\text{-}9)$$

where C is the bulk liquid phase concentration (g/cm^3); K_f is the external mass transfer coefficient (cm/s); ε is the liquid volume fraction in the kinetic bottles; R_p is the particleradius (cm); Cs is the liquid phase concentration at the surface of the particles (g/cm^3); and t is time (s).

Liquid Phase-Solid Phase Boundary Condition

By equating the liquid phase and solid phase fluxes at the surface and assuming that only the macroporous region is available for radial transport

$$fD_s\rho_c\frac{\partial q_m}{\partial r}\Big|_{R_p} = K_f(C - C_s) \qquad (2\text{-}10)$$

Where, ρ is carbon density of the carbon particles, g/cm^3.

The initial and boundary conditions for this model are:

$$q_m(r,0) = 0 \qquad (2\text{-}11)$$

$$q_b(r,0) = 0 \qquad (2\text{-}12)$$

$$\frac{\partial q_m}{\partial r}(0,t) = 0 \qquad (2\text{-}13)$$

$$q_m(R_p,t) = g\{C_s(t)\} \qquad (2\text{-}14)$$

Equation 2-14 stipulates that the solid phase concentration at the outer surface of the carbon grain is in equilibrium with the immediately adjacent liquid phase concentration. Thus, $g\{C_s\}$ is the isotherm model expression which is identified and calibrated by analyzing the batch isotherm data.

A computer program, which solves the Peel (1980) dual rate model equation via orthogonal collocation was developed by Narbaitz (1985). This program was tested using Peel's phenol data and mass transfer coefficients and found to yield very similar results (Narbaitz, 1985). A feature of this model is that by setting f=1 the model reduces to the homogeneous solid surface diffusion model. Narbaitz (1985) also, used this computer program for other simulations and found it to yield good results.

2.7 Effect of pH on Adsorption Equilibria

This part of the literature survey explains the changes in measured adsorption of various types of organic compounds caused by lowering or raising the hydrogen ion concentration. The extent of the changes depend on the physicochemical properties of individual organic solutes. Several types of organic compounds are discussed separately.

These include: organic acids in general, phenolic compound, organic bases, ampholytes, and anionic surface-active agents. Although phenolic compounds can be considered as weak acidic organics, they are discussed separately because they are the focus of the present research.

2.7.1 Organic Acids

Many of the physical and chemical properties of organic compounds change upon ionization. A study on adsorption of three herbicides: 2,4-dichlorophenoxyacetic acid (2,4-D), 2methoxy-3,6 dichlorobenzoic acid and 3-amino-2,5 dichlorobenzoic acid on activated carbon (Pittsburgh Chemical Company, type BL) were reported by Ward and Getzen (1970). There was a marked increase in the removal of all solutes from aqueous solution on lowering the pH below 7. At pH 3 approximately half of the acid in a 10^{-4} molar solution was adsorbed by 0.01 g of GAC in 4 hours. At pH 7 the removal generally ranged from 8-22% and at pH 11 from 2.5-15% depending on the solute present. However, Ward claimed that adsorption in the acid region is greater than that expected from the molecular-ionic ratio of the bulk solution. This was explained in terms of an enhanced specific ion adsorption resulting from increased proton concentration as the pH is lowered and a subsequent alteration in the surface properties of the AC. Maximum adsorption was attained near the point where $pH=pK_a$.

The experimental isotherm of Benzoic Acid (BA)(pK_a=4.19) on B10(II) activated carbon illustrated the important influence of pH on adsorption capacity (Muller et al., 1980). Changing the equilibrium pH from approximately 4 to 11 results in a capacity decrease of approximately 90%. Similar results were reported by Cooney and Wijaya (1987) for

the adsorption of a series of aromatic carboxylic acids: benzoic acid (pK_a 4.19), o-phthalic acid (pK_a's 2.95 and 5.41) and 1,2,4 benzene tricarboxylic acid (pK_a's 2.52, 3.84. and 5.2) (Figure 2.8). It is clear that for pHs below 3, the adsorbabilities of all three species are very high, since the species are predominately in a non-ionized state. As the pH rises, and the degree of ionization increases, the adsorbabilities all fall sharply to much lower values. In general, Cooney and Wijaya (1987) concluded that the neutral forms of the species adsorb more extensively than their ionized forms. They hypothesised that charges cause repulsion of adsorbed ions from the carbon surface.

Influence of pH on the removal of Mississippi River organics, which are composed principally of neutral and acidic organic compounds, by GAC showed that operation at a low pH improved the performance of the GAC columns and resulted in lower organic concentration in the effluent (Semmens et al., 1986). This study demonstrated that for an effluent value of 1 mg TOC/l the operating capacity of a carbon column can be increased by a factor of 400 to 500 percent by reducing the pH of adsorption from 8.7 to 5. Semmens et al. (1986) indicated that the influence of pH on the adsorption behaviour of GAC may be caused by the acidic character of a fraction of the organics being removed. The surface of GAC is negatively charged in the neutral pH. A reduction in pH can be expected to improve adsorption since the production of carboxylic functional groups on both the organic acids in solution and the carbon surface reduces electrostatic repulsion forces and promotes a greater degree of adsorption.

2.7.2 Phenolic Compounds

Isotherms of phenol and 4-nitrophenol (4NP) on a coconut-shell AC show that at various

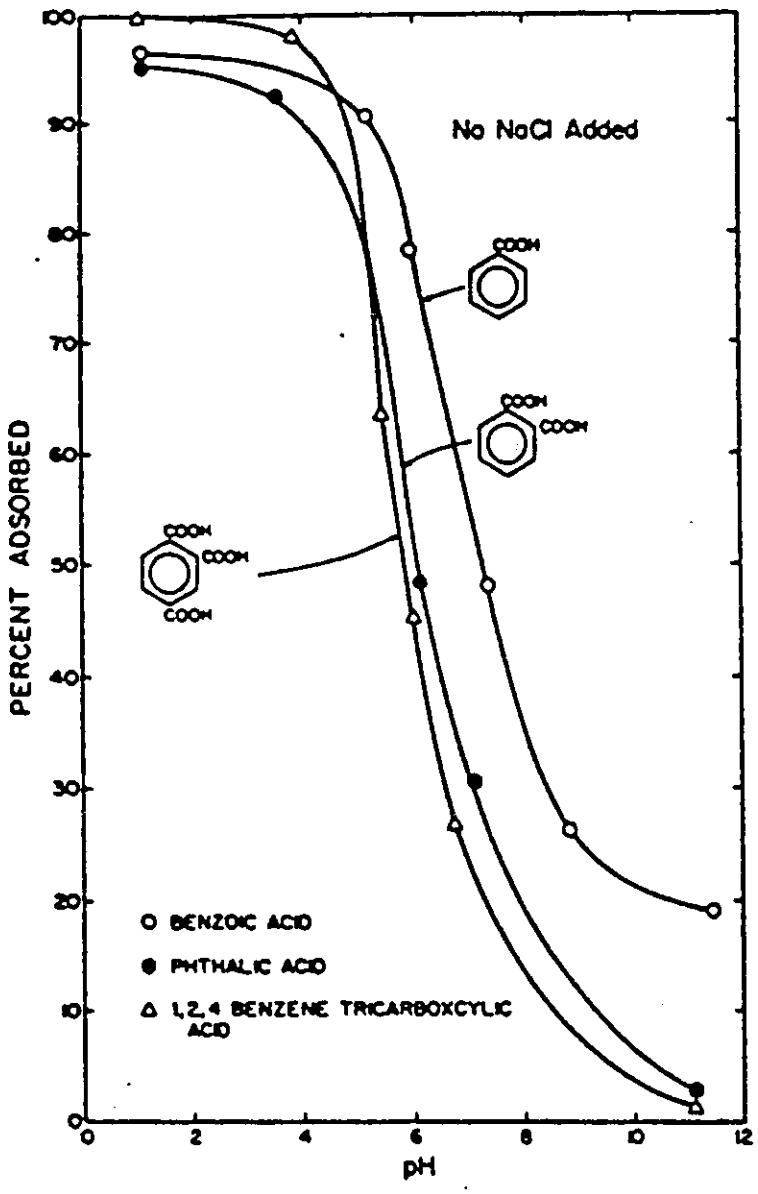


Fig. 2.8 Adsorption of aromatic carboxylic acids onto activated carbon as a function of pH.

(source: Cooney and Wijaya, 1987).

pHs the adsorption capacity of anionic forms is less than that for the corresponding neutral species (Snoeyink et al., 1969). Fig. 2.9 shows that there is no marked effect of pH on the sorption of the neutral form of 4NP (pK_a=7.1) in the pH range from 2 to 6.5. However, the capacity for the neutral phenol (pK_a=9.9) molecules decreases significantly with decreasing pH in the same range (Fig. 2.10). Snoeyink et al. (1969) suggested that the hydrated proton competes effectively with phenol for active sites. Similar results for adsorption of phenol on Hydraffin 71 AC and 2,4-dichlorophenol (pK_a 7.85) on Columbia LCK AC (Fig. 2.11) were reported by Seidel and Radeke (1990), and Zogorski and Faust (1978), respectively.

The experimental isotherm of 4NP (pK_a=7.1) on B10(II) activated carbon illustrated the important influence of pH on adsorption capacity (Muller et al., 1980). Changing the equilibrium pH from approximately 7 to 11 reduced the adsorption of 4NP at high solute concentration by 70%. Below pH values of 6.8 no further increase in adsorption capacity was noted. Similar results for adsorption of 2,4-dinitrophenol on Columbia LCK carbon (Fig. 2.12) and 4NP on GAC (Cal. 24/32 mesh) are reported by Zogorski and Faust (1978), and Suzuki and Takeuchi (1986), respectively. These studies also indicated that solutes of unionized form are more easily adsorbed onto activated carbon than those of ionic form. The repulsive forces between the anionic sorbate and the adsorbent was considered as the cause for the significant decreases in adsorption capacity at high pH.

Gomez Serrano et al. (1992) studied the adsorption of 4NP from a $NaOH/H_3PO_4$ bufferred aqueous solution on 1.5 mm particle size AC (supplied by Merk) at pH 2, 7, and 8.5. At acidic pHs, the 4NP adsorption was found to be markedly higher than at neutral and

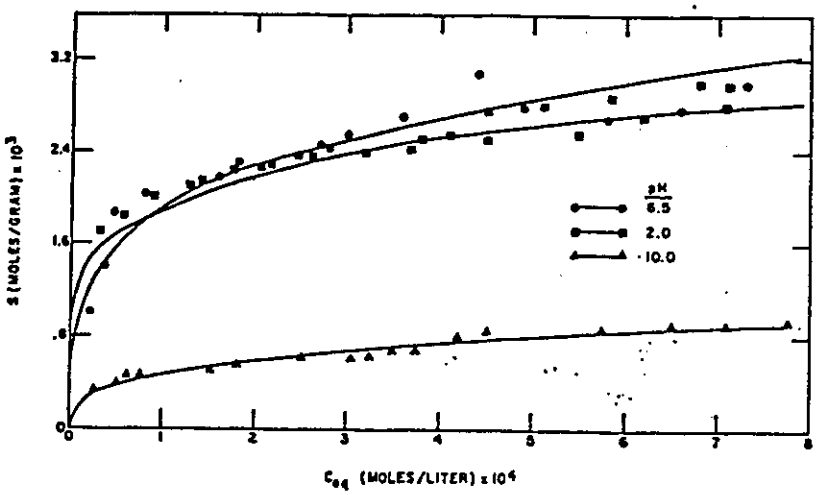


Figure 7. Isotherms for *p*-nitrophenol at different pH

Fig. 2.9 Isotherms for p-nitrophenol (4NP) at different pH on coconut-shell based GAC (Columbia, Lc Grade). (source: Snoeyink et al., 1969)

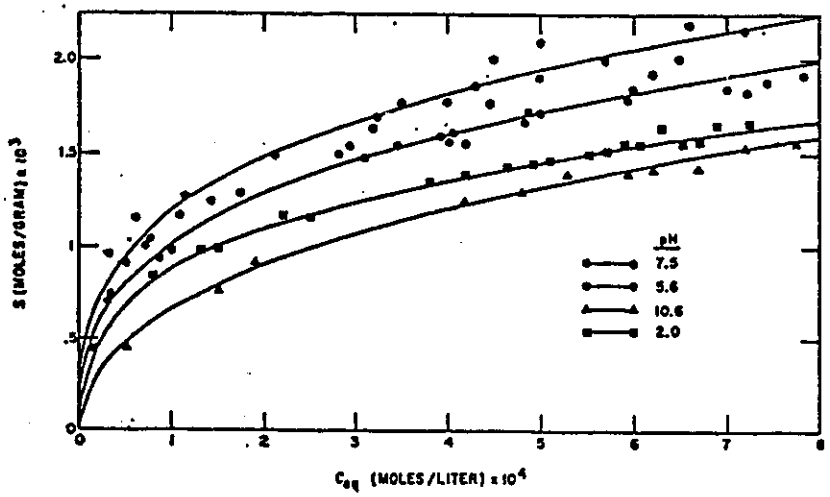


Fig. 2.10 Isotherms for phenol at different pH on coconut-shell based GAC (Columbia, Lc Grade). (source: Snoeyink et al., 1969)

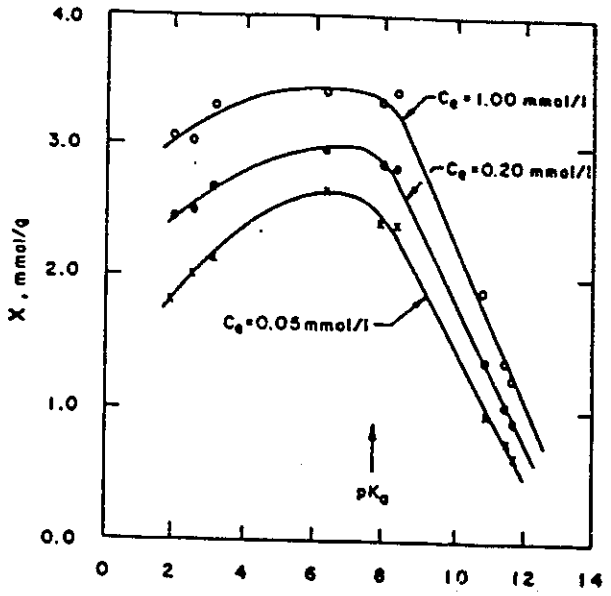


Fig. 2.11 Effect of pH on the adsorption of 2,4-dichlorophenol on GAC (Columbia, LCK).(source: Zogorski and Faust,1978)

(source: Zogorski and Faust, 1978)

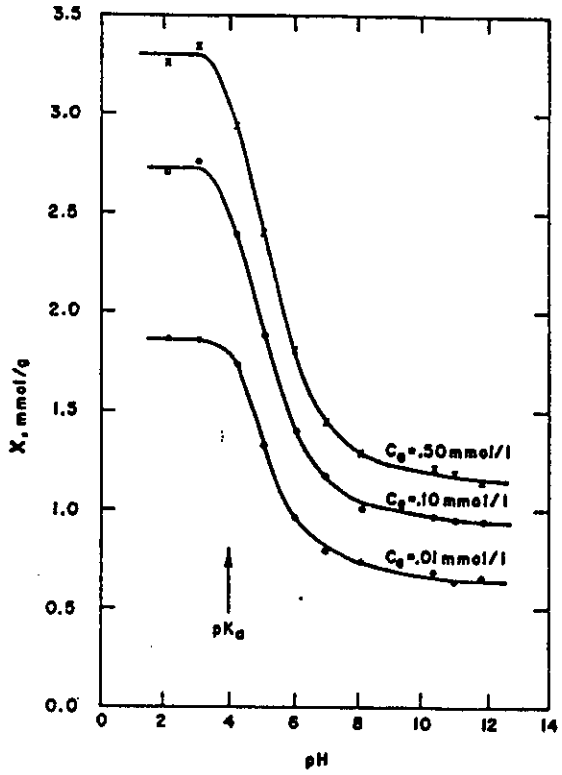


Fig. 2.12 Effect of pH on the adsorption of 2,4-dinitrophenol on GAC (Columbia, LCK).(source: Zogorski and Faust,1978)

weakly basic pHs. They hypothesized that the greater 4NP adsorption at pH 2 is consistent with a lesser competition for active sites between 4NP and anion species from H_3PO_4 dissociation. At neutral and basic pHs, OH^- competes more successfully with 4NP for active centres on the adsorbent surface.

Summarizing, for all organic acids and phenolic compounds, decreased adsorption has been observed as pH increases. Table 2.1 indicates that maximum adsorption is generally attained at pHs slightly lower than the pK_a's and the following mechanisms may be responsible for a large decrease in the amount adsorbed at pH values greater than the pK_a of the adsorbate.

1- The dissociated form is more soluble in solution (Mattson and Mark, 1971) thus, is less adsorbable.

2- The nature of the carbon surface is apparently altered in some manner by the acid or base used for pH adjustment (Ward and Getzen, 1970). The surface of activated carbon is negatively charged in the neutral pH ranges as a result of the dissociation of surface carboxylic groups. A reduction in pH can be expected to improve adsorption since the protonation of carboxylic functional group on both the organic acids in solution and the carbon surface reduces electrostatic repulsion forces (Semmens et al., 1986) therefore, promoting a greater degree of adsorption.

3- The anionic form of compounds may have different mechanisms of adsorption.

4- Repulsive forces between the anionic adsorbate species and adsorbate-adsorbent can also be significant at high pH. Increased negative surface charges at high pH values may be caused by physical adsorption of OH^- or by dissociation of very weakly acidic surface functional groups (Cooney and Wijaya, 1987 and Snoeyink et al. 1969).

TABLE 2.1: Adsorption of organics at different pHs

Organic Compound	pKa	pK_b	Isoelec-tric point	pH Range Studied	pH for Max. Ads.
Benzoic Acid[a]	4.2	--	--	3,7,11	3
phenoxyacitic Acid[a]	3.03	--	--	3,7,11	3
2,4-dichlorophenylacetic Acid[a]	3.92	--	--	3,7,11	3
Phenol[b]	9.89	--	--	2,5,6, 7.5,10.6	7.5
Urea[c]	--	13.9	--	7,11,8	11.8
Nicotine[d]	--	10.9	--	1 to 12	8.2-12
Sulphanilamide[f]	--	--	6	1.3,5.9,12.2	5.9
Benzoic Acid[e]	4.19	--	--	1,5,6,7,9, 11	1-3
Phthalic Acid[e]	2.955 5.41	--	--	1,3.5,6,7,11	1-3
Tricarboxcylic acid[e]	2.52 3,84 5.2	--	--	1,4,5,6,7, 11	1-3
Aniline[**]	--	4.63		1,3,3.5,4,5.6. 8,9.5,11	6-12
phenylenedi-amine[**]	--	2.65 4.88	--	1.5,2.5,35,6, 6.5, 9.5, 12	6-12
picolin[+]	--	7.5	--	3,5,7,8	8
Phenylanine[++]	--	--	5.45	1,3,6.9, 11	6
Anthranilic Acid[++]	--	--	3.5	1,2,3,3.5,6.5, 7,9,9.5, 11.5	3.5

Sodium dodecylbenzene sulfonate[$]	--	--		3.95, 6.85, 9.55	7
Phenol[1]	9.9	--	--	2,5.6,7.510.6	7.5
P-nitrophenol[1]	7.1	--	--	2,6.5,10	6.5
2,4-Dichlorophenol[2]	7.85	--	--	2,3,6,8, 11,12	4-6
2,4-Dinitrophenol[2]	4	--	--	2,3,4,5,6,7,8, 10, 11,12	2-3
P-nitrophenol[3]	7.1	--	--	2,7,8.5	2
Sodium alkylbenzene soulphonate[$]	1.5	--	--	1.9,4,6,7.8,8. 7	

[a]Organic acid (Ward and Getzen, 1970)
[b]Organic acid (Snoeyink et al., 1969)
[c]Organic base (Sung, 1968)
[d]Organic base (Andersen, 1947)
[f]Ampholyte (Andersen, 1947)
[g]Anionic surfactant (Weber and Morris, 1963)
[*]Organic acid (Cooney and Wijaya, 1987)
[**]Organic base (Cooney and Wijaya, 1987)
[+] Organic base (Seidel and Radeke, 1990)
[++]Ampholyte (Cooney and Wijaya, 1987)
[$]Anionic surfactant (Leyava-Ramos, 1989)
[1]Phenolic compound (Snoeyink et al., 1969)
[2]Phenolic compound (Zogorski and Faust, 1978)
[3]Phenolic compound (Gomez Serrano et al., 1992)

5- The lighter and hence more mobile OH^- anion may compete more successfully with adsorbates for active sites on the adsorbent surface at high pH (Gomez Serrano et al, 1992).

2.7.3 Organic Bases

Cooney and Wijaya (1987) showed that aniline (pK_a=4.63) and m-phenylenediamine (pK_a's 2.65 and 4.88) adsorb poorly (Figures 2.13. and 2.14) at low pH where these species have positive charges. As the pH rises and the charges go from positive to zero the percent adsorption rises to around 77 percent. Cooney and Wijaya (1987) also studied the adsorption of quinine, a dibasic organic species, which showed a steady rise in percent adsorption with pH at its charge goes progressively from +2 to +1 to zero. They concluded that the neutral forms of the species adsorb more extensively than their ionized forms.

Seidel and Radeke, (1990) studied adsorption of α-picolin (pK_b 7.5) from aqueous solution at different pHs onto the activated carbon Hydraffin 71. For this weak base the effect of pH on adsorption capacity was contrary to the effect of pH on adsorption of organic acids. Adsorption decreased considerably with increasing degree of dissociation at pH < 7.5.

Thus, as with organic acid, it may be postulated that maximum adsorption of organic bases can be attained at a pH close to the pK_b. More research is needed to confirm the above conclusion.

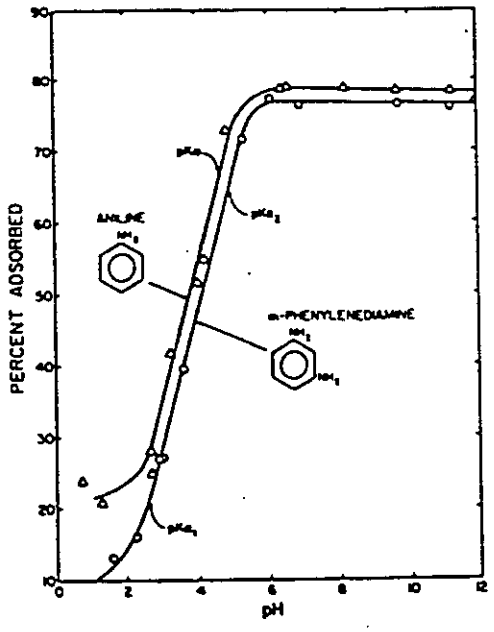


Fig. 2.13 Adsorption of aniline and m-phenylenediamine to activated carbon as a function of pH.
(source: Cooney and Wijaya, 1987)

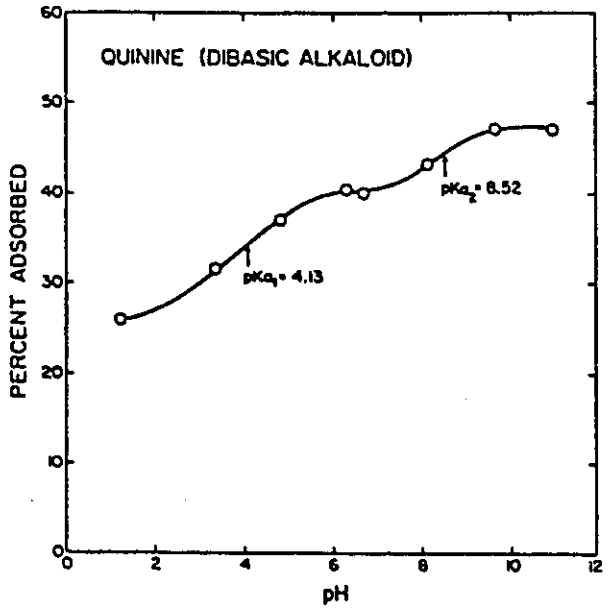


Fig. 2.14 Adsorption of quinine to activated carbon as a function of pH. (source: Cooney and Wijaya, 1987)

2.7.4 Ampholytes

Amphoteric compounds have the capacity to be both an acid and a base. Figures 2.15 and 2.16 show the behaviour of two amphoteric molecules studied by Cooney and Wijaya (1986). It is clear that at low pH (the +1 charge state) and at high pH (the -1 charge state) adsorption is lower. At intermediate pHs, where the molecules are more electrically neutral, the adsorption values reach a maximum. Cooney and Wijaya (1987) indicated that the neutral forms of the species adsorb more extensively than their ionized forms. The effect of pH on the adsorption of ampholyte sulphanilamid, was studied by Anderson (1947). The pHs were adjusted to 1.3, 5.97 and 12.2. It appeared that the adsorption of sulphanilamide is greatest around the isoelectric point. The explanation may be that at the isoelectric point, similar numbers of acidic end and basic groups of the compounds are ionized and the compound bears a net charge of zero. There are less repulsion forces between adsorbed compound and carbon surface.

2.7.5 Anionic Surface Active Agents

Adsorption of an anionic detergent ,sodium dodecylbenzene sulfonate (SDS), from aqueous solutions onto a wood activated carbon was studied at various pHs (Leyva-Ramos, 1989). The adsorption capacity is considerably affected by pH and maximum adsorption took place at a pH of approximately 7.

Weber and Morris (1963) reported that alkybenzene sulfonate is highly affected at low pHs. The adsorption of ionic surfactants is not always dependent upon the state of the ionization of the organic compound. The pK_a of alkylbezenesulfonate acid is 1.5 while, the pH for maximum adsorption is above 1.5 (pH 1.9-4). It is believed that as the ionic

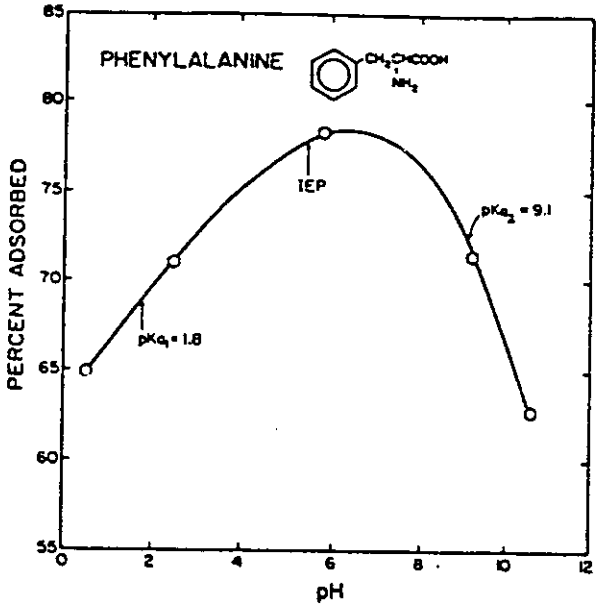


Fig. 2.15 Adsorption of phenylalanine to activated carbon as a function of pH. (source: Cooney and Wijaya, 1987)

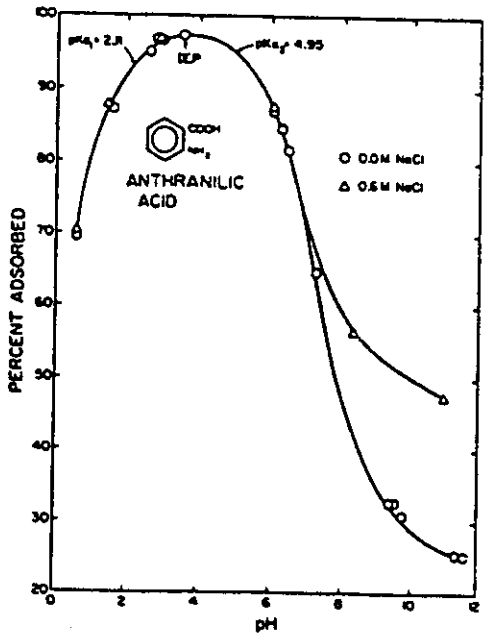


Fig. 2.16 Adsorption of anthranilic acid to activated carbon as a function of pH, with and Without added NaCl. (source: Cooney and Wijaya, 1987)

organic compounds become more complex (such as ionic surfactants with longer hydrocarbon chains and higher molecular weight), the significance of ionisation becomes of decreasing importance. Weber and Morris (1963) indicated that, the increase in adsorption observed at lower pHs may be due to alteration in the carbon surface, particulary its electrokinetic character, with changing hydrogen ion concentration.

Summarizing, the discussion presented previously show that the effect of pH on activated carbon adsorption depends to a significant extent on the nature of organic compound being adsorbed. The modification of adsorptive mechanisms following pH adjustment involve: ionisation of the adsorbates; alteration of the carbon surface; electrical attractive or repulsive forces between the adsorbate and the adsorbent.

Because of the complexity of pH effects, one can not accurately predict the influence of pH on adsorption of a specific organic compound. Experimental data are required to define it. This survey indicates there is a lack of information on the adsorption of 2NP and there is very limited information on the impact of GAC type on the pH dependency of adsorption of phenolics. Thus there is a need for this study.

2-8 Effect of pH on Adsorption Kinetics

Figure 2.17 shows the effect of solution pH on the observed rate of uptake of 3-dodecylbenzenesulfonate (pK_a 1.5), an anionic surface active agent, by 0.126 mm Columbia carbon (Weber and Morris, 1963). The authors mentioned several possible explanations for the observed pH effects. Because most carbons bear net negative charges, the uncharged molecular species of the alkylbenzenesulfonates would be expected to be

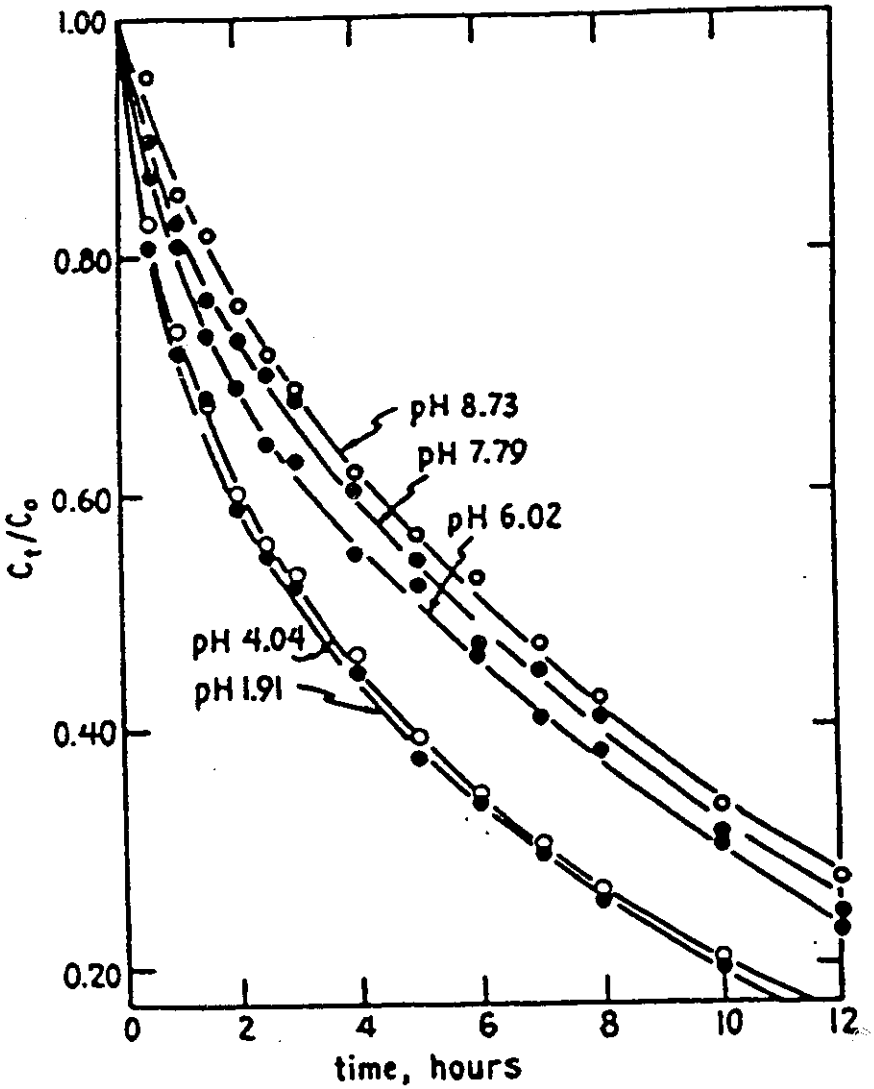


Fig. 2.17 Effect of pH on rate of 3-dodecylbenzenesulfonate adsorption onto Columbia carbon.

(source: Weber and Morris, 1963)

taken up by the carbon more rapidly than the negatively charged ionic species. The effect of hydrogen ion concentration is observed even in pH ranges for which the relative changes in absolute concentration of the two species of solutes are negligible. Weber and Morris (1963) suggested the increase in rate observed for decreasing pH may be due to alteration in the carbon surface, particulary its electrokinetic character, with changing hydrogen ion concentration. Therefore, a decrease in pH probably results in a reduction of the negative charges at the surface of the carbon subsequently enhancing the adsorption of the negatively charged alkylbenzenesulfonates.

The dependence of the initial removal rate of Columbia LCK carbon adsorption with hydrogen ion concentration for 2,4-dinitrophenol (pK_a=4.1) and 4-chlorophenol (pK_a= 9.4) are shown in Figures 2.18 and 2.19 (Zogorski and Faust, 1976-b). The rates of adsorption of these two compounds are most rapid at hydrogen ion concentrations greater than 10^{-5} (for 2,4-dinitrophenol) and $10^{-7.5}$ (for 4-chlophenol). Also, it is evident that the presence of high concentration of hydrogen ions does not influence the initial removal rate of adsorption of these phenolics. Moreover, increasing the pH value from 5 to 6.3 decreased the removal rate of 2,4-dinitrophenol by 20% and further increasing the pH beyond 6.3 appears to have no subsequent influence. While, a very rapid and almost linear decrease in the removal rate of 4-chlorophenol occurs at pH values greater than 9. The repulsive forces between adsorbate/adsorbent and adsorbate/adsorbate were hypothesized for decrease in initial removal rate at high pHs.

Gomez Serrano et al. (1992) studied the kinetic adsorption of 4NP on 1.5 mm activated carbon (supplied by Merk) at pH 2 and 8.5. They concluded that the initial removal rate

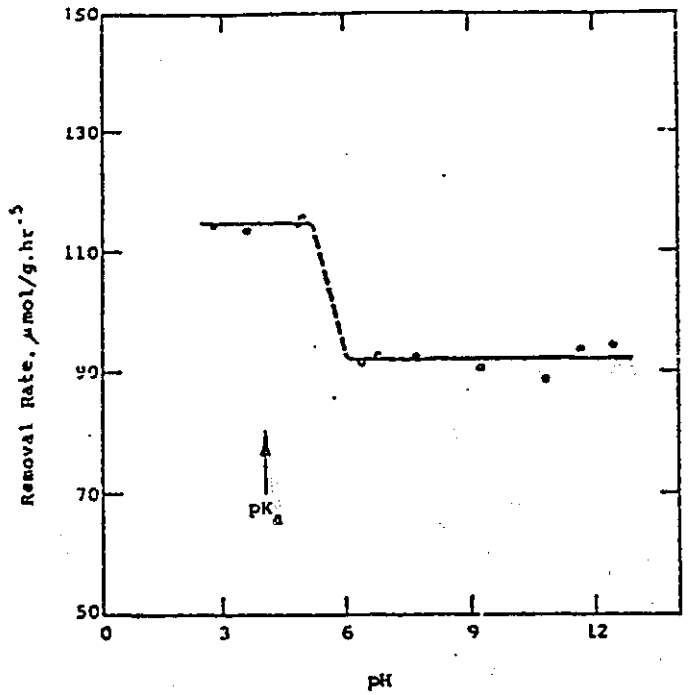


Fig. 2.18 Effect of pH on the rate of adsorption of 2,4-dinitrophenol on GAC (Columbia, LCK). (source: Zogorski and Faust, 1976-b)

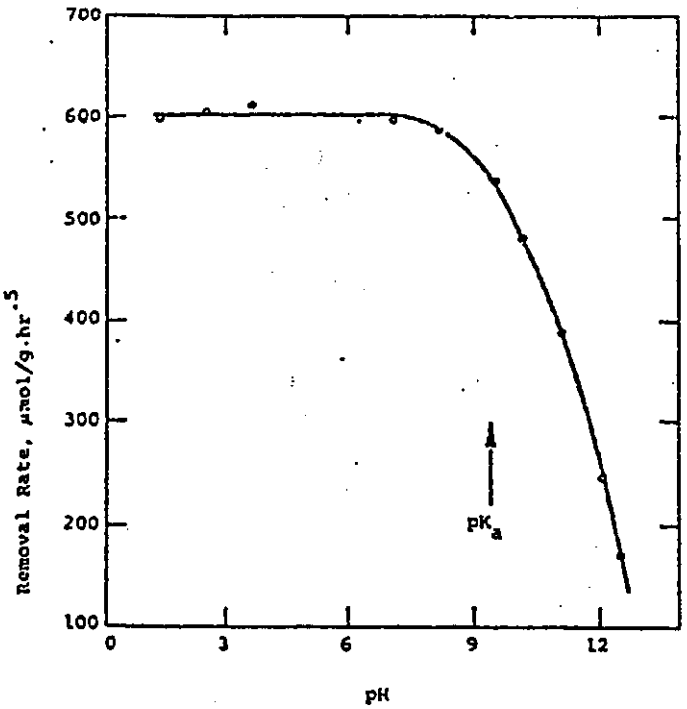


Fig. 2.19 Effect of pH on the rate of adsorption of 2,4-dichlorophenol on GAC (Columbia, LCK). (source: Zogorski and Faust, 1976-b)

was faster at acidic pH than basic pH.

There is very limited information available concerning the effect of pH on the adsorption rate of organics. Thus, this topic merits further research and it will be investigated in this thesis. There is a need to identify the impact of pH on the kinetic model's parameter values. Modelling of the kinetic experiments is necessary to identify the impact of pH on the kinetic aspects of adsorption as opposed to the equilibrium aspects.

2.9 Effect of pH on Desorption

Summers and Roberts (1988) conducted desorption experiments with four humic substances under a variety of experimental conditions. Desorption was found to occur at pH values above 10.5 and the mass desorbed ranged from 0 to 25% (at pH 10.5) of the original mass adsorbed. Desorption at elevated pH was explained in terms of surface electrostatics. Increasing pH to 11 during desorption results in repulsion between negatively charged humic macromolecules and the adsorbent surface.

Davis (1980) observed that lacustrine organic matter adsorbed on aluminum oxide at pH 5, partially desorbed at pH 9 and completely desorbed at pH 11.

NaOH has been used as a reactive chemical in the regeneration of GAC used for treatment of phenolic compounds (Himmelstein et al., 1973; Fox et al., 1970; Goto et al.,1986; and Newcombe and Drikas, 1993). Adsorbed phenol reacts with the caustic soda to form sodium phenate which is readily desorbed and carried out of the carbon bed in the regenerant stream. Goto et al. (1986) found that total amount of sodium phenate

desorbed from GAC was only 70% of adsorbed phenol and adsorptive capacity of GAC gradually decreased with multiple regeneration cycles.

2.10 Effect of pH on Desorption Kinetics

There is no information available related to the effect of pH on desorption kinetics.

2.11 Research Needs

The literature indicates that there is limited information on the effect of pH on adsorption equilibria and kinetics of organics on activated carbon and an almost total lack of information related to the effect of pH on desorption and desorption kinetics. Such information is critical for understanding the mechanisms and modelling of electrochemical GAC regeneration systems. To address these needs, the effect of pH on adsorption and desorption and their kinetics of two organic compounds (phenol and 2-nitrophenol) on two activated carbons (F-400 and WV-B) will be studied.

CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

3.1 Introduction

The effect of pH on adsorption equilibria, desorption equilibria, adsorption kinetics and desorption kinetics was evaluated using sets of batch reactors. The batch technique was selected because of its simplicity and the ease of evaluating results. Actual applications of GAC is via continuous flow column-type operations. However, the evaluation of the fundamentals of adsorption is much simpler in a batch reactor and the basic relationship developed can be applied to predict the behaviour of continuous flow adsorption systems.

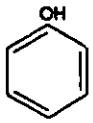
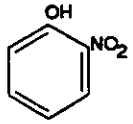
3.2 Adsorbates

Two organic chemicals: 2-nitrophenol (2NP) and phenol were used in this research. The experiments used laboratory reagent grade(min assy 99% by HPLC) 2-nitrophenol (Fluca Cheemie AG, Switzerland) and ACS grade (>99% purity) phenol (Aldrich Chemical Co, W, USA). The characteristics of phenol and 2-nitrophenol are given in Table 3.1.

Deionized distilled water (Milli-Q water) filtered through a Millipore purification system (Model 10 M Ω cm, Millipore Corp., Bedford, MA) was used for all parts of this study.

Phosphate buffer at 0.05 M was used in the solutions to minimize pH fluctuations. Solutions were adjusted to a desired pH by using HCl (assay 36.5%-38% ACS grade,

TABLE 3.1 Adsorbates Characteristics

	Phenol	2-nitrophenol
tructural formula		
Empirical formula	C_6H_6O	$C_6H_5NO_3$
Formula weight	94.11	139.11
Boiling point	182 °C	215 °C
Dissociation constant	9.99	7.23
Melting point	40-42 °C	45-46 °C
Solubility in water	93000 (mg/l)	2000 (mg/l)
Flash point	79 °C	73.5 °C
Henry's Law Constant ($atm.m^3/mol$) @ 25 °C	2.7E-7	3.5E-6
Odor	Sweet tarry odor	aromatic odor
Appearance	White crystals which slowly turns brown on exposure to air	Pale yellow crystals with an

BDH Chemicals, Toronto) and NaOH (assy 50%, Fisher scientific, New Jersey). These solutions required different proportions of analytical grade KH_2PO_4 and Na_2HPO_4 (BDH Chemicals, Toronto) to obtain specified pH. The pH was measured by a digital pH Meter (Accumet 910, Fisher Scientific, New Jersey) at the beginning and the end of each experiment. The phenol and the 2-nitrophenol solutions were prepared by adding them to buffered Milli-Q water in a glass carboy and mixing them overnight to obtain a uniform concentration.

3.3 Adsorbents

Two adsorbents: Filtrasorb 400 (Calgon Corp. Pittsburg, Pa.) and Westvaco Carbon (Westvaco Chemical Division, Covington, Virginia) were used in this study. Fibtrasorb 400 (F-400) is manufactured from bituminous coal and Westvaco Carbon (WV-B) is made from wood. Specifications of these carbons are given in Table 3.2. The F-400 activated carbon was sieved to obtain a 12*16 mesh size (average mesh diameter = 1.4mm). The Westvaco carbon was used as received from the manufacturer (14*35 mesh size, average mesh diameter = 1 mm). Considerable care was taken in this research to clean the adsorbents before using them in the experiments. After the carbon samples were sieved, the usable fraction was prepared by boiling in Milli-Q water for 30 minutes, cooling and settling then washing 3 times in Milli-Q water to remove fines and impurities that may have desorbed from the GAC. All GAC samples were then placed in glass drying pans and dried in an oven at 105 °C for 24 hours. Finally, the GACs were cooled and stored in desiccators until used.

TABLE 3.2 Adsorbents properties

	F-400	WV-B
Total surface area (m^2/g)	900-1100	1400-1600
Bulk density (g/cm^3)	0.401	0.257
Apparent particle density (g/cm^3)	0.75	0.45
Pore volume (cm^3/g)	0.85-0.95	-----
Mesh size	12*16	14*35
Mean particle diameter (mm)	1.4	1
Original raw material	Bituminous coal	Wood

3.4 Analytical Techniques

Phenol and 2-nitrophenol, were found to have UV absorption spectra with peaks at 268 ηm and 276 ηm, respectively. Their concentration was measured with a High Pressure Liquid Chromotograph(model 1090 HPLC, Hewlett Packard, Palo Alto, Ca, U.S.A.) and using integrated peak area. The HPLC detection limit was 1 mg/l. HPLC information file is presented in appendix V. Concentrations versus area calibration curves were prepared for both compounds using standards prepared in Milli-Q water. These calibration curves (Figs. 3.1 and 3.2) indicated a linear relationship between concentration and area in the 1.0 to 100 mg/l range for phenol and in the 1.0 to 150 mg/l range for 2-nitrophenol . Samples over 100 mg/l were diluted to bring them into the linear range. As a check on the HPLC measurements, three standard were used in each set of 20 samples. The analysis was conducted at the Institute for Environmental Chemistry, National Research Council of Canada by Ms. Karen Lamb.

3.5 Adsorption Equilibrium Studies

Adsorption isotherms were developed to describe the adsorptive properties of F-400 and WV-B carbons under different pH conditions. The isotherms were conducted by the bottle point method, using a range of carbon masses and the same solution of known initial concentration. The activated carbon and solution were contacted in 500 ml glass bottles with teflon lined caps. Each bottle was prewashed with chromic acid, rinsed 3 times with hot tap water and 3 times with distilled water and dried in an oven at 105 °C prior to usage. Clean bottles were rinsed twice with the solution to be used in the experiment prior to filling it with GAC and the solution. In each set of experiments, activated carbon was accurately weighed and added to the bottles. Because dried activated carbon gains weight

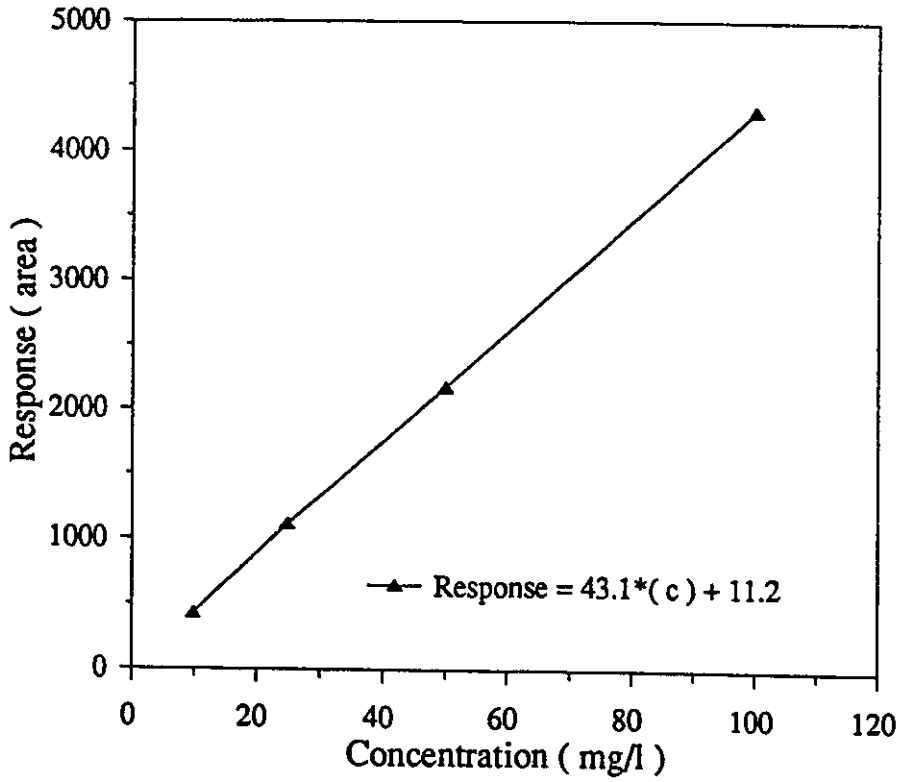


Fig. 3.1 Phenol Calibration Curve

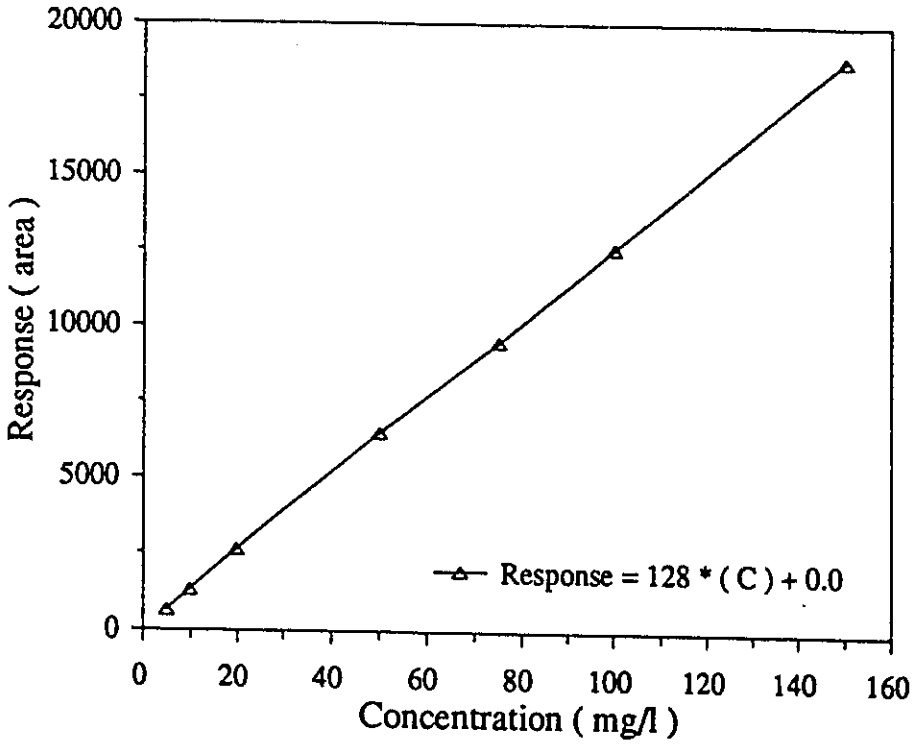


Fig. 3.2 2NP Calibration Curve

rapidly on exposure to air by absorbing moisture, care was taken to have desiccatory media in the balance chamber and to weigh the adsorbent as quickly as possible. To provide necessary mixing, the bottles were placed in an end-over-end tumbler that rotated the bottles at approximately 10 revolutions per minute. The tumbler was operated in a constant temperature room at 22±1 °C. Each set of experiments had three controls and two blanks, one blank contained only Milli-Q water and the other Milli-Q water plus one gram of GAC. Blanks were used to identify possible leaching from the bottles or the GAC. No leaching was detected. The controls were used to determine the possible adsorbate losses. The bottles were filled as much as possible, without overspilling to avoid loss of GAC, as some of the GAC floated to the surface of the liquid. The bottles were filled with the solution in random order to minimize systematic errors. The controls were filled among the other bottles as well. After two weeks (the assumed equilibrium time) the GAC was separated from solution by vacuum filtration through a pre-washed 0.45 μm pore size MSF cellulose nitrate membrane filter (Micro Filtration System, Dublin, Ca., U.S.A). The filters were soaked in Milli-Q water overnight to leach potential organic contaminants. Before each filtration, the glass filter holder apparatus was taken apart and was washed with an Alconox detergent (Alconox Inc. N.Y., U.S.A.) solution. It was then rinsed with hot tap water and Milli-Q water and then reassembled with a membrane filter in place. Around 150 ml of solution was filtered to rinse the filter apparatus and collection bottles. A 2 ml sample was taken from the second 150 ml volume of filtered solution and stored in a refrigerator until analyzed. The filtered solution was then analyzed as described in previous section.

3.6 Desorption Equilibrium Studies

The GAC was loaded with 2-nitrophenol solution at pH 4.6 using the bottle-point technique. The desorption solution (buffered Milli-q water or 1% NaCl solution) and the bottles were prepared before the end of the loading experiment. The loaded activated carbon was separated from solution as described in the previous section, then transferred into a clean 500 ml glass bottle, filled with Milli-Q water or 1% NaCl solution depending on the case. Bottles were then placed in a end-over-end tumbler and rotated for two weeks. Other procedural steps were the same as for the adsorption isotherms (section 3.5).

3.7 Adsorption Kinetic Experiments

Kinetics measure the change in liquid phase concentration with time. These experiments were conducted via the bottle-point technique with two critical modifications: all bottles used the same GAC dosage, and each bottle had a different contact time. To maintain a constant carbon dosage the target GAC masses were adjusted based on the volume of the individual bottles. The contact time of each bottle was calculated as the difference between the halfway point of the filling of the bottle and halfway point of the filtration step.

3.8 Desorption Kinetic Experiment

Desorption kinetics tests determined the change in liquid phase concentration with time, resulting from desorption. The approach was essentially the same as that in Desorption Equilibrium Studies (section 3.6) except using different contact time for each bottle and the GAC dosage in all the bottles was the same. The GAC was preloaded with a 2NP

solution at pH 4.6 using the bottle-point isotherm technique. The desorption solution was buffered Milli-Q water.

3.9 Effect of pH on Adsorption Studies

Effect of pH on adsorption of phenol and 2NP was tested for both F-400 and WV-B carbon by using a single GAC dosage in triplicate. Other steps were the same as in adsorption equilibrium studies (section 3.5).

3.10 Effect of pH on Desorption Studies

For the desorption studies GAC was preloaded at pH 4.6 for 2NP and at pH 7 for phenol. Triplicate bottles were used at each pH. Other procedure were the same as in the desorption squilibrium studies (section 3.6).

3.11 Experimental Plan

To reach the goal of this research a variety experiments were conducted. These experiments were intended to illustrate the impact of pH on adsorption equilibria, adsorption kinetics, desorption equilibria and desorption kinetics. 2NP was selected as the base adsorbate for all experiments and in some cases phenol was tested to obtain more information about those conditions. The experimental plan is shown in Table 3.3.

TABLE 3.3 Experimental Plan

Experiment		Compound	GAC	pH	Initial concentration (mg/l)	Contact time (day)
Isotherm		2NP	F-400	1,4.6,7, 13	500	14
Isotherm		2NP	WV-B	1,4.6,13	500	14
Desorption isotherm in Milli-Q water		2NP	F-400	4.6	0	14
Desorption isotherm in 1% NaCl solution		2NP	F-400	4.6	0	14
Adsorption loadindg		2NP	F400 & WV-B	1,4.6,8.5 10,11.5, 13	500	14
Adsorption loading		Phenol	F-400 & WV-B	4.6	300	14
Desorption	Loading	2NP	F-400 & WV-B	4.6	500	14
	Desorption	2NP	F-400 & WV-B	1,4.6,7, 10,13	0	14
Desorption	Loading	Phenol	F-400 & WV-B	7	300	14
	Desorption	Phenol	F-400 & WV-B	7	0	14
Adsorption kinetics		2NP	F400 & WV-B	1,4.6,13	500	up to 6
Desorption kinetics	Loading	2NP	F-400 & WV-B	4.6	500	14
	Desorption	2NP	F-400 & WV-B	1.4.6,13	0	up to 6

CHAPTER 4

EFFECT OF pH ON ADSORPTION AND DESORPTION EQUILIBRIA

4.1 Introduction

The influence of pH on adsorption is complex and potentially could have a significant effect on the results of experiments. This chapter presents the results of experiments conducted to identify the effect of pH on adsorption and desorption equilibria of two compounds; phenol and 2-nitrophenol (2NP) on two GACs (F-400, and WV-B).

4.2 Isotherm Studies

The dependence of the isotherm of 2NP upon the pH of the solution is presented in Fig 4.1. and Fig. 4.2. As seen in these figures, 2NP adsorption by GAC is markedly enhanced at the acidic pH, with no appreciable difference between pH 1 to 7. However, at pH 13 the adsorption capacities are markedly lower, which was expected based on the pK_a of 7.23 and on the literature reports on the adsorption behaviour of other phenolics.

The data fit the Freundlich isotherm model since it yields a straight line in log-log plot (Fig.4.3). The values of the regressed coefficients are shown in Table 4.1. The values of 1/n vary only slightly with pH up to 7 and it increased for pH 13 for F-400, but for WV-B they are almost the same. For F-400 the values of k peaks at pH 4.6 and decrease sharply at pH 13, while for WV-B the values of k are virtually constant at pH less than its pK_a (pH 7.23) and decrease sharply at pH 13. These results are consistent with those

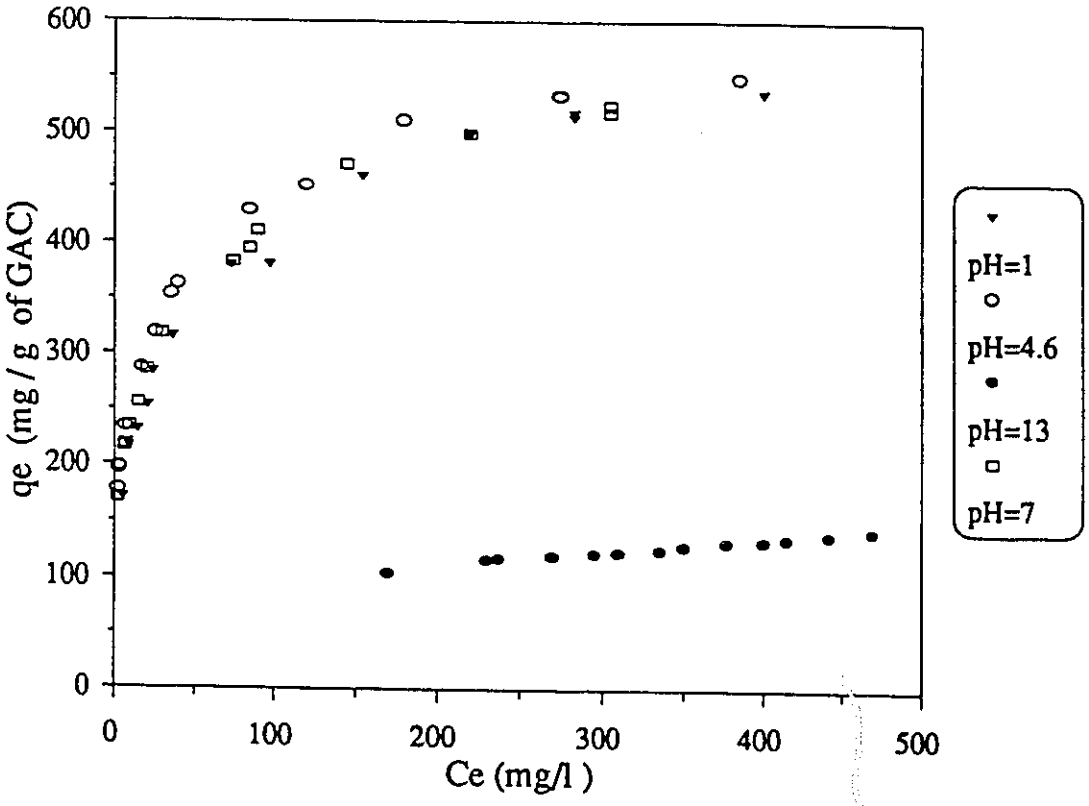


Fig. 4.1 Effect of pH on adsorption isotherms of 2NP on F-400

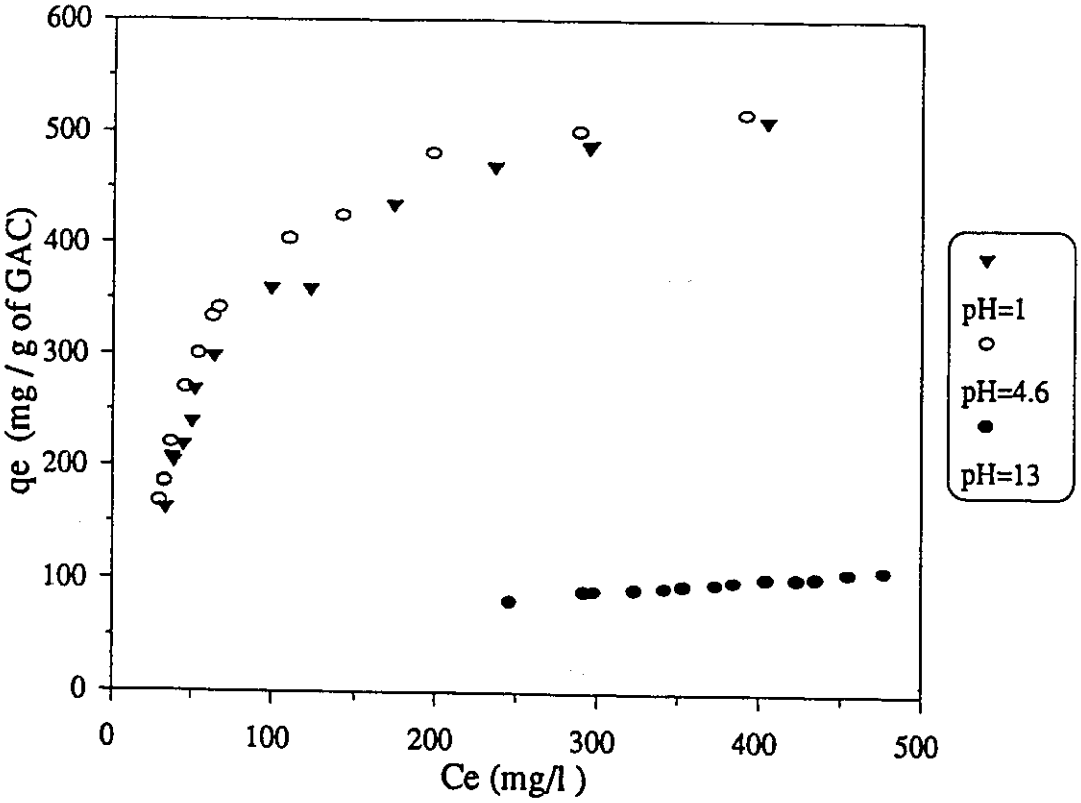


Fig. 4.2 Effect of pH on adsorption isotherms of 2NP on WV-B

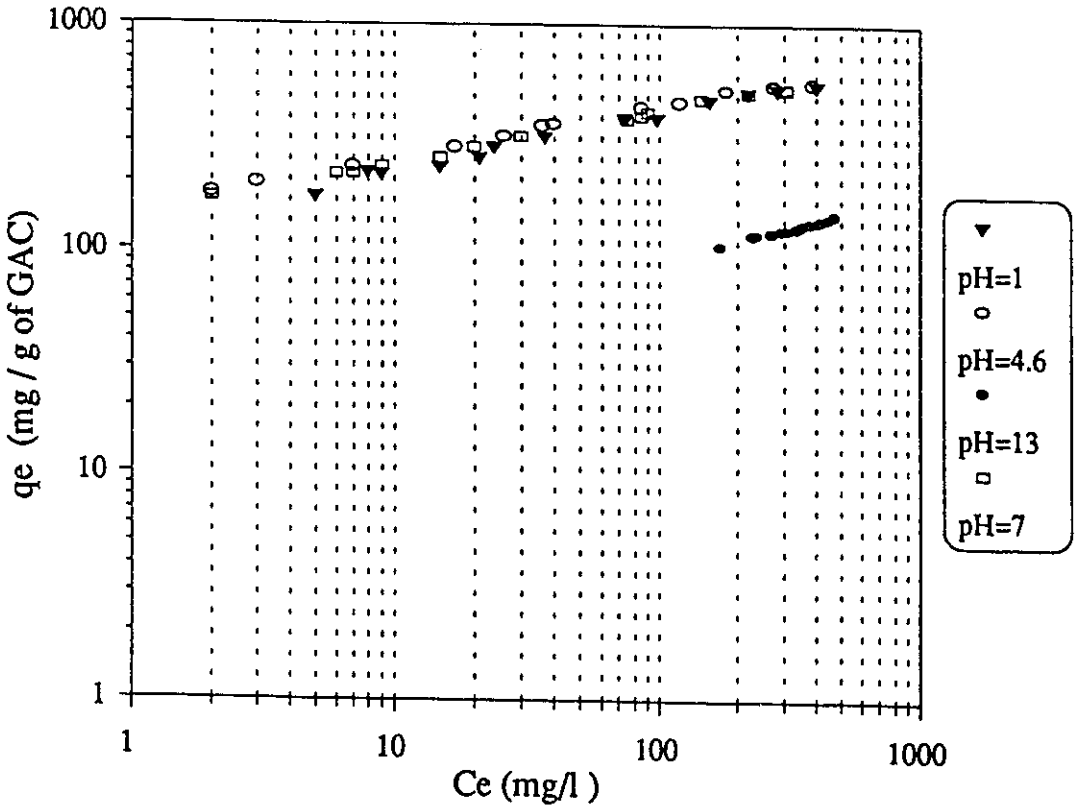


Fig. 4.3 Effect of pH on adsorption isotherms of 2NP on F-400

Table 4.1: 2-nitrophenol Freundlich Isotherm Parameters
at various pHs and Their Standard Errors.

pH	F-400 Carbon		WV-B Carbon	
	k	1/n	k	1/n
1	120±5	0.259±0.008	44±4	0.428±0.031
4.6	155±4	0.223±0.004	49±6	0.421±0.041
7	143±3.5	0.231±0.004	----	----
13	24.3±0.3	0.285±0.010	7.5±0.1	0.434±0.015

of Zogorski (1975) for the adsorption of 2,4-dinitrophenol on LCK carbon. Also the values of K and 1/n are comparable with those of Vidic et al. (1993).

4.3 Effect of pH on Adsorption

A single mass of GAC (in triplicate) was also used to investigate the effect of pH on adsorption. Adsorption of 2NP onto the two activated carbons is plotted in Fig. 4.4. Adsorption of 2NP is almost constant over the pH range 1 to 7 and drops off rapidly at pH values greater than its pK_a (pH 7.23). Fig. 4.4 also shows that both carbons are similarly impacted by pH. However, F-400 carbon has more adsorptive capacity than WV-B carbon in adsorbing 2NP. This excess capacity varies with pH. At pH less than pK_a of 2NP (pH 7.23), it shows that F-400 has 5% to 10% more adsorption capacity than 2NP, while at pH greater than pK_a F-400 has 15% to 50% more adsorption capacity. This difference in carbons performance could be due to different mechanism of adsorption.

Experimental data for phenol and two activated carbons show they have similar adsorption capacities and are similarly impacted by pH (Fig.4.5). Maximum adsorption of phenol on F-400 occurs over the pH range 4.6 to 7. In the case of WV-B carbon it is almost constant for pHs less than 7 and it drops off at pH values greater than 7. Note that the pK_a of phenol is 9.99. A slight decrease of phenol adsorption is observed at low pHs for F-400, where this solute is in the completely molecular form. Similar results were reported by Snoeyink (1968) and Seidel and Radeke (1990). They attributed the decrease in the adsorption of phenol on F-400 at low pH to competitive adsorption of hydrogen ions. The ability of hydrogen ions to adsorb onto activated carbon was observed by Snoeyink (1968). The amount of hydrogen ions adsorbed depends upon the type of acid,

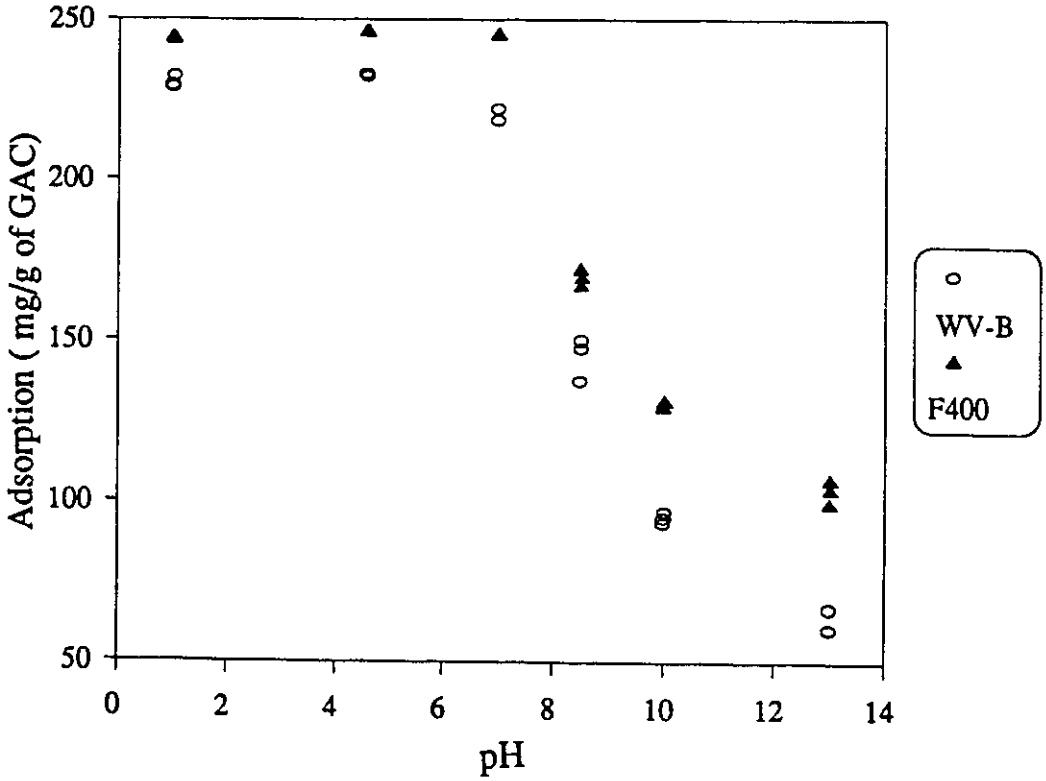


Fig. 4.4 Effect of pH on adsorption of 2NP on F-400 and WV-B (C_i=500 mg/l, GAC=1 g)

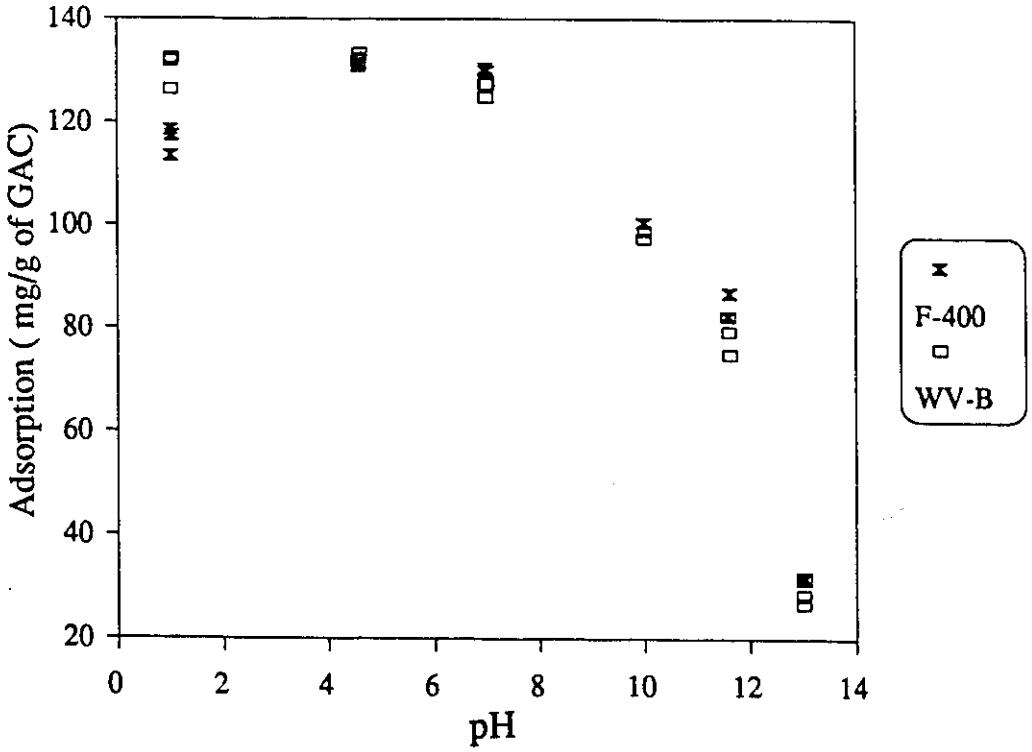


Fig. 4.5 Effect of pH on adsorption of phenol on F-400 and WV-B (C_i=300 mg/l, GAC=1 g)

the hydronium ion activity, and the type of adsorbent. The adsorptive capacity of activated carbon for hydronium ions varied between 0.0 to 0.0004 mol/g (Snoeyink, 1968). Mattson and Mark (1971) have hypothesized that the sorption of phenols on active carbon surfaces occurs at carbonyl oxygen or similar functional groups sites. It is reasonable to expect that hydrogen ions would also interact with the carbonyl oxygen groups on the carbon surface (Zogorski, 1975). Such an interaction would decrease the capacity of the carbon surface for phenol as seen in Fig 4.5.

Except at pH 1, Fig. 4.5 shows almost the same adsorption capacity for both carbons in adsorbing phenol. It is noticeable that WV-B carbon has greater surface area per gram of carbon than F-400 and thus is expected to have greater adsorptive capacity than F-400. The better than expected performance of F-400 carbon may be due to having a larger number of adsorption sites that are more prone to adsorb phenol and hydronium ions. And at these sites there is competition between the undissociated form of phenol and hydronium ions, which becomes more noticeable at higher hydronium ion concentrations. Note that there is no decrease in adsorption of 2NP at low pH when F-400 carbon was used. Apparently 2NP competes better with hydronium ions than phenol, which may be explained by the stronger acidity of 2NP (pK_a = 7.23) over phenol (pK_a = 9.99).

In general, adsorption of 2NP and phenol is much higher at low pH (undissociated form of compounds) than high pH (dissociated form of compounds). Some factors such as high solubility of the dissociated form of the compound, alteration of the carbon surface by acid or base, competition of OH^- for active sites and repulsive forces between the anionic species may have caused such a result.

4.4 Adsorption-Desorption Isotherm

To determine the effect of NaCl on the extent of desorption of 2NP on F-400 carbon, single-solute desorption isotherms were conducted with Milli-Q water and a 1% NaCl solution at pH 4.6. NaCl is the electrolyte used in electrochemical regeneration by Cen (1994). The desorption experiment with NaCl solution may explain its impact on electrochemical regeneration, if any.

The plotted results in Fig 4.6 show that adsorption is reversible in Milli-Q water and this confirms work of Vidic et al. (1993). Fig. 4.7 shows that 2NP adsorption is reversible in NaCl solution. Thus, the NaCl solution does not have a significant effect on reversibility of 2NP at pH 4.6.

4.5 Effect of pH on Desorption

Batch desorption experiments were conducted with loaded GAC (at a single phase concentration) and buffered Milli-Q water at different pHs. The GAC was loaded with solutions of undissociated phenolics (pH 4.6 for 2NP and 7 for phenol).

The results of 2NP desorption from carbons at different pHs are plotted in Fig. 4.8. This figure shows that maximum desorption of 2NP occurs at pH values greater than pK_a (pH=7.23) and decreased dramatically at pH values less than pK_a. It is evident from the figures that the dissociated form of compounds desorb much more than undissociated form. The mass of 2NP desorbed from WV-B is greater than that from F-400 and these differences are less at low pHs than at high pHs. This is consistent with the lower affinity of WV-B in adsorbing 2NP (Fig. 4.4). Apparently 2NP adsorbs with a stronger bond to

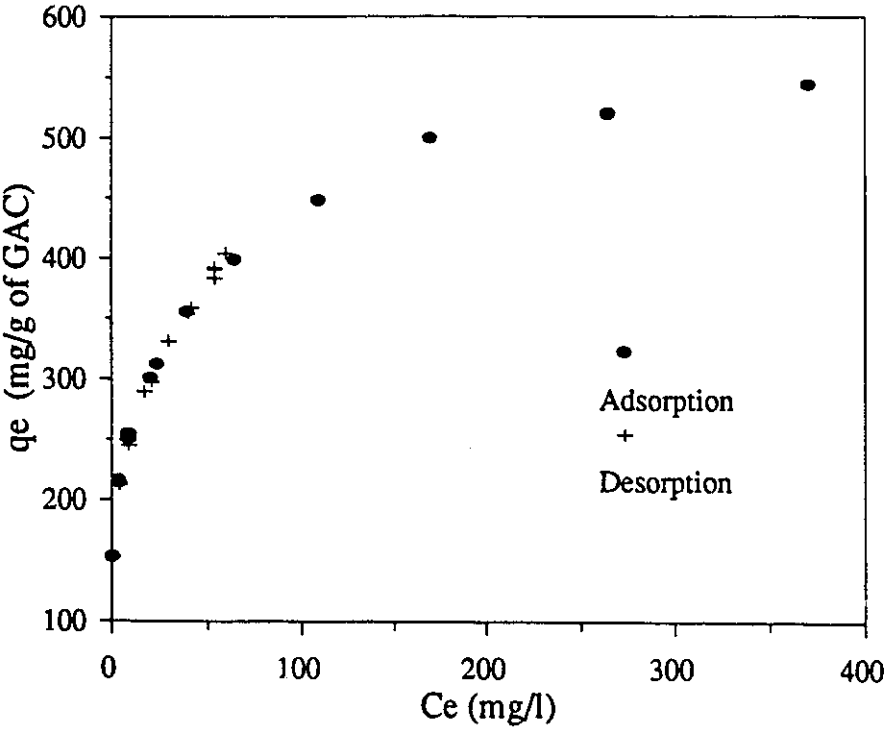


Fig. 4.6 2NP adsorption and desorption isotherms at pH 4.6 (F-400, desorption solution: Milli-Q water)

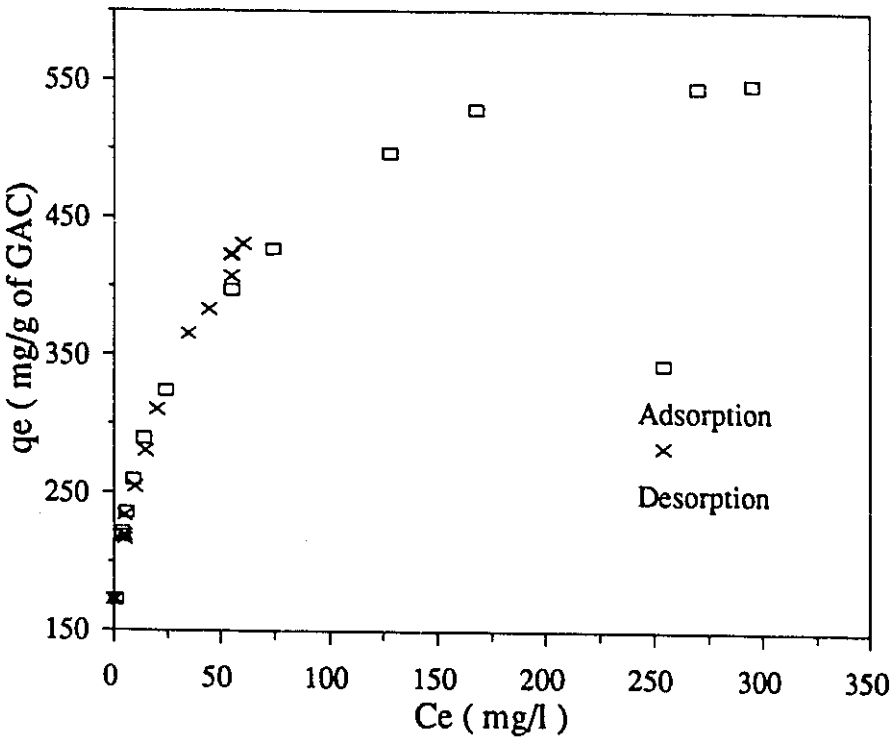


Fig. 4.7 2NP adsorption and desorption isotherms at pH 4.6 (F-400, desorption solution: 1% NaCl solution)

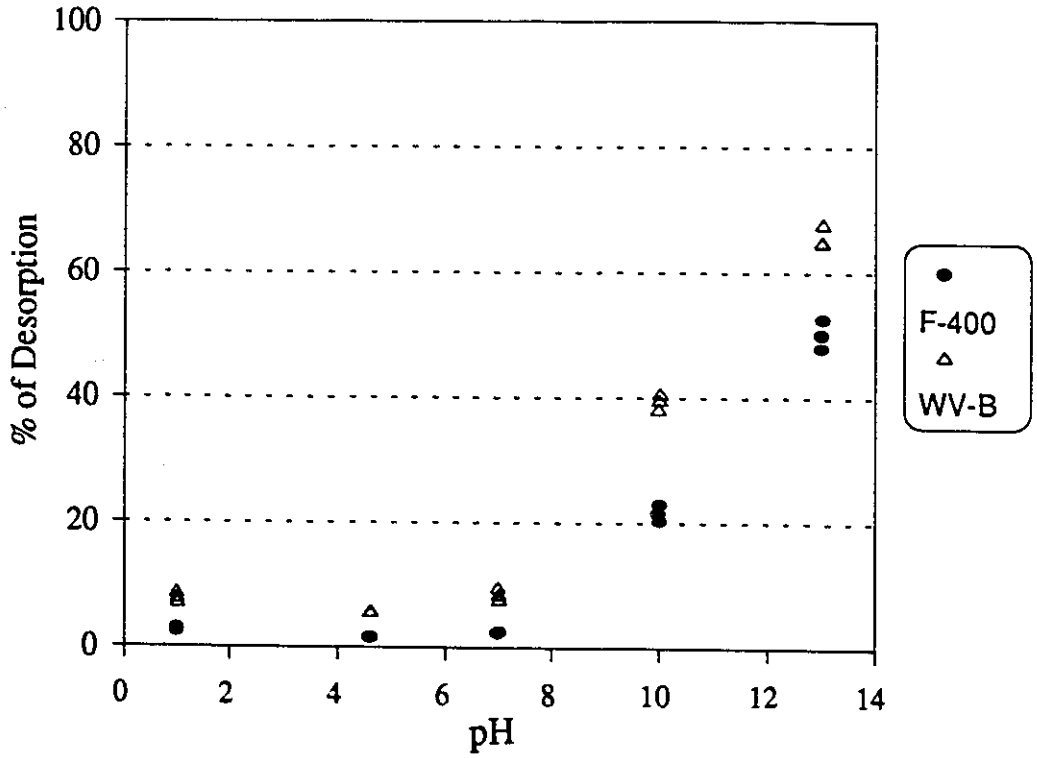


Fig. 4.8 Effect of pH on desorption of 2NP from F400 and WV-B

F-400 than to WV-B.

As Fig. 4.9 shows minimum desorption of phenol occurs at pH values smaller than the pK_a (pH=9.99) and increased sharply at pH values greater than pK_a. Although the two GACs have almost identical phenol adsorption capacity (Fig. 4.5), they show different desorptive behaviour (Fig. 4.9). The amount of phenol desorbed is greater in the case of WV-B. This additional desorption is almost constant over all pHs less than the pk_a, while it increases at high pH. This difference apparently shows that phenol/WV-B carbon bonds are weaker than phenol/F-400 carbon bonds. These results are consistent with reports that adsorption of phenol on WV-B is reversible while, its adsorption on F-400 is partially irreversible (Vidic et al., 1993; Narbaitz and Cen, 1994; Yonge et al., 1985).

The large amount of desorption at pH values greater than the pK_a of the adsorbate, suggests higher regeneration probability at the cathode in electrochemical regeneration process. This confirms Nabaitz and Cen's (1994) hypothesis regarding higher cathodic regeneration due to local pH effect at the cathode.

Much higher desorption at high pH, suggests that the amount of dissociation of adsorbate influences the extent of desorption. This variation of desorption with degree of dissociation is not unexpected, since the dissociated form is more soluble in solution (Mattson and Mark, 1971). Moreover, based on the different interpretations of the effect of pH on adsorption in the literature, the following mechanisms may influence the desorption.

1- At high pH, where the compounds are in ionic form, the adsorbate-adsorbent bond is

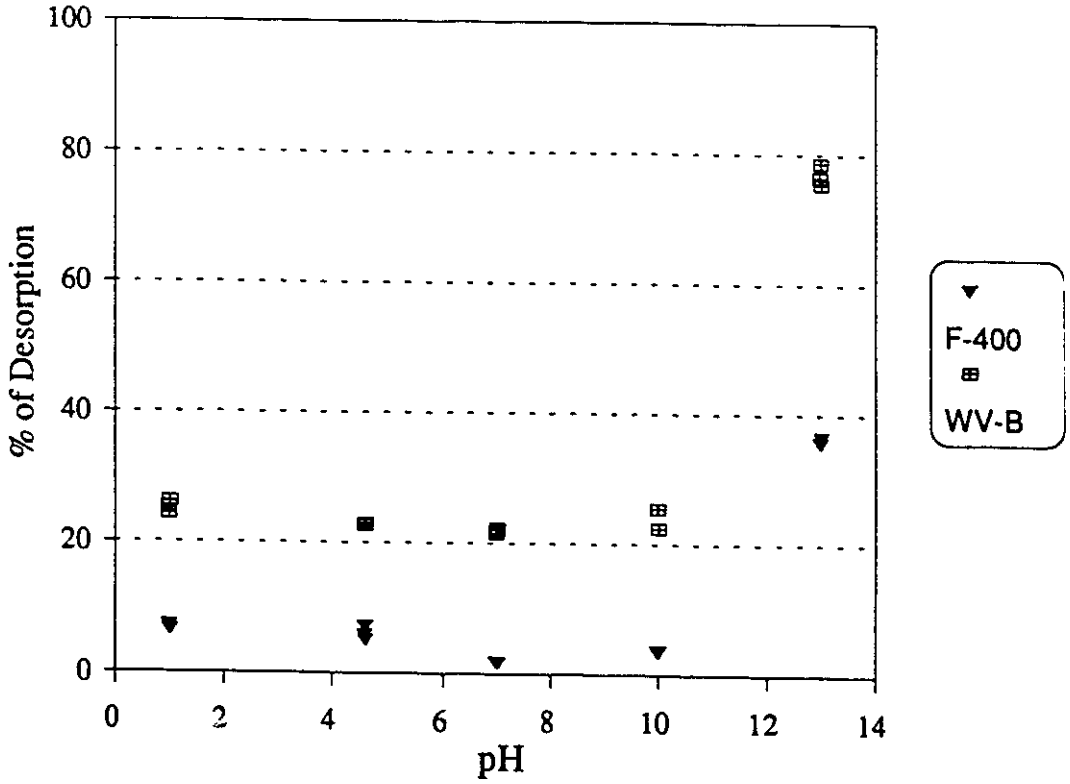


Fig. 4.9 Effect of pH on desorption of phenol from F400 and WV-B

weaker than adsorbate-solution bond.

2- Repulsive forces between the anionic sorbate and adsorbent can become significant at high pH values, which may increase the amount of desorption (Summers and Roberts,1988).

3- Competitive adsorption between anionic adsorbed and excess OH^- ions. OH^- ions are lighter and hence more mobile and may compete more successfully.

4- The surface of activated carbon may be altered in some manner by the base used for pH adjustment. Adsorption of OH^- will increase negative charge of activated carbon surface, enhancing repulsive forces between it and the anionic sorbate.

To investigate the reversibility of 2NP at different pHs from both carbons a number of calculations were made in Tables 4.2 and 4.3. They include the solid phase concentration after adsorption loading at pH 4.6 (qe_{ads}); the solid phase concentration after desorption cycle (qe_{des}) at different pHs; and, assuming full reversibility the predicted solid phase concentration from the adsorption isotherm for the pH of the desorption solution,qe_{rev}. These tables also present the confidence interval of qe_{rev}. These tables show that qe_{des} falls within the confidence interval of the predictions based on the adsorption isotherms at the same pH and assuming full reversibility. Thus there is full reversibility and the impact of pH on desorption can explained strictly based on the adsorption behaviour at the various pHs. Thus,the adsorption isotherms at the appropriate pH can be used to predict desorption.

4.6 Solute Comparison

When comparisons of the sorption of different solutes are needed, the number of moles

Table 4.2 Comparision of the experimental and the predicted qe_{rev} after desorption for 2NP on F-400 at various pHs.

Ce_{des}[1] (mg/l)	qe_{ads}[2] (mg/g)	Desorption pH	qe_{des}[3] (mg/g)	predicted qe_{rev}[4] and its confidence* limit (mg/g)
13	246	1	239.5	233.4 (223.5, 243.7)
13	246	1	240.2	233.4 (223.5, 243.7)
14	245.5	1	238.9	237.9 (227.9, 248.5)
8	246	4.6	242	246 (239.4, 253)
8	245.5	4.6	241.5	246 (239 , 253)
8	246	4.6	242	246 (239 , 253)
12	246	7	239.5	253.1 (247, 259)
12	246	7	239.8	253.1 (247, 259)
12	246	7	240	253 (247, 259)
250	246	13	120.8	117 (111, 124)
260	246	13	123	118 (112, 125)
230	246	13	117	114 (108, 121)

[1] Ce_{des} is equilibrium liquid phase concentration after desorption cycle.
[2] qe_{ads} is equilibrium solid phase concentration after adsorption loading at pH 4.6.
[3] qe_{des} is equilibrium solid phase concentration after desorption cycle at desorption pH.
[4] predicted equilibrium solid phase concentration based on full reversibility and the adsorption isotherm for the pH equal to the desorption pH.
* the confidence limits are predicted from the confidence limits of the Frundlich model's K.

Table 4.3 Comparison of the experimental and the predicted qe_{rev} after desorption for 2NP on WV-B at various pHs.

Ce[1] (mg/l)	qe_{ads}[2] (mg/g)	Desorption pH	qe_{des}[3] (mg/g)	Caculated qe[4] (mg/g)
36	234	1	213	204 (185 , 225)
34	234	1	217	199.6 (181 , 220.5)
34	234	1	215.5	192 (181 , 220.5)
27	234	4.6	219.9	196 (171 . 225)
28	234	4.6	220.5	199.6 (174 , 229)
27	234	4.6	220.5	196 (171 , 225)
270	234	13	82.5	85 (78 , 92.6)
300	234	13	82	89 (81 , 97)
300	234	13	84	89 (81, 97)

[1] Ce is equilibrium liquid phase concentration after desorption cycle.
[2] qe^{ads} is equilibrium solid phase concentration after adsorption loading at pH 4.6.
[3] qe^{des} is equilibrium solid phase concentration after desorption cycle at desorption pH.
[4] qe is caculated equilibrium solid phase from adsorption isotherms at desorption pH

of sorbate removed per gram of carbon should be plotted against the reduced concentration (Snoeyink et al., 1969). The reduced concentration is defined as the actual concentration of the adsorbate in bulk solution phase (c_e) divided by the compounds solubility (Cs) in this phase at the temperature of the experiment. Dividing the solute concentration by solubility is an attempt to normalize the amount of energy required to move different adsorbates from the bulk phase to the surface of the adsorbent. So, the reduced concentration has the effect of eliminating differences in equilibrium sorption characteristics due to solubility. Differences in equilibrium sorption curves plotted in this method should then be due to differences in the nature of sorbate-surface bonding, sorbate-sorbate interaction, or to differences in the types of sites at which sorption occurs (Snoeyink et al., 1969).

The quantities of undissociated form of 2NP and phenol sorbed on the F-400, is given as functions of C_e/C_s in Fig. 4.10. As can be seen phenol adsorbs more than 2NP on F-400 carbon and it can be due to different adsorption mechanisms. However, without eliminating the effects due to solubility 2NP adsorbs more than phenol onto both GACs regardless of pH (Figures 4.11). Similar results are obtained for WV-B carbon (Appendix A).

The extent of dissociation has a significant impact on adsorption and desorption processes. To find if 2NP and phenol behave similarly with respect to the extent of dissociation, the relative amount adsorbed term vresus the term pH-pK_a are plotted for F-400 (Fig. 4.12). Relative amount of adsorption was calculated arbitrarily as : Adsorption(pH)/Adsorption(max.). This figure shows that 2NP and phenol behave

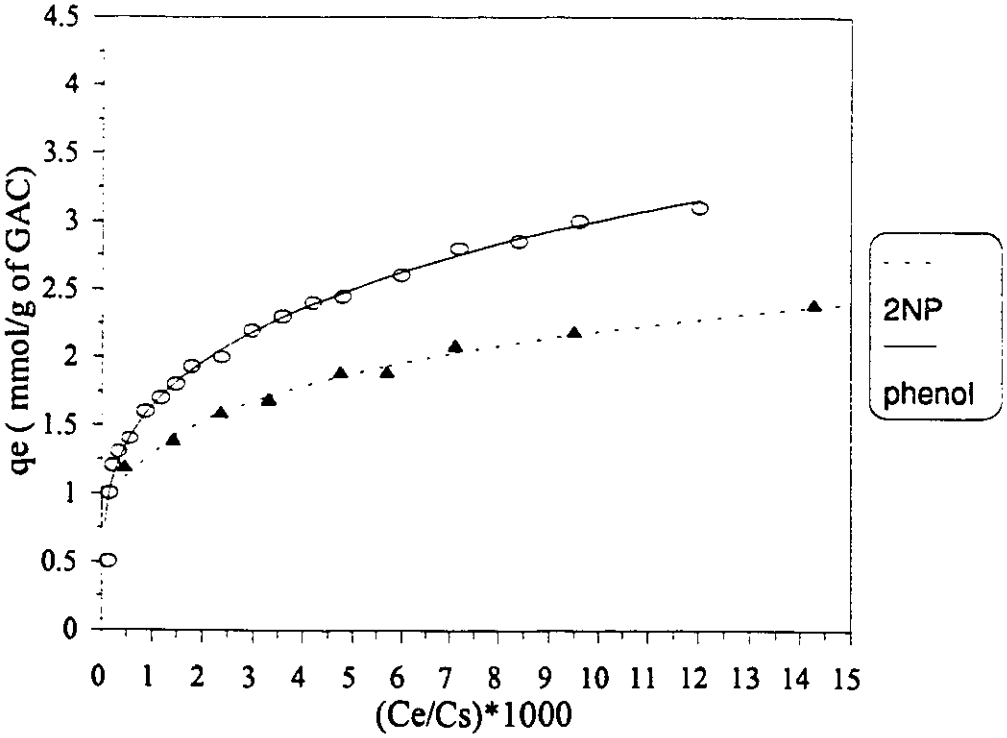


Fig. 4.10 Sorption capacity versus reduced concentration (pH 4.6 , F400)

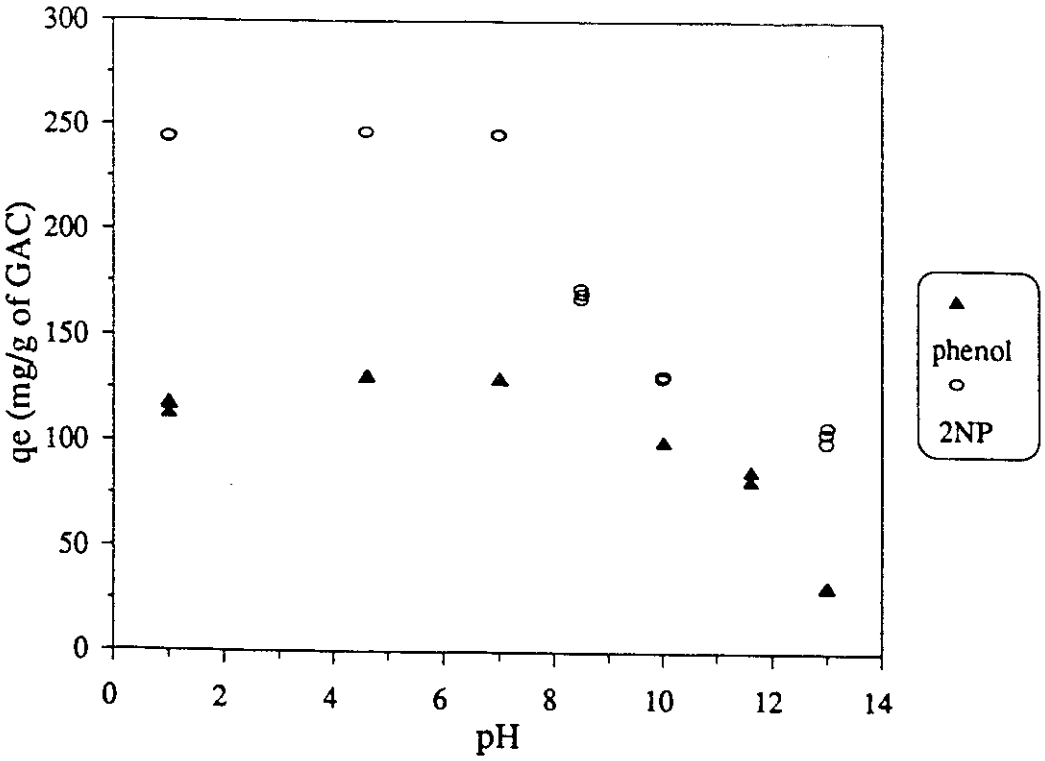


Fig. 4.11 Sorption capacity versus pH
(F400 carbon)

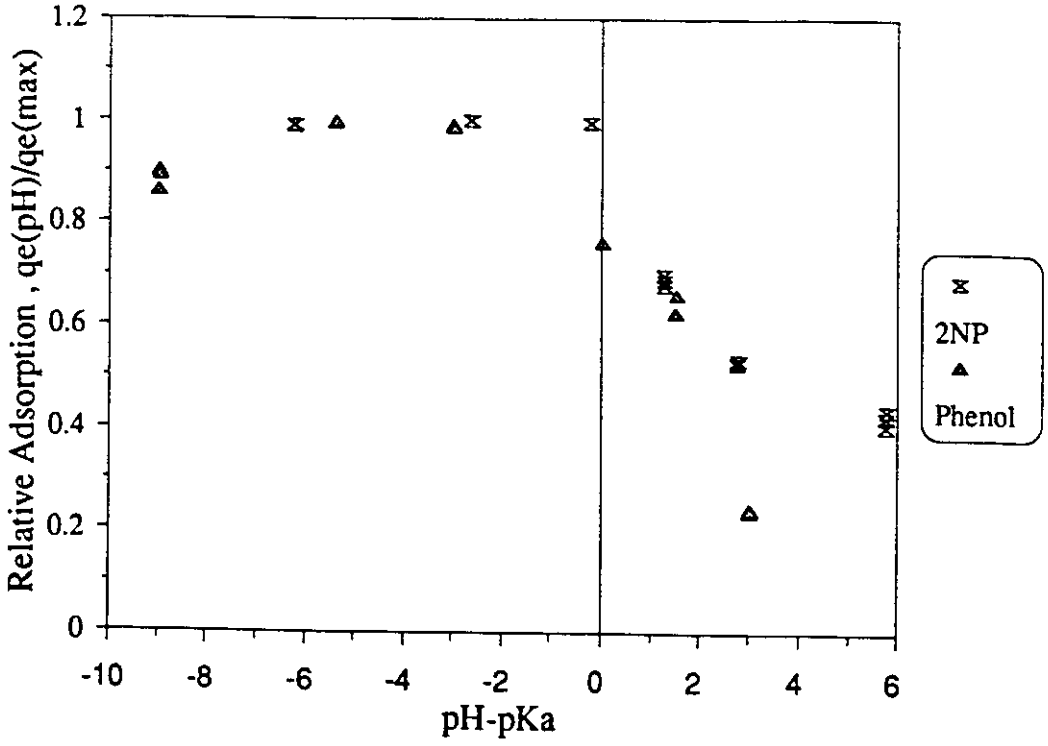


Fig. 4.12 Relative adsorption on F-400 versus dissociation of the adsorbate

similarly when plotted in this way. There are some differences in adsorption characteristics at pH 13 and slight differences at pH=pK_a. The same type of results are obtained for 2NP and phenol on WV-B carbon (Appendix B). 2,4-dichlorophenol and 2,4-dinitrophenol showed similar adsorptive characteristics when they were plotted in this method (Zorgorski, 1975). Zorgorski suggested that different phenols behave similarly with respect to extent of dissociation, while, results of the present research are in fair, if not total agreement with that hypothesis.

Also, the desorption experimental data were evaluated to determine if 2NP and phenol behaved similarly with respect to extent of dissociation. Fig. 4.13 shows the relative amount of desorption versus pH-pK_a for F-400 carbon. Relative amount of desorption was calculated arbitrarily as: Desorption(pH)/Desorption(Max). The term pH-pK_a was selected as a tool for comparing the two compounds on the same basis. As seen although 2NP and phenol follow similar patterns, they show somewhat different desorptive characteristics when plotted in this fashion. Similar results are obtained for WV-B carbon (Appendix C).

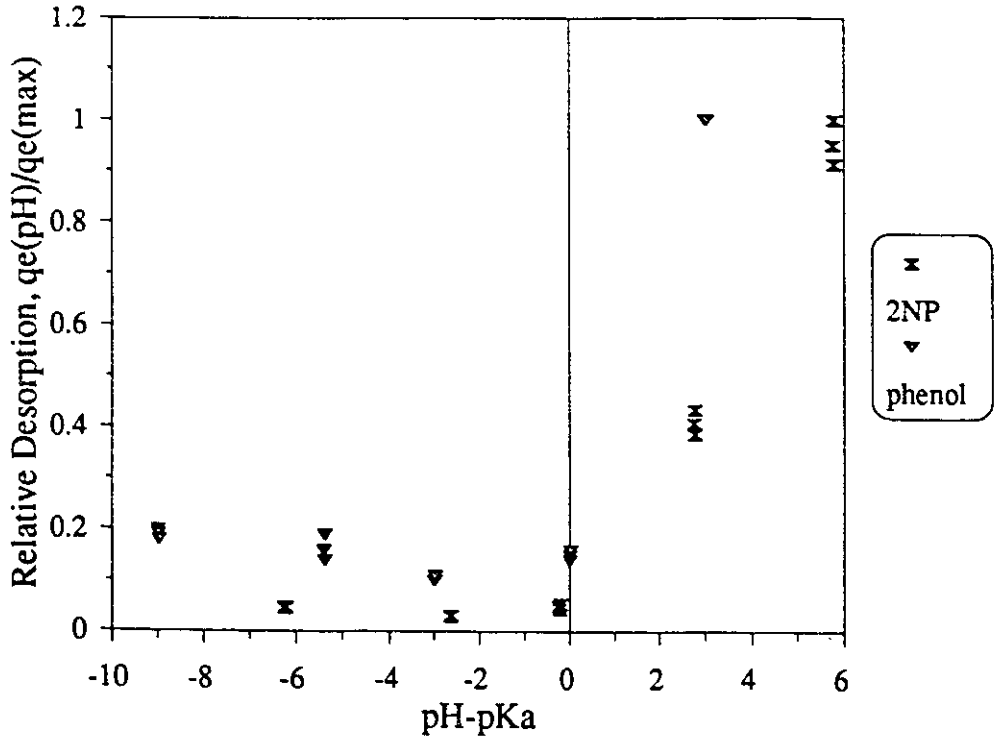


Fig. 4.13 Relative desorption from F-400 versus dissociation of the adsorbate

CHAPTER 5

EFFECT OF pH ON KINETICS

5.1 Introduction

Adsorption and desorption are time-dependent processes. It is important to know the rate of uptake for design and performance evaluations. Also, the rate of desorption is important in design and evaluation of water-based regeneration systems. There are many systematic factors affecting rates of adsorption and desorption. This chapter present results on adsorption and desorption kinetics of 2NP on F-400 and WV-B carbons under different condition of pH. Moreover, the adsorption kinetics of 2NP on these carbons is simulated by a dual internal resistance model.

5.2 Adsorption Kinetics

Several experiments were conducted to determine the effect of pH on the adsorption kinetics of 2NP on F-400 and WV-B. The results of experiments are plotted in Figures 5.1 and 5.2. As these figures show the adsorption reaches equilibrium quickly and around 80-90% of the uptake occurs in less than 5 hours.

Linearization of the initial adsorption data is obtained by plotting the amount adsorbed per unit weight of adsorbent(q_t) versus $t^{0.5}$ (Zogorski, 1975; Faust and Aly ,1987). The adsorption rate, determined from the slope of the line with the units of $mg/g/h^{0.5}$; $mol/g/h^{0.5}$ or equivalent. They are not true reaction rates but relative rates useful for

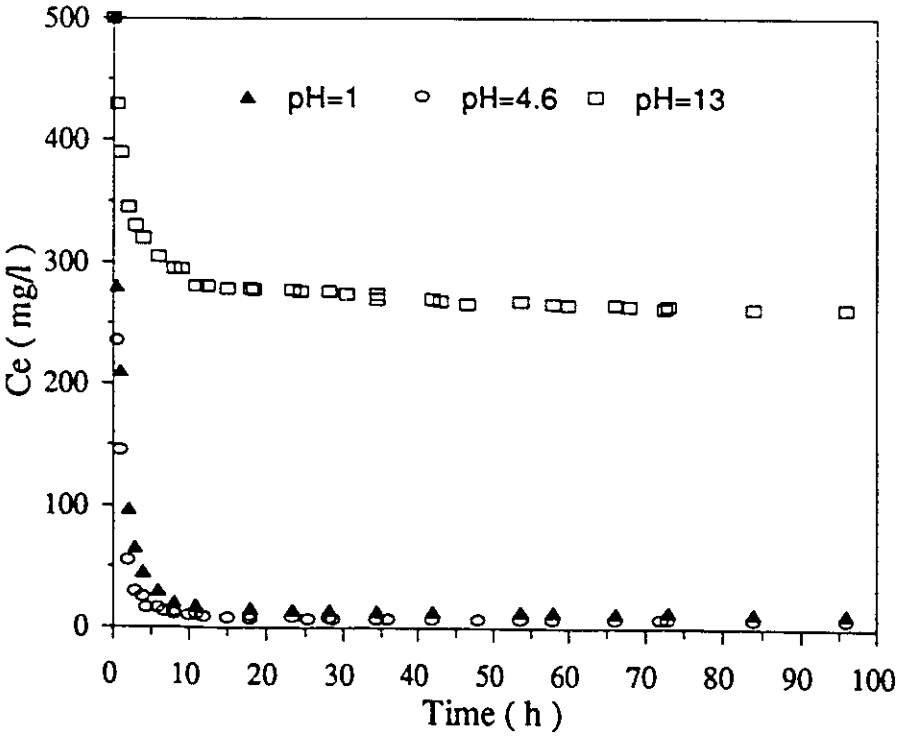


Fig. 5.1 Effect of pH on adsorption kinetics of 2NP on F-400

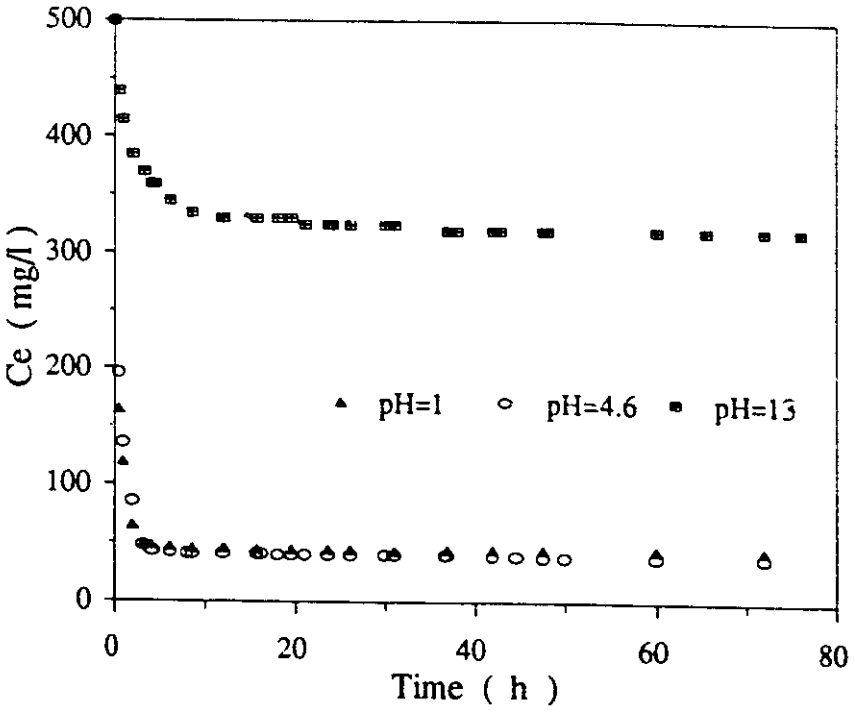


Fig. 5.2 Effect of pH on adsorption kinetics of 2NP on WV-B

comparative purposes. Figures 5.3 and Appendix D present these type of graphs for the adsorption of 2NP on F-400 and WV-B respectively. The initial adsorption rates which are the slopes of the lines are shown in Table 5.1 for both types of GACs. The time required for the first 50 percent of the ultimate removal to occur, t_{50}, is also present in this table. These values were read directly from the amount removal versus $t^{0.5}$ plots, after determining the ultimate removal via the appropriate adsorption isotherm. The values of t_{50} are used in conjunction with the removal rate to interpret the kinetic data in Table 5.1.

The dependence of removal rate of 2NP with hydronium ion concentration is shown in Figs. 5.1, 5.2, 5.3 and Table 5.1. Several observation are evident from these kinetic studies. First, at low pH, which molecules are in undissociated form, rate of adsorption is faster than at high pH (dissociated form of molecule). Second, Table 5.1 shows the maximum rate of adsorption occurs at pH 4.6 and there is a sharp decrease in the removal rate above a pH greater than pK_a of 2NP (pH 7.23). Also, the presence of high concentrations of hydronium ions does not have much influence on the rate of adsorption of 2NP, as indicated by the results at pH 1 and 4.6 in Table 5.1. Finally, an increase in t_{50} value occurs at pH values greater than the pK_a values of the adsorbate. However, the magnitude and nature of the pH effect varies from adsorbent to adsorbent. Similar results are reported by Weber and Morris (1963) for phenol and Zogorski (1975) for 2,4-DCP and 2,4-DNP.

5.3 Adsorption Kinetic Simulation

In order to separate impact of pH on kinetic effects independently of equilibrium effects, several simulations of the data are presented in this section. The impact on kinetics will

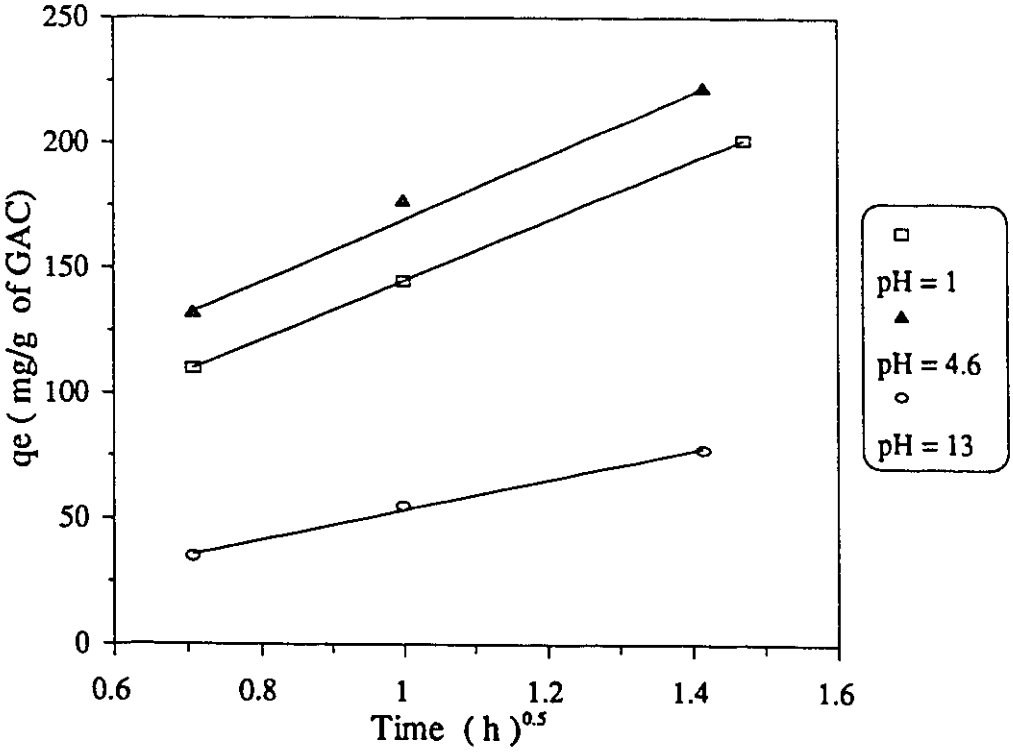


Fig. 5.3 Initial adsorption rate of 2NP on F-400

Table 5.1 Initial adsorption rate of 2-nitrophenol

pH	F-400			WV-B		
	Initial rate ($mg/g.h^{0.5}$)	Max. qe_{ads} (mg/g)	t_{50} (h)	Initial rate ($mg/g.h^{0.5}$)	Max. qe_{ads} (mg/g)	t_{50} (h)
1	120±0.2	231	0.6	70±3	217	0.4
4.6	126±12	234	0.4	77±12	220	0.35
13	60±4	96	0.9	39±2	60	0.9

manifest itself as differences in the values of the kinetic model's parameters. The dual rate kinetics model (Peel, 1980) was used to simulate the results of 2NP adsorption kinetic studies. The reason for selecting this model are:

1- It has been shown to describe adsorption of a variety of different organics, particularly some phenolics, which could not be modelled properly using models with single internal resistance (Peel, 1980; and Famularo et al., 1980).

2- By changing the values of two parameters, this model reduces to the homogeneous solid surface diffusion model, so it can also be easily used for comparisons.

The 2NP adsorption kinetics experiments on F-400 and WV-B carbons at different pHs were regressed using a non-linear least squares routine. The data were analyzed using both the Peel (1980) dual rate model and the homogeneous solid surface diffusion model (HSSD). The results of the regression of these data are shown in Figures 5.4 to 5.9 and Table 5.2 for F-400 and Table 5.3 and Appendixes E; F; and J for WV-B. As can be seen from these graphs, the adsorption occurs relatively rapid, reaching equilibrium in about 10 hours. Also, there is almost no significant difference between the simulation by the two models for the same pH conditions. The similarities are also reflected in Tables 5.2 and 5.3, as the sums of squares only differ by 1 percent for WV-B and 2 percent for F-400 at pH 4.6. The confidence interval of f (the fraction of the adsorption capacity in the macropores) include 1, and the confidence interval of the surface diffusion, D_s, and K_b the pseudo mass transfer coefficient for transport from the macropore to the micropore or branch pores, includes 0.0 . Due to these results the branch pore transfer resistance is not required, and the HSSD model can represent the kinetics of this compound.

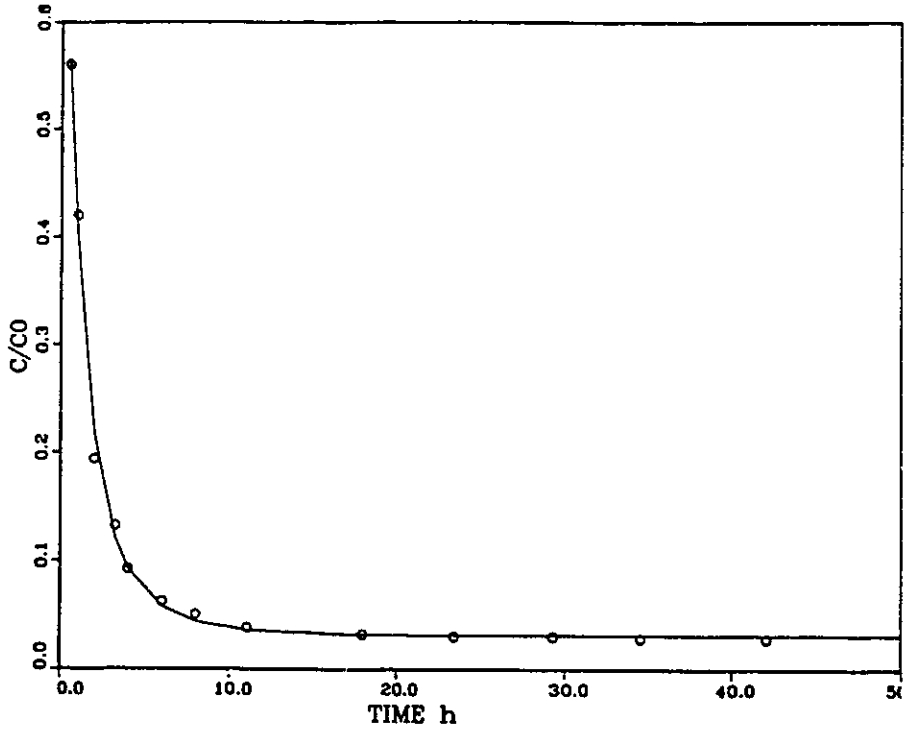


Fig. 5.4 2NP adsorption kinetics on F-400 at pH 1 simulated by the HSSD Model

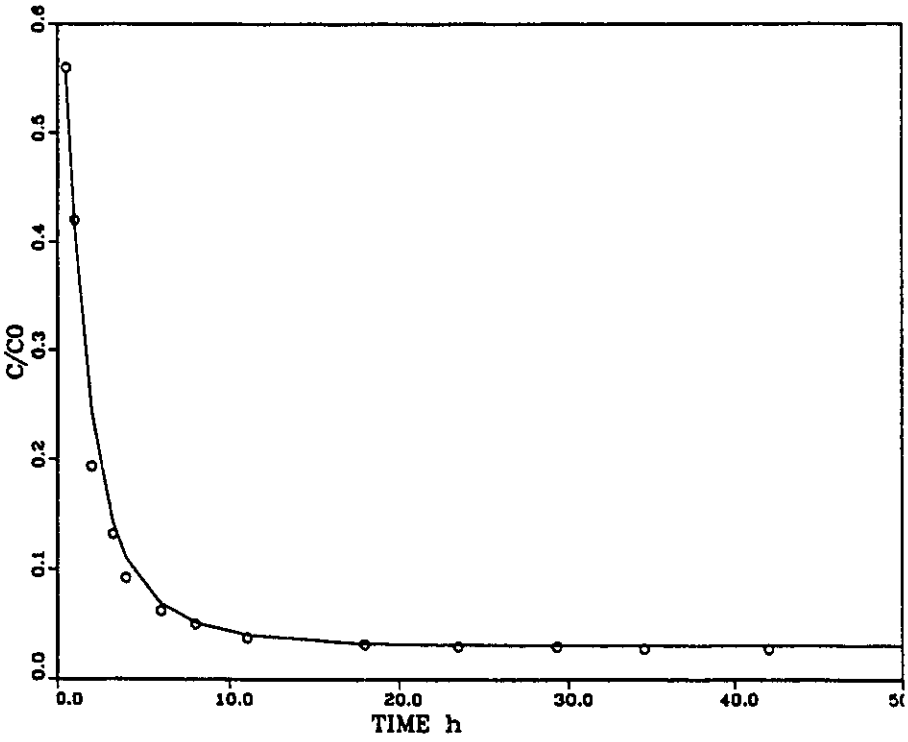


Fig. 5.5 2NP adsorption kinetics on F-400 at pH 1 simulated by the Dual rate Model

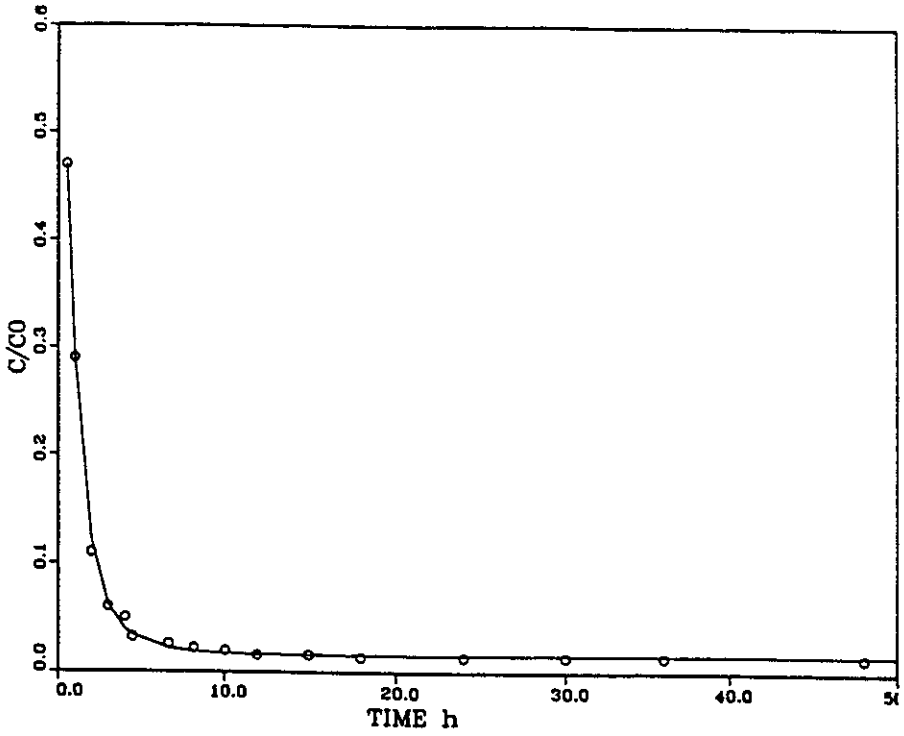


Fig. 5.6 2NP adsorption kinetics on F-400 at pH 4.6 simulated by the HSSD Model

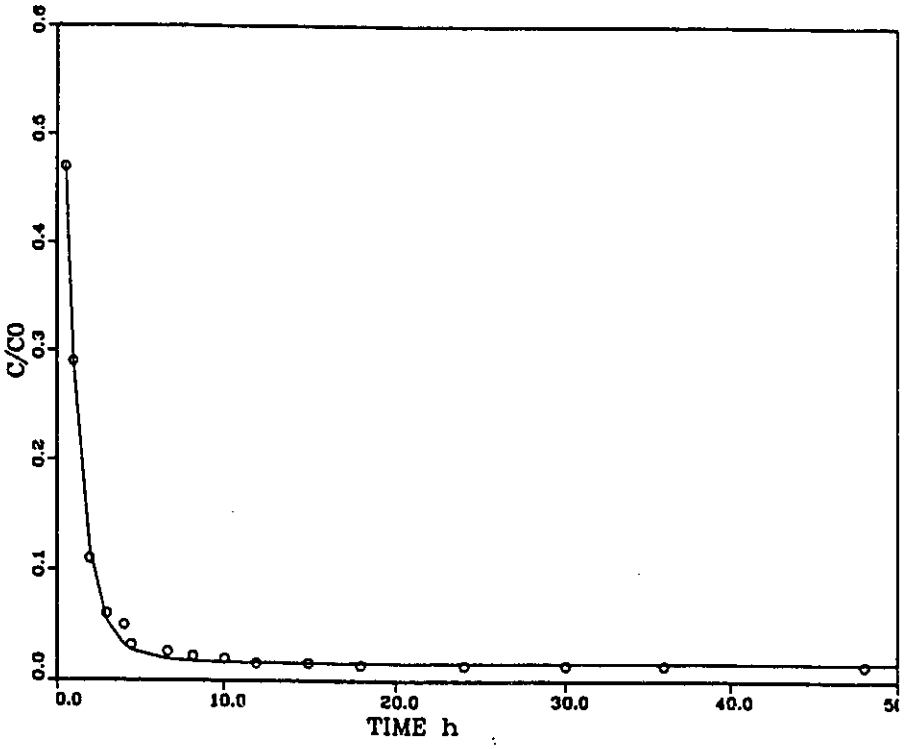


Fig. 5.7 2NP adsorption kinetics on F-400 at pH 4.6 simulated by the Dual rate Model

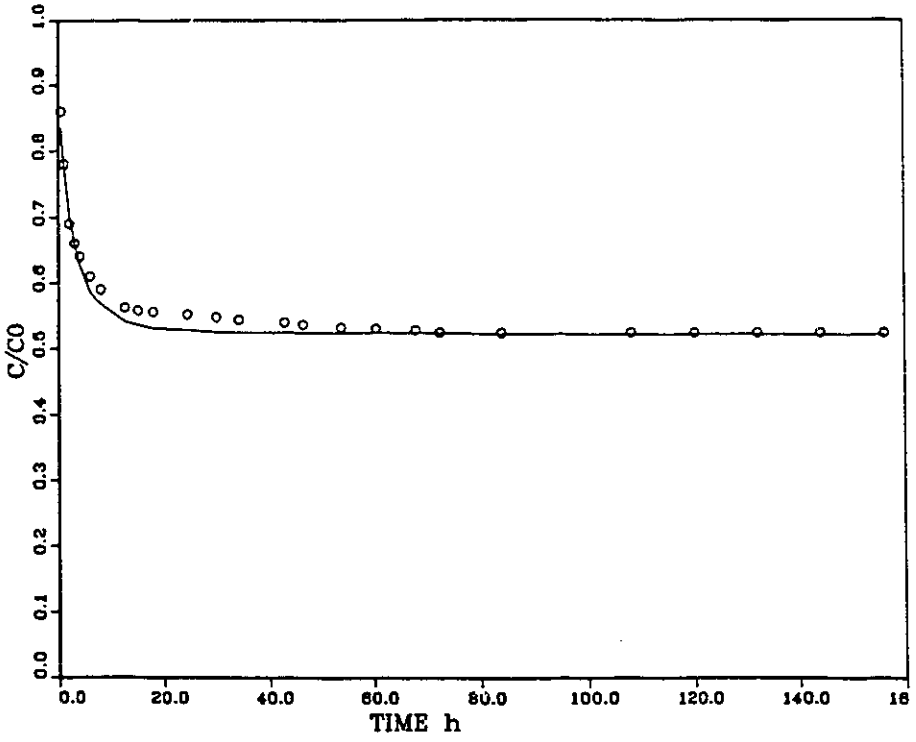


Fig. 5.8 2NP adsorption kinetics on F-400 at pH 13 simulated by the HSSD Model

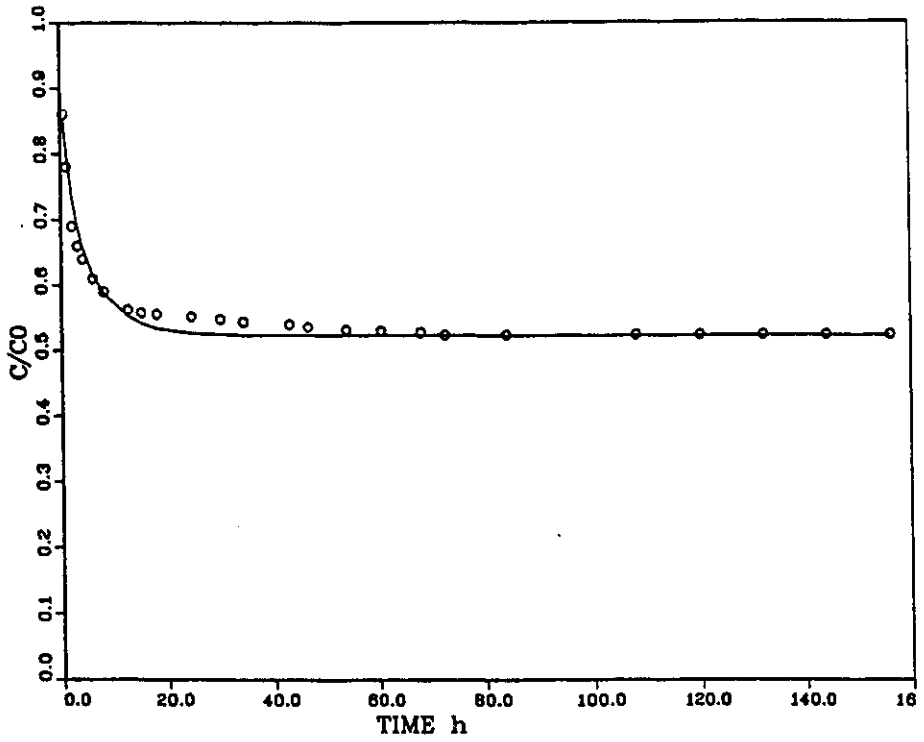


Fig. 5.9 2NP adsorption kinetics on F-400 at pH 13 simulated by the Dual rate Model

Table 5.2 Regressed parameter values and their 95% confidence interval from the 2NP batch kinetic tests on -400 at different pHs.

pH		Peel's Dual Rate Model	HSSD Model
1	sum of squares	0.9203471E-2	0.1098938E-1
	K_f (cm/sec)	0.9393E-2 (0.4549E-2, 0.1424E-1)	0.6658E-2 (0.2872E-2, 0.1044E1)
	D_s (cm^2/s)	0.7933E-7 (-0.1395E-5, 0.1553E5)	0.7510E-7 (0.4417E-7, 0.1060E6)
	f	0.7744 (-0.1360E2, 0.1515E2)	1
	K_b (1/sec)	0.1248 (-0.1531, 0.4028)	0
4.6	sum of squares	0.2910985E-2	0.2951305E-2
	K_f (cm/sec)	0.1261E-1 (-0.4623E-1, 0.7145E1)	0.8334E-2 (0.5074E-2,0.1159E-1)
	D_s (cm^2/s)	0.2401E-6 (-0.4401E-6, 0.9202E6)	0.1082E-6 (0.6890E-7, 0.1475E6)
	f	0.5485 (- 0.4862, 1.5833)	1
	K_b (1/sec)	0.8846E-4 (-0.8055E-4, 0.2575E3)	0
13	sum of squares	0.4119914E-2	0.6116286E-2
	K_f	0.1964E-1 (0.2245E-3, 0.3906E-1)	0.5772E-1 (0.4475E-1, 0.6425E1)
	D_s (cm^2/s)	0.9260E-7 (-0.4708E-7, 0.2323E6)	0.7503E-7 (0.7299E-7, 0.9185E7)
	f	0.7576 (-0.3936, 1.909E1)	1
	K_b (1/sec)	0.2203 (-0.1106, 0.1546)	0

Table 5.3: Regressed parameter values and their 95% confidence interval from the 2NP batch kinetic test on WV-B carbon at different pH.

pH		Peel's Dual Rate Model	HSSD Model
1	sum of squares	0.7243842E-1	0.7850915E-1
	K_f (cm/sec)	0.5528E-1 (-0.2437, 0.3543)	0.5601E-1 (0.5403E-1, 0.5803E-1)
	D_s (cm^2/sec)	0.1496E-6 (0.1322E-6, 0.1670E-6)	0.1002E-6 (0.8447E-7, 0.1159E-6)
	f	0.7933 (0.5574, 0.1029E1)	1
	K_b (1/sec)	0.0714E-4 (-0.1382E-4, 0.2810E4)	0
4.6	sum of squares	0.5918594E-1	0.5929693E-1
	K_f (cm/sec)	0.5427E-1 (-0.3598, 0.3706)	0.5545E-1 (0.5344E-1, 0.5746E-1)
	D_s (cm^2/sec)	0.8994E-7 (-0.1655E-6, 0.3454E6)	0.7066E-7 (0.6038E-7, 0.8094E-7)
	f	0.7530 (-0.1791, 0.1685E1)	1
	K_b (1/sec)	0.2625E-2 (-0.4292, 0.4345)	0
13	sum of squares	0.2994341E-2	0.3065427E-2
	K_f (cm/sec)	0.4993E-2 (0.4002E-2, 0.5985E-2)	0.5970E-1 (0.5814E-1,0.6126E-1)
	D_s (cm^2/sec)	0.4570E-7 (-0.6753E-8, 0.9815E7)	0.6066E-7 (0.5926E-7, 0.6206E-7)
	f	0.936 (0.2945, 0.1577E1)	1
	K_b (1/sec)	0.6105E-1 (-0.5375E-1, 0.1148)	0

The results of simulation in Tables 5.2 and 5.3 also show that the 95% confidence interval of D_s at pH 4.6 include the D_s of pHs 1 and 13. This point indicate that D_s, the surface diffusion coefficient, is almost the same at all pHs. For F-400 the external mass transfer coefficient, K_f, is almost the same for pHs 1 and 4.6 while, it increases for pH 13. However, for WV-B the values of K_f for the three pH values are relatively close. Other similar studies in the literature did not model the experiments using the HSSD model or other state-of-the art models. Thus, there is no information on the impact of pH on the kinetic model's parameter values.

The adsorption mechanism responsible for the slow adsorption was hypothesized to also cause irreversible adsorption because both phenomena are caused by steric or chemical restrictions (Peel, 1980; and Narbaitz, 1985). The data from these kinetic experiments confirm this hypothesis. The 2NP adsorption which showed no slow adsorption, was completely reversible.

5.4 Desorption Kinetics

It should be noted that the GAC used in the desorption kinetics at different pHs, was preloaded at pH 4.6. The desorption of 2NP from F-400 and WV-B carbons was studied and are shown in Figures 5.10 and 5.11. The linearization form of the data for the initial part of the reaction are plotted in Figures 5.12 and Appendix H. In these figures the amount of desorption per unit weight of adsorbent are plotted versus $t^{0.5}$. The desorption rate, determined from the slope of the line and are shown in Table 5.4. The following points may be noted from Figures 5.10, 5.11, 5.12 and Table 5.4. First, the time required for the desorption process to reach steady state is somewhat shorter than the time required

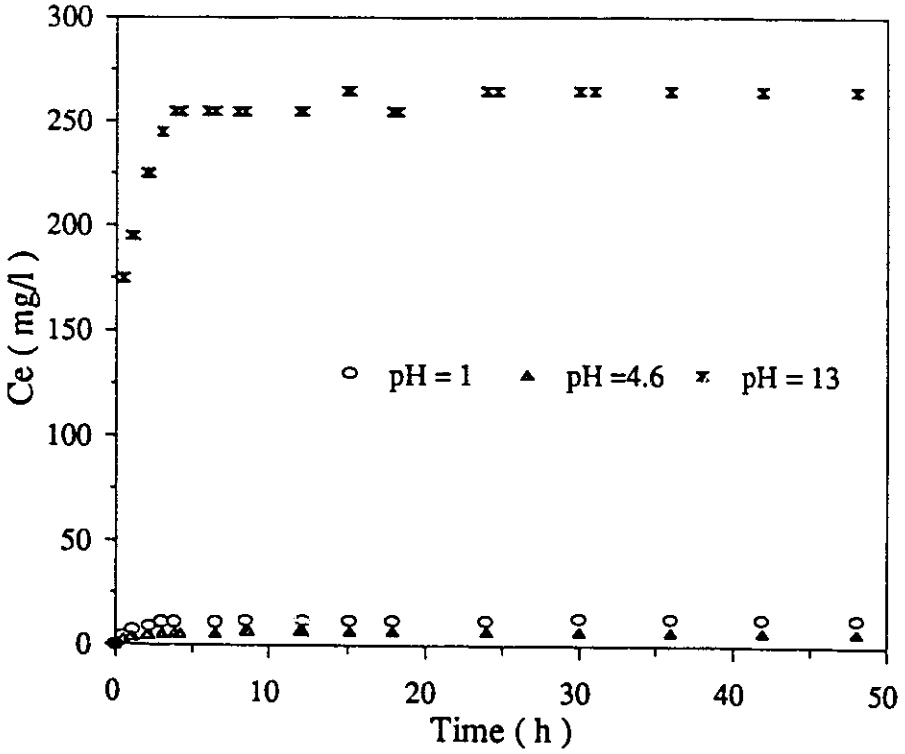


Fig. 5.10 Effect of pH on 2NP desorption kinetics from F-400

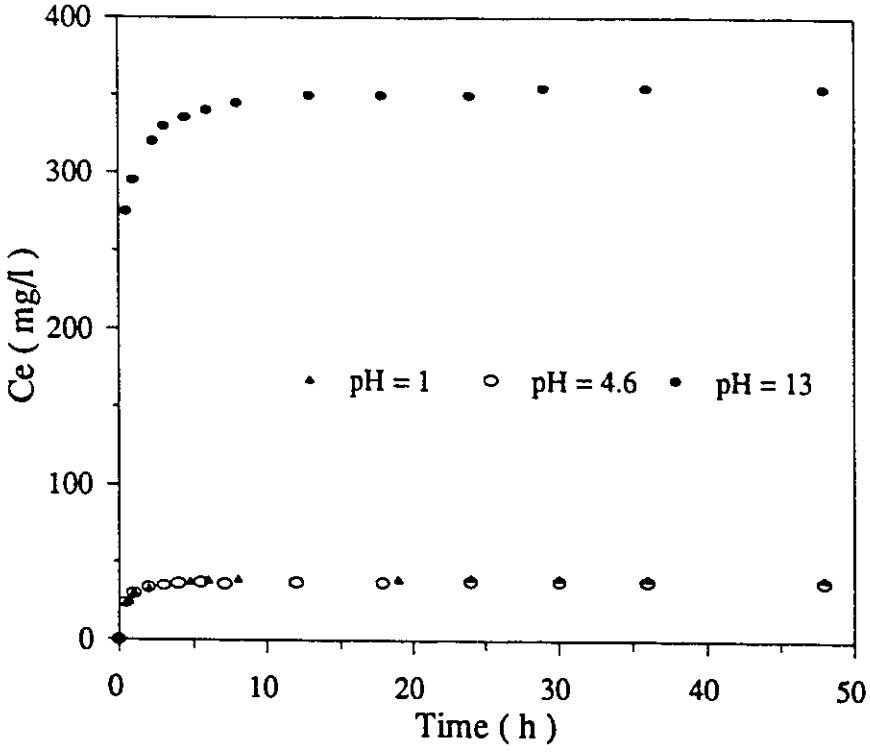


Fig. 5.11 Effect of pH on 2NP desorption kinetics from WV-B

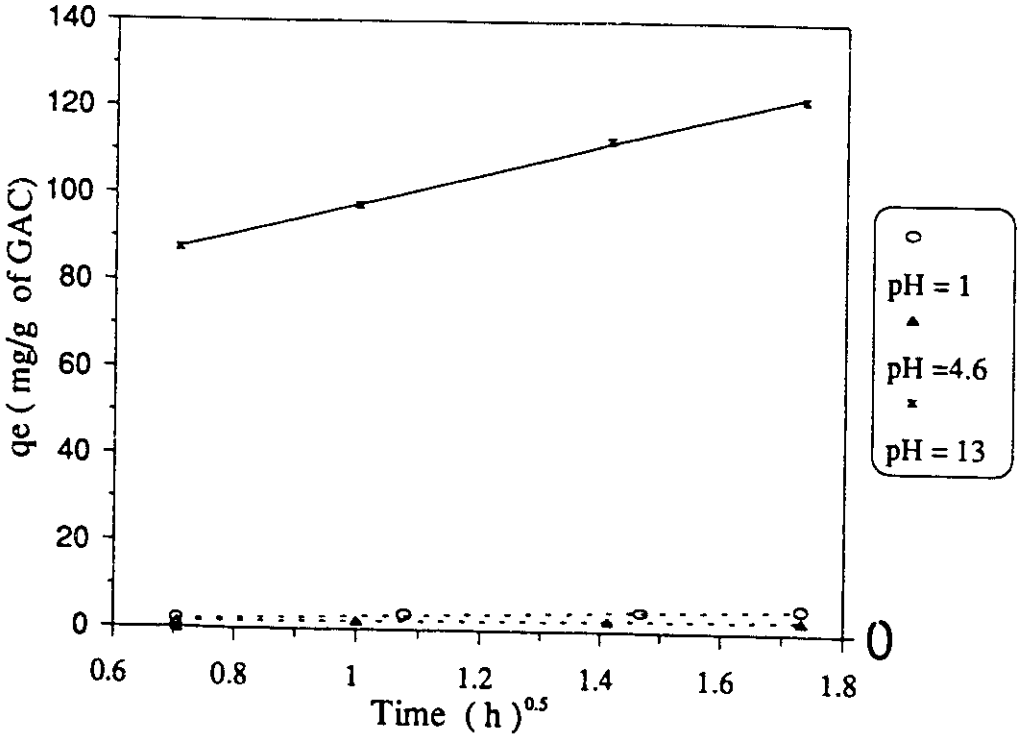


Fig. 5.12 Initial rate of 2NP desorption from F-400

TABLE 5.4 Initial Desorption Rate of 2-nitrophenol

pH	F400			WV-B		
	Initial rate ($mg/g*h^{0.5}$)	qe_{ads}-qe_{des} (mg/g)	t_{50} (h)	Initial Rate ($mg/g*h^{0.5}$)	qe_{ads}-qe_{des} (mg/g)	t_{50} (h)
1	3.3±0.2	6.5	1.0	6.9±1.5	18	0.4
4.6	1.43±0.07	4	0.5	6.2±1.8	13	0.3
13	34.4±0.6	125	0.25	27.5±2	150	0.15

to achieve steady-state condition for uptake of the solute. Second, the rates observed for desorption are lower than the rates for adsorption for the same conditions of solution. Third, a rapid initial desorption of 80% to 90% of the final desorption was followed by a slower desorption.

Figures 5.10 and 5.11 and Table 5.4 show the pH dependence of the desorption of 2NP from activated carbons. The maximum rate of desorption occurs for the dissociated form of the molecule (pH 13) and a sharp decrease in the desorption rate observes for pH less than pK_a. As shown by Table 5.4 this high rate is primarily due to the high driving force for desorption, i.e. the difference between the 2NP solid phase concentration before and after desorption. An increase in t_{50} values occurs at pH less than pK_a. However, the magnitude and nature of the pH effect varies from adsorbent to adsorbent.

CHAPTER 6

CONCLUSIONS

6.1 Conclusions

Based on the findings of this investigation on the effect of pH on adsorption and desorption of 2NP and phenol compounds on GACs (F-400 and WV-B), the following conclusions are made:

1- The extent of dissociation had a significant impact on the adsorption of 2NP and phenol on F-400 and WV-B. For each of the GACs, both adsorbates followed similar adsorption patterns with respect to the extent of dissociation. Also for each sorbate, both GACs exhibited similar adsorption patterns with respect to the extent of dissociation and pH. At pHs less than the pK_a, where the adsorbates are in the undissociated form, the adsorption capacities were constant and decreased markedly as the pH increased beyond the pK_a.

2- Desorption isotherms showed that the adsorption of 2NP on F-400 is fully reversible and the presence of 1% NaCl has no significant influence on the reversibility at pH 4.6.

3- Single point loading experiments showed the 2NP adsorbs reversibly on WV-B and F-400 at various pHs. Thus, the desorption equilibrium conditions at various pHs can be predicted by the adsorption isotherms for the pH in the desorption solution.

4- Much higher desorption occurs at pH values greater than pK_a and decreases dramatically at pH values less than pK_a for both compounds. This suggest higher

regeneration probability at the cathode in electrochemical regeneration process, since it has a high localized pH.

5- For the undissociated form of compounds after eliminating differences in equilibrium sorption characteristics due to solubility, F-400 adsorbs more phenol than 2NP. This difference indicates that different adsorption mechanisms were involved. This was expected based on literature reports of phenol irreversible adsorption due to chemisorption.

6- The initial adsorption and desorption rate are significantly affected by pH. Adsorption kinetics of 2NP onto both carbons were adequately described by the homogeneous surface diffusion model. The branch pore mass transfer resistance model is not required in this case. This appears to confirm literature reports linking the need for such a model to cases with irreversible adsorption.

7- The adsorption kinetics simulations indicate that the surface diffusion coefficient, D_s, within the HSSD model is essentially the same at all pHs.

6-2 Recommendation For Future Research

The logical extension of this research would be to conduct adsorption and desorption experiments at different pHs and considering the following variables: 1- Type of operation, 2- Different organic compounds, 3- Different activated carbons, 5- Different temperatures 5- Different initial concentration of organics, 6- Presence and absence of molecular oxygen. Also modelling of desorption kinetics and competitive adsorption-desorption experiments at different pH conditions should be completed.

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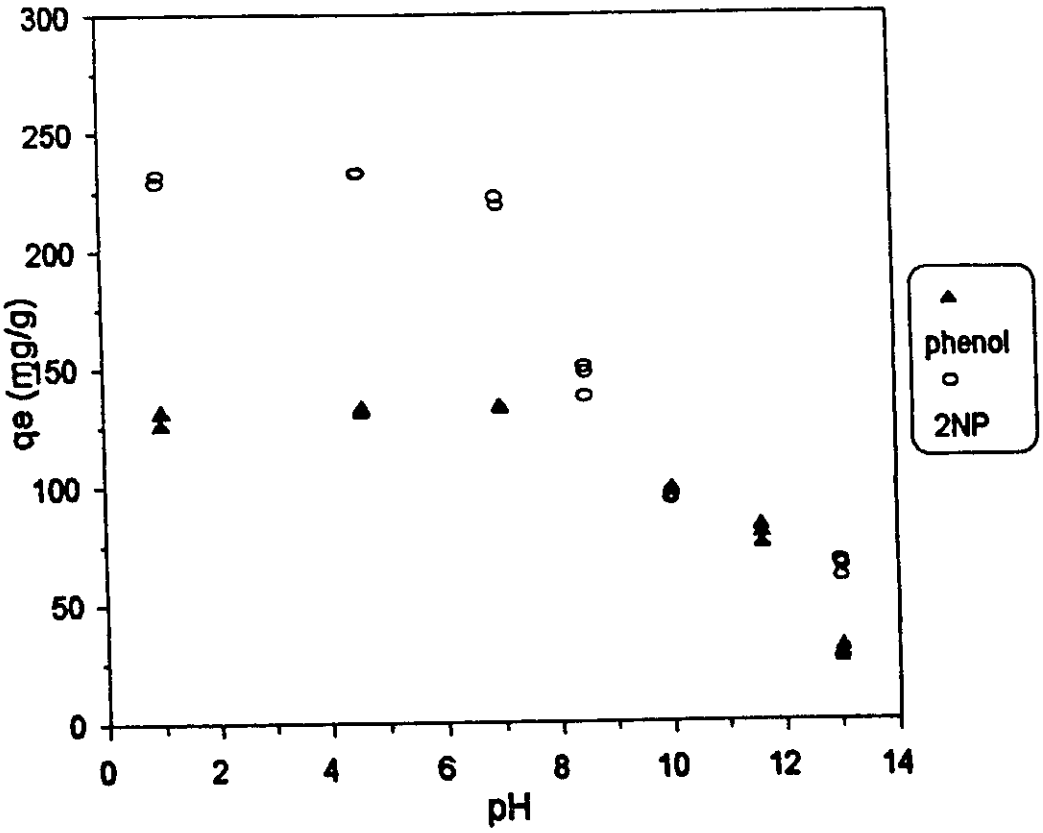
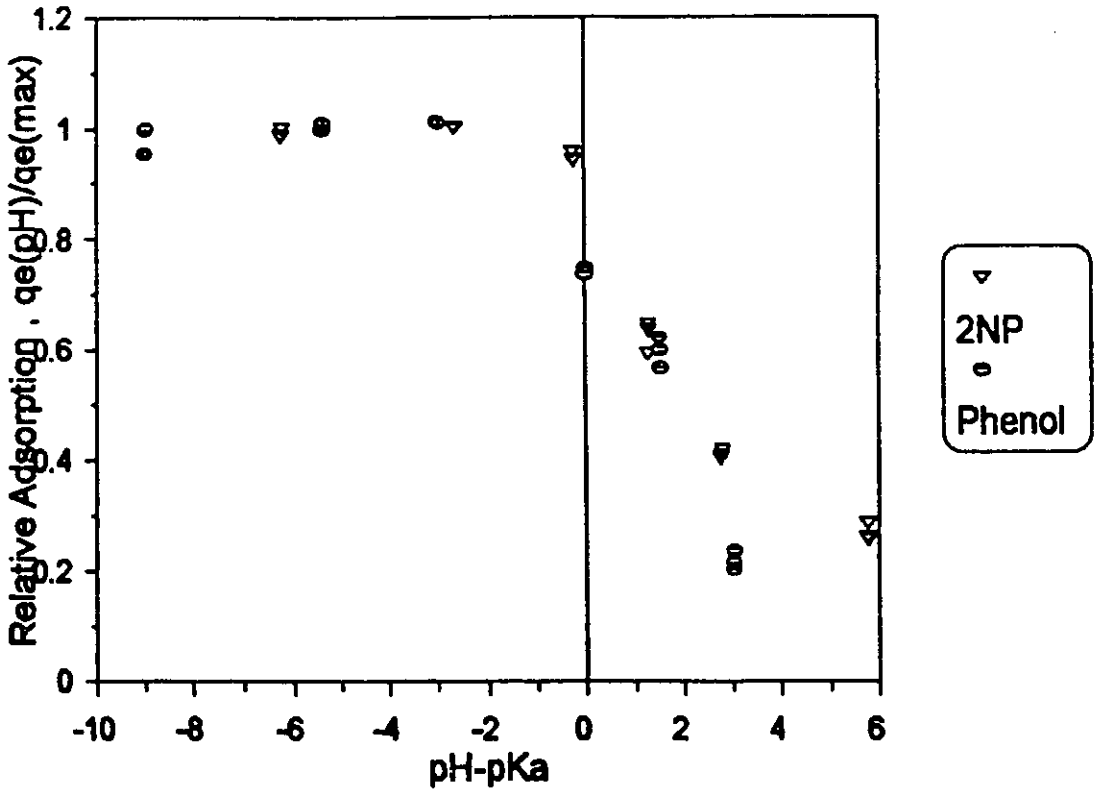
APPPENDIX A



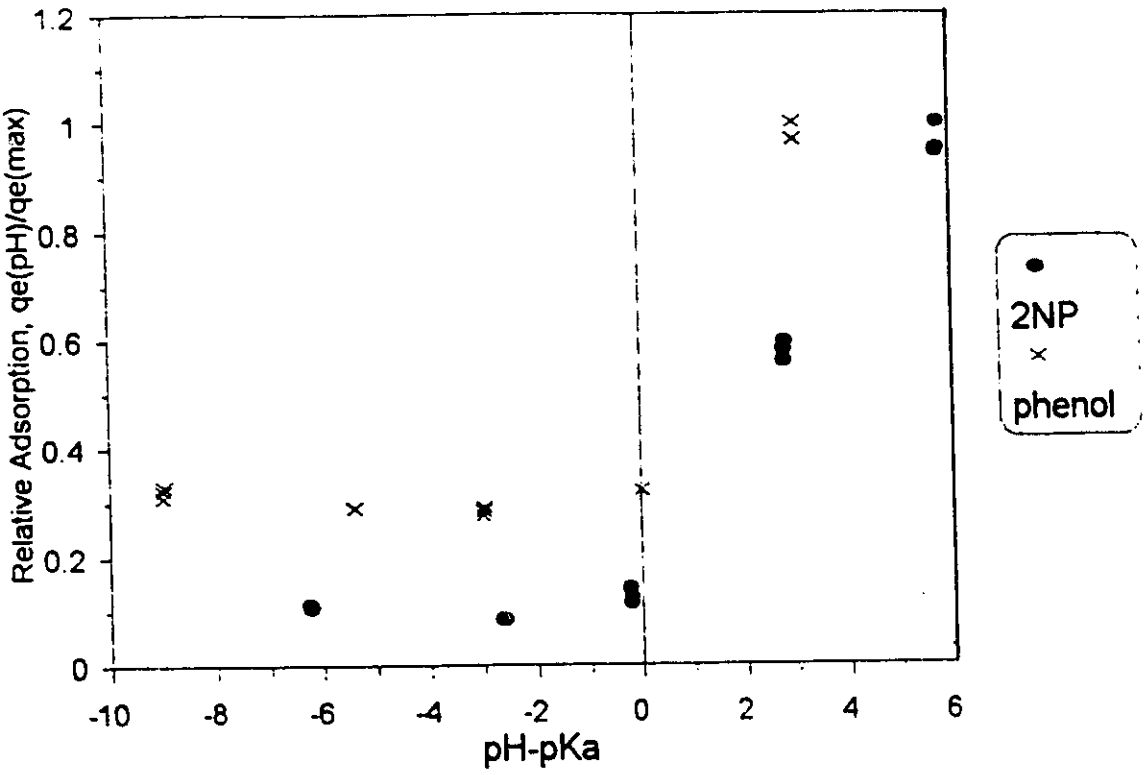
WV-B Soptive capacity versus pH

APPENDIX B



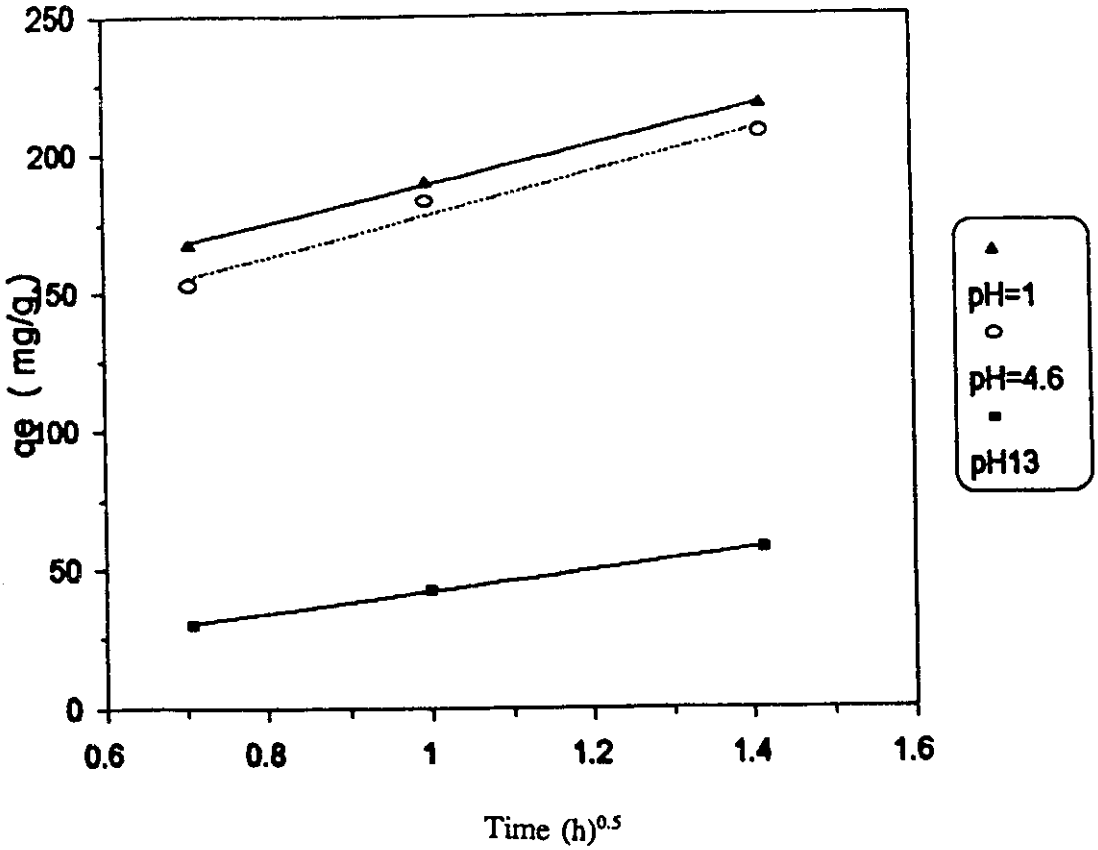
Effect of dissociation of the adsorbate on the relative adsorption on WV-B

APPENDIX C

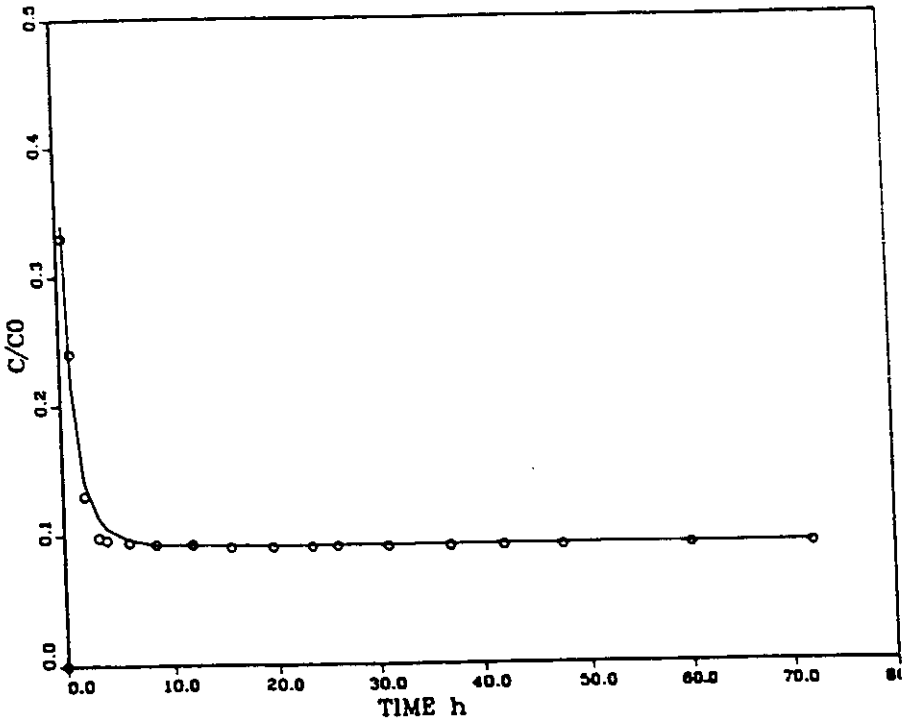


Effect of dissociation of the adsorbate on the relative desorption on WV-B

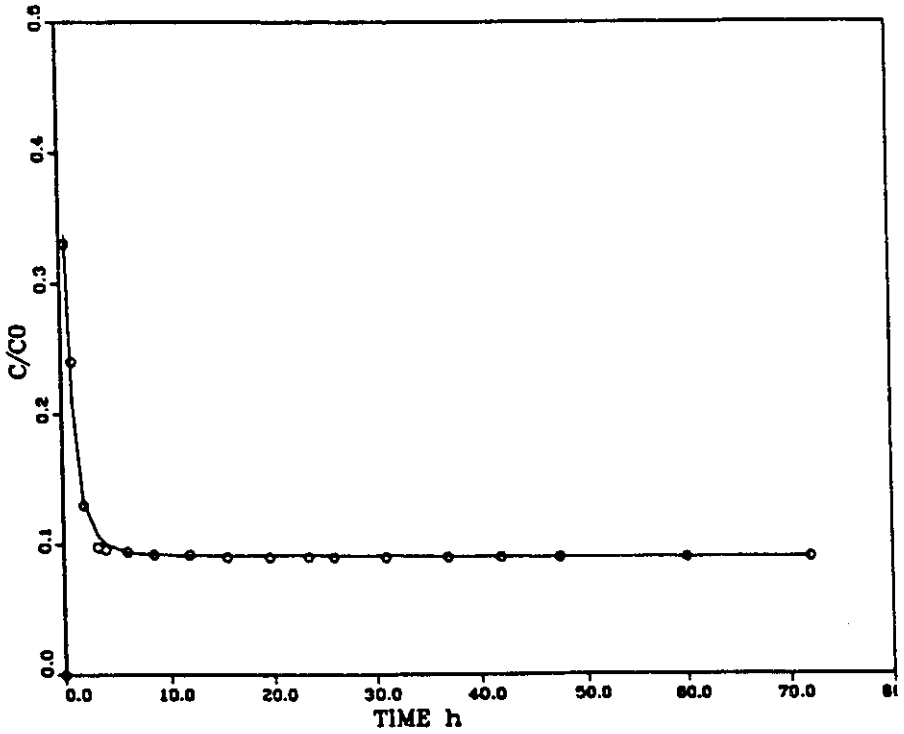
APPENDIX D



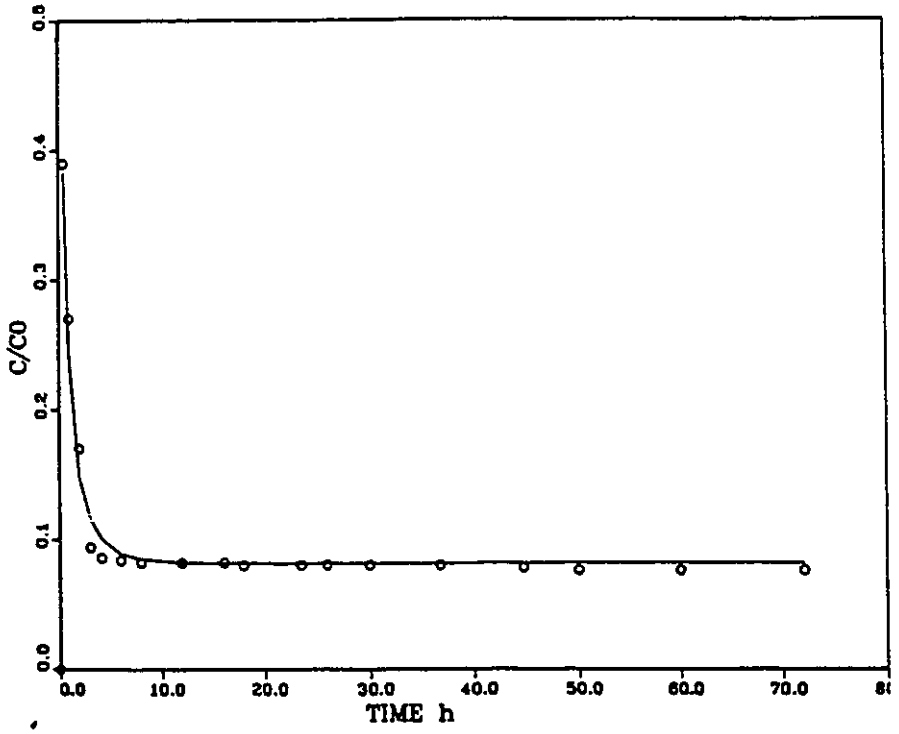
Initial adsorption rate of 2NP on WV-B



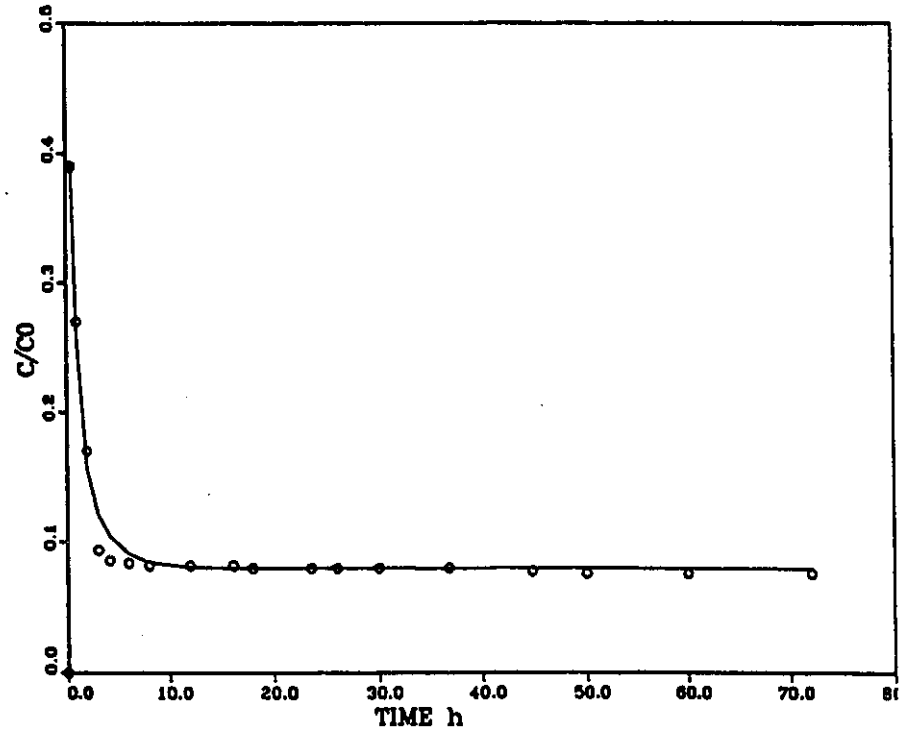
2NP adsorption kinetics on WV-B at pH 1 by the HSSD model



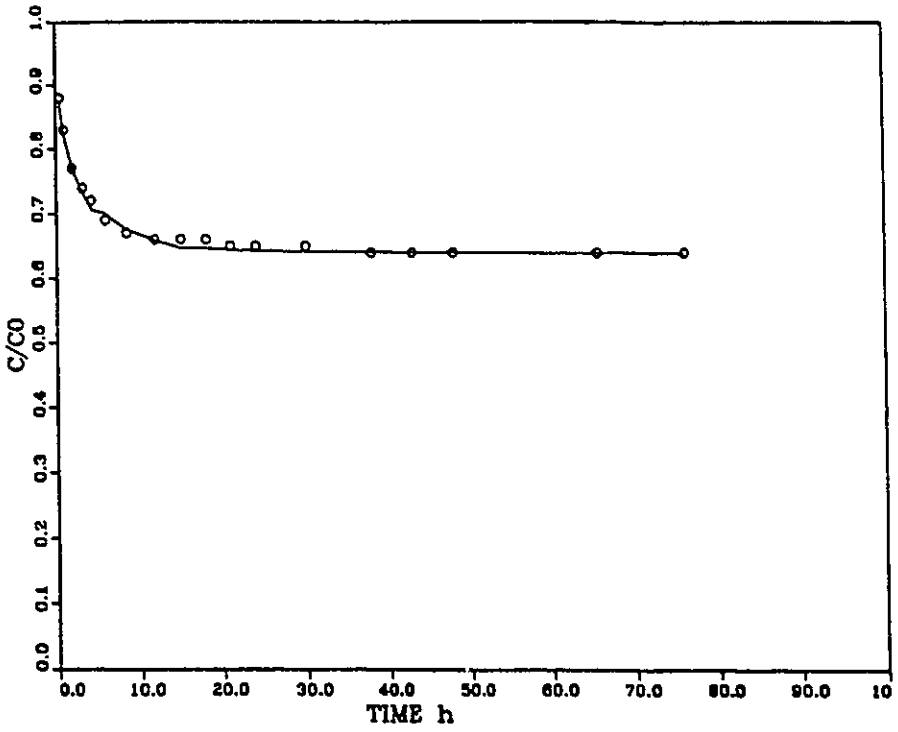
2NP adsorption kinetics on WV-B at pH 1 by the Peel's dual rate model model



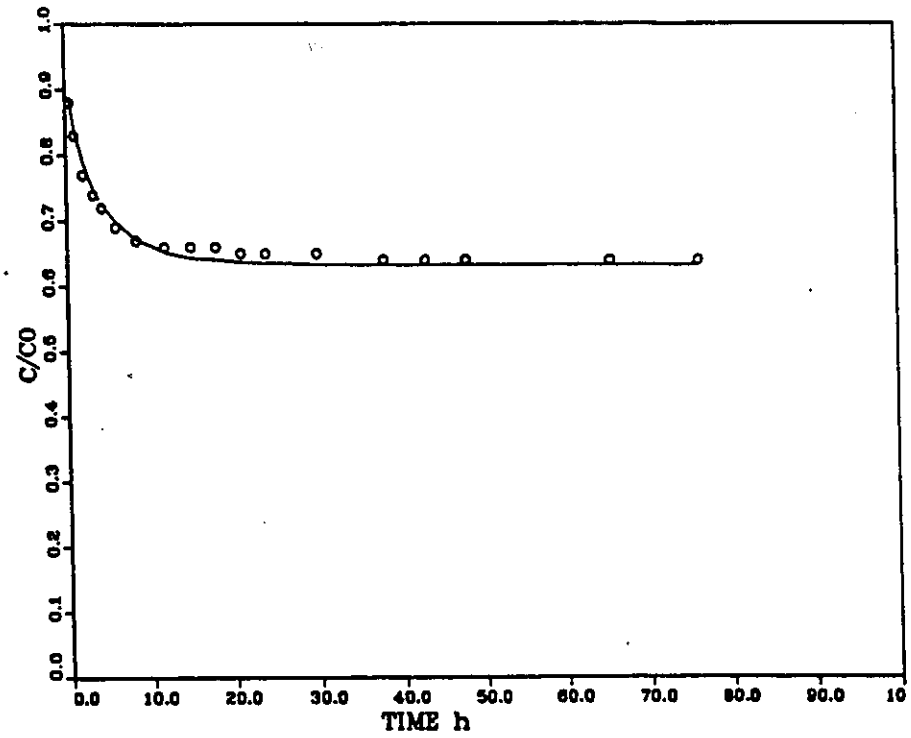
2NP adsorption kinetics on WV-B at pH 4.6 by the HSSD model



2NP adsorption kinetics on WV-B at pH 4.6 by the Peel's dual rate model model

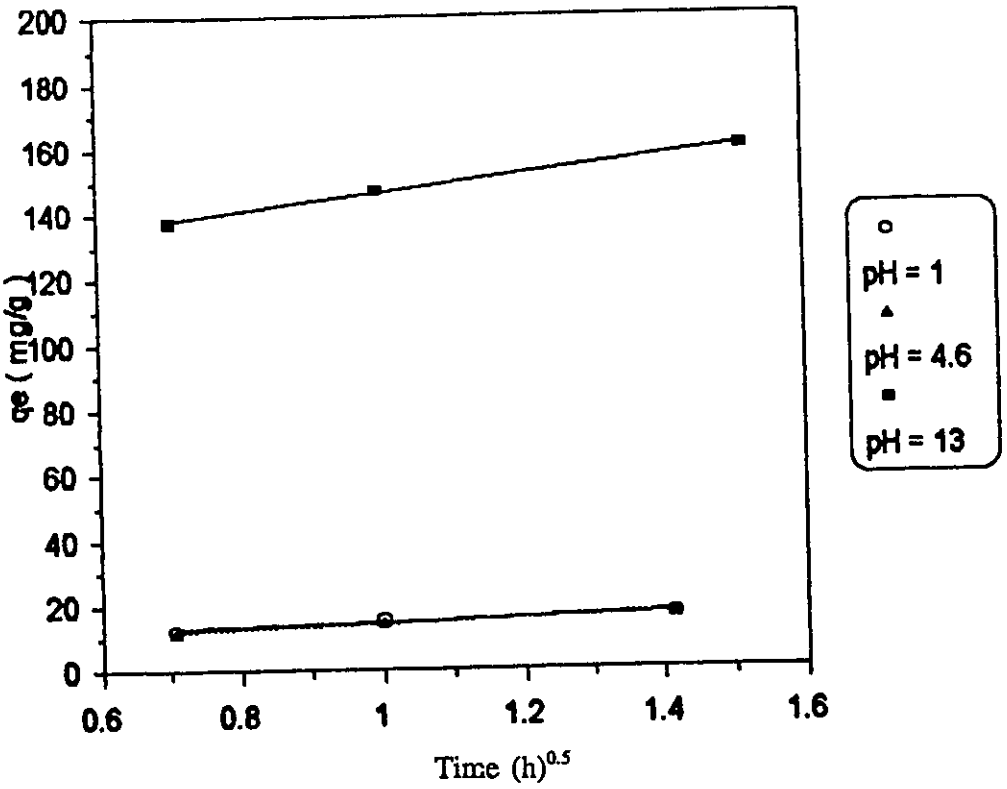


2NP adsorption kinetics on WV-B at pH 13 by the HSSD model



2NP adsorption kinetics on WV-B at pH 13 by the Peel's dual rate model model

APPENDIX H



Initial desorption rate of 2NP from WV-B

Effect of PH on Isotherms of 2-nitrophenol on carbon F400

Co = 500 mg / l

#	Ce(mg)	V (l)	G.A.C.	pH=1 qe(mg/g)	pH=4.6 qe(mg/g)	pH=13 qe(mg/g)
1	5	0.518	1.5	170.94		
2	8	0.535	1.2	219.35		
3	9	0.528	1.2	216.04		
4	15	0.477	1	231.345		
5	21	0.476	0.9	253.3378		
6	24	0.477	0.8	283.815		
7	37	0.477	0.7	315.5014		
8	74	0.536	0.6	380.56		
9	98	0.474	0.5	381.096		
10	155	0.534	0.4	460.575		
12	220	0.534	0.3	498.4		
11	283	0.478	0.2	518.63		
13	283	0.474	0.2	514.29		
14	400	0.536	0.1	536		
20	2	0.536	1.5		177.952	
21	3	0.475	1.2		196.7292	
22	3	0.478	1.2		197.9717	
23	7	0.475	1		234.175	
24	17	0.535	0.9		287.1167	
25	26	0.538	0.8		318.765	
26	36	0.534	0.7		353.9657	
27	40	0.473	0.6		362.6333	
28	85	0.518	0.5		420.94	
29	120	0.476	0.4		452.2	
30	180	0.479	0.3		510.9333	
31	275	0.474	0.2		533.25	
33	275	0.475	0.2		534.375	
32	385	0.478	0.1		549.7	
15	170	0.475	1.5			104.5
16	230	0.518	1.2			116.55
17	237	0.536	1.2			117.4733
18	270	0.519	1			119.37
19	295	0.535	0.9			121.8611
39	310	0.518	0.8			123.025
40	335	0.535	0.7			126.1071
41	350	0.518	0.6			129.5
42	377	0.538	0.5			132.348
43	400	0.533	0.4			133.25
44	415	0.478	0.3			135.4333
45	442	0.477	0.2			138.33
46	442	0.477	0.2			138.33
47	470	0.475	0.1			142.5

APPENDIX K

2NP adsorption isotherm at pH 4.6 and its desorption in Milli-Q water F400

Co = 485 mg/l

#	V (l)	GAC (g)	Ceads (mg/l)	Ce des (mg/l)	qe ads (mg/g)	qe des (mg/g)
3	0.476	1.5	1	1	153.5893	153.272
4	0.535	1.2	4	4	214.4458	212.6625
5	0.538	1.2	4	4	215.6483	213.855
6	0.534	1	9	8	254.184	249.912
7	0.473	0.9	9	9	250.1644	245.4344
8	0.519	0.8	21	17	301.02	289.9913
9	0.474	0.7	24	21	312.1629	297.9429
10	0.479	0.6	40	30	355.2583	331.3083
11	0.475	0.5	65	42	399	359.1
12	0.478	0.4	110	54	448.125	383.595
13	0.476	0.3	170	60	499.8	404.6
14	0.472	0.2	265	54	519.2	391.76
15	0.473	0.2	265	54	520.3	392.59
16	0.473	0.1	370	40	543.95	354.75

APPENDIX L

'Effect of pH on adsorption of 2-nitrophenol on F-400

Bottle	V (l)	Ce(mg/l)	pH	GAC (g)	qe (mg/g)
10	0.534	11	1	1.068	244.5
11	0.478	12	1.01	0.956	244
12	0.534	11	1.02	1.068	244.5
13	0.474	7	4.6	0.948	246.5
14	0.536	7	4.61	1.072	246.5
15	0.475	7	4.62	0.95	246.5
19	0.535	9	7	1.07	245.5
21	0.475	9	7.01	0.95	245.5
23	0.475	9	7.02	0.95	245.5
6	0.477	155	8.5	0.954	172.5
7	0.477	165	8.51	0.954	167.5
4	0.477	160	8.52	0.954	170
27	0.473	240	10	0.946	130
29	0.476	237	10.01	0.952	131.5
29.1	0.476	237	10.02	0.952	131.5
32	0.478	300	13.01	0.956	100
33	0.475	291	13.02	0.95	104.5
31	0.474	285	13.02	0.948	107.5

APPENDIX M

Effect of pH on adsorption of 2-nitrophenol on westvaco carbon

Ci = 500 mg/l

Bottle	V (l)	Ce(mg/l)	PH	G. A. C.(g)	qe(mg/g)
4	0.477	42	1	0.954	229
5	0.476	43	1.01	0.952	228.5
6	0.477	36	1.02	0.954	232
1	0.518	35	4.6	1.036	232.5
2	0.536	36	4.61	1.072	232
3	0.529	35	4.62	1.058	232.5
7	0.477	56	7	0.954	222
8	0.535	56	7.01	1.07	222
9	0.474	63	7.02	0.948	218.5
1	0.518	225	8.5	1.036	137.5
2	0.536	200	8.51	1.072	150
3	0.529	205	8.52	1.058	147.5
10	0.534	313	10	1.068	93.5
11	0.477	310	10.01	0.954	95
12	0.534	306	10.02	1.068	97
13	0.474	366	13	0.948	67
14	0.536	379	13.01	1.072	60.5

APPENDIX N

Effect of pH on desorption of 2NP on F-400

Bottle	Loading at pH = 4.6 Ceads.(mg/	V (l	'GAC (g)	q1 qeads.(mg/g)
18	9	0.519	1.038	245.5
39	8	0.518	1.036	246
41	8	0.518	1.036	246
43	8	0.533	1.066	246
44	9	0.478	0.956	245.5
45	8	0.477	0.954	246
46	8	0.477	0.954	246
47	8	0.475	0.95	246
48	8	0.536	1.072	246
49	8	0.471	0.942	246
50	8	0.534	1.068	246
51	8	0.501	1.002	246
52	8	0.475	0.95	246
53	8	0.498	0.996	246
54	7	0.474	0.948	246.5

'Desorption in buffered Milli-Q water for various pHs

				qedes.(q2)	PH	q1-q2
1	12	0.517	1.038	239.523121387	7	5.976879
2	12	0.535	1.036	239.803088803	7.01	6.196911
41	12	0.518	1.036	240	7.02	6
3	8	0.528	1.066	242.037523452	4.6	3.962477
4	8	0.477	0.956	241.508368201	4.61	3.991632
45	8	0.477	0.954	242	4.62	4
5	13	0.475	0.95	239.5	1	6.5
6	13	0.477	1.072	240.215485075	1.01	5.784515
7	14	0.477	0.942	238.910828025	1.02	7.089172
8	250	0.535	1.068	120.765917603	13	118
9	260	0.474	1.002	123.005988024	13.01	122.994
10	230	0.534	0.95	116.715789474	13.02	129.2842
11	110	0.478	0.996	193.208835341	10	52.79116
12	100	0.534	0.948	189.670886076	10.01	56.32911
13	100	0.474	0.948	196.5	10.02	50

APPENDIX P

'Effect of pH on desorption of 2NP on WV-B

'Loading at pH = 4.6 Bottle :	'Cads(mg/	V (l)	GAC (g	q1 qads (mg/g)
21	33	0.474	0.948	233.5
22	32	0.478	0.956	234
23	31	0.475	0.95	234.5
24	33	0.535	1.07	233.5
25	32	0.538	1.076	234
26	32	0.533	1.066	234
27	31	0.473	0.946	234.5
28	32	0.518	1.036	234
29	32	0.476	0.952	234
30	32	0.477	0.954	234
31	32	0.474	0.948	234
32	32	0.478	0.956	234
33	34	0.475	0.95	233
34	33	0.472	0.944	233.5
35	29	0.473	0.946	235.5

Dsorption in byffered Milli-Q water for various pHs

				q2	q1-q2	PH
14	36	0.536	0.948	213.14556962	20.35443	1
15	34	0.475	0.956	217.106694561	16.89331	1.01
16	34	0.518	0.95	215.961052632	18.53895	1.02
17	27	0.536	1.07	219.974766355	13.52523	4.6
18	28	0.519	1.076	220.494423792	13.50558	4.61
19	27	0.535	1.066	220.44934334	13.55066	4.62
20	40	0.536	0.946	211.83615222	22.66385	7
21	40	0.475	1.036	215.66023166	18.33977	7.01
22	40	0.478	0.952	213.915966387	20.08403	7.02
23	180	0.475	0.954	144.377358491	89.62264	10
39	170	0.519	0.948	140.930379747	93.06962	10.01
40	170	0.536	0.956	138.686192469	95.31381	10.02
43	270	0.533	0.95	81.5157894737	151.4842	13
44	300	0.478	0.944	81.593220339	151.9068	13.01
46	300	0.477	0.946	84.2315010571	160	13.02

2-nitrophenol adsorption kinetics on F400

Bottle	Time (h)	pH=1 Ce(mg/l)	pH=4.6 Ce(mg/g)	pH=13 Ce(mg/g)
	0	500	500	500
76	0.5	280	235	430
77	1	210	145	390
78	2.16	97	55	345
79	3	66	30	330
80	4	46	25	320
81	6	31	16	305
82	8	21	13	295
83	11	19	11	281
85	18	16	10	279
86	23.5	15	9	278
87	28.3	15	8	276
88	34.5	14	7	274
89	42	14	7	270
90	53.8	14	7	268
91	58	14	7	266
92	66.3	13	7	265
93	73	14	7	264
94	84	13	7	262
95	98	13	7	262

APPENDIX R

Adsorption kinetics 2-nitrophenol , Westvaco carbon (

Co = 500 mg/g

Bottle	time(h)	pH=1 Ce(mg/g)	pH=4.6 Ce(mg/g)	pH13 Ce(mg/g)
	0	500	500	500
34	0.5	165	195	440
35	1	120	135	415
36	2	65	85	385
38	3.25	49	47	370
39	4	48	43	360
40	6	47	42	345
41	8.5	46	41	335
42	12	46	41	330
43	15.7	45	41	330
44	19.5	45	40	330
45	23.5	45	40	325
46	28	45	40	325
47	31	44	40	325
48	37	45	40	320
49	42	45	39	320
50	47.5	45	38	320
51	60	45	38	320
52	72	45	38	320

APPENDIX S

Effect of pH on desorption kinetics (2-nitrophenol , F400 carbon)

C0 =		0 mg/l	pH = 1	pH =4.6	pH = 13
Bottle	Time(h)	T^0.5	Ce(mg/g)	Ce(mg/g)	Ce(mg/g)
	0	0	0	0	0
1	0.5	0.707107	4	3	175
2	1.16	1.077033	7	4	195
3	2.16	1.469694	9	5	225
4	3	1.732051	11	6	245
5	3.84	1.959592	11	6	255
16	6.5	2.54951	11	6	255
7	8.5	2.915476	12	7	255
6	12.25	3.5	12	7	255
9	15.16	3.893584	12	7	266
10	18	4.242641	12	7	255
11	24	4.898979	12	7	265
12	30	5.477226	13	7	265
13	36	6	13	7	265
14	42	6.480741	13	7	265
15	48	6.928203	13	7	265

APPENDIX T

Effect of pH on desorption kinetics of 2NP from WV-B

Bottle	time(h)	pH = 1 oe(mg/l)	pH = 4.6 Ce(mg/l)	pH = 13 Ce(mg/l)
1	0.5	25		
2	1	31		
3	2	34		
5	4.75	38		
6	6	39		
7	8	40		
9	19	40		
10	24	41		
11	30	41		
12	36	41		
13	48	41		
	0		0	
40	0.5		24	
41	1		30	
42	2		34	
43	3		35	
44	4		36	
45	7.1		36	
46	5.5		37	
47	18		37	
48	12		37	
49	24		38	
50	30		38	
51	36		38	
52	48		38	
	0			0
61	0.5			275
62	1			295
63	2.3			320
64	3.1			330
65	4.5			335
66	6			340
67	8			345
68	13			350
69	18			350
70	24			350
71	29			355
72	36			355
73	48			355

HPLC file information

F I L E I N F O R M A T I O N

PARAMETER FILE
Param. File Name METHOD:PHK.A
Last Change Date 1 Dec 92 12:04 pm

Information : PHENOL SEPARATION (GRADIENT).
Last Altered By : KAREN LAMB

DATA FILE
Data File Name DATA:JN15B00A.D

Operator Name :
Sample Name : WATER
Further Comments :

L I Q U I D C H R O M A T O G R A P H initial parameters

Flow :	0.300 ml/min		
Solvent A :	40.0 % HPLC Methanol pH 4.7		
B :	0.0 % MQW		
C1 :	60.0 % Na acetate 0.05M pH 4.7	: narrow	
Oven Temperature :	40.0 C		
Max Pressure :	300 bar	Min Pressure :	off
Stop Time :	26.00 min		
Post Time :	6.00 min	Contacts :	0000
Injection Volume :	25.0 ul	Slowdown :	2

L I Q U I D C H R O M A T O G R A P H timetable

Time (min)							
12.00	Solvent	A:	80.0 %	B:	0.0 %	C1:	20.0 %
13.00	Solvent	A:	90.0 %	B:	0.0 %	C1:	10.0 %
18.00	Solvent	A:	90.0 %	B:	0.0 %	C1:	10.0 %
20.00	Solvent	A:	40.0 %	B:	0.0 %	C1:	60.0 %

I N J E C T O R P R O G R A M

Slowdown Draw & Eject :	2
Mix :	2
Hold after Draw & Eject :	0

0.0 ul accumulated in Syringe with Line# 0

Line#	Function
1	Inject

D I O D E - A R R A Y D E T E C T O R signals & spectra

SIGNALS	A	B	C	D	E	F	G	H
Sample (nm)								
Wavelength :	268	off	off	off	off	off	off	off
Bandwidth :	4							
Reference (nm)								
Wavelength :	550							
Bandwidth :	100							

Store Spectrum : peak controlled about 2656 Records acquired during Run
Threshold : 0.1 mAU

Peakwidth :	0.070 min
Stop Time :	20.00 min
Post Time :	0.10 min
Prerun Balance :	Yes

Sampling Interval	320 ms
Spectrum Range from :	210 nm
to :	400 nm
step :	2 nm