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ELECTROCHEMICAL REGENERATION OF GRANULAR ACTIVATED CARBON

by

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under the Supervision of Dr. R. M. Narbaitz

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ABSTRACT

Laboratory experiments have investigated the feasibility of granular activated carbon (GAC) regeneration via an electrochemical technique. GAC was loaded with phenol by batch adsorption tests, electrochemically regenerated and finally reloaded with phenol. Regeneration was conducted by placing GAC on a platinum electrode within a batch reactor filled with electrolyte (generally a 1% NaCl solution), and applying a current to the reactor. Limited experiments show that cathodic regeneration is more efficient than anodic regeneration; the investigation concentrates on the former. Although anodic regeneration is more efficient in destroying residual phenol in the electrolyte, cathodic regeneration can also eliminate these residuals by using longer regeneration times and/or higher currents.

Increasing the regeneration current and time could increase the regeneration efficiency (RE) up to 94 percent. Lower currents applied for longer regeneration times yield similar results with slightly lower energy consumption. REs are also significantly affected by the electrolyte type, electrolyte concentration, and GAC particle size, but not by the carbon loading. Multiple regenerations only reduce the REs by an additional 2 percent per cycle. Preliminary analysis indicates that electrochemical regeneration is less expensive than thermal regeneration as it has no obvious carbon losses. Since this electrochemical regeneration process is technologically feasible and probably more economical than thermal regeneration, it merits further investigation.

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Two forms of activated carbon, granular and powdered, have been used in controlling taste and odor problems in drinking water for the past fifty years. Activated carbon has received more attention in recent years due to its capacity to remove toxic and synthetic organic compounds and disinfection by-products from water. Powdered activated carbon (PAC) is a more suitable adsorbent for contact processes. The major advantages of PAC are its rapid adsorption kinetics, its low investment cost and the possibility of easily adjusting carbon dose to match the requirements of varying contaminant type and concentration. Granular activated carbon (GAC) has been chosen as an adsorbent in packed beds because of some inherent advantages over PAC contact processes. These include higher percentage of contaminant removals, lower carbon usage rates for multiple applications and easier regeneration of the spent carbon. Moreover, the sludge disposal problems associated with PAC and the possibility of GAC reuse have favoured the application of GAC. The United States Environmental Protection Agency (USEPA) has thus designated GAC adsorption as the "best available technology" for treating a variety of synthetic organic chemicals being regulated under the 1986 amendments to the U.S. Safe Drinking Water Act (Oxenford and Lykins, 1991).

A major drawback of activated carbon adsorption technology has been the high cost

of GAC and its regeneration. This has prevented it from being applied more widely in the water treatment industry. Carbon regeneration or replacement costs may represent up to 50% of the total expenditure of GAC treatment systems. The cost can be significantly reduced by regenerating spent GAC rather than replacing it with virgin carbon (Adams and Clark, 1989; Adams *et al.*, 1988; Clark and Lykins, 1989).

Regeneration techniques fall into three categories: thermal, chemical, and biological regenerations. At present, thermal regeneration is used almost exclusively in water and wastewater treatment applications. It involves gradually heating the GAC up to 800°C in furnaces with an oxygen deficient atmosphere. This causes the adsorbed impurities to volatilize and desorb without burning the GAC. The high temperature also oxidizes some of the desorbed contaminants. This process has always resulted in regeneration efficiencies greater than 90%. However, the process is characterized both by the loss of carbon (perhaps 5-10% during each cycle) due to oxidation and attrition, and by the high energy cost of heating the GAC to 800-850°C (Clark and Lykins, 1989). Usually a minimum activated carbon usage of 680 kg/day is needed before the capital cost of an on-site regeneration facility can be justified. At present, there are no commercial carbon regeneration facilities available in Canada and the loaded carbon is either sent to regeneration facilities in the US or discarded in landfills where the captured organics may be released, contaminating ground water.

Chemical and biological regeneration processes have not been sufficiently successful to warrant commercial applications. Recent electrochemical oxidation studies using carbonaceous electrodes have raised the possibility of regenerating GAC by making it part of the electrodes of an electrochemical reactor.

1.2 Aim and Objectives

The aim of this thesis is to investigate the technical feasibility of electrochemical regeneration of GAC. Electrochemical regeneration of loaded GAC is expected to destroy adsorbed organic pollutant molecules instead of simply transferring them to another phase. The specific objectives of the thesis are:

1) To determine the main factors affecting the efficiency of GAC regeneration. Key variables in the process include GAC location, regeneration current, regeneration time, electrolyte concentration, electrolyte type, carbon particle size, and mass of contaminant on GAC. Their influences on the regeneration process will be evaluated in terms of regeneration efficiency.

2) To determine long-term feasibility of this electrochemical regeneration process by conducting experiments of multiple adsorption, regeneration and readsorption cycles.

3) To compare the operating energy consumption between thermal regeneration and electrochemical regeneration.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Since the 1950's, there has been an increase in the use of synthetic organic chemical (SOCs) and an increase in the sensitivity of analytical methods for detecting them in waters. The detection of SOCs in drinking water has been of great concern because many SOCs are carcinogens or suspected carcinogens. Activated carbon adsorption has emerged as a very important technology as it is one of the most effective methods of removing them from drinking water and wastewater. Numerous studies on water purification have been carried out, but this literature review is focused upon those pertinent to GAC adsorption equilibria and regeneration.

2.2 Adsorption Equilibria

Adsorption from aqueous solutions involves accumulation of contaminants (or adsorbates) on the solid surface of a material, called the adsorbent. Adsorption occurs initially at a rapid rate and then decreases with time. As the adsorption process proceeds, some of the adsorbed contaminants may be desorbed into solution. Equal amounts of contaminant are eventually adsorbed and desorbed simultaneously, and this leads to the formation of an adsorption equilibrium state. The quantity of contaminant adsorbed onto a unit mass of GAC is defined as the adsorptive capacity of GAC. The adsorption

equilibrium depends upon a number of factors such as adsorbent, adsorbate (contaminant), temperature, and pH.

2.2.1 Adsorption isotherm

Adsorptive capacity of activated carbon is usually measured utilizing adsorption equilibrium tests conducted at a constant temperature (e.g. isotherm tests). Experiments are performed by contacting the solution of interest in a series of bottles with different masses of activated carbon (adsorbent), until the equilibrium is reached. The carbon and solution are then separated. The solution is called the "equilibrium liquid phase concentration" (C_e). The amount of contaminant adsorbed per unit mass of activated carbon, namely the "solid phase concentration (i.e. adsorptive capacity)" (q_e), can be calculated by a mass balance formula:

$$q_e = \frac{(C_o - C_e) \cdot V}{M} \qquad (2.1)$$

where C_o is initial liquid phase concentration (mg/l), V is volume of contaminant solution (l), and M is mass of activated carbon (g).

Graphs of the equilibrium solid phase concentration as a function of the equilibrium liquid phase concentration are also termed the "adsorption isotherms". Figure 2.1 shows a typical adsorption isotherm. Adsorbed quantities at the equilibrium usually increase with solution concentration. As each bottle in the above experiment yields one point on the adsorption isotherm graphs, it is frequently called the bottle-point technique.

The results of isotherm experiments yield curves of many different shapes. Most isotherms are described by using the Freundlich Model, the Langmuir Model and the BET

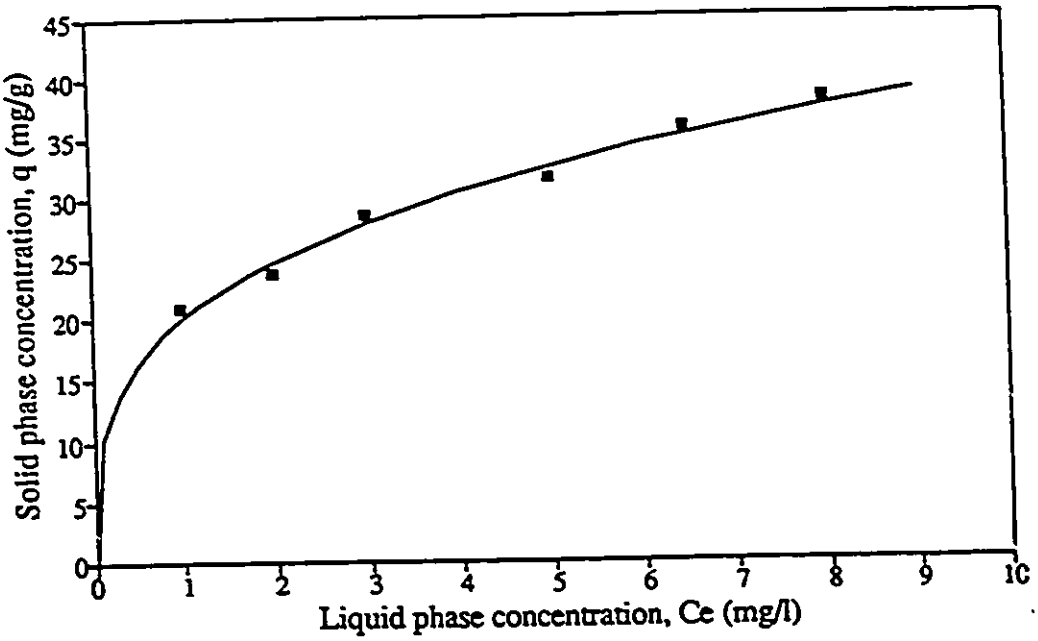


Figure 2.1 Typical isotherm graph.

Model. The Freundlich Model and its modifications have been found to best describe the adsorption of most contaminants from water. This empirical model is:

$$q_e = KC_e^{1/n} \tag{2.2}$$

where K and 1/n are Freundlich coefficients. This model corresponds to a heterogeneous adsorbent with adsorption sites that have different energy levels.

2.2.2 Factors affecting adsorption equilibrium

The adsorption of organic chemicals is controlled by a number of factors such as properties of the chemicals, type of activated carbon, pH, temperature, presence or absence of oxygen (e.g. Peel and Benedek, 1980; Randtke and Snoeyink, 1983; Vidic *et al.*, 1990). For water treatment, several types of activated carbon are suitable for use. They include those manufactured from coconut shells, peat, sawdust, wood char, lignin, petroleum coke, bone char, anthracite coal, and molasses (Faust and Aly, 1987). Some of these materials yield products of a unique porous nature that makes them suitable for specialized applications. For example, high-density coconut shells produce a carbon with a considerably finer pore size distribution and a greater apparent density than those produced from paper mill waste (Hassler, 1974). Thus, this carbon is preferred for applications such as gas adsorption and is less suitable for wastewater treatment because of the fine pores. Coal-based and lignite-based activated carbon have significant pore volumes in the transitional pore range permitting ready access of liquids to the micropore structure, resulting in rapid attainment of adsorption equilibrium for smaller molecular adsorbates. In addition, accessibility to the internal pore structure improves subsequent adsorption for

larger molecules and colloidal substances. During the manufacture of GAC, fluctuations in some variables influencing the process may cause variations in quality among batches of any type of GAC. Fortunately, manufacturers produce various grades of GAC, and the quality of each grade falls within a set of specifications established by the manufacturer, thereby limiting variation among batches of a given grade.

Most researchers employ varying experimental procedures to collect isotherm data. These procedures differ in carbon preparation, particle size, buffer application, temperature and equilibration time allowed. As a result, many different isotherms for the same compound and the same activated carbon have been reported in literature. Peel and Benedek (1980) have found that this is attributed to difficulties defining the attainment of true equilibrium. GAC takes up to a month to reach equilibrium while only 3 to 5 days are required for PAC. The equilibrium time is also dependent on the type of adsorbates. For adsorbing humics, more than a week may be necessary, even for PAC. Peel and Benedek (1980) also reported that particle size, the presence or absence of a weak buffer and the initial concentration of adsorbate had no effect on the equilibrium relationship for phenol and *o*-chlorophenol. This conclusion was supported by data from several other investigators (e.g. Martin and Al-Bahrani, 1978; Randtke and Snoeyink, 1983). But some researchers noticed that some of these variables did have certain impact on the adsorption isotherms (e.g. Weber and Morris, 1964; Crittenden and Weber, 1978; van Vliet *et al.* 1980). The following discussion focuses on the impact of particle size, pH, temperature and the presence or absence of molecular oxygen on the adsorption isotherms.

2.2.2.1 Particle size

Activated carbons have a surface area ranging between 400 and 1,800 m^2/g or more. When GAC is crushed to a powder, the internal surface area and pore diameters will remain the same. The increase in the outer surface area represents less than 1 percent of the total surface area, and thus this outer area plays an insignificant part in the equilibrium adsorption capacity. Consequently, the equilibrium capacity for an adsorbate should be independent of the adsorbent's particle sizes. This has been proven by many studies (e.g. Peel and Benedek, 1980; Martin and Al-Bahrani, 1978). The few exceptions can be explained either by a) the accompanying reduction of large pores critical for the adsorption of large molecular adsorbates; b) insufficient contact time to reach equilibrium with the GAC; or c) uneven activation of the GAC particles. Randtke and Snoeyink (1983) have reported that GAC exhibited almost no difference in activity with particle size for a low-molecular-weight adsorbate, such as *p*-nitrophenol. It exhibited some difference for high-molecular-weight adsorbates, however, such as peat fulvic acid, because of differences in pore-size distribution (Randtke and Snoeyink, 1983). Weber and Morris (1964) point out a decrease in adsorptive capacity with increasing particle size, and they argue that, this is because the rate of saturation of large particles is much slower than that of small particles. Tests that do not allow enough time for the entire particles to reach equilibrium with the bulk solution will show that the small particles have higher adsorptive capacities. Activation conditions may be such that the inner cores of larger particles are not completely activated, resulting in a decrease in adsorptive capacity with increasing particle size. If unevenly activated GAC particles are ground and sieved to obtain PAC, the adsorption capacity of the PAC will be dependent on the location of the GAC particles from which it

originates. For example, if the PAC originates from the partially activated GAC particle core, it can have a lower adsorptive capacity than the unground GAC (Narbaitz, 1986).

As adsorption on the particles is a diffusion-limited process and the rate of adsorption is inversely proportional to the square of the particle diameter, small particles adsorb contaminants more quickly and reach equilibrium much faster than large ones.

2.2.2.2 Temperature

The effect of temperature on adsorption isotherms has been investigated by a number of researchers (e.g. Snoeyink *et al.*, 1969; Weber, 1972; Zogorski and Faust, 1978). Weber (1972) reported that the adsorptive capacity increased with decreasing temperature. The same phenomenon was also found by Zogorski and Faust (1978) (Figure 2.2). However, the influence of temperature on the adsorption process was reduced when phenol content was 200 µmol/l or higher. Snoeyink *et al.* (1969) states that the influence of temperature (11, 25, and 37°C) on phenol adsorption is insignificant in the range of 100 to 1000 µmol/l.

Usually, the adsorption process is a combination of physical adsorption and chemisorption. If the major adsorption mechanism is chemisorption, it frequently results in irreversible adsorption. If the adsorption of a compound is reversible, it is then considered to be physical adsorption. The extent of physical adsorption decreases with increasing temperature.

As a diffusion-limited process, the rate of adsorption of the organic from solution increases as the temperature of the system is increased. Zogorski *et al.* (1976) show that raising the temperature from 10 to 30°C increases the removal rate of phenol and 2,4-

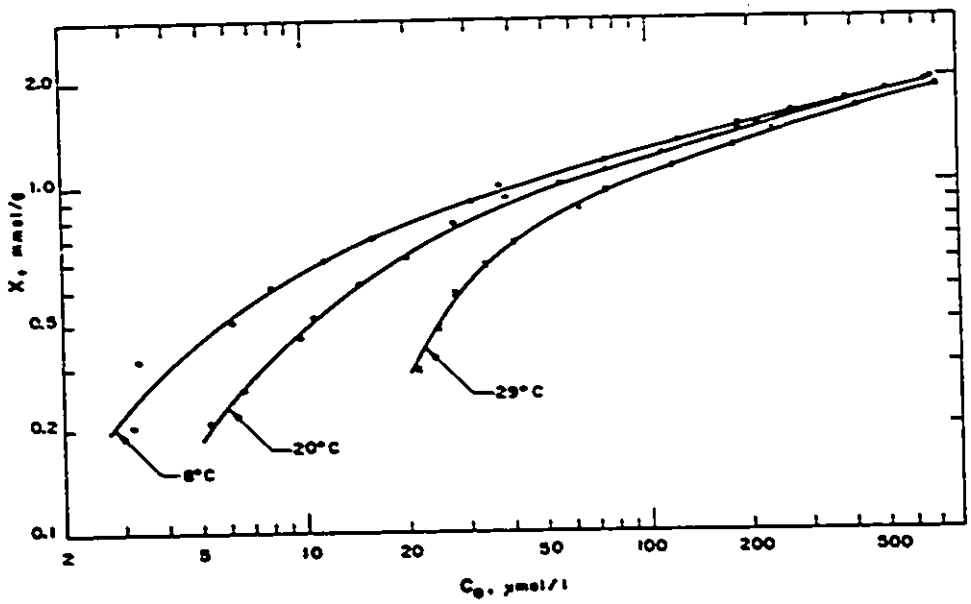


Figure 2.2 Influence of temperature on the adsorption of phenol at pH 6.3 (source: Zogorski and Faust, 1978).

dichlorophenol by 21% and 28%, respectively. The decrease in equilibrium adsorptive capacity due to the increase in temperature is offset by the increased rate of adsorption. Thus, the temperature does not have a significant effect on the overall pollutant removal efficiency of activated carbon. According to Weber (1972), normal temperature variations have only minor effects on activated carbon adsorption processes at water treatment plants.

2.2.2.3 pH

Adsorption is influenced by pH in a number of ways (Weber, 1972). First, H^+ and OH^- are adsorbed quite strongly and this in turn affects the adsorption of other ions in solution. Second, compounds that ionize are affected because the un-ionized and the different ionized species of a compound are adsorbed differently. As shown by Zogorski and Faust (1978), the adsorptive capacity of phenolics increases slightly or remains constant with increasing pH up to the acidity equilibrium constant pK_a, then decreases substantially as the pH increases further (Figure 2.3). Finally, the carbon activation process and the activation temperature in particular, affect the capacity of the product to adsorb acids and bases.

The adsorption of phenol, selected as an adsorbate in this study, is affected by pH. Snoeyink *et. al.* (1969) conducted phenol adsorption isotherms for a coconut-shell based carbon (Columbia, LC Grade) at pH values of 2.0, 5.6, 7.5, and 10.6 (Figure 2.4). A summary of this plot, plus additional data points at pH 4.0 and 10.0, are listed in Table 2.1. Results showed that the highest adsorptive capacity was obtained at pH 7.5. Since the Pk_a of phenol is 9.89, the principal adsorbing species above this pH is anionic, and a reduction in the extent of adsorption is expected. The repulsive forces between the

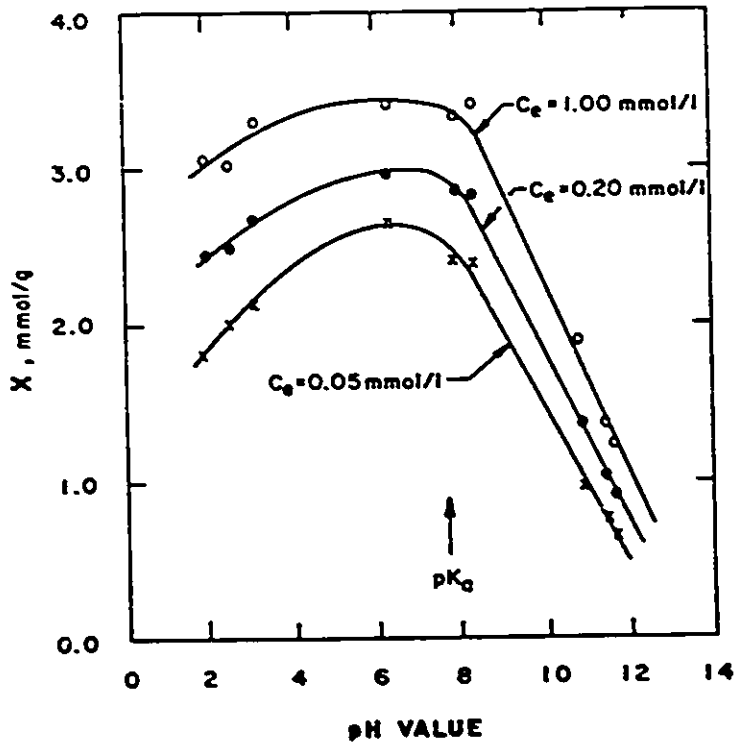


Figure 2.3 Effect of pH on the adsorption of 2,4-dichlorophenol on GAC (Columbia, LCK) (source: Zogorski and Faust, 1978).

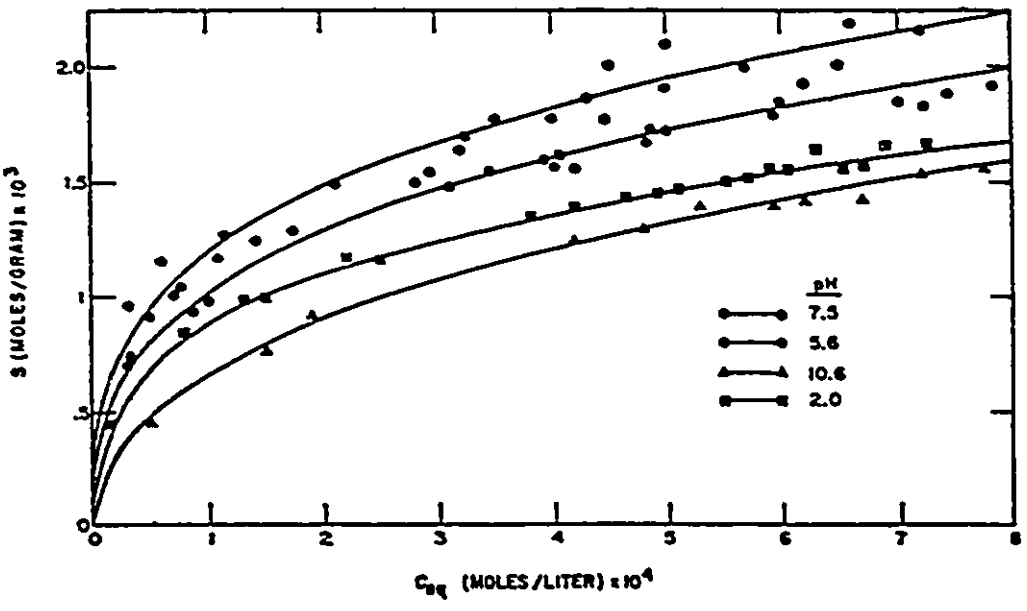


Figure 2.4 Isotherms for phenol at different pH on coconut-shell based GAC (Columbia, LC Grade) (source: Snoeyink *et al.*, 1969).

Table 2.1. Effect of pH on the adsorption of phenol on GAC (Columbia, LC Grade) (from Snoeyink *et al.*, 1969).

pH	q (moles/gram)x10^3 ($C_{eq} = 7x10^{-4}M$)
2.0	1.67
4.0	1.88
5.6	1.93
7.5	2.15
10.0	1.75
10.6	1.50

adsorbate anion and the carbon surface, and those between the adsorbate species themselves, would tend to cause such decreases. However, the reason for the observed reduction in quantity adsorbed with decreasing pH below pH 7.5 is unclear. Apparently, the nature of carbon surface is altered to some degree by the acid used for pH adjustment. The decrease in capacity for phenol with decreasing pH can be explained partly by the competitive effect of the increased quantity of acid adsorbed with decreasing pH. According to the results of Mattson *et al.* (1969), the adsorption of phenol on activated carbon surfaces occurs at carbonyl oxygen sites. It is reasonable to expect that protons would interact competitively with carbonyl oxygen to reduce phenol adsorption, as pH decreases.

2.2.2.4 Molecular oxygen

Recently, Vidic *et al.* (1990) and Vidic and Suidan (1991) report significant increases in GAC adsorptive capacity of phenol, *o*-cresol, and 3-ethylphenol, as well as natural organic matter, as a result of the presence of molecular oxygen in the test environment (aerobic conditions). Experimental data have shown that this increase in capacity cannot be attributed to biological degradation of these adsorbates. It is speculated, that this phenomenon is due to the polymerization of adsorbate on the carbon surface in the presence of molecular oxygen. However, the adsorptive capacity of GAC for aliphatic organic compounds, such as trichloroethylene, and 2-,3-,4-nitrophenol is not significantly influenced by the presence of molecular oxygen (Vidic and Suidan, 1991; Vidic *et al.*, 1993). Sorial *et al.* (1993) suggest that for *p*-chlorophenol the presence of molecular oxygen can cause an increase in the adsorptive capacity of activated carbon manufactured

from bituminous coal and lignite coal. One wood-base carbon shows no effect of molecular oxygen on the adsorption behaviour.

2.3 Previous Studies on Activated Carbon Regeneration

Although the internal pore structure of activated carbon particles provides a very high surface area, this surface area is finite and eventually becomes covered with adsorbate. Adsorption, which is a surface phenomenon, ceases at this stage. When GAC becomes exhausted or when the effluent from a GAC bed or column reaches the maximum allowable discharge level, the GAC must be replaced by fresh or regenerated GAC. The life of GAC used in water treatment plants for taste and odor removal is in the range of 3 to 5 years. However, for other applications such as the removal of disinfection by-products, the on-stream life of activated carbon beds could be reduced to 3 to 6 months (Schuliger *et al.*, 1987). In this situation, the economics could be very favourable for on-site regeneration. The adsorption capacity of spent GAC can be regenerated by thermal, chemical, or biological techniques. This section provides a brief review of previous studies on activated carbon regeneration.

2.3.1 Thermal regeneration

Thermal regeneration of GAC has been a standard process in the United States since the early 1950's. The process is also used extensively world-wide for reactivating GAC used in the treatment of potable water. It is the most exclusive regeneration method used in water applications.

The thermal regeneration process itself involves three steps: drying, baking

(pyrolysis of adsorbates) and activating (oxidation of the residue from the adsorbate). As spent wet carbon enters a furnace, it is heated to less than 100°C and dried during the first step. During baking, the temperature increases from 100 to 815°C, at which the adsorbed organics are thoroughly carbonized. This is accompanied by both the evolution of gases and the formation of a carbon residue in the micropores of the activated carbon. The objective of the regenerating step is to oxidize the carbon residue with minimum damage to the basic pore structure, thereby maximizing the restoration of the GAC's original properties. Activating gas temperature during this step is about 927°C (1700°F), while the carbon temperatures range from 815 to 900°C. Flue gas supplemented by varying amounts of additional steam and limited oxygen produces the desired oxidizing atmosphere (U.S. Environmental Protection Agency, 1973).

The most important phase of the regeneration process is the activation, with the critical parameters being carbon temperature, duration of activation, and steam or carbon dioxide concentration in the activating gas mixture. If the temperature increase (controlled by heat input) is too fast for a given time of regeneration, the process will cause an attack to the base GAC, which can result in enlarged pores and reduced adsorptive capacity because of the reduction in the surface area. On the other hand, too slow of a temperature increase for a given regeneration time will result in regeneration furnaces that are larger than necessary and possibly in failure to remove all of the adsorbate. This can also cause reduced adsorptive capacity because of the inaccessibility of partially filled pores.

Studies of thermal regeneration have focused on the optimum conditions to restore the maximum GAC capacity and to retain, as much as possible, the original pore structure. Several researchers have shown that the time and temperature of regeneration (activation

rate) can be adjusted to control the capacity. Jüntgen (1976) stated that a GAC loaded with phenol could be regenerated repeatedly with no decrease in capacity if an optimum time of regeneration was chosen. Chihara *et al.* (1982) found an optimum regeneration time for the recovery of sucrose adsorption capacity, which yielded a GAC with a capacity almost equal to virgin carbon (98.5%) for the first cycle, but decreasing slightly with each successive cycle. Cairo *et al.* (1982) observed a regenerated GAC capacity close to virgin carbon for methyl ethyl ketone (MEK) and n-butanol probes at 850°C during laboratory studies. By comparison, regeneration of GAC at 962°C resulted in a lower overall capacity. van Vliet and Venter (1984) were able to restore only 70 percent of the virgin micropore volume (on a unit bed volume basis) after the fourth regeneration cycle. This spent GAC came from a GAC contactor treating secondary effluent. The optimum regeneration conditions were 8-minute oxidation at 800°C in an infrared furnace.

Waer *et al.* (1992) have investigated fluidized-bed regeneration to determine the effects of regeneration temperature and time on volume losses and recovery of adsorptive capacity. The results indicated that for coal-based GAC loaded with naturally occurring organic material and methylene blue, GAC capacity was returned to that of virgin carbon at a temperature of 850°C in 15 minutes. Shorter time and lower temperatures resulted in a loss of adsorptive capacity. Longer times resulted in increased capacity for large molecules but the same or reduced capacity for small adsorbates. This is consistent with the results of Juhola (1970), which suggest that volume losses are due to submicron particles breaking off the particle exterior rather than the result of oxidation.

Juhola (1970) was the first to find evidence that the accumulation of inorganics on GAC used in tertiary wastewater treatment caused increased mass losses during

regeneration under constant oxidizing conditions. An analysis of GAC ash indicated accumulation of calcium, magnesium, potassium, sodium, iron, and chromium on GAC during loading process. Cannon *et al.* (1993) studied the impact of several thermal regeneration strategies on GAC that had been in service nearly four years in a water treatment plant. This GAC (F-200) contained 2 percent calcium. When calcium appeared inside the spent GAC, it always caused micropores to be converted to small mesopores during thermal oxidation. Pyrolysis of this spent GAC at 850°C created a product that had 6 percent fewer micropores, 13 percent more mesopores, and the same surface area as a virgin GAC F-200. It caused 14-16 percent mass loss and 3-4 percent bed volume loss. When this pyrolyzed spent GAC received 2-3 minutes of steam oxidation at 850°C, the regenerated GAC became nearly identical to virgin GAC F-400. It had almost the same amount of GAC loss as that without steam. Low temperature (below 750°C) with both steam and CO_2 caused lower volumes of small pore and lower surface areas.

In contrast, when the calcium was leached out of the spent GAC with acid, thermal oxidation only increased the micropore volume. However, acid-washed spent GAC exhibited far lower oxidation reaction rates than spent GAC which had not been acid-washed. It has been suggested that the slight improvement cannot justify the added nuisance and expense incurred by employing an acid-washing step before regenerating coal-based GACs that contain < 2% calcium (Cannon *et al.*, 1993).

Knappe *et al.* (1992) also studied the effect of calcium on thermal regeneration of GAC. They found that the presence of internally loaded Ca (0.03% to 4.1%) greatly increased regeneration mass losses (≈ 35%) compared with non-Ca-loaded GAC (≈ 11%) when samples were regenerated under the same conditions. These increased mass losses

resulted not only in a reduction of micropore volume, BET surface area, and iodine number but also in an increase of macropore volume. Regenerating GAC at 850°C with steam alone performed better than regeneration with both steam and CO_2 because the milder regeneration conditions without CO_2 were less destructive to the GAC structure. Regeneration at 850°C plus CO_2 increased the mass losses with increasing Ca loading. At a regeneration temperature of 750°C, CO_2 addition resulted in negligible reductions of micropore volume, BET surface area, and iodine number in the presence of Ca. Therefore, regeneration of GAC can be performed at a lower temperature in the presence of Ca if the accumulation of ash in the regenerated product does not affect capacity.

The main disadvantages of the thermal regeneration are: a) the loss of carbon (5-10% per cycle) due to oxidation and attrition; and b) the energy cost of heating the GAC to approximately 800°C. Table 2.2 shows the in-furnace and total mass losses for five regeneration facilities and one regional regeneration (sharing of a regeneration furnace among three small users to minimize the regeneration cost). The transport loss is fairly constant at 2-3 percent, although Schuliger and MacCrum (1974) have reported a much higher transport loss. Kornegay (1987) presented information on procedures to minimize transport losses. In-furnace losses vary widely. The highest carbon losses for the Connecticut Water Company are attributed to the type of carbon used. Because the lignite-based carbon is softer than coal-based, abrasion losses are suspected to be greater with this material. The lost GAC needs to be replaced with virgin GAC. Clark and Lykins (1989) have shown that the cost of purchasing replacement GAC can be up to four times greater than the energy costs for thermal regeneration systems.

A third disadvantage of thermal regeneration is the very high unit costs associated

Table 2.2 In-furnace and total GAC losses for five regeneration facilities for water treatment applications (data source: Lykins, 1987; Clark and Lykins 1989; Gammie and Giesbrecht, 1986).

Location	Facility (lb/d)	In-furnace loss (%)	Total loss (%)	GAC type	Type of furnace
Cincinnati, Ohio	500	12.2	15.3	Coal-based	Fluid bed
Manchester, N.H.	500	10.9	12.9	Coal-based	Fluid bed
Jefferson Parish, La.	215	7.0	9.0	Coal-based	Infrared
Evansville, Ind.	100	5.0	8.0	Lignite-based	Infrared
Manchester, N.H. serving:					
Connecticut water company	500		23.5	Lignite-based	Fluid bed
Danvers, Mass.	regional		11.5	Coal-based	
Lowell, Mass.			15.3	Coal-based	
Regina, Saskatchewan	14,000		6.5	Coal-based	Fluid bed

with small facilities and their operations. When spent carbon requirements are <1,500 lb/d (680 kg/d), the on-site regeneration alternative is not cost effective. Thus, replacement of spent carbon with virgin is recommended (Adams and Clark, 1989).

2.3.2 Chemical regeneration

Chemical regeneration has been used primarily in industrial systems designed to recover adsorbates. The basis of which is that organic adsorbates can be partially desorbed from GAC by conventional liquid solvents (e.g. Hassler, 1967; Modell *et al.*, 1980). The chemical regeneration of spent GAC can be achieved by two main categories of substances: inorganic chemical regenerants with oxidizing powers and organic chemical regenerants with solubilising powers.

Using GAC adsorbed with tertiary sewage effluent, Johnson *et al.* (1964) investigated nine inorganic oxidizing agents and his results indicated that the most effective regenerant was a 3% hydrogen peroxide solution with 71% adsorptive capacity recovery. In the next adsorption-regeneration cycle, the recovery was reduced to 47%. For the third cycle, the recovery fell further to 20%. Some of the other reagents evaluated were moderately successful for the first adsorption-regeneration cycle, namely, Sodium dichromate (61%), sodium peroxide (60%), sodium persulphate (55%) and potassium persulphate (49%). However, their percentages of regeneration tailed off considerably to 20% or less for the second cycle; zero recovery was achieved for the third cycle. Chlorine water, bromine water, potassium permanganate and ozone water were found to have very limited carbon-regenerating powers. Distilled water was found to induce some desorption (regeneration) but the recovery was less than 5%.

Sodium hydroxide has been used as a reactive chemical in the regeneration of GAC used for treatment of phenolic brine from the Dow phenol plant in Midland, Mich (Himmelstein *et al.*, 1973; and Fox *et al.*, 1970). This system was operated for more than 100 adsorption-regeneration cycles over a two-year period. The spent GAC is contacted with a 4% aqueous solution of sodium hydroxide. 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. The regenerant need not be treated further because the caustic soda-sodium phenate solution is suitable for recycle to the phenol plant as a raw material and the residual caustic is a component in the production of phenol. This particular situation makes the system commercially effective. The regeneration powers of NaOH have also been demonstrated by Goto *et al.* (1986) and Newcombe and Drikas (1993). Goto and coworkers found that the total amount of sodium phenate desorbed from GAC was only 70% of adsorbed phenol and adsorptive capacity of GAC gradually decreased during the repetition process.

Modell *et al.* (1980) have evaluated the use of supercritical carbon dioxide in the regeneration of carbon. Fluids above their critical temperatures and pressures exhibit good solubilising powers (a property of liquid solvents, but not of gases) and favourable mass transfer properties for rapid desorption (a property of a gas phase, but much less so for a liquid phase). Using very small amount of activated carbon exhausted with phenol, supercritical carbon dioxide was applied to recover over 80% of the virgin carbon capacity. Repeated cycles of exhaustion and regeneration indicated that this level of recovery could be maintained. Studies by deFilippi *et al.* (1980) and Picht *et al.* (1982) demonstrate that supercritical carbon dioxide can effectively regenerate activated carbon loaded with a broad

range of organic compounds and the regeneration method can favourably influence the economics of the carbon used as an adsorbent. Tan and Liou (1989) also report that the adsorptive capacity of regenerated activated carbon loaded with toluene is close to that of the virgin carbon and remains stable after several regeneration cycles.

The regeneration of activated carbon loaded with phenol using wet air oxidation has been studied by Mundale *et al.* (1991) and Ding *et al.* (1987). As much as 90-95% of virgin carbon capacity was achieved under certain conditions (temperature of 150°C and oxygen partial pressure of 0.5 MPa). Further increase in temperature (180°C or higher) caused a reduction in adsorption capacity. They conclude that such a loss could be attributed to the formation of oxygenated-chemical-structured groups on the adsorbing surfaces.

Cooney *et al.* (1983) chose methanol as the best solvent among nineteen other solvents, because it poorly adsorbs the activated carbon and water washing is quite successful in removing a large part of the methanol. Apart from this, methanol can restore 88% of the fixed-bed adsorptive capacity for phenol after one regeneration, and 81% of the capacity after five cycles.

A detailed study on the chemical regeneration of exhausted activated carbon for a wide range of adsorbates and regenerants has been carried out by Martin and Ng (1984, 1985 and 1987). Eleven adsorbates and twenty-eight regenerants were used to examine the importance of the relationship between molecular size, structure and properties of the adsorbate and those of regenerants. It was indicated that organic chemical regenerants could achieve regeneration efficiencies in excess of 80% in many instances. Alcohols performed well as regenerants. Inorganic chemical regenerants were found to be generally ineffective,

even when the adsorbates were capable of being readily oxidized. The efficacy of organic solubilising regenerants decreased as their molecular weights and sizes increased. The smaller the regenerants, the further it could penetrate into the micropores of the carbon and displace the adsorbate. Thus, the regenerants chosen should be smaller than the smallest adsorbate to be removed. Also the organic regenerants should be readily water-soluble since carry-over of regenerants into the re-adsorption phase reduces the adsorption capacity for a subsequent application. This conclusion is in agreement with the results of Cooney *et al.* (1983).

Martin and Ng (1987) have evaluated the chemical regeneration of activated carbon loaded with nitrobenzene, Rhodamine B and humic acid using several regenerants. Regeneration efficiencies of more than 95% were easily achieved using formic acid and acetic acid. Multiple cycles of exhaustion-regeneration showed little loss of adsorptive capacity. However, acetone, ethanol and methanol showed a decline in regeneration efficiency to 80% after 15 cycles for Rhodamine B, and only achieved moderate regeneration efficiency for humic acid.

Compared with the thermal regeneration, chemical regeneration possesses some advantages: a) It can be done relatively fast *in situ*, thus minimizing downtime for the adsorbers and eliminating unloading, transporting and repacking of the carbon; and b) No carbon attrition occurs, the cost of replacing this carbon is thus avoided. However, the main disadvantage associated with chemical regeneration is the low regeneration efficiency. Most of regeneration systems have achieved efficiencies below 70%. This results in an increase in regeneration times (e.g. in a two year period more than 100 adsorption-regeneration cycles were required (Himmelstein *et al.*, 1973)). Also the regeneration

capacity is highly dependent on the GAC, the contaminant, the regenerant, and the regeneration conditions. This technique has not been used in water treatment system, since it dose not adequately reactivate the carbon for uses requiring removal of organic present in low concentrations. However, it is most likely suitable for regenerating GAC used in wastewater treatment.

2.3.3 Biological regeneration

Many studies on biological regeneration have been carried out, however, most do not refer to a separated regeneration process in terms of thermal or chemical regeneration. Biological regeneration is usually discussed with respect to the addition of powdered activated carbon to a biological wastewater treatment process, or to increased adsorptive capacities as a result of microbial growth on the activated carbon (e.g. Lowry and Burkhead, 1980; Suidan *et al.*, 1981; Khan *et al.*, 1981; Kim *et al.*, 1986). Only a few studies related to separate biological regeneration processes have been reported. Rodman *et al.* (1978) used activated carbon to decolorize 50,000 gallons per day of a yarn spinning mill effluent. Activated carbon columns were used in the treatment mode for 10 hours per day, and regenerated by passing an aerobic microbial culture through the column during the next 14 hours. The process was operated continuously for 98 days, with similar results. Although regeneration occurred, the adsorption capacity of regenerated carbon was significantly lower than that of virgin carbon.

Sigurdson and Robinson (1978) have investigated the *in situ* biological regeneration of activated carbon loaded with phenol by a pure-culture of *pseudomonas putida*. The regenerated carbon was found to have only 47% of the adsorptive capacity of the fresh

carbon. No further loss in adsorptive capacity was observed in two subsequent regeneration cycles. It was hypothesized that extracellular metabolites competing for adsorption sites on the activated carbon were responsible for the observed decline in the adsorption capacity for phenol.

Wallis and Bolton (1982) found a similar reduction in adsorptive capacity for GAC (Nuchar, 12/40 mesh, Westvaco Corp.) loaded with phenol and regenerated using *P. putida*. Up to 87% of the activated carbon's original adsorptive capacity was recovered using an optimum regeneration time of 29 hours. Reduction in the adsorptive capacity of the activated carbon was noted with both prolonged activated carbon-culture contact and with multiple regenerations. It was speculated that microbial fouling of the pore openings and/or adsorption of microbially produced compounds was responsible for the observed decline in adsorption capacity.

Hutchinson and Robinson (1990 a and b) have described microbial regeneration of activated carbon (F-300, Calgon) loaded with a single-solute (phenol) and a bisolute system containing phenol and *p*-cresol, by a pure culture of *Pseudomonas putida*. Bacterial fouling of the column occurred when fermentation broth was contacted directly with carbon during the regeneration, and regenerated activated carbon was characterized by an almost immediate breakthrough of phenol on subsequent loading. It was likely that the bacterial fouling produced an additional mass transfer resistance that greatly reduced adsorption rates during loading. Regenerated carbon using cell-free permeate filtered from the fermentation broth exhibited only a gradual deterioration in the breakthrough performance with successive regeneration. Up to 56% of virgin carbon adsorptive capacity was achieved for the first regeneration cycle, and decreased further with subsequent regenerations.

Hutchinson and Robinson (1990 b) conclude that bioregeneration process does not appear to be appropriate for regenerating activated carbon used in tertiary wastewater treatment. The limitation on desorption rates and the presence of residual phenolics preclude the restoration of adsorption capacity to the point where the activated carbon could not be used for polishing wastewater.

2.3.4 Electrochemical regeneration

The use of electrochemical techniques for the destruction of organic contaminants in water has received much attention (e.g. Sharifian and Kirk, 1986; Smith de Sucre and Watkinson, 1981; Murphy *et al.*, 1992). Dabrowski *et al.* (1975) have investigated electrochemical oxidation for destroying phenolic wastes in a pilot plant and Chettiar and Watkinson (1983) have applied it to synthetic wastewater solutions. However, electrochemical oxidation techniques have not been used commercially because of their low efficiencies (low reaction rate). One reason for the low reaction rates is electrode fouling caused by electrochemical oxidation products. The oxidation products block the electrode surface and reduce further reactions. Therefore, a reticulate glassy carbon and carbon felt were employed as electrodes (Gattrell and Kirk, 1990; Kudo and Wayner, 1990). In the study by Kudo and Wayner (1990), carbon felt was used as an electrode with a large surface area for adsorbing organics. This inspired the present study on the electrochemical regeneration of spent GAC, which uses the spent GAC as an electrode in an electrochemical reactor.

An initial computer literature search failed to identify papers on this subject. After the completion of the experimental work described in this thesis, a report on

electrochemical regeneration was discovered accidentally. Searches of five additional databases identified one more report and several translated Russian papers, which are discussed below.

Wills (1971) investigated the electrochemical carbon activation process by anodically electrolyzing the carbon surface in 20% hydrochloric acid. In his tests, current densities ranged from 0 to 125 mA/cm^2, and were held constant in the given test. A treatment time of 5 minutes was used. After each treatment, the sample was cathodically electrolyzed at a current density of 38 mA/cm^2 for one minute to free the surface of adsorbed chlorine. Carbon slabs (Graphite 39, 18 and 2690, Union Carbide Carbon, Catalog N. 52306) were loaded with Dieldrin. Results showed that activated carbon adsorptive capacity using electrochemical regeneration was 10% greater than that of the virgin carbon.

Owen and Barry (1972) studied the electrochemical regeneration of carbon which was used for treatment of municipal secondary effluent. Their regeneration system circulated a brine solution through the electrolytic regeneration cell and the exhausted carbon column (Figure 2.5). Electrochemical regeneration was able to restore working capacity to 42 to 61% of the corresponding virgin capacity over the range of experimental conditions investigated. Cost analysis showed that electrochemical regeneration is potentially a much less costly method of regenerating carbon than thermal regeneration.

Several Russian researchers applied the electrochemical technique to regenerate activated carbon (Slavinskii *et al.*, 1984; Sveshinikova *et al.*, 1987; Khabalov *et al.*, 1989; and Lazareva *et al.*, 1991). In the study of Slavinskii's *et al.* (1984), an anode was a bed of GAC loaded with *p*-nitrotoluene and the cathode was the column shell (vertical cylindrical

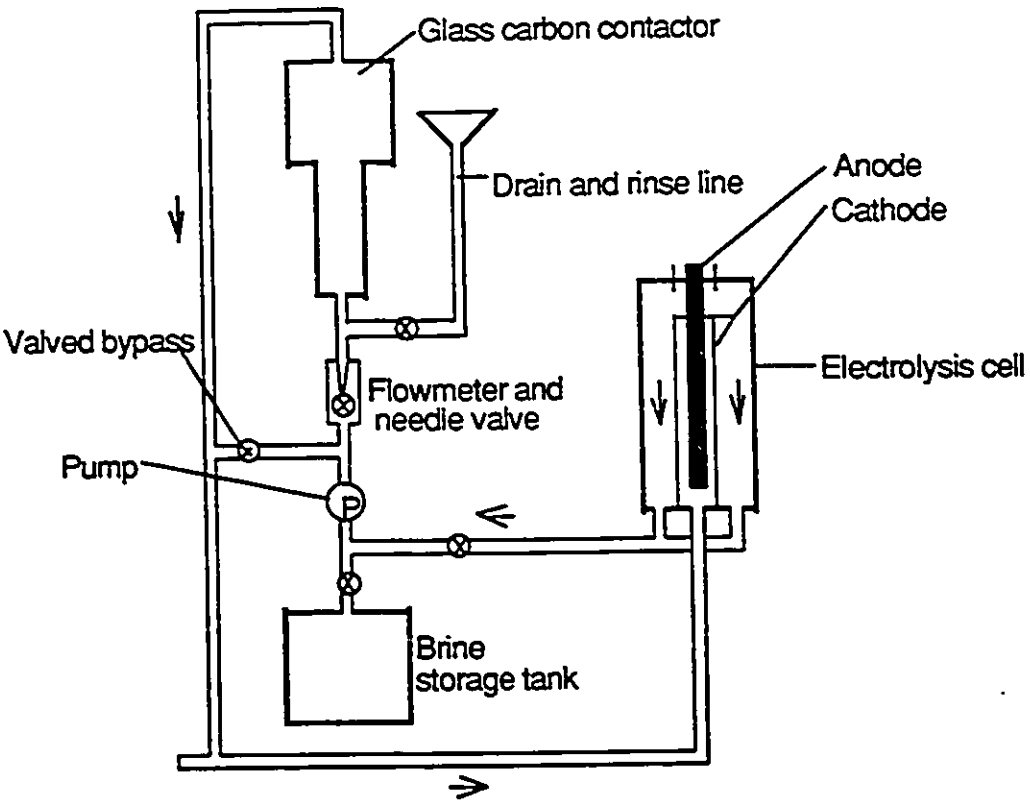


Figure 2.5 Diagram of brine recirculating in regeneration apparatus (source: Owen and Barry, 1972).

steel conductor), and the electrolyte was a sodium chloride solution. In order to prevent the bulk anode (the activated carbon) from contacting the column shell (the cathode), the column was lined with a special perforated cylinder of polycaprolactum. It was shown that adsorptive capacity of the carbon after the first regeneration cycle was 97.4% of the initial capacity, then remained almost constant for four cycles. The optimum regeneration conditions were a current of 30 A/m^2, an electrolyte concentration of 0.2 M NaCl, and a treatment time of 30 minutes.

Sveshinikova *et al.* (1987) investigated electrochemical regeneration of activated carbon loaded with phenol in a plexiglass laboratory cell. Graphite rods were used as the current conductors, and electrolyte was a NaCl solution. It was indicated that the optimum conditions were electrolysis for 1 to 1.5 hours using a 1 ampere current and a 20 g/l NaCl solution. Under these optimum conditions, regenerated carbon capacity of type A decreased slightly during the first five adsorption-regeneration cycles, then remained practically constant in the subsequent cycles (about 70% of initial adsorptive capacity). After five adsorption-regeneration cycles, the adsorptive capacity of type B decreased to 40% of the virgin capacity and remained unchanged for subsequent cycles. Lazareva *et al.* (1991) also suggested the possibility of repeated adsorption and electrochemical regeneration of carbon adsorbent loaded with dyes. Khabalov *et al.* (1989) studied the influence of pore structure on the desorption and regeneration processes. They found that electrochemical regeneration could only be applied in practice to adsorbents with an extensive mesopore structure.

2.4 Conclusions

The above review yields some important points. First, adsorptive capacity of activated carbon depends not only on the adsorbate and adsorbent, but also on experimental procedures. Factors such as equilibration time, pH, temperature, and presence or absence of molecular oxygen in experimental bottles can exert significant effects on the GAC adsorptive capacity.

Second, thermal regeneration can achieve more than 90% of regeneration efficiency and is used universally for the regeneration of GAC from water and wastewater applications. The main drawbacks of thermal regeneration are significant GAC losses and high unit costs associated with small regeneration facilities. Chemical regeneration has severe limitations owing to the low percentage of recoverable adsorptive capacity, the need for solvent recycle and the disposal problems created by the desorbed contaminants. Biological regeneration studies indicate that it yields low regeneration efficiencies and is a time consuming process.

Electrochemical regeneration possesses several potential advantages over thermal regeneration. They include minimal carbon loss, high regeneration efficiency, and particularly, its suitability for use in treatment facilities of small and moderate sizes. Studies carried out by Will (1971) and Owen and Barry (1972) on electrochemical regeneration of GAC have achieved moderate capacity restoration. Although Russian researchers obtained high restoration of GAC adsorptive capacity, the translated papers lack details on experimental setup and procedures used.

This study is designed to contribute to a better understanding of electrochemical GAC regeneration by conducting experiments on electrochemical regeneration and by

investigating the impact of various process variables (such as regeneration current, time, electrolyte concentration, electrolyte type, GAC particle size, and amount of contaminant on GAC) on this process.

CHAPTER THREE

EXPERIMENTAL MATERIALS AND METHODS

3.1 Materials

3.1.1 Adsorbate and chemicals

Phenol was chosen as an adsorbate in this study because it can be easily analyzed by HPLC and UV spectrophotometry, and is a common contaminant in industrial wastes. ACS reagent grade phenol (purity > 99%) was used (Aldrich Chemical Co., Milwaukee, WIS). All solutions were prepared in distilled-deionized and GAC filtered water (DDFW) buffered with a 0.01 M phosphate at pH 7.0. To obtain this pH, the buffered solutions were prepared with 0.806 g/l KH_2PO_4 (Fisher Scientific Co. Fair Lawn, NJ) and 0.579 g/l Na_2HPO_4 (Anachemia Chemicals Ltd., Montreal, PQ). The pH was monitored throughout the experiments, and it remained in the range of 6.9 to 7.1.

Deionized-distilled and GAC filtered water (DDFW) was used for preparing the phenol solutions and electrolytes, and for cleaning the glassware. The gravity fed GAC filter produced 1-2 liters of water per hour and was packed with activated carbon from the same batch as that used in the experiments. The phenol concentration of DDFW was always undetectable (<< 0.1 mg/l).

Several types of salts were used as electrolytes in this study. They were sodium chloride (Canlab, Mississauga, ON.), sodium sulfate, sodium bicarbonate (Fisher

Scientific Co. Fair Lawn, NJ), and sodium acetate (Anachemia Canada Inc., Montreal. PQ). All chemicals were of ACS reagent grade.

3.1.2 Adsorbent

The adsorbent in this study was Filtrasorb F-400 (Calgon Carbon Corp., Pittsburgh, Pa.), which was prepared from bituminous coal, and supplied in the 12/40 mesh-size range. The activated carbon was prepared by sieving to three different particle sizes (i.e. 12/16, 16/18, and 30/40) to produce more uniformly-sized particles. After having been sieved, the carbon was washed with DDFW to remove carbon fines. The carbon was then boiled in the water for about 30 minutes to remove/desorb any contaminants that may remain on the carbon. The boiled carbon was allowed to cool and settle, and rinsed with DDFW to remove the fines. This procedure was repeated. Finally the carbon was dried in an oven at 105°C for three days and stored in a desiccator.

3.2 Analytical Instruments

Phenol concentrations were determined by the Institute for Environmental Chemistry, National Research Council of Canada (N.R.C.C.) with a high performance liquid chromatography (HPLC) (Hewlett Packard-1090 HPLC, Palo Alto, CA). The HPLC was equipped with a diode array detector and HP-300 work station for integration of peak areas. Detection wavelength was 268 ηm which corresponds to absorbance maximum for phenol. 25 µl of sample was injected onto a Shandon Hypersil ODS C18 (2.1mm id x 10cm x 5µm) column maintained at 40°C. Flow rate of the mobile phase was 0.3 ml/min and the composition of solvent is shown as follows (Table 3.1):

Table 3.1 HPLC conditions for phenol analysis

Time	Solvent A	Solvent B	Solvent C
	HPLC Methanol pH 4.7	MQW	Na acetate 0.05M pH 4.7
0	40%	0.0%	60%
12	80%	0.0%	20%
13	90%	0.0%	10%
18	90%	0.0%	10%
20	40%	0.0%	60%

For reference purposes, samples were also measured with a Beckman model UV-40 spectrophotometer (Toronto, ON). Calibration-curve shows a linear relationship between absorbance and concentration in the range of 20 to 120 mg/l phenol concentration. The samples were diluted before analysis if the phenol concentration was higher than 120 mg/l.

3.3 Electrochemical Reactor

The GAC regeneration was carried out in an electrochemical batch reactor composed of a two-compartment regeneration cell that was submerged in a one-liter crystallizing dish filled with an electrolyte (Figure 3.1). Platinum sheets were secured to the bottom of each of the two plexiglass rings (2cm high, 7.6cm in diameter). The two compartments were formed by stacking the rings on top of each other and placing a third platinum sheet on top of the upper ring. A plexiglass disk was placed on top of the upper platinum sheet to keep it in place. This arrangement kept the particles on the platinum

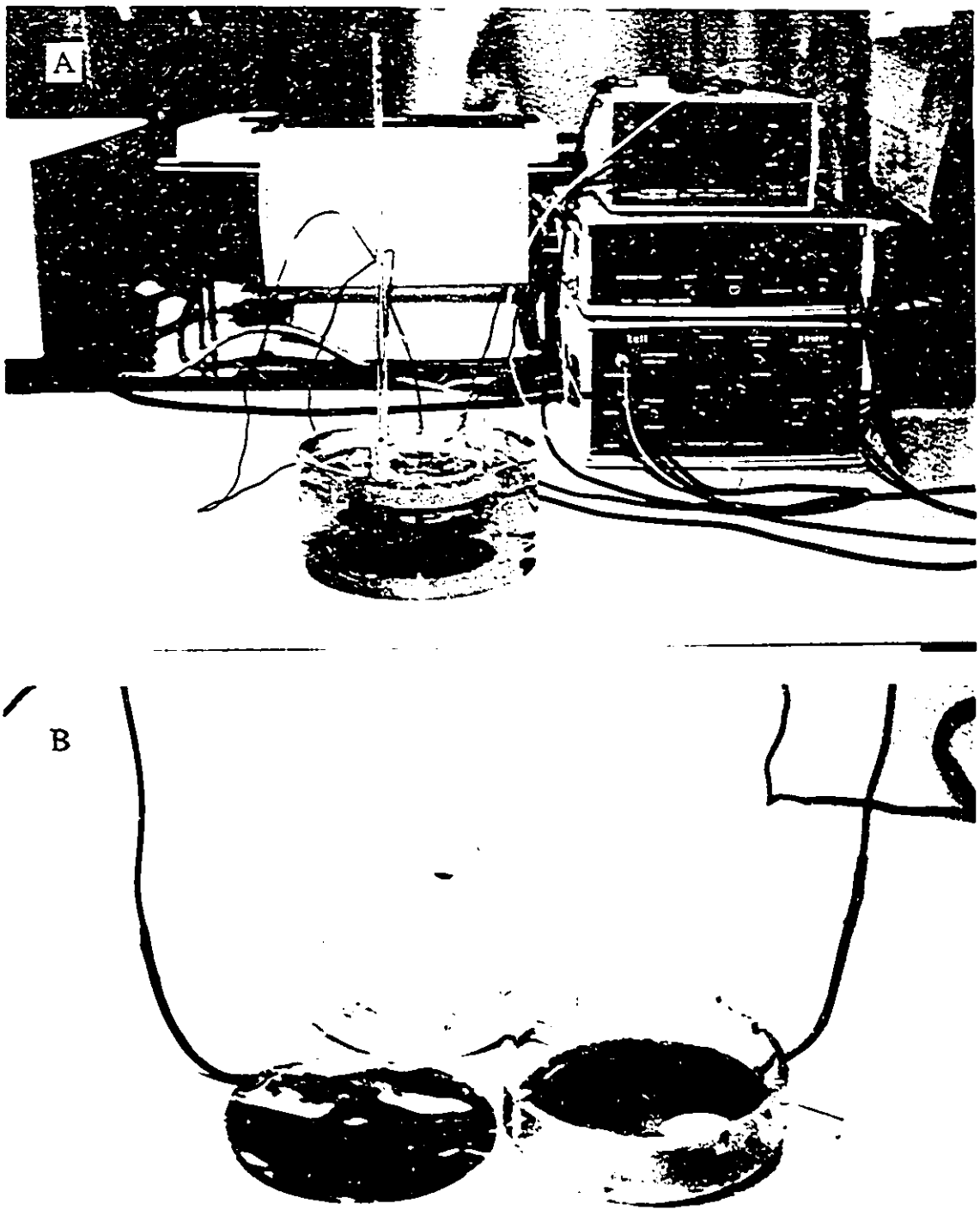


Figure 3.1 The experiment set up: A) the electrochemical reactor, B) the platinum electrodes.

electrodes and maintained the platinum electrodes 2cm apart. The three equidistant electrodes were necessary to maintain constant current densities when GAC was simultaneously regenerated at the two lower electrodes. The plexiglass rings were slightly inclined and had several perforations on their top edge to allow bubbles generated at the electrodes to escape. The perforations also permitted some electrolyte to flow into and out of the cell compartments. There is no mixing or forced flow in this system. The electrolyte, which is necessary for electron transfer, was a 1% NaCl solution; however, a few tests were conducted using solutions of Na_2SO_4, $NaHCO_3$, CH_3COONa, and other concentrations of NaCl. All experiments used a monolayer of GAC to ensure direct contact with the platinum electrode (Figure 3.2).

The power was supplied by a potentiostatic controller (model 410, Electrosynthesis, Buffalo, NY) and an accessory power supply (model 420A, Electrosynthesis, Buffalo, NY). The potentiostatic controller was used as a constant current source by connecting an external resistor between the working and reference terminals (Figure 3.3). Since a 1.0 ohm resistor was used, the output current was 1 ampere per volt of set potential. A digital coulometer (model 640, Electrosynthesis, Buffalo, NY) was also used to check the current.

3.4 Adsorption Studies

Four different types of adsorption tests were conducted in this study: adsorption isotherms, adsorption kinetics, desorption isotherms and loading tests associated with the regeneration tests. The first three types of experiments were conducted to help interpret the results of the latter type.

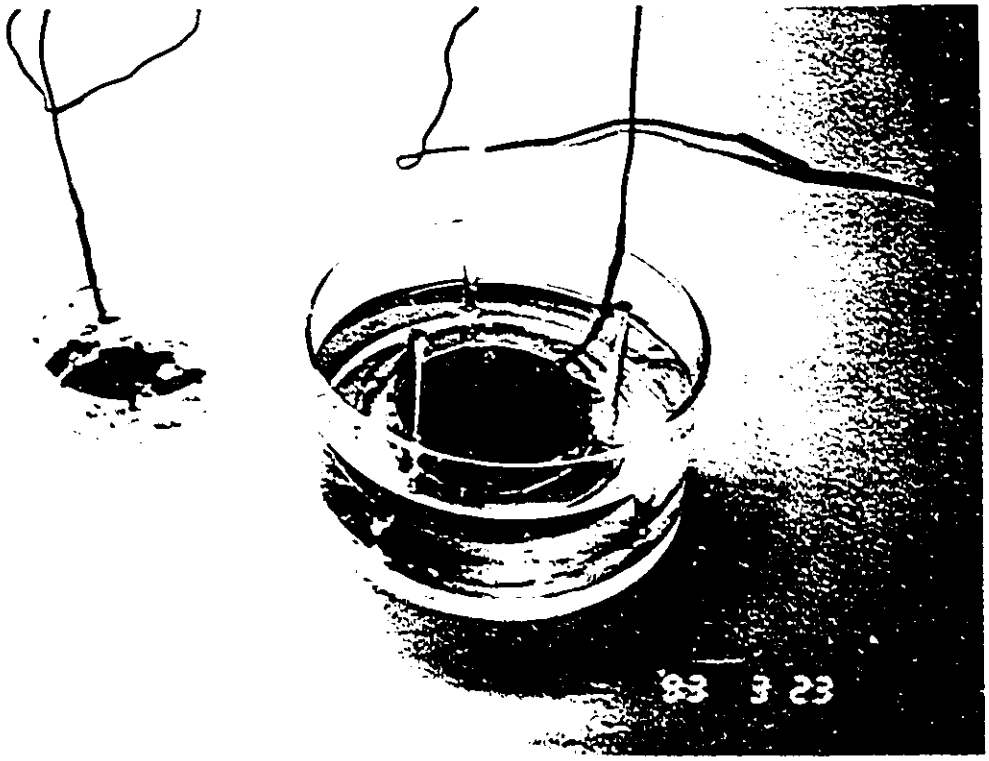


Figure 3.2 The pattern of GAC placed on the electrode.

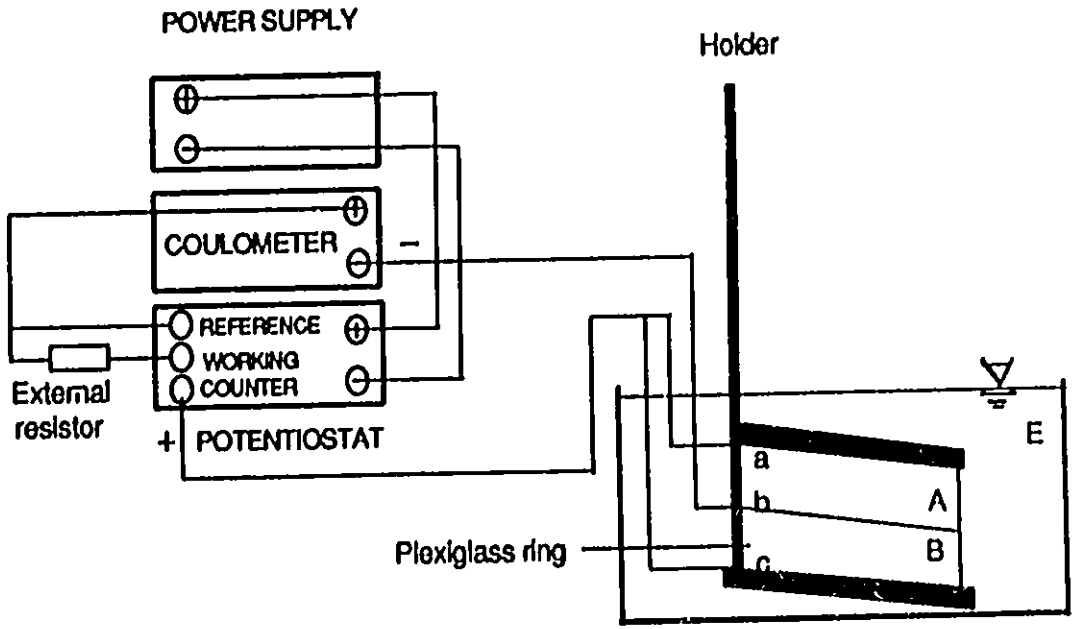


Figure 3.3 The electrochemical reactor used in experiment: a, b, and c - platinum plates; A - anode compartment, B - cathode compartment, and E - electrolyte.

3.4.1 Adsorption equilibria experiments

The adsorption isotherm represents the equilibrium at a constant temperature between the quantity of contaminant adsorbed per unit mass of adsorbent, q, and the concentration of adsorbate in the bulk solution. The isotherms were obtained by the bottle-point technique. Varying amounts of GAC were accurately weighed and placed in a series of glass bottles. The 500-ml bottles, which actually ranged from 474 to 538 ml, were used for 12/16 and 16/18 mesh-size GAC particles, and 160-ml bottles were used with 30/40 mesh GAC particles. The bottles were then filled with 300 mg/l phenol solution. The bottles were sealed with Teflon-lined caps (500-ml bottles) or Teflon-lined septa (160-ml bottles) and rotated in a tumbler for at least six days. The tumbler was designed to gently tip the bottles end-over-end at approximately 10 r.p.m. to provide mixing and to keep the carbon fully in suspension so that particle attrition could be minimized.

The adsorption tests were run at room temperatures (21 ± 2°C). Two control bottles without carbon were used in each set of adsorption tests to check for adsorbate volatilization, adsorbate degradation and/or adsorption onto the walls of the container during the equilibration period. At the end of the contact period, the loaded GAC and solution were separated by vacuum filtration through a 0.45-μm cellulose nitrate membrane (Micro Filtration Systems, Dublin, CA). The filtrate was then analyzed and carbon solid phase concentration (loading) was calculated by a mass balance relationship.

3.4.2 Batch kinetic experiment

Adsorption of organic compounds from aqueous systems onto activated carbon is a

time-dependent process. Previous studies have indicated that the equilibrium time varies with different experimental conditions (e.g. Peel and Benedek, 1980; Martin and Ng, 1984; and Vidic *et al.*, 1990). A batch kinetic experiment was also carried out in this study to determine the time needed to reach the equilibrium between GAC (F-400) and the 300 mg/l phenol solutions. The kinetic experiment in the study was a series of 160-ml glass bottles with a constant GAC dosage and varying contact times. The test was carried out with mesh size of 12/16. The amounts of GAC were weighed and placed carefully in corresponding bottles, filled with phenol solution. Thereafter, bottles were sealed and placed in the tumbler for different specified mixing time intervals. The rest of the procedure is the same as that for the adsorption test.

3.4.3 Desorption isotherms

A batch desorption test was performed by the bottle-point technique. In this technique, previously loaded GAC samples (from an adsorption equilibrium test) served as the adsorbent and a 1% sodium chloride solution as the adsorbate. This adsorbate is the standard electrolyte used in electrochemical regeneration tests and was chosen for comparing the extent of desorption (and thus regeneration) in the absence and presence of a current.

The procedure of the desorption test involved placing a set of experimental units (bottles) in the tumbler to saturate the GAC (i.e. adsorption test). After adsorption equilibrium had been reached, the bottles were removed from the tumbler. The loaded GAC and the solution were separated by vacuum filtration through a membrane filter. The filtrate was then analyzed and the bottles were cleaned carefully. The GAC particles on the

membrane filter were then flushed back into the bottles which were then filled with a 1% NaCl solution (adsorbate free). Then the bottles were sealed and returned to the tumbler for desorption tests. The equilibration period for this test was three weeks as opposed to two week for the adsorption cycle.

3.4.4 Adsorption tests associated with the regeneration

The regeneration efficiencies were evaluated via three experiments in series: a) bottle-point isotherms, used to load the virgin GAC with a contaminant, b) regeneration of the loaded GAC, and c) repetition of adsorption procedure with the regenerated GAC. The GAC loading tests were conducted by the same procedure as the adsorption isotherms except that a single carbon dose was utilized and the tests were carried out in triplicate. The loaded GAC was then temporarily stored in small glass jars while awaiting regeneration.

In the second step of the tests, the loaded GAC was electrochemically regenerated in the previously described reactor. Following the electrochemical regeneration, the GAC was separated from the electrolyte by vacuum filtration through a membrane filter. The third test was the readsorption test. The regenerated GAC was transferred to a clean 500 ml (or 160 ml) bottle. The actual bottle used in the readsorption test is the same as that used in the adsorption cycle to maintain the ratio between carbon mass and liquid constant. The bottle was again filled with 300 mg/l phenol solution to repeat the adsorption procedure.

3.5 Experimental Plan for the Regeneration Experiments

The aim of these experiments is to investigate the technical feasibility of electrochemical regeneration by conducting a sensitivity analysis of the process. The key

process variables include GAC location, regeneration current, time, electrolyte concentration, electrolyte type, GAC particle size and mass of contaminant on the GAC.

3.5.1 Electrodes

Several GAC samples were anodically or cathodical electrolyzed by placing GAC on different electrodes: a) the anode; b) the cathode; c) the anode and cathode simultaneously; d) the anode and cathode simultaneously but reversing the polarity at the middle point of the experiment (three-hour regeneration time). The purpose of these tests was to determine which electrode achieves better regeneration efficiency.

3.5.2 Current and time

After testing the electrodes, we selected the cathode electrode over the anode because of its higher regeneration efficiency. The experiments were then conducted by using a standard set of conditions and by changing one variable at a time. These standard conditions were 1.2 g GAC loaded with a phenol loading of approximately 107 mg/g, 12/16 mesh size GAC, 1% NaCl solution as an electrolyte, a five-hour regeneration time, and a 50 milliampere regeneration current.

The regeneration current tests ranged from 10 mA to 300 mA and regeneration time from 1.5 to 10 hours. A high current can rapidly oxidize the phenol, but may also deteriorate the carbon surface and pore structures. Thus regenerations with low currents (10 mA) and long regeneration times (up to 40 hours) were also evaluated.

3.5.3 Electrolytes

Electrochemical regeneration was conducted in an electrolyte solution with a high ionic conductivity to reduce the electrical resistance between the anode and cathode to workable levels. For the electrooxidation process to be effective, an acid, base or salt must be added to the water to form an electrolyte. A 1% NaCl solution was chosen as a standard electrolyte in this study because it satisfies these requirements and is inexpensive. Other tests for evaluating the effect of electrolyte on regeneration efficiency used several different NaCl concentrations between 0.01% and 5%, different electrolyte such as 1% $NaHCO_3$, 1% Na_2SO_4, 1% CH_3COONa, and Ottawa tap water (water quality is presented in appendix A).

3.5.4 Carbon particle sizes and dosage

The activated carbon itself has two variables: particle size and loading. GAC from the three different particle fractions (i.e. 12/16, 16/18 and 30/40) was loaded to have the same solid phase concentration. In order to have a monolayer of particles on the electrode for the smallest particle size fraction (i.e. 30/40 mesh), the mass of carbon was reduced to one-third of that used for other two fractions.

3.5.5 Multiple adsorption and regeneration cycles

In order to investigate the long-term feasibility of the electrochemical regeneration process, multiple cycles of adsorption, regeneration and readsorption tests were conducted. The regenerations were carried out under the standard conditions for five cycles.

CHAPTER FOUR

EQUILIBRIUM STUDIES

4.1 Introduction

This chapter describes and discusses the results of a series of fundamental adsorption experiments conducted to help interpret the electrochemical regeneration tests. These adsorption experiments include a complete adsorption isotherm, a batch adsorption kinetic test, and desorption tests. The results of the electrochemical regeneration experiments are discussed in chapter five.

4.2 Adsorption Equilibrium

4.2.1 Phenol adsorption isotherms

Adsorption properties of activated carbon are defined by its adsorption equilibrium capacity and by its adsorption kinetics. The equilibrium adsorption capacity of activated carbon is commonly represented by adsorption isotherms, which are plots of the equilibrium solid phase contaminant concentration (or loading) versus the equilibrium liquid phase concentration. Isotherm data are usually obtained by using the bottle-point technique described in chapter three. As mentioned earlier, there is no standard procedure for such tests. As a result, many different isotherms for the same adsorbate-adsorbent pair have been reported in literature (e.g. Peel and Benedek, 1980; Vidic *et al.*, 1990;

Crittenden and Weber, 1978). Therefore, in order to evaluate the adsorptive capacity of activated carbon, it is necessary to determine the adsorption isotherms for specific experimental conditions utilized in the loading part of the regeneration experiments. Carbon loadings were also chosen, in this thesis, as one of the variables affecting the electrochemical regeneration.

In this study, 10 sets of loading tests were conducted as the first step of electrochemical regeneration and desorption tests. The results are presented in Figures 4.1 and 4.2 (data in appendix B). All the data on the adsorptive capacity of GAC were modelled with the Freundlich isotherm equation (2.2) and regressed by a non-linear least squares method using Statgraphics Plus (Manugistics Inc., 1993). The estimated values of K and 1/n for all test sets are listed in Table 4.1, together with their standard errors. The standard errors for both coefficients are within 3% of the mean value (except for set three which will be discussed later). Thus, the experimental data are described well by this two-parameter isotherm equation. The loading test data and Freundlich isotherms from sets no. 2 and no. 5 are given in Figure 4.1 (as examples). Those data fit equation (2.2) quite well.

The calculated Freundlich coefficients differ slightly from set to set (Table 4.1). For example, parameters K and 1/n for set no.4 were estimated to be 45.73 and 0.263, while they were 43.03 and 0.278 respectively for set no. 5. This is probably due to variations in test conditions. If all data are plotted on one graph, it shows a slight scattering (Figure 4.2). Close examination of the data notes that data from sets no. 3 and no. 8 are above and below the remaining data, respectively, although they are supposed to line up along one single line. This is likely caused by changes in GAC moisture content and room temperature. In all circumstances, the solid line in Figure 4.2 is the best fit for all sets

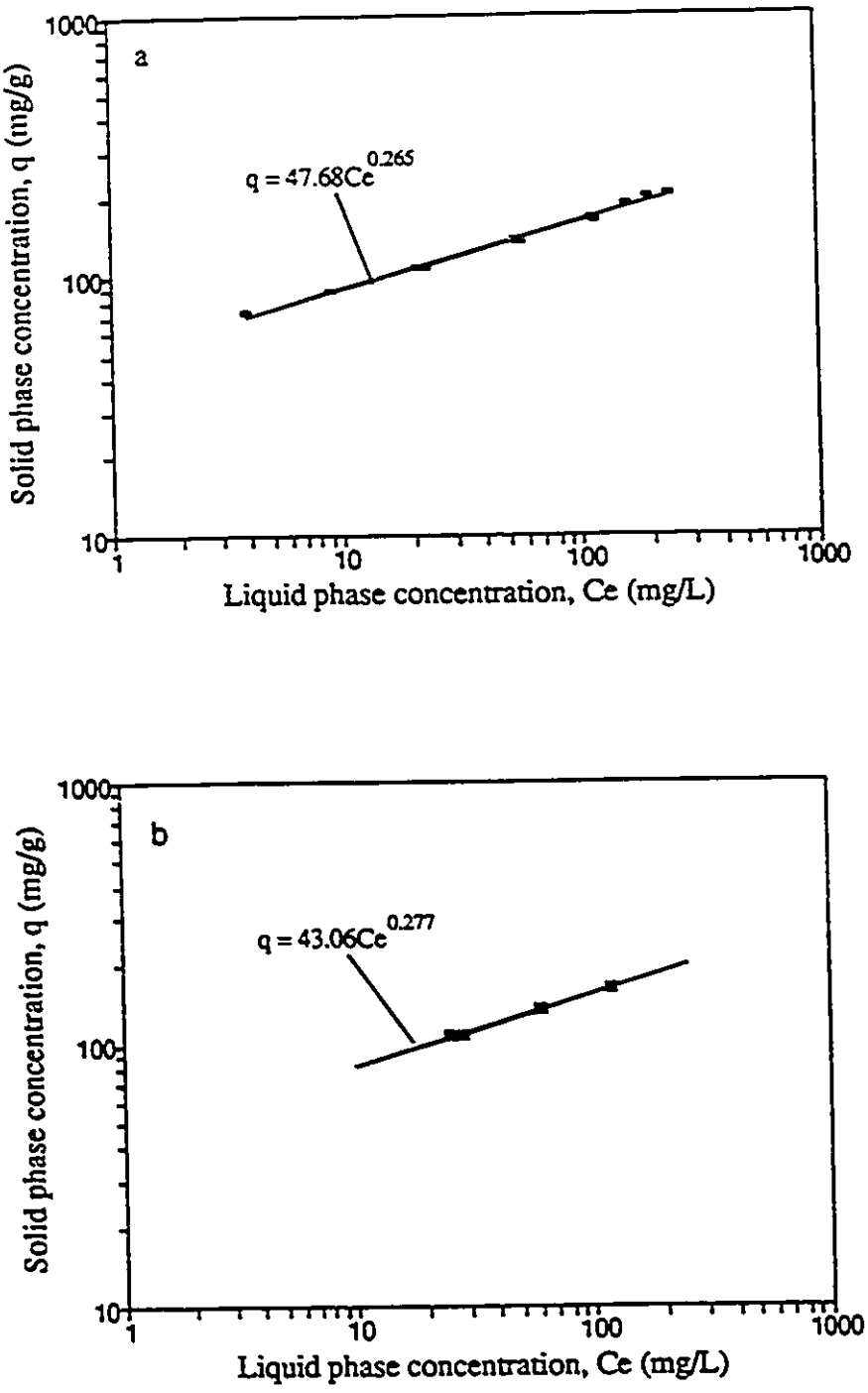


Figure 4.1 Freundlich adsorption isotherms for phenol on activated carbon: a) data from set no. 2, b) data from set no. 5.

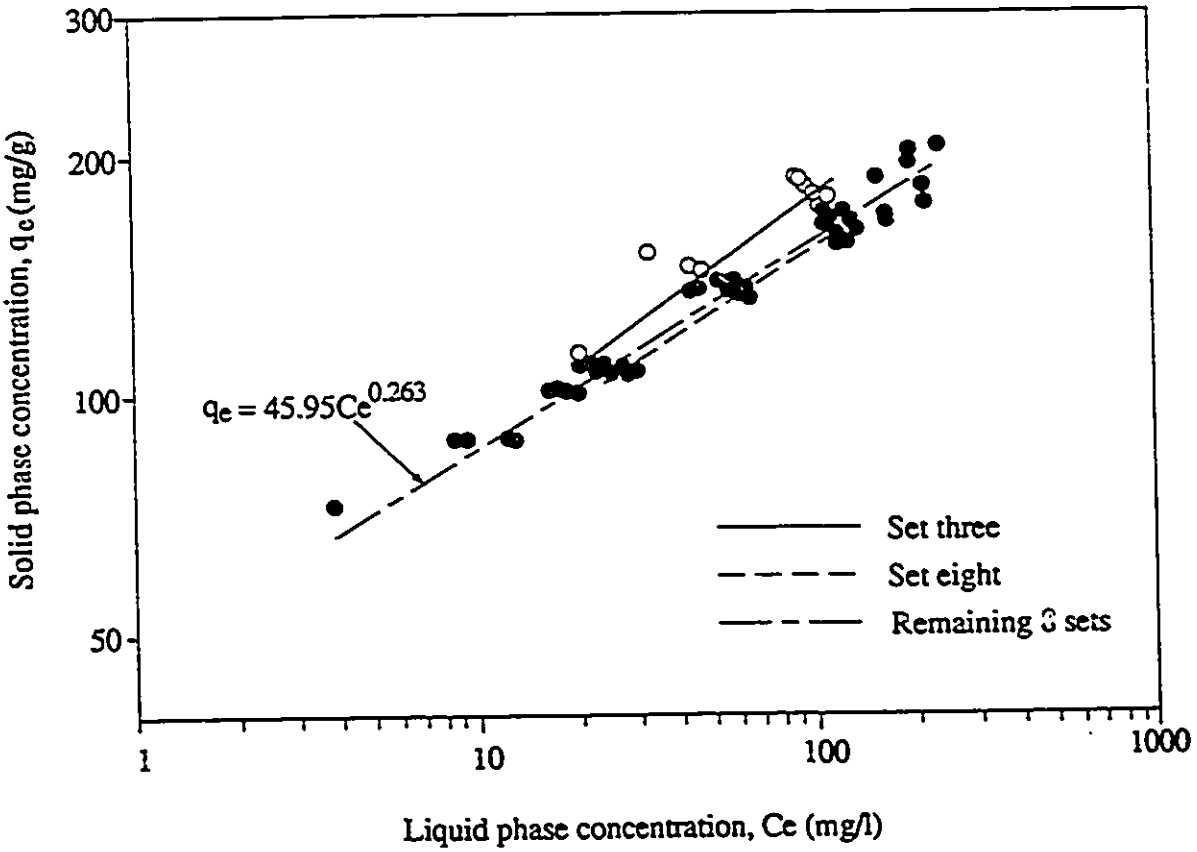


Figure 4.2 All sets of phenol adsorption data and isotherms.

Table 4.1 Freundlich isotherm constants for phenol.

Test set no.	K ± Standard error $(mg/g)/(mg/l)^{1/n}$	1/n ± Standard error	Loading points
1	48.45 ± 1.4782	0.254 ± 0.0077	3
2	47.68 ± 0.9524	0.265 ± 0.0044	8
3	45.77 ± 6.3141	0.290 ± 0.0329	3
4	N/A@	N/A	2
5	43.06 ± 0.9254	0.277 ± 0.0051	3
6	N/A	N/A	1
7	45.79 ± 0.3996	0.256 ± 0.0021	3
8	N/A	N/A	2
9	48.38 ± 0.852	0.243 ± 0.004	6
10	N/A	N/A	1
eight sets*	45.95 ± 0.6364	0.263 ± 0.0034	

@ N/A = no attempt made for regression due to insufficient data.

* These eight sets exclude the sets no. 3 and no. 8.

(eight sets) of adsorption data except for the no. 3 (dotted line) and no. 8 sets (dashed line). The values of K and 1/n are listed in Table 4.1.

For set no. 3, most of GAC samples were quickly weighed and apparently there was insufficient time for them to equilibrate with ambient conditions. According to Randtke and Snoeyink (1983), an activated carbon that was dried at 110°C may gradually gain as much as 5 to 10 percent in weight when exposed to ambient temperature and humidity. This makes it difficult to accurately weigh freshly dried carbon. One remedy is to allow the carbon to equilibrate with ambient condition first and then reweigh it. The drier carbon will yield a lower apparent carbon dose resulting in a higher contaminant loading. Therefore, the dryness of GAC has to be taken into consideration as it affects carbon weight. Initially, in the experiment, GAC was dried and stored in a glass jar. When the GAC is weighed for a set of adsorption test, the carbon might capture certain moisture from the air every time the jar is opened. Thereafter, if the remaining GAC is left in the jar for use in subsequent tests, it would be heavier than its initial weight. Thus the data from subsequent sets of the experiment would have a lower apparent capacity and yield a higher equilibrium liquid phase concentration.

In order to demonstrate how the remaining GAC behaved in term of adsorptive capacity, two replicates were conducted by using the GAC left in the jar after one set of adsorption tests. The results of these tests are shown in Figure 4.3 as triangles. This figure also includes the equilibrium adsorption data from the previous loading test (shown as empty squares) and the fitting curve for comparison. The data in Figure 4.3 indicate that moisture content has a weak effect on adsorptive capacity. Indeed, about 2.4% of capacity was lost and the equilibrium concentration was increased by 11% (GAC = 1.2 g) when

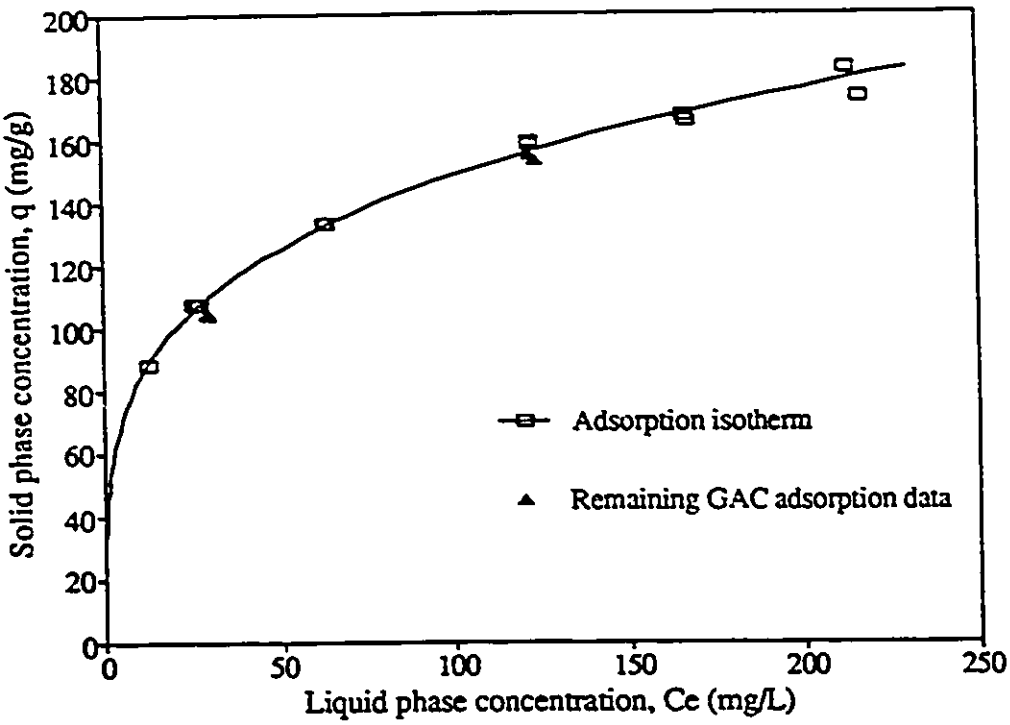


Figure 4.3 Effect of GAC moisture on its adsorption capacity.

remaining GAC was used for succeeding adsorption tests (see appendix B2). In order to avoid this error, dried GAC was placed in several small jars and each jar was used for only one set of loading tests. The remaining GAC was redried before the next set of loading tests.

The significantly higher adsorptive capacities of set no. 3 may also be due to the lower-than-normal room temperature (≈ 19°C) during the contact period because of cold weather. Physical adsorption increases with decreasing temperature (Faust and Aly, 1987). The isotherm capacity of set no. 8 was slightly lower than those of other sets. This is believed to be brought about only by a higher-than-average room temperature, which remained constant at 25°C during this adsorption test. Since the room temperature was not specially controlled, water temperature sometimes went up to 23°C in the mid-afternoon and down to 19°C in the early morning, depending on the weather. This may cause some variations in the adsorption data, despite Snoeyink *et al.* (1969) found that temperature has only a minor effect on GAC adsorptive capacity.

For comparison purposes, Figure 4.4 and Table 4.2 present the phenol/Filtrasorb F-400 adsorption isotherms obtained in this study, together with those previously published. Although some differences in equilibrium capacity exist due to variations in carbon properties and environmental conditions, the observed differences are greater in magnitude than might reasonably be attributed to such causes (carbon properties and environmental conditions). There is a substantial volume of evidence in the literature showing that the effects of environmental conditions such as temperature, pH, and buffer strength are usually insignificant. Peel and Benedek (1980) conclude that the differences can be attributed to an insufficient contact time. It can be seen from Table 4.2 that Peel and

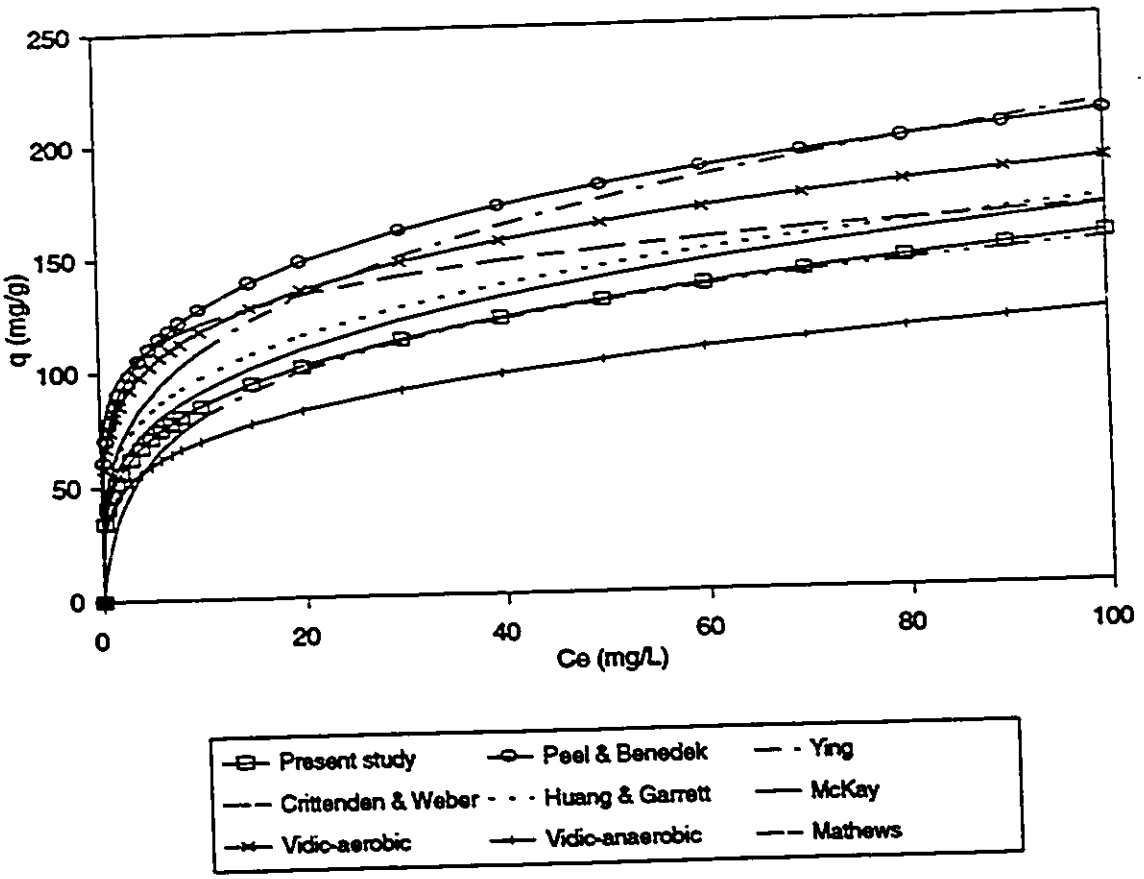


Figure 4.4 Published phenol adsorption isotherms for Filtrasorb F-400.

Table 4.2 Published phenol isotherm data for Filtrasorb F-400.

Time period	Isotherm mg/g of C; mg/L	Particle size	pH	Temp. °C	Source
6-7 days	$q = 46.76C_e^{0.2584}$	12/16, 16,18	7.0	room	present study
23-40 days	$q = 78.1C_e^{0.212}$	16/30, 200	7.0	20	Peel & Benedek (1980)
6 days-6 weeks	$q = 56C_e^{0.288}$	30/35	0.01M-PO_4	room (?)	Ying (1978)
several weeks	$q = \frac{16160C_e}{1 + 183.9C_e^{0.8617}}$	50/60	7.0	room (?)	Crittenden & Weber (1978)
24 hours	$q = 56C_e^{0.24}$	10/30		23.5	Huang & Garrett (1977)

Table 4.2 Published phenol isotherm data for Filtrasorb F-400. (continued).

Time period	Isotherm mg/g of C; mg/L	Particle size	pH	Temp. °C	Source
4 days-4 weeks	$q = 50C_e^{0.26}$	25/35		18	McKay *et al.* (1984)
2 weeks	Aerobic: $q = 74.02C_e^{0.201}$ Anaerobic: $q = 40.03C_e^{0.239}$	12/14, 16/20	7.0 0.1M-PO_4	35	Vidic *et al.* (1990)
N/A	$q = \frac{43.29C_e}{1 + 0.7138^{0.7942}}$	30/35, 60/100	7.0	room (?)	Mathews (1975)

Benedek (1980) and Ying (1978) used long contact periods. The isotherms reported by them exhibit much higher adsorptive capacities than others (see Figure 4.4). By contrast, the isotherm obtained by Crittenden and Weber (1978) does not show such high capacity although an equilibrium time of several weeks was used. In the studies of Peel and Benedek (1980), it was assumed that all phenol concentrations were eventually constant. Through our controls, it was found that phenol experienced 1-3 % of removal under normal environment (room temperature 21 ± 2°C). The longer the equilibrium time, the more phenol may be removed. Hence, the phenol concentration (C_o) in the control bottle was used rather than the initial concentration which was added to the isotherm bottles for determining the adsorptive capacity of GAC.

Vidic *et al.* (1990) and Vidic and Suidan (1991) report that the phenol isotherms under aerobic conditions have yielded capacities approximately 42-85% higher than those obtained in the absence of molecular oxygen. The molecular oxygen may arise from three sources: air entrapped within the pores of GAC particles, the dissolved oxygen present in the water used in preparing the adsorbate solution and the head space in the bottles. Anaerobic conditions are a requirement for the elimination of the interference of molecular oxygen. Oxygen associated with these three sources is eliminated by stripping with nitrogen gas. As a result, the aerobic isotherm is higher than the majority of other isotherms and the anaerobic isotherm is the lowest (Figure 4.4). The isotherms obtained by this study and others (e.g. Huang and Garrett, 1977; McKay *et al.*, 1984; Mathews, 1975) are located in between. The large headspace in the Vidic and Suidan (1991) experiments seems to explain the high aerobic isotherm capacity since the oxygen content in the air is much higher than that dissolved oxygen in solution. In this study, the bottles used range

between 474 ml and 538 ml in volume and were completely filled to eliminate the headspace. As there was no headspace, there was no molecular oxygen transfer from headspace into both the solution and the GAC. However, the phenol solutions were nearly saturated with dissolved oxygen. Thus, these experimental conditions were between the aerobic and anaerobic; the adsorption isotherm is higher than the anaerobic isotherm and lower than the aerobic isotherm obtained by Vidic and coworkers (see Figure 4.4).

4.2.2 Batch kinetic experiment

One of the most important considerations in determining an equilibrium isotherm is the selection of an equilibration (contact) time sufficiently long to ensure that the equilibrium is actually reached or closely approached. Various equilibrium times have been used for phenol adsorption isotherms (see Table 4.2). A two-week contact time was chosen for this study and used for loading tests in sets one through four. However, since the evaluation of the regeneration efficiency is based on three tests: loading, electrochemical regeneration and reloading, the two-week contact time makes this process very lengthy as more than four weeks are needed to finish these three tests. Thus, a kinetics experiment was conducted to determine the necessary contact time for GAC adsorption.

In the batch kinetic experiment, a phenol solution was contacted with a fixed dose of GAC in 52 bottles and the changes in concentration with time in the liquid phase were monitored. The results are shown in Figure 4.5 in terms of reduced concentration versus time (data are tabulated in appendix C). The curve indicates that about 75% of the capacity was consumed in the first 4 hours and that subsequent approach to equilibrium was rather

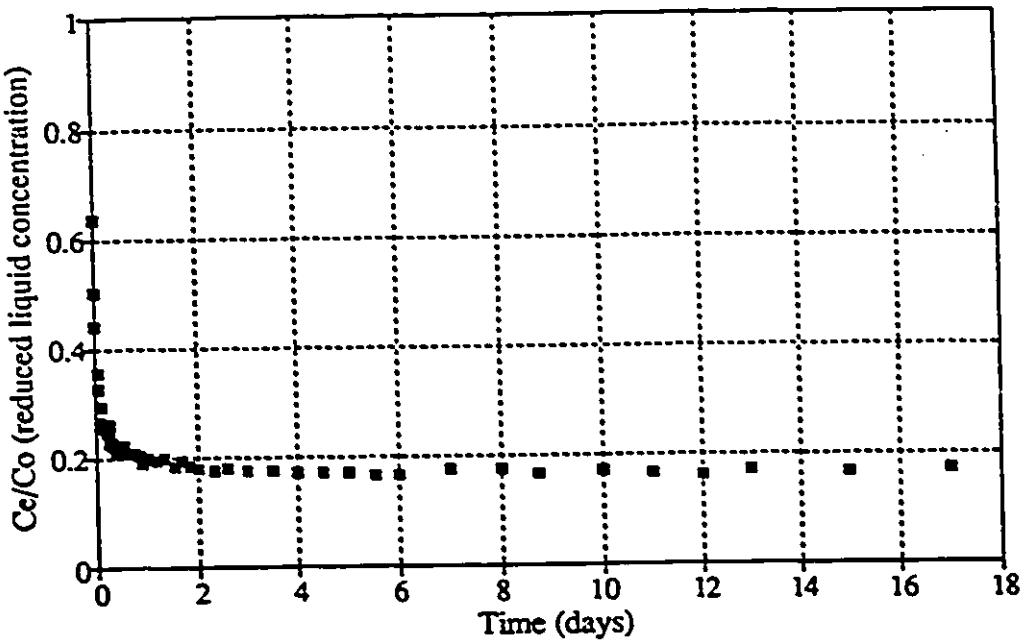


Figure 4.5 Batch kinetic data of phenol adsorption.

gradual. When no further changes in concentration were observed, the equilibrium was assumed to be reached. For this test, the change in concentration between the fifth and sixth days was less than 1.5 mg/l, within the accuracy of the measuring techniques. The result indicates that a contact time of five to six days is required for GAC and phenol solution to reach the adsorption equilibria. Consequently, a six-day contact time was used for subsequent loading and reloading tests.

4.3 Desorption Isotherms

Most research pertaining to desorption has been performed on single-solute systems by using batch desorption procedures (e.g. Yonge *et al.*, 1985; Snoeyink *et al.*, 1969; Wilczak and Keinath, 1993). The first step of the desorption test is the same as the adsorption test. After the adsorption equilibrium, the GAC is periodically allowed to settle to the bottom of the reaction vessel. At the same time, the adsorbate solution concentration is measured. Second, a certain amount of adsorbate solution is decanted and replaced with distilled water. Third, GAC is allowed to re-equilibrate with the new solution, after the decantation and replacement procedure is repeated. Finally, this process is repeated until the resultant liquid-phase adsorbate concentration is less than the detectable limit. The solid-phase loading on the GAC is calculated after each desorption cycle by using (Yonge *et al.*, 1985):

$$(q_D)_i = \frac{m_A - \sum_{i=1}^{n} (m_D)_i}{M} \tag{4.1}$$

where $(q_D)_i$ is the equilibrium solid-phase loading at ith desorption cycle (moles per

gram), m_A is the mass of adsorbate adsorbed in the initial adsorption step (moles), $(m_D)_i$ is the mass of adsorbate desorbed after ith desorption cycle (moles), and M is the mass of GAC in the desorption vessel (grams). The q_D is plotted as a function of the residual concentration of adsorbate in solution. Figure 4.6 shows an example of multiple desorption cycles of phenol for two different masses of coconut-shell carbon conducted by Snoeyink *et al.* (1969). The solid circles and triangles represent the equilibrium conditions at the end of each cycle. The cycles were ceased when phenol was no longer desorbed.

Unlike in the above multicycle desorption experiments. a single desorption cycle was utilized in this study to obtain the desorption isotherms. The adsorption and desorption isotherms for phenol are illustrated in Figure 4.7 (data are listed in Appendix D). As the GAC samples loaded during the adsorption isotherm tests were also used to conduct the desorption isotherm tests, this graph shows the bottle numbers from the isotherms in relation to the adsorption and desorption data. According to Narbaitz (1986), when the desorption experiments consist of separate desorption of carbon masses from individual adsorption bottles, the desorption isotherms are the inclined loading-lines which connect the corresponding desorption points and equilibrium adsorption points generated from the same GAC sample. These desorption isotherms are shown as dashed lines in Figure 4.7. The solid line is the adsorption isotherm. The difference between the adsorption and desorption isotherms indicates the occurrence of hysteresis due to irreversible adsorption.

A complete desorption isotherm is usually obtained by several desorption cycles until the contaminant is no longer desorbed. In this particular study, subsequent desorption cycles were not necessary because the experiment was performed to help interpret the batch

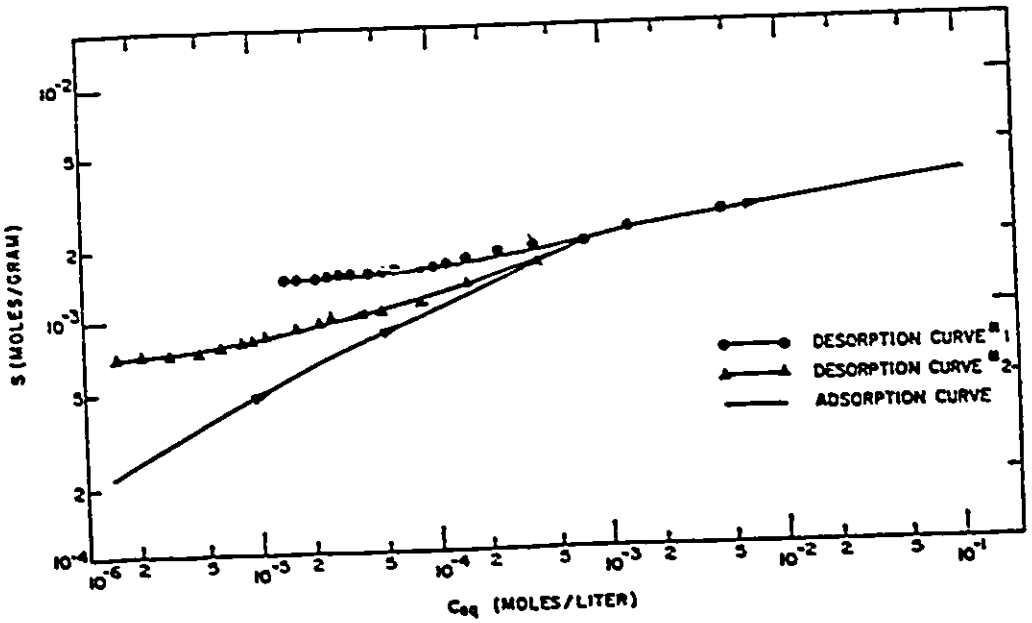


Figure 4.6 Adsorption and desorption isotherms of phenol (source: Snoeyink *et al.*, 1969).

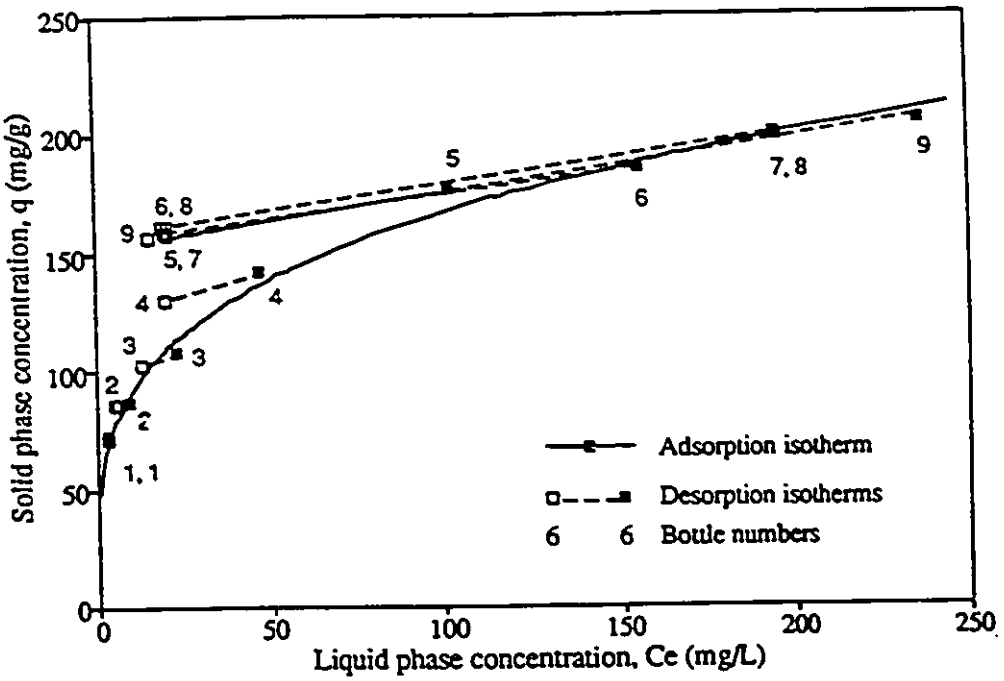


Figure 4.7 Phenol adsorption and desorption isotherms. Desorption tests were conducted in 1% NaCl solution.

electrochemical regeneration which consists of a single batch desorption step. In addition, equilibrium desorption concentrations are quite low; a second desorption cycle would have yielded little additional information. Only 1-24% of adsorbed phenol could be desorbed from the GAC (Table 4.3). The percentage of desorbed phenol was determined by:

$$\%Desorbed = \frac{q_e - q_D}{q_e} \cdot 100\% \qquad (4.2)$$

where q_e is equilibrium solid phase loading after the adsorption step and q_D is equilibrium solid phase loading after the desorption cycle, which can be calculated by equation (4.1). Results show that the percentage of desorbed phenol increases with increasing carbon loading. That is, the more phenol was adsorbed on GAC during the adsorption test, the more phenol was desorbed from GAC in the desorption test. For example, for the GAC loading of 108.33 mg/g, which was used in most of the electrochemical regenerations, only 5.3mg/g of phenol could be desorbed, or 4.9 percent of the adsorbed phenol. If the GAC loading was 205.18 mg/g, the GAC desorbed 48.72mg/g phenol or 23.74 percent. This may be explained by Vidic's hypothesis. Vidic and Suidan (1991) indicate that polymerization reactions between the adsorbate and molecular oxygen take place on the surface of GAC when adsorption tests are conducted under oxic conditions. Thus, a fraction of adsorbate (12.2 to 32.8% for *o*-cresol) could be desorbed from GAC in extraction experiments and was strongly influenced by the amount of adsorbate adsorbed per unit mass of GAC. Whereas approximately 90% of *o*-cresol could be desorbed when the adsorption tests were in anoxic conditions. The adsorptive capacity of phenol was significantly affected by the molecular oxygen and polymerization reactions on the GAC

Table 4.3 The percentages of phenol desorption in batch tests.

No.	Adsorption tests		Desorption tests		Desorbed
	C_e (mg/l)	q_e (mg/g)	C_D (mg/l)	q_D (mg/g)	(%)
1	3.8	72.72	3.31	71.89	1.14
2	8.9	87.54	6.2	85.64	2.16
	9.1	87.49	5.91	85.69	2.06
3	22.73	108.33	13.4	103.03	4.9
4	47.5	141.97	20.2	130.44	8.12
5	102.0	176.58	20.9	157.59	10.76
6	155.67	186.06	20.46	158.83	14.64
7	194.66	199.67	19.38	161.27	19.23
8	195.33	198.01	20.7	161.61	18.38
9	236.33	205.18	15.9	156.46	23.74

surface. As a result, only part of the adsorbed phenol could be desorbed.

It is important to note that the contact time for these desorption tests was three weeks while the electrochemical regeneration tests lasted only 2.5 to 10 hours. It is clear that phenol is a compound displaying partially irreversible adsorption. These results are similar to those obtained by Snoeyink *et al.* (1969), who have shown that 50% of adsorbed phenol was desorbed from coconut-based GAC in distilled water, and by Yonge *et al.* (1985) who have shown only 15% adsorption reversibility for phenol adsorbed on F-400 GAC. Thus, without the aid of a current or other enhancement means, the desorption is very limited.

4.4 Conclusions

Ten sets of loading tests were completed. The data of each set fits the Freundlich isotherm model quite well. Although the Freundlich coefficients, K and 1/n, show variations from set to set, the standard deviations for both coefficients regressed by using eight more reliable data sets are within 1.5% of the mean value. This indicates that the adsorption data are reliable. An additional test showed that increases in moisture content due to exposure to the air during weighing exerted an insignificant impact on adsorption capacity.

Long-term (17 days) GAC adsorption kinetic test demonstrates that it takes six days to attain the equilibrium between the solid and liquid phase concentration. Desorption studies indicate that a significant fraction of adsorption on GAC is irreversible and only a fraction of adsorbed phenol can be desorbed from GAC in the 1%-NaCl solution. The percentage of desorbed phenol increases with increasing carbon loading. For the loading of

108 mg/g, used for most of electrochemical regenerations, the percentage of desorption is 4.9 percent. Thus, the long term desorption without the aid of a current is very limited.

CHAPTER FIVE

ELECTROCHEMICAL REGENERATION OF GRANULAR ACTIVATED CARBON

5.1 Introduction

This chapter presents the results of an investigation into the feasibility of using an electrochemical technique to regenerate spent GAC. Regeneration efficiency is determined based on adsorption, electrochemical regeneration, and readsorption tests. The evaluation of the electrochemical process was made through a sensitivity analysis of key process variables affecting the regeneration efficiency.

5.2 Evaluation of Regeneration Efficiency

5.2.1 Methods of evaluation

The evaluation of a regeneration process is based on the characteristics of the GAC regeneration. In thermal regeneration, the quality control of regenerated carbon is performed by measuring the apparent density of regenerated carbon and by laboratory tests of measuring the capacity of regenerated carbon to adsorb a standard iodine solution (e.g. Iodine Number) (U.S. Environmental Protection Agency, 1973). Because dry-regenerated carbon can be sampled from the outlet of a furnace, the apparent density can be easily determined by weighing the regenerated GAC of certain volume. In chemical regeneration,

there are two ways of expressing the restored carbon capacity for batch regeneration tests. The first is by regeneration efficiency (RE), which can be calculated as follows (Martin and Ng, 1984 and 1985):

$$\text{Regeneration Efficiency (RE)} = \frac{q_r}{q_{e1}} \cdot 100\% \qquad (5.1)$$

where q_{e1} is the adsorptive capacity of virgin carbon obtained by equation (2.1) and q_r is the capacity of regenerated carbon after the readsorption equilibrium. This approach is also sometimes used to assess the effectiveness of thermal regeneration.

A second method is by determining the percentage of desorbed contaminants (e.g. Cooney *et al.*, 1983; Tan and Liou, 1989). In this kind of solvent regeneration experiments, it is assumed that all the desorbed contaminant is in the solvent. Evaluation of regeneration efficiency (effectiveness of solvent) is based on measuring the equilibrium concentrations of the adsorbates. From the measurements, it is possible to determine the quantity of both adsorbate originally adsorbed onto the carbon and adsorbate subsequently desorbed from the carbon by the solvent. Then, the percentage of desorption (i.e. adsorbed contaminant desorbed in the solution) can be calculated (Cooney *et al.*, 1983). Many researchers have employed carbon columns in adsorption and regeneration tests (e.g. Cooney *et al.*, 1982; Picht *et al.*, 1982; Goto *et al.*, 1986). The carbon capacities are calculated through integration of the area above the breakthrough curves.

Since the electrochemical regeneration is conducted via batch tests, evaluation of regeneration efficiency is based on cycles of adsorption, regeneration and readsorption. The standard RE method (equation (5.1)) is selected over others in this study for two

reasons. First, the apparent density and Iodine Number measurements are usually not accurate enough in laboratory studies to determine RE, and GAC drying procedure may cause certain amount of phenol to be removed from the carbon. Second, the electrochemical process may desorb phenol from GAC and oxidize it in the electrolyte, or it may destroy phenol on the GAC with or without modifying the GAC surface, or both. If the phenol is oxidized, it is impossible to determine the percentage of phenol desorbed by measuring the phenol concentration in the electrolyte solution.

5.2.2 Discussion of evaluation methods

From the desorption tests, we know that phenol desorption is very limited without the aid of a current. Control experiments of 1.5-hour and 2.5-hour long were carried out in the electrochemical reactor with no current going through the cells. In such a short time (compared with three-week desorption period), the amount of desorbed phenol should be negligible and the calculated RE should approach zero. It was surprising, however, that the regeneration efficiencies calculated by equation (5.1) were 60.47%, 60.16%, 27.7%, and 26.24%, respectively (Table 5.1). Thus several questions arose: how could a certain amount of capacity be restored without the current? Did the desorption occur in the 1%-NaCl solution? Measurement of phenol concentration shows that there was almost no phenol desorption (< 1.5 mg/l) in the electrolyte solution (see Table 5.1). Repeated experiments showed similar results, which means that the problem lies in the evaluation method itself. This method (i.e. equation (5.1)) assumes that the regeneration process destroys or removes all the adsorbate from the surface of spent GAC, however, this is not necessarily the case in reality, particularly when the degree of regeneration is low.

Table 5.1 Experimental results of regeneration without current.

Adsorption test		Regeneration conditions		Desorbed phenol	Readsorption test			Standard method	New method
C_{e1} (mg/L)	q_{e1} (mg/g)	Current	Time	(mg/l)	C_{e2} (mg/L)	Δq_2* (mg/g)	q_{e2} (mg/g)	RE (%)	REFF (%)
22.36	108.21	0	1.5h	0	131.22	65.43	172.67	60.47	0.89
22.38	108.09	0	2.5h	0	132.05	65.09	172.95	60.16	0.30
115.35	164.00	0	1.5h	0	246.45	45.42	203.09	27.70	3.86
113.3	165.83	0	2.5h	0.1	248.54	43.51	203.53	26.24	3.50
25.54	106.49	0	2.5h	1.4	145.23	60.03	169.41	56.38	-2.71
111.93	167.61	0	1.5h	0	247.33	42.11	208.08	23.81	0.98
111.04	168.36	0	2.5h	0	247.33	42.10	208.08	25.00	1.41
25.63	106.46	0	0		141.53	61.50	168.26	57.77	-0.29
120.11	158.61	0	0		257.33	35.89	196.91	22.63	-1.52

* $\Delta q_2 = (C_o - C_{e2})V/M$

In order to improve this evaluation method, the relationship between different components of the regeneration tests needs to be analyzed further. An extreme case of totally ineffective regeneration can be taken as an example. During the first adsorption cycle virgin GAC is loaded with the contaminant. Adsorptive capacity of virgin GAC q_{e1} is calculated by following expression:

$$q_{e1} = \frac{(C_o - C_{e1}) \cdot V}{M} \tag{5.2}$$

where C_{e1} is first cycle equilibrium liquid phase concentration (mg/l) and q_{e1} is equilibrium solid phase concentration.

After an adsorption equilibrium, the loaded GAC undergoes a completely ineffective regeneration. The adsorptive capacity of loaded GAC will still be q_{e1}. Then this GAC will get reloaded in the second adsorption cycle identical to the first. The GAC will continue to adsorb the contaminant from the solution until a new equilibrium between solid and liquid phases is reached. This additional loading occurs because the solid phase concentration q_{e1} is much lower than q_{eo}, the solid phase concentration which is in equilibrium with the initial liquid phase concentration. The additional adsorptive capacity (Δq_2) attributed to the second cycle is:

$$\Delta q_2 = \frac{(C_o - C_{e2}) \cdot V}{M} \tag{5.3}$$

where C_{e2} is readsorption equilibrium liquid phase concentration. The total adsorptive capacity (q_{e2}) of GAC after the readsorption cycle equals:

$$q_{e2} = q_{e1} + \Delta q_2 \tag{5.4}$$

In the completely ineffective regeneration, since GAC does not undergo regeneration, q_{e2} should be described by the original Freundlich model (i.e. $q_{e2} = K C_{e2}^{1/n}$). To demonstrate, two GAC samples were tested in such manner, i.e. by placing loaded GAC back into a readsorption test directly after achieving the first adsorption equilibrium. The results are given in the last two rows of Table 5.1. These two samples plus those control samples which were in the electrochemical reactor with no current for a certain time period are subject to completely ineffective regeneration. The readsorptive and total capacities of GAC were calculated by equations 5.3 and 5.4, and shown in Table 5.1 as well. All adsorption data from Table 5.1 and the best fit to Freundlich isotherm are presented in Figure 5.1, together with readsorption data. This figure shows that the GAC samples yielding the filled squares in the first adsorption cycle reach the higher solid phase concentrations (the empty square symbols) at the completion of the second adsorption cycle. As expected, the total adsorptive capacities after the second adsorption cycle are well described by the original Freundlich isotherm (shown as a line in Figure 5.1).

Since most regeneration techniques do not fully restore the GAC's adsorptive capacity, it is necessary to examine the case of partial regeneration of activated carbon. Partial regeneration may result from the permanent reduction of the adsorption capacity caused by the destruction of the adsorptive sites or from plugging of pores. Another possibility is that the GAC surface and structure are not altered and the partial regeneration is caused by failure to remove all the adsorbate from GAC adsorption sites. The analysis below will address the last mechanism.

For the cases with low regeneration efficiencies there is residual contaminant on the

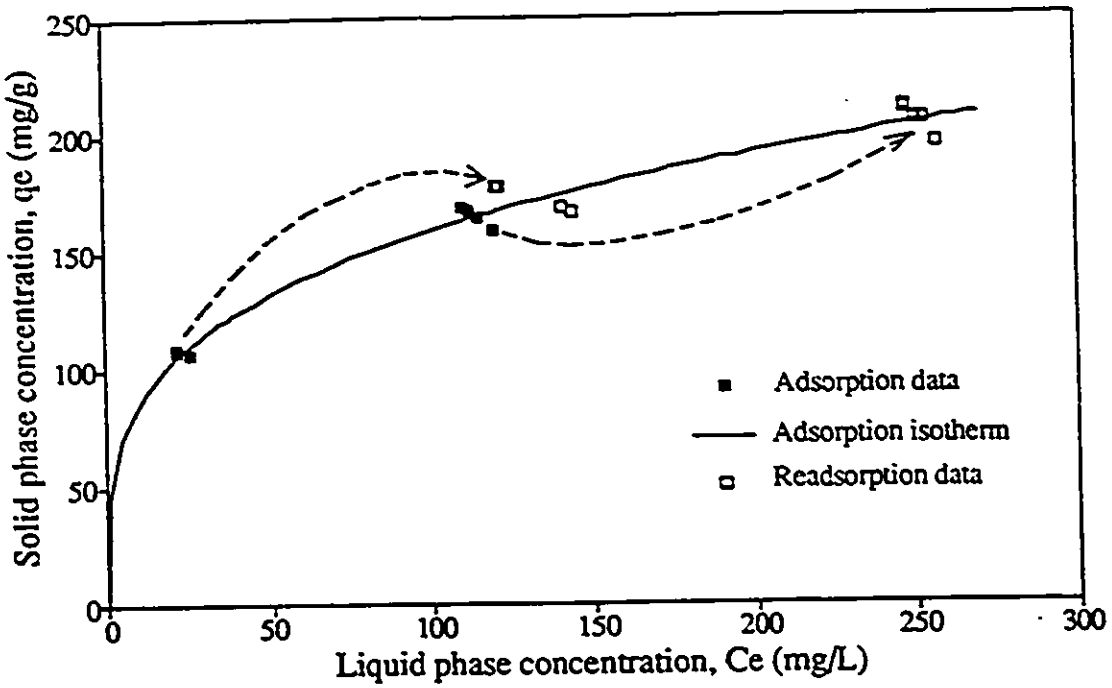


Figure 5.1 Adsorption data and isotherm, along with readsorption data without electrochemical regeneration.

GAC at the end of regeneration cycle, the residual solid phase concentration is q_{rs} and regenerated capacity is q_{Reg}:

$$q_{Reg} = q_{e1} - q_{rs} \tag{5.5}$$

The regeneration efficiency, REFF, is then:

$$\text{REFF} = \frac{q_{Reg}}{q_{e1}} \cdot 100\%$$

$$= \frac{(q_{e1} - q_{rs})}{q_{e1}} \cdot 100\% \tag{5.6}$$

Unfortunately, REFF and q_{Reg} cannot be determined from experiments because q_{rs} cannot be measured directly. Assuming that the carbon surface is not altered, the total capacity after the readsorption cycle, q_{e2} can be described by the original Freundlich isotherm equation:

$$q_{e2} = q_{rs} + \Delta q_2 = KC_{e2}^{1/n} \tag{5.7}$$

Substituting equation (5.5) into (5.7), one obtains:

$$q_{e2} = q_{e1} - q_{Reg} + \Delta q_2 = KC_{e2}^{1/n} \tag{5.8}$$

and

$$q_{Reg} = q_{e1} + \Delta q_2 - KC_{e2}^{1/n} \tag{5.9}$$

Then the regeneration efficiency can now be estimated by a new formula:

$$\text{REFF} = \frac{q_{e1} + \Delta q_2 - KC_{e2}^{1/n}}{q_{e1}} \cdot 100\% \qquad (5.10)$$

This new formula is different from equation (5.1) in that it takes the residual contaminant on GAC into account in regeneration efficiency calculation.It is noted from equation (5.10) that if there is no residual contaminant on the GAC (RE = 100%), equations 5.6 and 5.10 reduce to equation (5.1).

Recalculating the data listed in Table 5.1 by equation (5.10) (the new method) shows that REs range from -2.71% to 3.86%, that is, they approach zero. These results indicate that completely ineffective regeneration did not restore any adsorptive capacity. By contrast, large values of RE were obtained by using the standard method (equation (5.1)) for the same data. For example, a RE of 60.47% was obtained with the standard method, while 0.89% with the new method. This is because the standard method considers readsorptive capacity Δq_2 as the regeneration capacity in equation (5.1), and thus over estimates the efficiency.

To gain a better understanding of the experimental results, both the standard and new REs were determined for sets of data (Table 5.2). It shows that the difference between the two methods for low current conditions is significant. For example, for GAC regeneration at 10 mA for 2.5 hours, the RE obtained by the standard method was 64.67%, which is roughly seven times higher than that by the new method (9.31%). But the differences decrease with increasing regeneration current and time. For regeneration conditions of 50 mA/5 hours and 10 mA/40 hours, the difference between REs calculated by the two methods was reduced to 22% and 13%, respectively. These differences may be due to the fact that the standard method includes the residual capacity q_{rs} in the readsorptive

Table 5.2 Regeneration efficiencies calculated with the standard and new methods (Carbon loading = 107 mg/g, electrolyte = 1% NaCl, and particle size = 16/18 mesh).

Regeneration conditions		Standard method	New method	Difference
Current (mA)	Time (hr)	RE (%)	REFF (%)	RE - REFF
10	2.5	64.67	9.31	55.36
	5.0	75.87	31.43	44.44
	7.5	82.44	45.91	36.53
	10	86.83	58.54	28.29
	15	90.40	68.35	22.05
	20	91.92	74.80	17.12
	40	94.80	82.77	12.63
50	2.5	84.72	54.38	30.34
	5.0	89.22	69.93	19.22
	7.5	92.93	76.03	16.90
	10.0	93.23	75.60	17.63
100	2.5	90.65	68.35	22.30
	5.0	92.84	75.48	17.36
	7.5	93.65	81.11	12.54
	10.0	93.87	80.47	13.40

readsorptive capacity. Since electrochemical regeneration cannot achieve full restoration, the equilibrium liquid phase concentration in the readsorption cycle is always higher than in the initial adsorption cycle. This results in an apparent additional adsorptive capacity and higher RE calculated by the standard method. Actually, part of the apparent adsorptive capacity is caused by the increase in equilibrium liquid phase concentration and is not the recovery of capacity.

The regeneration efficiency increases as the equilibrium liquid phase concentration in the readsorption cycle decreases. When a regeneration technique achieves complete restoration, there is no additional capacity because the equilibrium liquid phase concentration in readsorption cycle is the same as in the initial adsorption cycle. The REs determined by the two methods will then be the same. However, the experimental results showed that REs have approached the peak value (≈ 94%), this suggests that electrochemical regeneration could not achieve full recovery of GAC capacities for phenol on F-400 carbon. The reduced adsorption capacities may be due to alterations to the GAC surface and/or structure. Such a phenomenon would render the new calculation method incorrect. Although the results calculated by this new method seem more reasonable than those by the standard method, further investigation is needed to prove if its hypothesis of unchanged surface and structure is correct. As such experiments are beyond the scope of this thesis, the standard method is still used in this study.

5.3 Regeneration of GAC Using an Electrochemical Technique

An ideal regeneration process should regenerate the activated carbon and destroy the adsorbed contaminants so that they cannot be transferred to other media. It should

either directly destroy the contaminants without altering the surface of the GAC or desorb them from the GAC and destroy them in solution. The high adsorptive capacities of activated carbon are due to adsorption on its large internal surface area. The adsorption on the external surface of the particles is negligible compared with that on the internal surface. The electrochemical effect is expected to occur primarily on the external surface of the GAC particles, however, it may also affect the internal surface since the GAC is in direct contact with the electrodes. If the effects are only confined to the external surface, it is more likely that enhanced desorption and destruction of contaminants in the liquid phase is the prevailing regeneration mechanism.

As discussed in section 5.2, the regeneration process was evaluated using the standard method to calculate the RE, which is the adsorptive capacity achieved in the readsorption experiment divided by the virgin carbon adsorptive capacity (i.e. equation (5.1)).

The following section discusses the impact of GAC location, regeneration current, regeneration time, electrolyte concentration, electrolyte type, mass of phenol on the GAC, and particle size on RE. Unless otherwise stated, the experiments were conducted using a standard set of conditions with one parameter varying at a time. The standard set of conditions were: 1.2 g of 16/18 mesh GAC that was loaded with a phenol (approximately 107 mg/g), a 1% NaCl solution as an electrolyte, a five-hour regeneration time and a 50 mA regeneration current.

5.3.1 Cathodic versus anodic regeneration

In order to determine which electrode achieves better regeneration efficiency, three-

hour regeneration tests with a 50-mA current were conducted with GAC being placed on: a) the anode, b) the cathode, c) the anode and cathode simultaneously, and d) the anode and cathode simultaneously but reversing the polarity after 1.5 hours. As shown in Figure 5.2, the REs were approximately 80 percent. This contrasts with 4.9% desorption (regeneration) obtained without the benefit of an applied current (Table 4.3, when q = 108.33 mg/g). Thus, the electrochemical process greatly improved the recoverability of adsorption capacity.

Comparison of results obtained under regeneration conditions a, b and c shows that cathodic regeneration is 5 to 10% more efficient than anodic regeneration (Figure 5.2). On the other hand, the cathodic regeneration left a small amount of residual phenol in the electrolyte, while the anodic phenol residual was undetectable. The c and d regeneration tests had the same residual phenol concentrations because two samples were regenerated in one batch and the electrolytes from the two electrode compartments were mixed before analysis. It is believed that the residual phenol comes from the cathode compartment. Switching the polarity at half-time was not superior to other alternatives. It appears that phenol did not desorb well under straight anodic conditions, but once desorbed it was destroyed more efficiently. This can be explained by the localized conditions at the electrodes.

In the electrolysis of aqueous sodium chloride, sodium ions are attracted toward the negative pole (cathode) and chloride ions toward the positive pole (anode) (Figure 5.3). The electric charge in electrolytic conduction is carried by cations moving toward the cathode and anions moving toward the anode. For a complete circuit, electrode reactions must accompany the movement of ions. At the cathode some chemical species (not

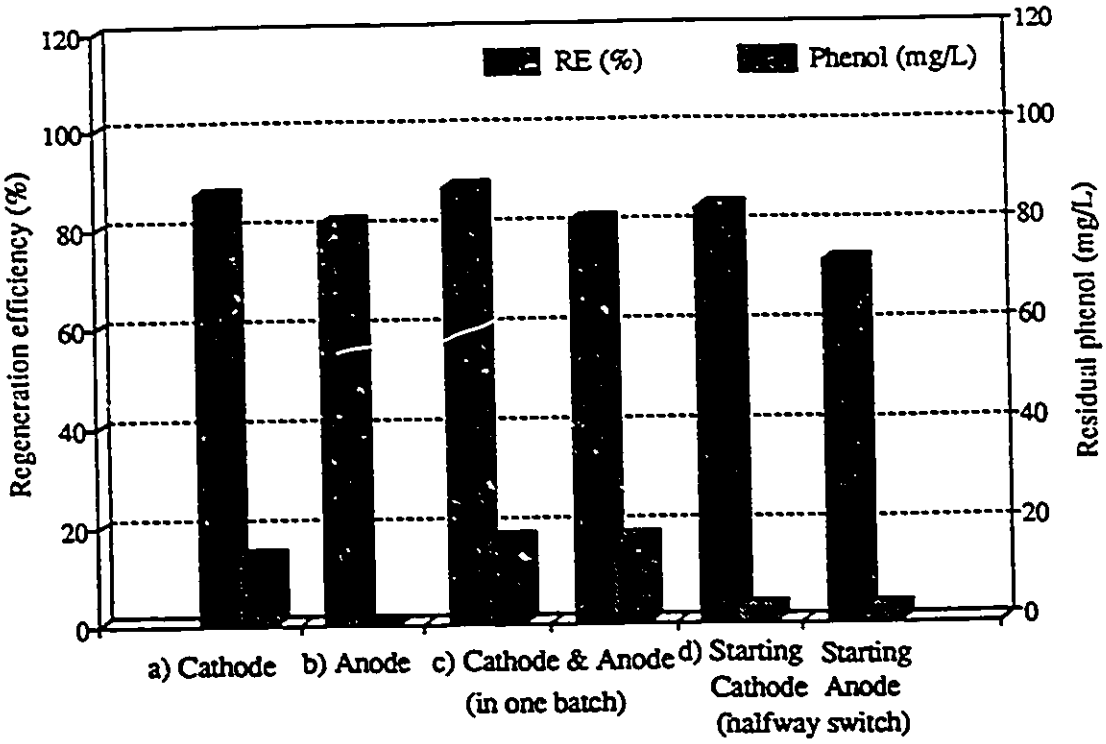


Figure 5.2 Variations of regeneration efficiency and residual phenol with GAC on different electrodes. (Regeneration current and time were 50 mA and 3 hours respectively).

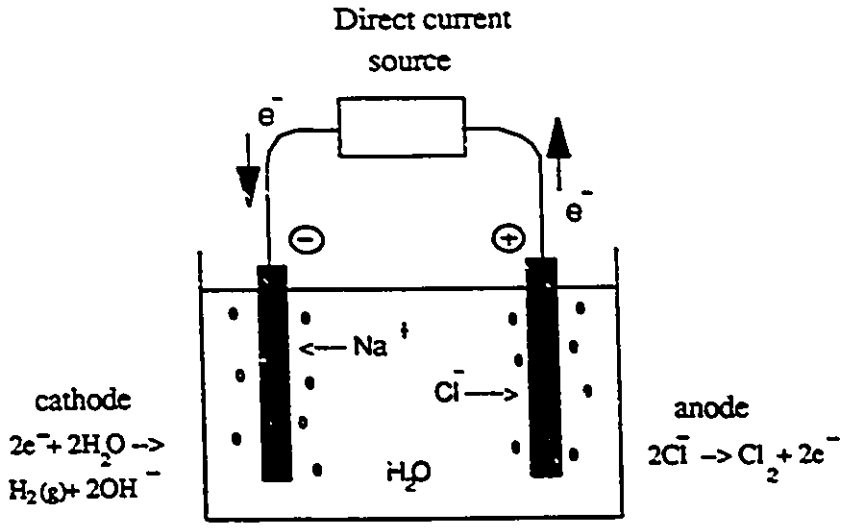


Figure 5.3 Electrolysis of sodium chloride solutions.

necessarily the charge carrier) accept electrons and are reduced. At the anode, electrons are received from some chemical species, which, as a consequence, are oxidized. The sodium ions are difficult to reduce. Therefore water is reduced and hydrogen gas is evolved at the cathode, and the solution surrounding the electrode becomes alkaline as described by the following equation:

$$2e^- + 2H_2O \text{ — } H_2\,(g) + 2OH^- \qquad (5.11)$$

Chloride ions are oxidized at the anode:

$$2Cl^- \text{ — } Cl_2\,(g) + 2e^- \qquad (5.12)$$

Since the sodium ion remains unchanged in solution, the reaction may be written as:

$$2H_2O + 2(Na^+,Cl^-) \xrightarrow{\text{electrolysis}} H_2(g) + Cl_2(g) + 2(Na^+,OH^-) \qquad (5.13)$$

It has been known that adsorption capacity for phenol decreases with increasing pH (see Table 2.1). At the reducing electrode, OH^- ions accumulate around the electrode which increases the local pH. This reduces the adsorbability of phenol and promotes phenol desorption from the GAC. Sodium hydroxide is a chemical regenerant with oxidizing powers to desorb the contaminants from GAC and has been investigated by a number of researchers (e.g. Goto *et al.*, 1986; Himmelstein *et al.*, 1973).

The anode is an oxidizing electrode. It is likely that the adsorbed phenol was rapidly oxidized when activated carbon was placed at the anode compartment, which explains the lack of phenol residual in the electrolyte. The driving force associated with the negligible phenol residual in the electrolyte led to further desorption and regeneration.

When the electrolyte consists of anions and cations that are not removed from the solution, such as sodium sulphate and sodium acetate, evolution of oxygen gas is observed at the anode (Mortimer, 1979). As mentioned earlier, the presence of molecular oxygen significantly increases the adsorptive capacity of GAC for phenol (Vidic and Suidan, 1991; Vidic *et al.*, 1990). The increase can be attributed to polymerization reactions that take place on the surface of activated carbon; the polymeric species formed by these reactions do not desorb under normal conditions. As large quantities of oxygen are generated at the anode, the regeneration process may have increased the extent of this type of chemisorption. Thus, it may reduce phenol adsorption in the next loading cycle. From this respect, cathodic regeneration seems better than the anodic.

Bubbles formed during regeneration migrated upwards and were temporarily trapped underneath the solid electrode above. When the bubbles coalesced and formed large bubbles (i.e. with several cm^2 in area), they could not easily escape from the electrode compartments via small holes on the plexiglass rings. The quantity of bubbles produced was proportional to the current applied. The bubbles caused two problems. First, as large area of the underside of top electrode was covered by the bubbles, the transfer efficiency may have been impaired. In later runs, the vents were enlarged, but the problem was not totally eliminated. On the other hand, rising bubbles may have a beneficial effect as they provided the only mixing that occurred in the cell. Second, the bubbles adhered to and carried carbon particles because of their relatively low density. Some small particles were carried out from the inner electrode compartments into the large crystallizing dish. This was particularly troublesome when GAC was being regenerated simultaneously at both electrodes, since it was impossible to distinguish the source compartments of carbon

particles that came into the large crystallizing dish. It is critical to retain all the GAC from individual samples together because the GAC will be used in the readsorption test, and the readsorptive capacity is used to evaluate the RE. Thus, all of the subsequent experiments were conducted with GAC at a single electrode. The cathode was selected over the anode electrode because of its higher REs. Longer regeneration time (5 hours) achieved similar results (cathodic regeneration RE = 90.61%, anodic regeneration RE = 78.55%). However, an extensive comparison of the REs and residual phenol concentration for both cases is required to establish if the regeneration at one electrode is superior to the other.

5.3.2 Effect of regeneration current and time

As designed, the power source supplies a constant current to the electrochemical cell. Here the current is used instead of current density because of its simplicity. The current density can be calculated by dividing the current by the electrode area, i.e. 45.36 cm^2. In these experiments, the regenerations of GAC were carried out at various currents, and the corresponding cell potential varied with current and electrolyte. The cell potential measurements for two different currents in 1% NaCl electrolyte are given in Figure 5.4 as an example. The cell potential values remained almost constant or slightly increased over an extended period. For applied currents of 50 mA and 100 mA, the cell potentials were almost the same because of the high conductivity of the electrolyte. The concentration of ions decreased with reaction as hydrogen gas was released at the cathode and chlorine gas at the anode. Then, the cell potential increased correspondingly to maintain a constant current. When certain aqueous solutions are electrolyzed, however, large amount of water is involved in the electrode reactions rather than the ions derived from the solute

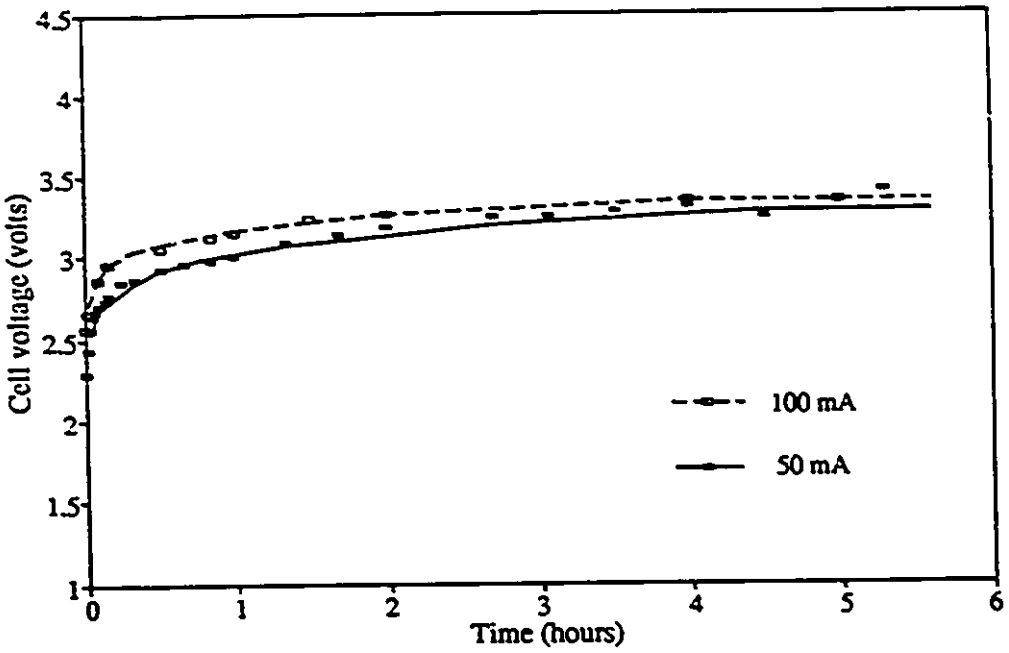


Figure 5.4 Cell voltage vs. regeneration time of electrochemical reactor operations for two regeneration currents in a 1% NaCl electrolyte.

(Mortimer, 1979).

Figure 5.5 shows GAC regeneration runs performed at various currents and durations (data are tabulated in appendix E2). The REs could be increased to 93% by increasing the current and/or time. The effect of current was very marked from 10 milliamperes (mA) to 30 mA and gradual from 30 mA to 100 mA. The effect of time shows a similar pattern to that of current, that is, the REs increase rapidly with increasing regeneration time in the range of 1.5 to 5 hours, followed by a more gradual increase of RE for longer times. Using the same type of electrochemical treatment on virgin GAC prior to loading (50 mA for 1.5 hours) had no impact on adsorptive capacity of GAC. Results of high-current runs with 2.5-hour regeneration period are presented in Figure 5.6a. Increasing the current beyond 100 mA does not enhance the RE, however it reduces the phenol residual in the electrolyte to undetectable levels (< 0.1 mg/l). It is noted from Figure 5.6a that to destroy all of the residual phenol, the current has to be significantly larger than the lowest current yielding the maximum RE. Longer regeneration times achieved similar results (Figure 5.6b). Comparison of Figures 5.6a and 5.6b indicates that high currents are more efficient at destroying the phenol in the electrolyte than low currents. This is attributable to the high oxidizing power at higher currents. The need for additional time suggests that there is a mass transfer limitation in the transport of phenol from the cathode, where the GAC is located, to the anode where the phenol oxidation is expected to occur. Future cells should incorporate mixing flows to reduce potential mass transfer limitations.

There is a slight variance between data. The analytical error of the phenol concentrations, that were used to calculate the GAC loading, was 3 percent. An evaluation of seven replicate tests has shown that the 95% confidence interval of regeneration

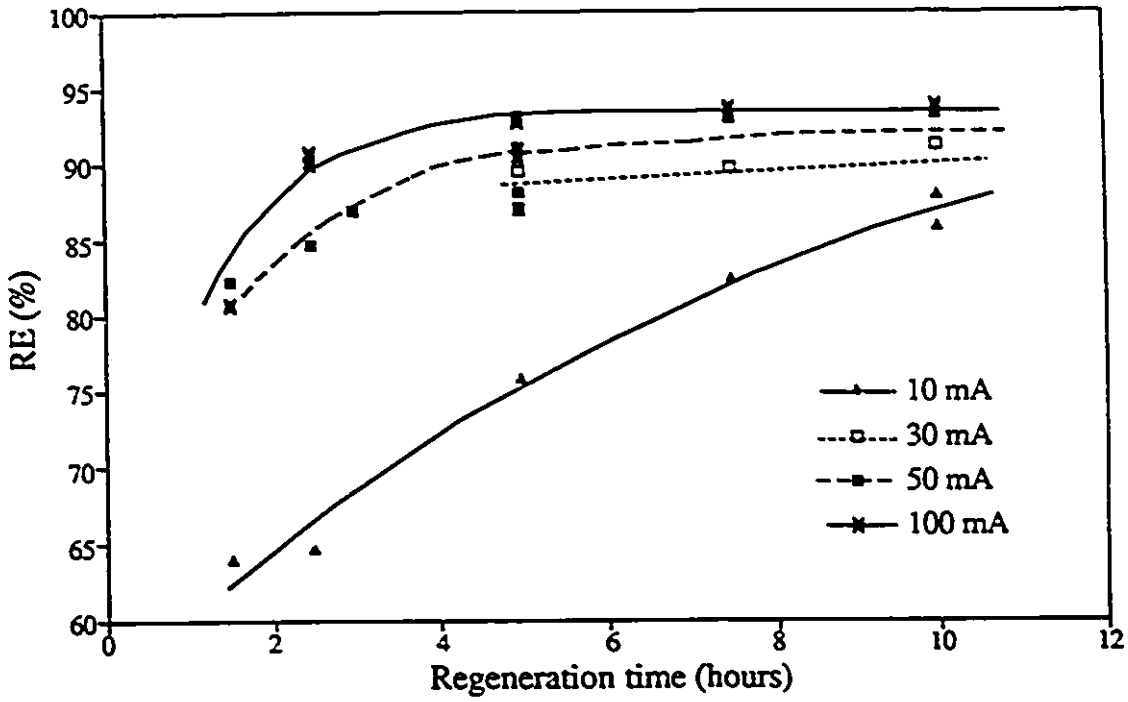
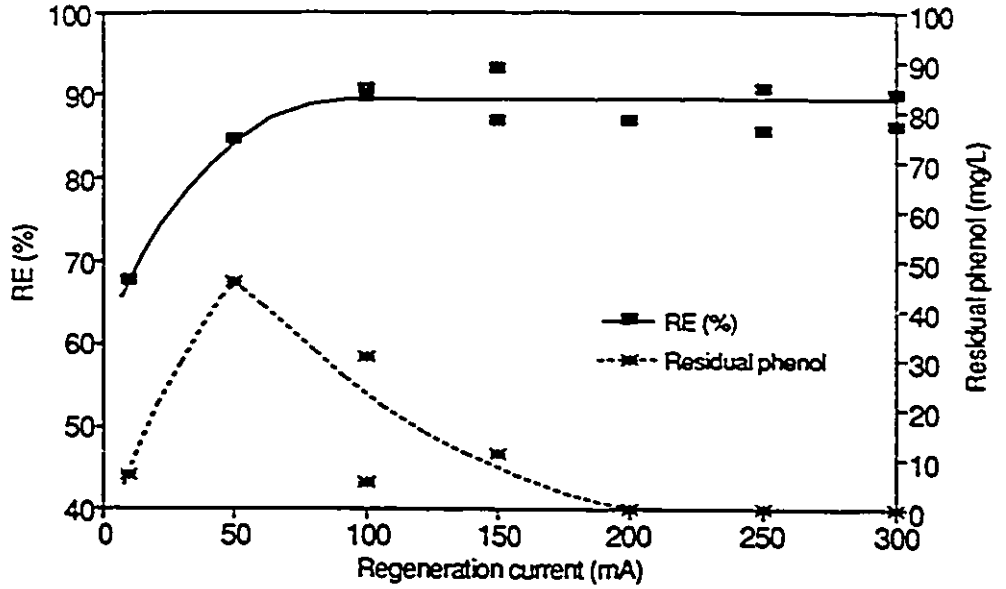


Figure 5.5 Relationships of regeneration efficiency with current and time.



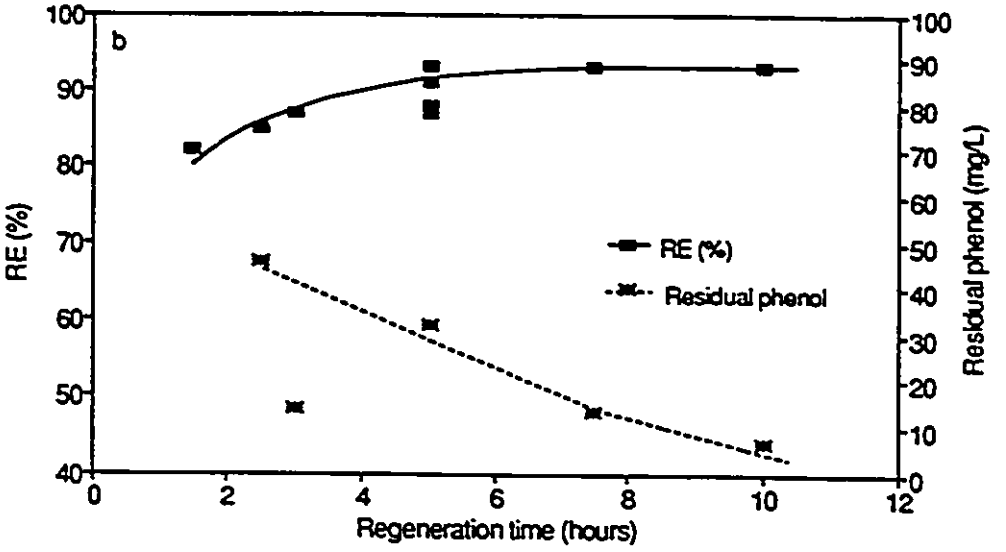


Figure 5.6 Variations of regeneration efficiency and residual phenol: a) with at 2.5 hrs. of regeneration time, b) with regeneration time at 50 mA of current.

efficiency is ± 7% of the mean. This is not surprising that the RE includes the combined errors of three experiments: loading, electrochemical regeneration and reloading.

A higher current can rapidly oxidize the phenol, but may also alter or deteriorate adsorption sites. Thus a lower current was hypothesized to be more effective. However regenerations at 10 mA (the lowest current tested) only yielded a maximum RE of 95% after 40 hours (Figure 5.7). On the other hand, low current and long regeneration time could achieve high coulombic efficiency, that is, a slightly lower energy consumption. Figure 5.8 represents the same regeneration current and time profiles in terms of RE versus the number of coulombs passed instead of the regeneration time duration. It shows that low currents produced higher REs for the same number of coulombs passed. Therefore, the coulombic efficiency for the GAC regeneration is somehow dependent on the current applied.

Chlorine odor was produced during the experiments. Cathodic regeneration caused the electrolyte in its compartment to become yellowish or brownish in colour during the first hours of regeneration. Anodic regeneration did not yield colour. The intensity of colour was proportional to the current applied and the time passed. Figure 5.9 exhibits changing colours of 1% NaCl-electrolyte after 4- and 5-hour regeneration with a current of 50 mA. With longer regeneration times and/or higher currents (such as 50 mA after 7.5 hours, 200 mA after 1.2 hours), the colour disappeared. With 300 mA current, the electrolyte was colourless throughout. Cathodic regeneration of virgin carbon did not yield a coloured electrolyte. The colour is presumably due to the by-products of phenol oxidation. The general oxidation pathways of phenol decomposition is given in Figure 5.10. Further oxidation leads to intermediates which are usually less stable than the

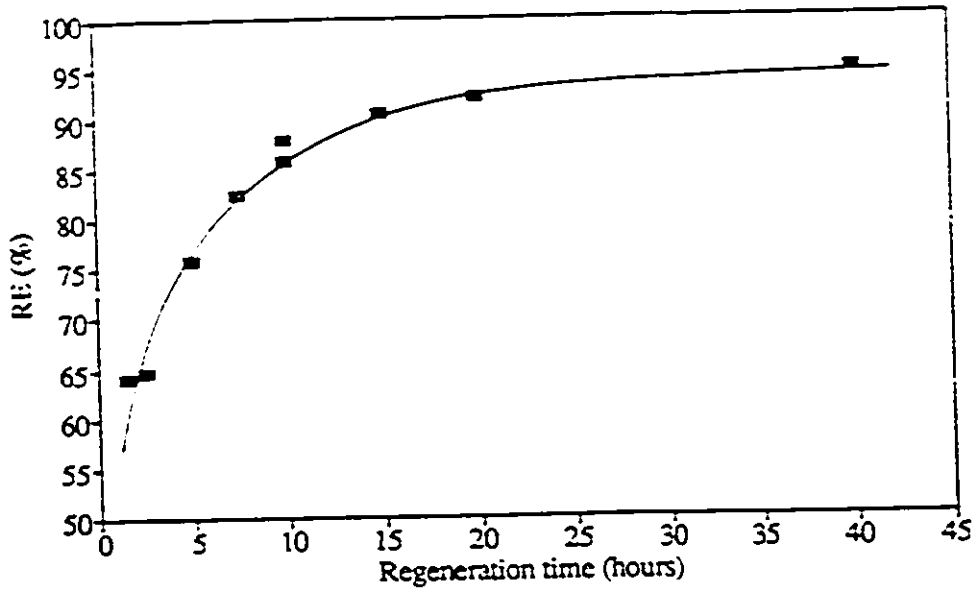


Figure 5.7 Effect of time on regeneration efficiency at a current of 10 mA.

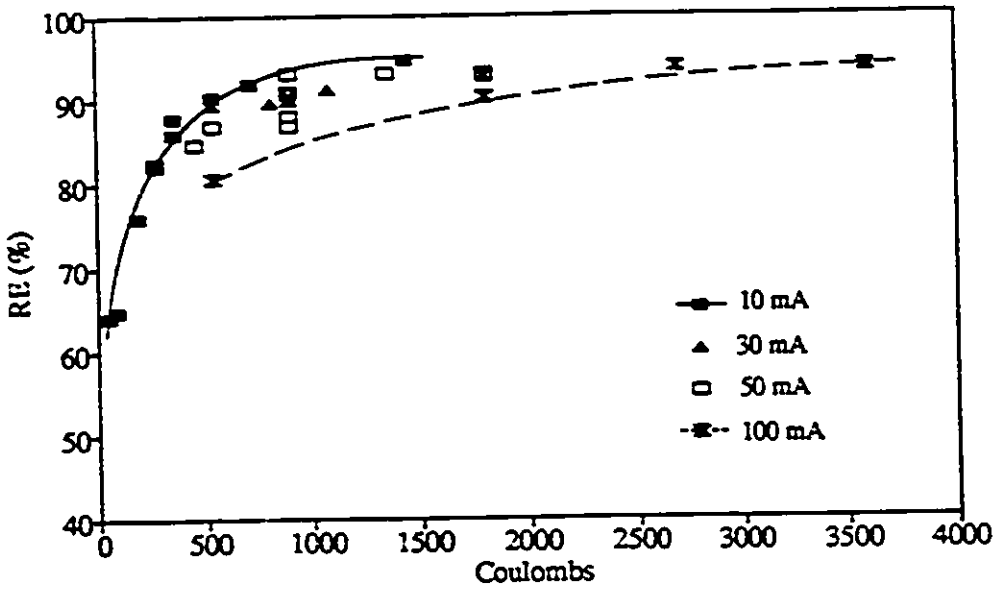


Figure 5.8 Regeneration efficiency vs. the number of coulombs passed for electrochemical regeneration of GAC.

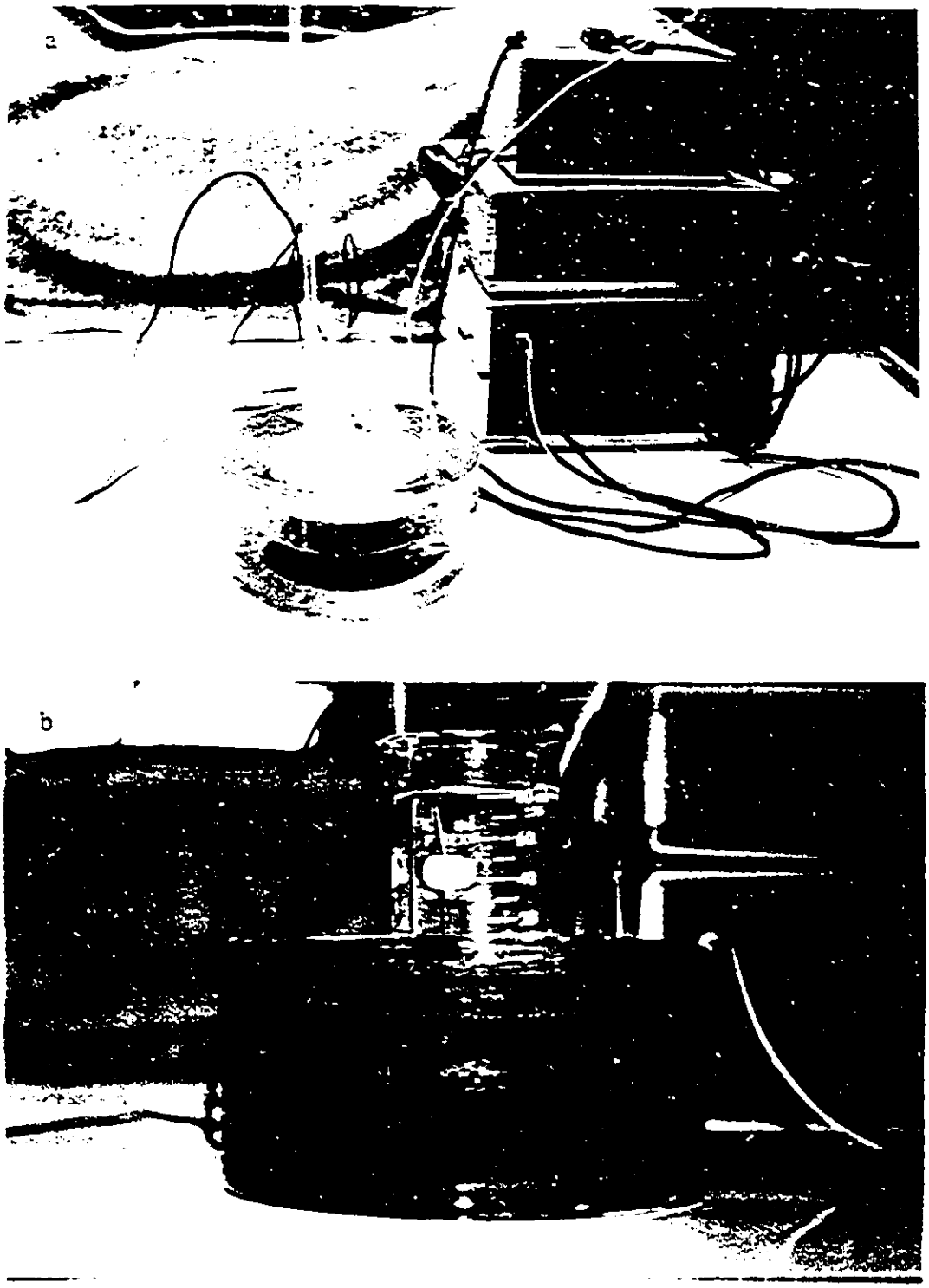


Figure 5.9 Photographs showing the changes in colour during regeneration: a) after 4 hours of regeneration and b) after 5 hours of regeneration with current of 50 mA and 1%-NaCl electrolyte.

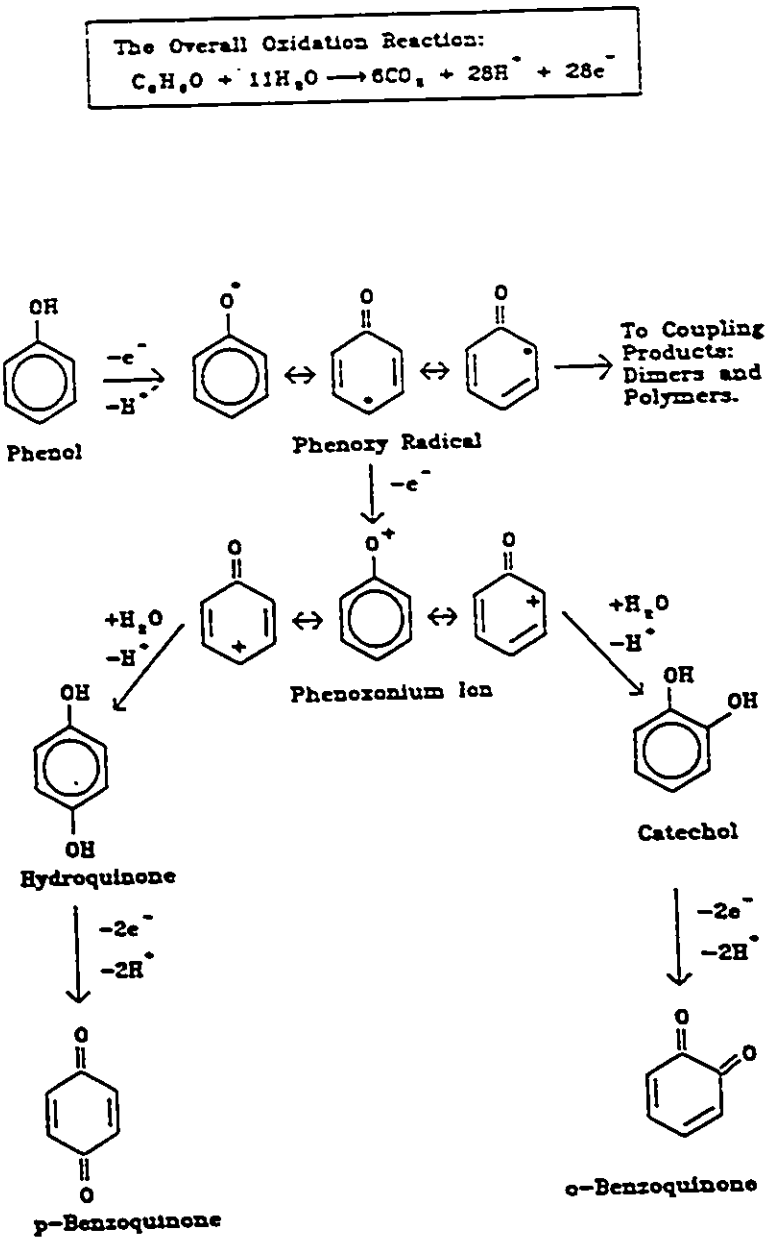


Figure 5.10 The oxidation pathways of phenol (source: Gattrell and Kirk, 1990).

quinone and quickly decompose forming a variety of products including maleic and oxalic acids and eventually CO_2. Catechol is grey in colour, *p*-benzoquinone is yellow and hydroquinone light brown. The coloured electrolyte may result from a combination of these compounds. Owen and Barry (1972) observed a similar phenomenon for a brine solution (e.g. electrolyte), it became a dark red-brown colour, and slightly opaque. The phenol by-products could not be measured in this investigation due to equipment limitations.

Sharifian and Kirk (1986) have monitored the concentration of phenol, benzoquinone, maleic acid, and carbon dioxide in an electrochemical reactor as a function of time (Figure 5.11). Here the carbon dioxide concentration is not a true concentration but is the number of moles of carbon dioxide purged from the electrolyte and is reported as mmol per liter of anolyte. As expected from the reaction sequence, benzoquinone concentration increases initially as phenol starts to be oxidized; its concentration begins to decrease after 1.5 hours due to oxidation. Maleic acid concentration builds up more slowly and begins to decay after 5 hours. At longer times, the rate of CO_2 production remains relatively constant over the 10-hour period and this indicates possibly complete oxidation. Sharifian and Kirk (1986) conclude that the carbon dioxide formation depends on the degree of oxidation and is favoured by high currents, acid concentration (electrolyte), temperature, and dissolved oxygen. Low concentration of phenol ($\leq$ 0.0035 M = 329 mg/l) displays greater conversion to carbon dioxide than does high concentration of phenol. At higher concentrations, there is a significant proportion of other by-products which contribute to the overall carbon mass balance.

Similar results were observed in these experiments. Since high currents and long

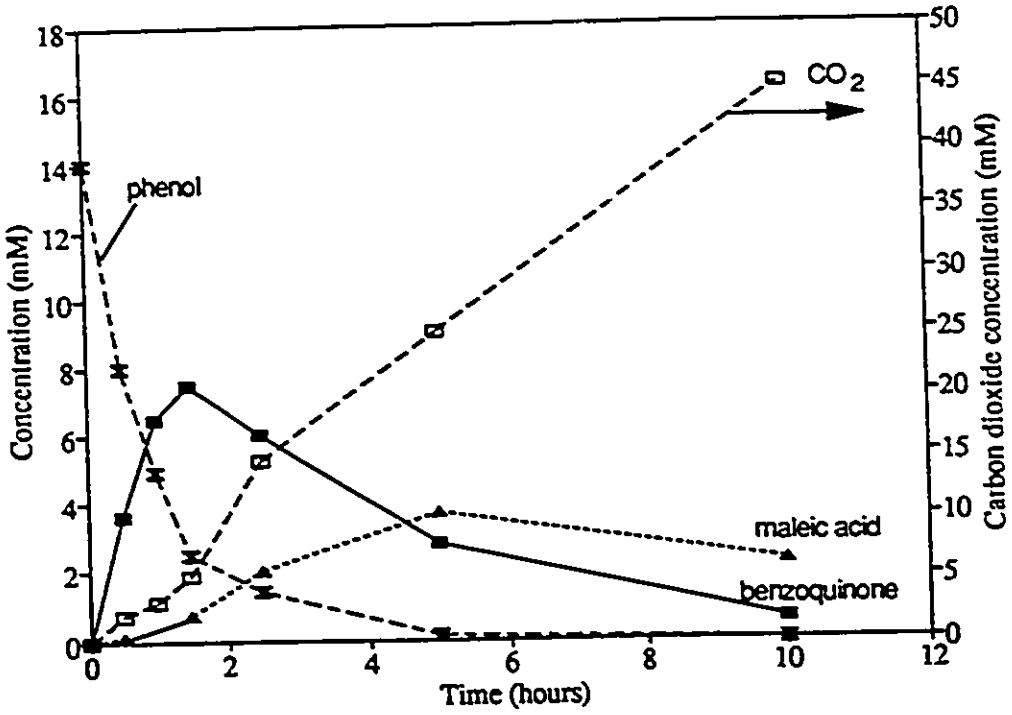


Figure 5.11 Concentration of phenol, benzoquinone, maleic acid, and carbon dioxide as a function of electrolysis time for 0.014 M phenol in 1.0 M sulfuric acid solution at a cell current of 2A. (source: Sharifian and Kirk, 1986).

regeneration times contribute to the destruction of all the residual phenol and oxidation of by-products, one could possibly take regenerated GAC out of the reactor, and then increase the current for a certain period to electrochemically oxidize the contaminated electrolyte before discharge or reuse.

5.3.3 Effect of electrolyte concentration and type

An evaluation of the effect of NaCl concentration on RE suggests that there is a significant effect as the concentration increases from 0.01% to 1% (Figure 5.12, data in appendix E3). Further increases did not appear to enhance the regeneration, however there was some scattering in the data. The concentration of 5% NaCl with a 50-mA current is most likely detrimental to the GAC and its surface, as it creates a 5 mm diameter black spot and several small spots on the surface of the cathode and produces a number of small particles as well. As a result, a low RE is obtained. This is likely due to the impaired effect of excessive chlorine which is generated by the high power input in conjunction with the high chloride content of electrolyte. The results were confirmed by regenerating 30/40 size GAC in a 10% NaCl solution. In this run, the cathodes had black spots, especially dark in the areas adjacent to the platinum sheet-wire joint. The black dots were also observed on the anodes. After filtration, a number of fine carbon particles remained on the membrane filter, which was not observed in other runs. Thus these conditions seem to lead to particle destruction. The concentration of 0.001% NaCl solution was also tested in this study. Although the potentiostatic controller was adjusted to 50 mA, the current through the regeneration cells was much lower than required, approximately 10 mA shown on the coulometer. This means that the concentration of ions in electrolyte was so low that it was

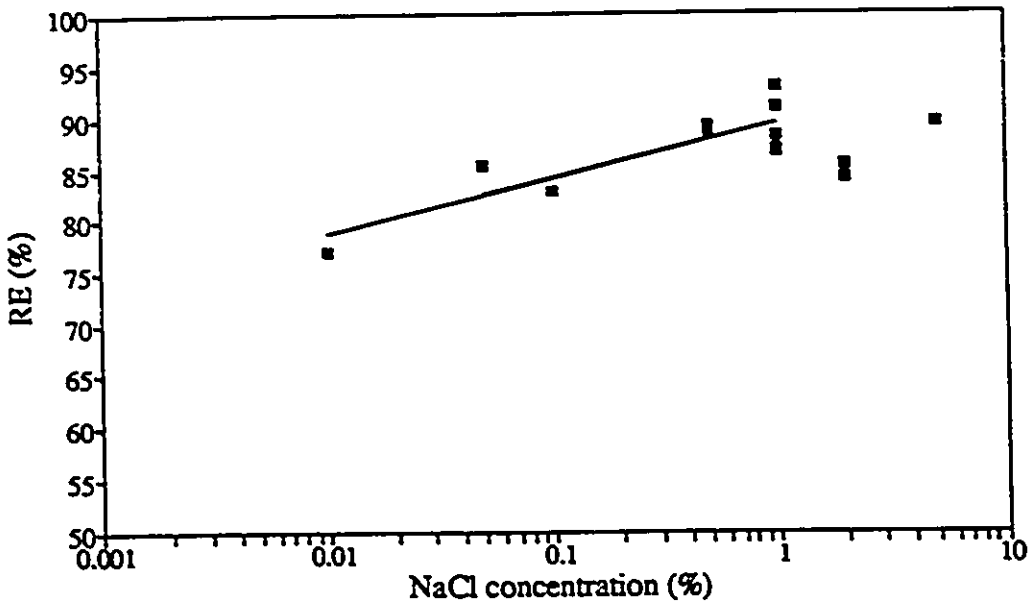


Figure 5.12 Semi-log plot of regeneration efficiency vs. NaCl concentration (particle size 16/18, regeneration current 50 mA and time 5 hours).

beyond the regulation limit of the potentiostatic controller. Thus, this point was not plotted in the figure.

As NaCl solution results in the generation of chlorine at the anode, alternative electrolytes would be preferable if they produce comparable REs. Changes of electrolyte to 1% of sodium bicarbonate, 1% sodium sulphate and 1% sodium acetate also affected the efficiency. Results are shown in Figure 5.13 (data in Appendix E3). The RE obtained by using $NaHCO_3$ as an electrolyte was significantly lower than that obtained by using NaCl. This may be caused by the bicarbonate ions acting as radical scavengers, as is the case in ozonization reactions (Aieta *et al.*, 1988), which would reduce the oxidation rate of phenol. Na_2SO_4 and CH_3COONa electrolytes yielded slightly lower REs than NaCl. These three kinds of electrolytes did not reveal any colour changes during the regeneration tests, but a layer of light brown precipitate was formed on the surface of anodes when CH_3COONa was used as an electrolyte. This is likely a reason for the lower GAC regeneration efficiency because adsorption of reaction products could rapidly cause electrode passivation, blocking further reaction. Phenol is well known for its ability to foul electrodes, and the tarry deposit which is produced on the electrodes during phenol oxidation is attributed to phenol polymerization products. These phenomena were also found by many other researchers who have investigated the electrochemical oxidation of phenolic wastes (e.g. Chettiar and Watkinson, 1983; Dabrowski *et al.*, 1975; Babai and Gottesfeld, 1980). They believed that the passive film is composed of a tightly adsorbed layer of oxidation and polymerization products at the electrode surface, which hindered the electron transfer and lowered the reaction rate. Gattrell and Kirk (1990) used a glassy carbon electrode with an inert electrolyte (Nafion 427 cation selection membrane) to

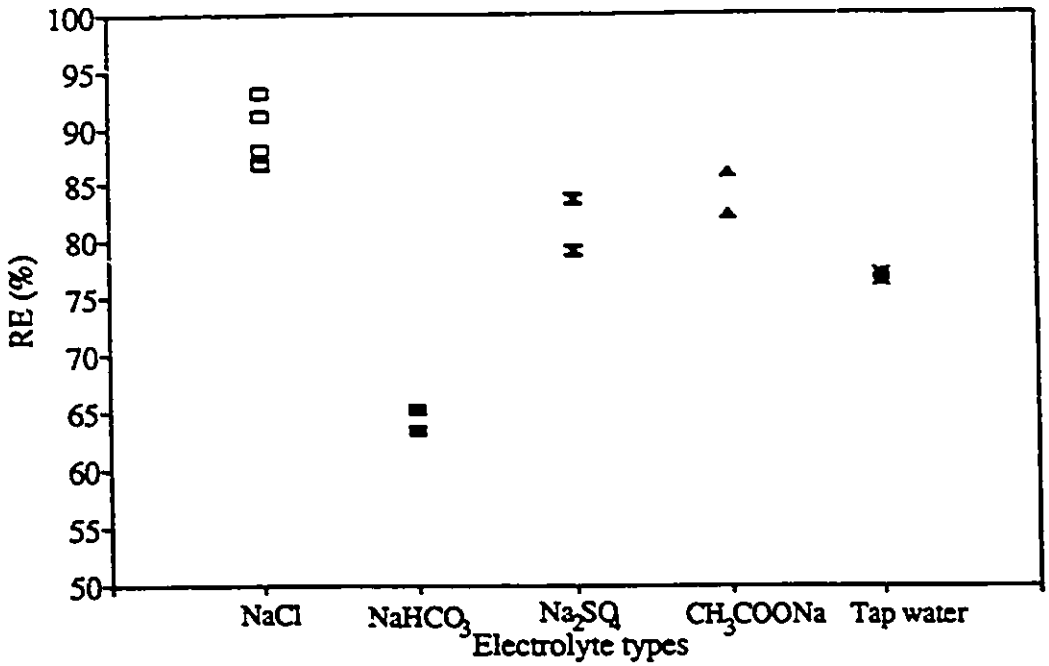


Figure 5.13 Comparison of regeneration efficiencies for different electrolyte types (regeneration current and time were 50 mA and 5 hours respectively).

minimize phenol polymerization.

From the economic point of view, tap water is probably a better electrolyte. Thus Ottawa tap water (drinking water) was used as an electrolyte in this study and result is also plotted in Figure 5.13. The performance was quite good as the RE was 76%. On the other hand, in order to apply a 50-mA constant current, the cell potential increased to about 15 volts (five times as much as that required for 1% NaCl electrolyte). This is because of the low concentration of ions in the water. Although the electrolyte is easy to obtain, the energy input is much higher than for the other alternatives. Also the RE is too low to be competitive with a 1%-NaCl electrolyte. Accordingly, groundwater may be a good electrolyte and it is worth study in the future.

It is hard to draw definite conclusions from the electrolyte samples tested due to the limited number of samples. Further investigation is needed into the effect of electrolyte type and concentrations, as well as their impact on other adsorbates.

5.3.4 Effect of particle size and loading

If desorption is the main mechanism for GAC regeneration, small particles will have better performance than large ones. Therefore, GAC particle size was chosen as one of the variables to be evaluated in the experiments. GAC of three different particle fractions (namely, 12/16, 16/18 and 30/40) was loaded to have the same solid phase concentration. The GAC mass (≈ 0.4g) for the 30/40 fraction was about one-third of the other two fractions whose mass was kept the same (≈ 1.2g). Figure 5.14 indicates that the REs are inversely proportional to average particle size. For example, a RE of 95% was obtained with 0.58mm GAC, while 70% with 1.44mm GAC. It is likely that the diffusion rate in

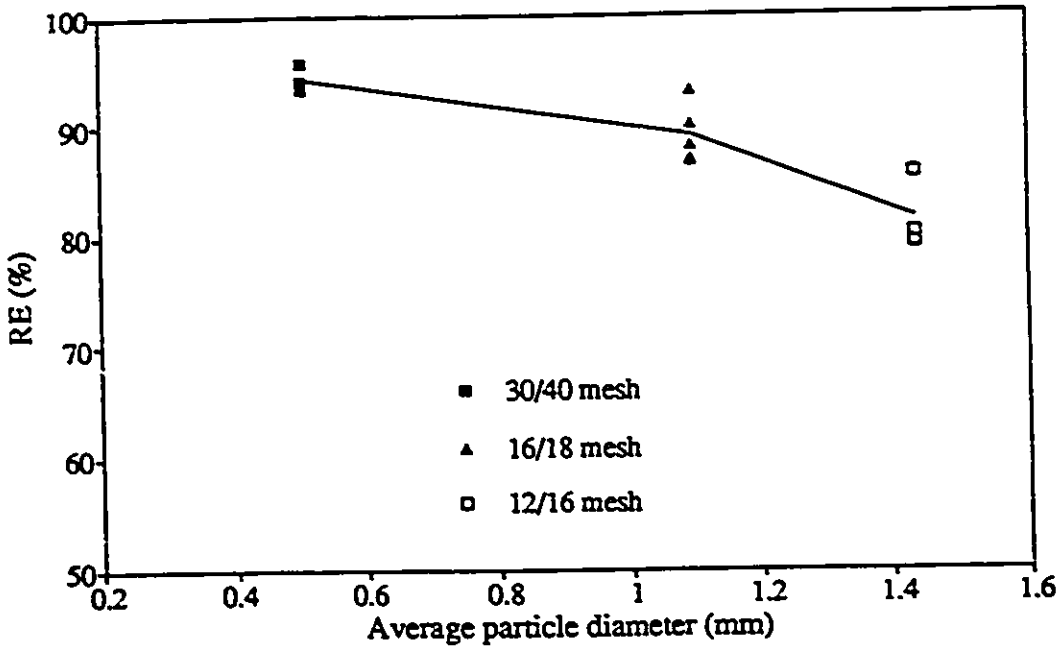
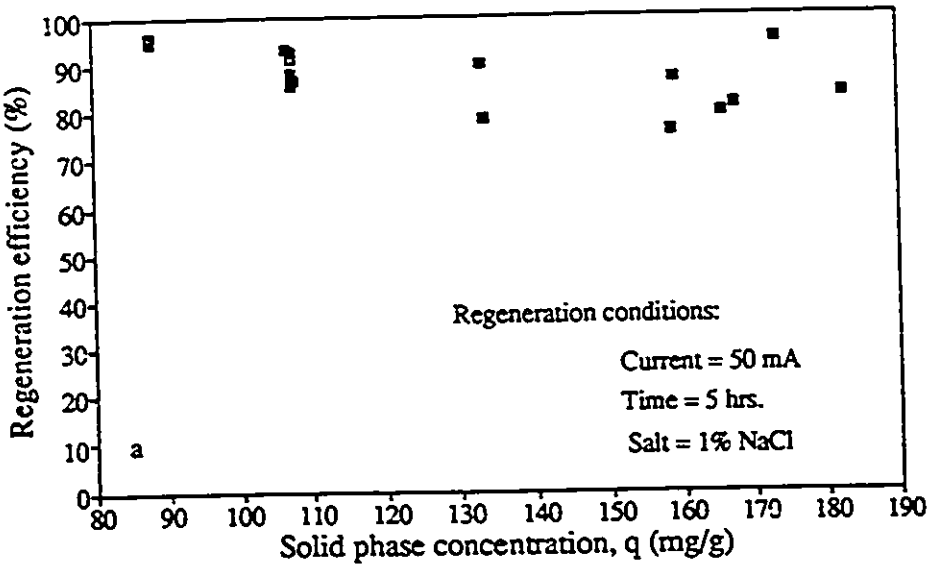


Figure 5.14 Effect of GAC particle sizes on regeneration efficiency (regeneration current and time were 50 mA and 5 hours respectively, electrolyte was 1% NaCl solution).

the GAC particles control the regeneration efficiency.

In a typical water or wastewater adsorption system, the overall rate of the adsorption process is frequently controlled by internal diffusion. It has been found that, in a regeneration process, increasing the pH of surrounding solution assists in phenol desorption from GAC surface. Therefore, the change in pH within small particles is quicker and the solution within internal pores in small particles reaches higher pHs faster than that in large particles. Desorption of phenol from small particles is, thus more effective than from large particles. This is due to the kinetic limitation of internal diffusion, as the rate of adsorption is inversely proportional to the square of the particle diameter. The experimental data did not show an inverse square relationship because the RE is a measure of total regeneration and not a measure of the regeneration rate. It was also noted that 12/16 and 16/18 mesh size GAC probably need longer regeneration times to reach the ultimate RE.

All of the GAC samples (particle size 16/18 mesh) used in generating the original isotherm, which had different GAC masses, were regenerated to study the effect of the quantity of adsorbed phenol on carbon regeneration. The solid phase concentrations of phenol on the GAC ranged between 87 and 182 mg/g. The carbon regeneration efficiency is plotted against the solid phase concentration of phenol in Figure 5.15a. It is indicated that there appears to be no significant difference among the various solid phase concentrations, only a slightly decreasing trend with increasing GAC loading. If the solid phase concentration is plotted versus liquid phase concentration with a log-log coordinate, the virgin and regenerated carbon adsorption isotherms can be established (Figure 5.15b). The closeness of these two isotherms indicates that the regeneration is quite efficient.



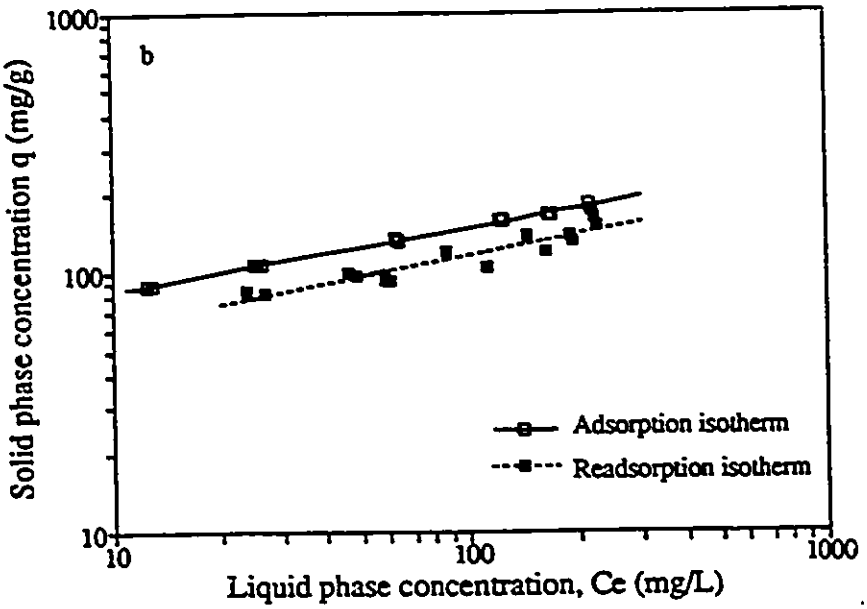


Figure 5.15: a) Effect of the GAC loading on regeneration efficiency, b) Adsorption isotherm and readsorption isotherm obtained after one cycle of regeneration.

5.3.5 Engineering implications

Multiple loading and regeneration cycles were conducted to investigate the long-term feasibility of the electrochemical regeneration process. The experiments were carried out with adsorption, regeneration and readsorption tests in series for five cycles. Regeneration conditions were the following: a 50 mA current, a 5-hour regeneration time, a 1% NaCl electrolyte solution, and a 107 mg/g carbon loading. Triplicates were run in these tests (see appendix E5). Figure 5.16 presents the results expressed in terms of RE (relative to the virgin adsorptive capacity) as a function of the number of cycles. The line drawn represents the best fit. The efficiency is 88% after the first cycle and then decreases at a rate of approximately 2% per cycle.

The major disadvantages associated with thermal regeneration are carbon losses and the high cost of energy. The lost GAC is usually replaced by fresh activated carbon. Clark and Lykins (1989) have shown that the cost of purchasing replacing carbon can be two to four times greater than the energy cost of a thermal regeneration system. In order to gain a better understanding of the process, it is important to quantify the GAC losses in electrochemical regeneration.

The GAC losses were measured under three different situations: a) loaded carbon, b) after one regeneration, and c) after six loading-regeneration cycles. The results are given in Table 5.3. The table shows that the carbon has lost 1.2 percent of its weight after the loading test. This may be caused by some carbon particle loss during the operation and weighing errors. After regeneration, the mass of carbon not only did not decrease, but increased by 9.4 percent. This increase is probably brought about by salt and residual phenol adsorbed on the GAC. For the next five cycles of loading and regeneration, the

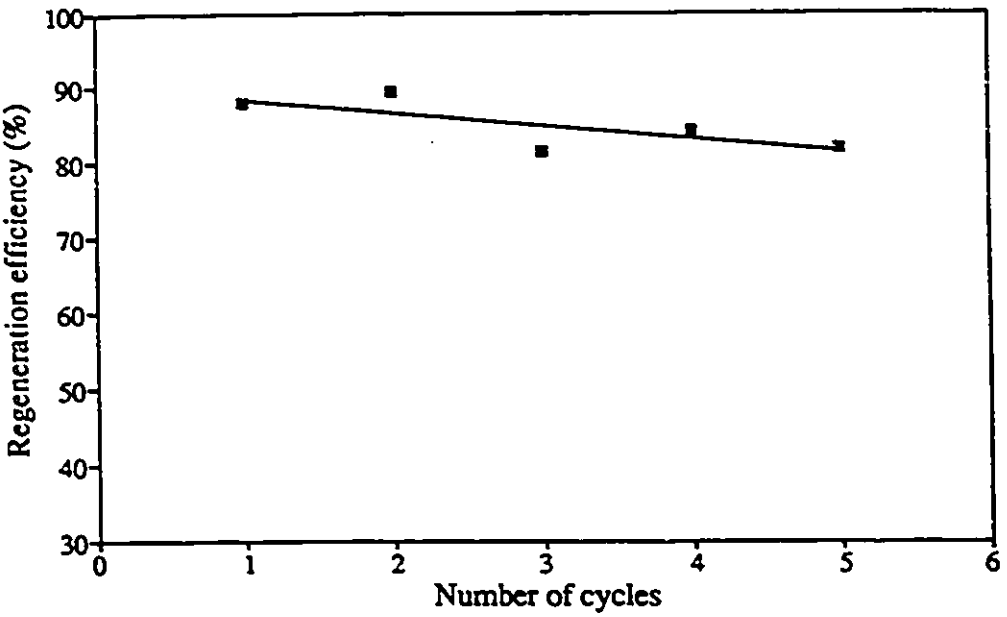


Figure 5.16 Repeated loading and regeneration cycles (regeneration conditions: 50 mA current, 5 hours regeneration time and 1% NaCl electrolyte solution).

Table 5.3 GAC losses for loaded carbon, after one regeneration, and after six loading-regeneration cycles.

	Initial mass (g)	Final mass (g)	Calculated phenol on GAC (g)	GAC loss (%)
Loaded GAC	1.1982	1.3127	0.1277	1.11
	1.1995	1.3126	0.1279	1.23
	1.2056	1.3206	0.1291	1.17
After one regeneration	1.1995	1.3129	N/A*	-9.45
	1.2057	1.3186		-9.36
	1.2065	1.3183		-9.27
After six regenerations	1.2020	1.3266	N/A	-10.37
	1.2040	1.3226		-9.85
	1.2066	1.3275		-10.02

* N/A = not available.

mass of GAC slightly increased because more compounds were adsorbed on the carbon surface, as indicated by decreasing RE. From the above discussion, we conclude that the electrochemical process yields no apparent GAC losses.

The substantial weight increase means that there was accumulation of salt or oxidation by-products which is bound to alter the carbon surface and pore structure to some extent. This in turn would result in a reduced adsorption capacity, which provides further reason for using the standard method to determine RE.

5.4 Conclusions

Electrochemical regeneration process has been evaluated using the standard method, which is based on the three tests in series: adsorption, regeneration and readsorption. Results indicate that application of a current greatly enhances the desorption and oxidation of phenol adsorbed on GAC.

Under the test conditions, the RE of cathodic regeneration is 5 to 10 percent higher than that of anodic regeneration. Thus, cathodic regeneration is chosen for subsequent experiments in the study. Anodic regeneration is superior in destroying residual phenol in the electrolyte, while cathodic regeneration also achieves destruction of such residuals using higher currents and/or longer regeneration times. It seems that phenol is desorbed from the GAC surface under the effect of cathodic polarization and alkaline conditions during electrolysis, and it is oxidized in the electrolyte by anodic oxidation. The apparent mass transfer limitations may be avoided by introducing mixing.

Regeneration current and time are the most important variables controlling the regeneration process. An increase in regeneration current and/or time increased the RE to a

maximum of 94 percent. The oxidation of phenol is more rapid under high currents, but the achievement of higher coulombic efficiency is favoured by low current combined with long regeneration time. The electrolyte type and electrolyte concentration significantly affected the REs. Comparisons of the electrolytes show that using 1%-NaCl solution, one can obtain the highest REs. However, chlorine is produced during the regeneration and the electrolyte becomes coloured apparently due to reaction intermediates, while other electrolytes do not. The colour disappears with longer regeneration times and/or higher currents. GAC particle size also plays an important role in the regeneration process. RE decreases with increasing GAC particle sizes, however, this may be a kinetics effect. Carbon loading has a weak effect on the RE.

Multiple adsorption and regeneration steps suggest that 88 percent of RE is achieved in the first cycle; subsequent regenerations reduce the RE by 2 percent per cycle. Measurement of GAC losses shows that there is no evident carbon losses in electrochemical regeneration process. Given the fact that phenol adsorption is fairly irreversible, GAC loaded with other contaminants will likely be regenerated to a higher degree with smaller power requirements.

CHAPTER SIX

ECONOMIC COMPARISON OF THERMAL AND ELECTROCHEMICAL REGENERATIONS

6.1 Introduction

An important consideration for selecting regeneration techniques is their cost. The most common technique practised for GAC regeneration is thermal regeneration. The cost of this method has been studied by many researchers (e.g. Lykins, 1987; Schuliger *et al.*, 1987; Loven, 1973). Preliminary costs for GAC treatment and regeneration systems are given in the literature (Adams and Clark, 1989, Adams *et al.*, 1988; Gumerman *et al.*, 1985). However, the electrochemical regeneration has been only investigated in the laboratory. There is no information on construction, building energy, operation and maintenance (O&M) labor costs for electrochemical regeneration. This chapter briefly discusses the operation costs (process energy consumption) with a comparison between thermal and electrochemical regenerations.

6.2 The Cost of Thermal Regeneration

Through the years, there have been many types of equipment used for thermally regenerating GAC. The main systems are multiple hearth GAC regeneration, infrared GAC regeneration, and fluid bed GAC regeneration. Multiple hearth is a traditional method of GAC regeneration, although fluidized bed and infrared furnaces have been recently applied

more frequently. Multiple hearth GAC regeneration uses a multiple hearth furnace operated under closely controlled conditions such as temperature, oxygen, and moisture content. Infrared GAC regeneration uses infrared energy to generate heat. The principal advantage of infrared regeneration is that the furnace can be rapidly put into or taken out of operation without furnace damage or excessive operational cost. Fluid bed furnaces suspend the carbon particles by an upward flowing gas stream. The velocity of the gas is controlled so that the weight of particles in the bed can be balanced by the upward forces of the gas. The use of fluid bed in this application offers the advantages of uniform temperatures within the bed and high heat and mass transfer rates. The temperature is controlled by steam injection.

Adams and Clark (1989) have developed cost estimating equations for analyzing the GAC treatment and regeneration systems. Figure 6.1 shows regeneration cost estimates (dollars per pound for 1983) for fluid-bed, infrared, and multihearth technologies as a function of the amount of spent carbon required for regeneration. Results indicate that regeneration unit costs ranged from about $0.70/lb for a very small regenerator to about $0.22/lb for a large regenerator. Significant cost savings are realized by carbon regeneration compared with the virgin carbon replacement costs of $0.80-1.00/lb.

As noted in Figure 6.1, the infrared regeneration appears to be cost effective for small systems, and fluid-bed regeneration appears to be cheaper when spent carbon is > $3x10^6$ lb/year. Multihearth regeneration appears to be slightly more expensive than fluid-bed and infrared systems. When projected spent carbon quantities are small, replacement with virgin GAC or use of off-site (regional, the sharing of a regeneration furnace among several users) regeneration may be more cost-effective than on-site regeneration. Figure 6.2 compares costs for on-site and off-site regeneration and for replacement of spent

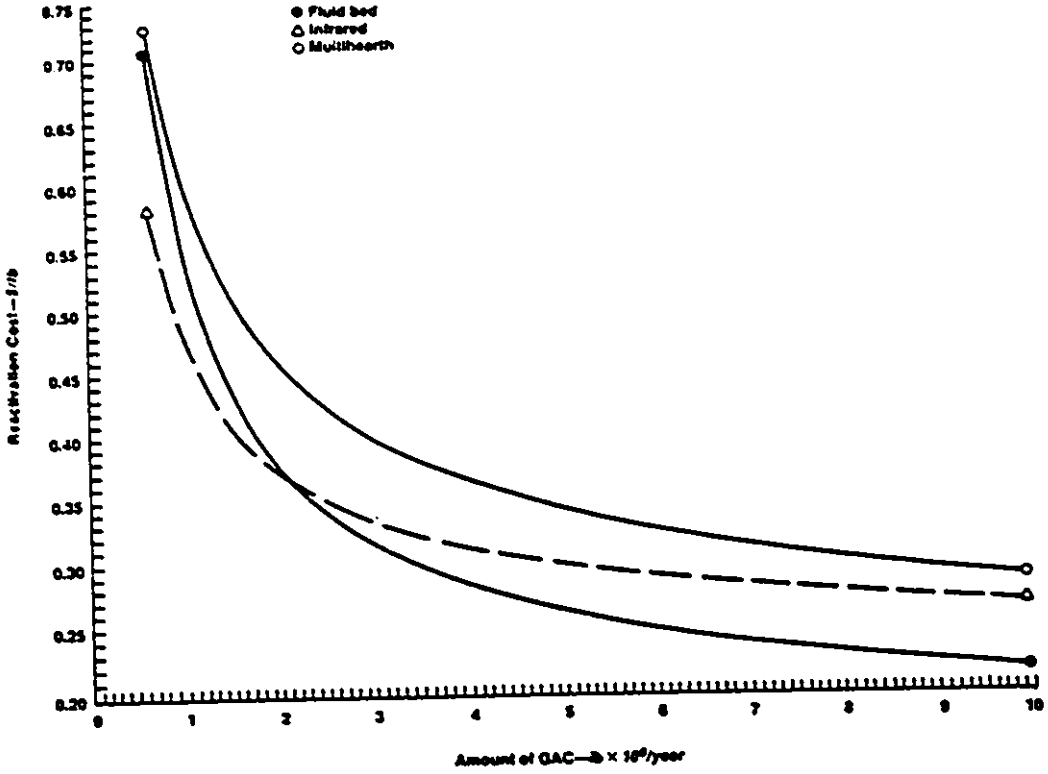


Figure 6.1 Cost estimates for on-site GAC regeneration (sources: Adams and Clark, 1989).

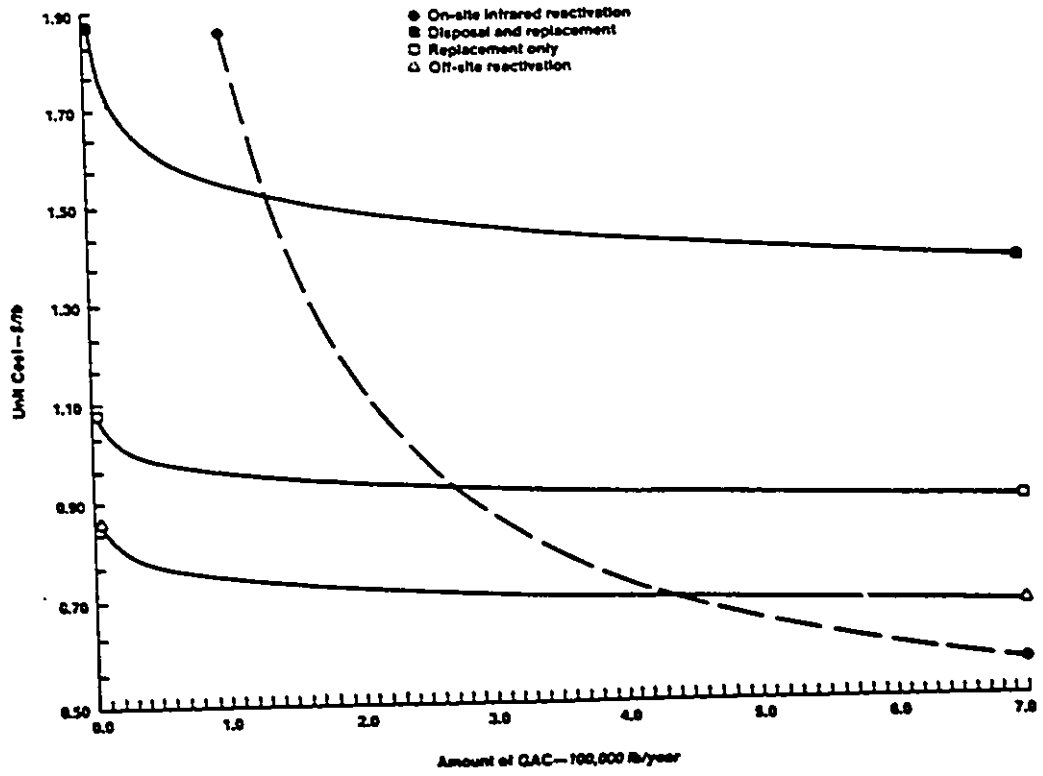


Figure 6.2 Cost estimates for GAC regeneration and replacement.

Note: The on-site regeneration assumes a 100 lb/day infrared regenerator. Off-site regeneration assumes a commercial operation that includes transport charges for up to 500 mi one way. The "replacement only" refers to the cost of purchasing virgin GAC, and "disposal and replacement" includes the cost of GAC and the disposal of spent carbon by incineration (plus transport charges) (source: Adams and Clark, 1989).

carbon with new GAC (with and without spent carbon disposal). It shows that when spent carbon requirements are < 1500 lb/day (680 kg/day, i.e. = 410,000 lb/year based on a 75 percent uptime factor), replacement of spent carbon with virgin GAC is more cost-effective. The evaluation of choices among on-site and off-site regeneration and virgin GAC replacement is important because the regeneration or replacement cost may represent up to more than 50 percent of the total cost of the GAC treatment system. The following section presents several examples of cost estimates for on-site and regional regeneration systems.

6.2.1 Costs of on-site regeneration systems

Water treatment at Manchester City (N.H.), consists of five sequential unit processes beginning with flash mixing, followed by flocculation, sedimentation, sand filtration, and GAC adsorption (Adams *et al.*, 1988). The GAC is regenerated on-site with a 500 lb/h fluid bed furnace. From June 1980 to March 1981, Manchester Water Works (MWW) regenerated 1,857,176 lb (843,158 kg) of carbon and their operation costs were analyzed by Adams *et al.* (1988). A summary of the unit cost (cost per pound/kilogram of GAC) by item is shown in Table 6.1. The cost-effectiveness of on-site fluid bed regeneration is clearly demonstrated, because carbon is regenerated at a total unit cost of $0.217/lb ($0.478/kg) versus a cost of purchasing virgin carbon at $0.615/lb ($1.36/kg). The largest single operating cost item is the makeup carbon associated with GAC losses from regeneration and on-site handling, representing 33 percent of total regeneration cost. The average total carbon loss resulting from on-site transport and regenerating is 11.5 percent by volume. Total overall labor expense, including labor overhead, represents about

Table 6.1 Costs of on-site regeneration per pound (kilogram) of GAC at Manchester Water Works, June 1980-March 1981 (Source: Adams *et al.*, 1986).

Cost item	Unit cost*	
	$/lb GAC	$/kg GAC
Makeup carbon	0.0707	0.1559
Labor expenses	0.0630	0.1388
Fuel oil	0.0223	0.0492
Electrical power	0.0050	0.0110
Water	0.0074	0.0163
Parts and service calls	0.0267	0.0587
Laboratory	0.0010	0.0022
Depreciation	0.0213	0.047
Total cost	0.2174	0.4792

* Unit costs based on regeneration of 1,857,176 lb (842,415 kg) of GAC

29 percent of the total system cost. Capital cost (depreciation) represents about 10 percent of the total system cost. Fuel oil and electrical power only represent 10.3 and 2.3 percent of the total system cost respectively, that is, $0.0273/lb ($0.06/kg). Electrical power consumption is 0.093 kW•h/lb (0.205 kW•h/kg) GAC based on an average cost of $0.0523/kW•h.

Table 6.2 summarizes the cost over eight years 1983-1988 of operation. Subsequent experience with on-site fluid bed regeneration at MWW demonstrated again that it is an economical process.

Jefferson Parish Water Treatment Plant, La. has used a 215lb/h infrared GAC regeneration furnace. The average GAC transport and regeneration cost for the first 11 regenerations is shown in Table 6.3 (in 1983 dollars). The fraction of the transport cost is GAC loss at $0.015/lb. The major regeneration cost is electricity at $0.059/lb (@ $0.06/kW•h), followed closely by GAC loss at $0.052/lb. Maintenance is also a considerable cost. Labor was $0.031/lb and materials were $0.017/lb. Operating labor cost was $0.014/lb, and water and laboratory costs were $0.007/lb and $0.002/lb, respectively. Amortized unit cost based on 10 percent for 20 years, was $0.06/lb, for a total regeneration cost of $0.242/lb. Thus, the transport and regeneration costs are estimated to be around $0.262/lb. It shows that infrared regeneration of spent GAC is more economic than replacement with virgin carbon ($0.75/lb).

As compared with fluid bed, infrared furnace has high electricity consumption and low GAC losses. But the total regeneration cost for both system are almost the same.

6.2.2. Cost of regional regeneration

Table 6.2 Summary of on-site regeneration at Manchester Water Works for 1980-1988 (Source: Adams *et al.*, 1988).

Year	Regeneration cost ($/lb)	Virgin GAC Cost ($/lb)	Amount regenerated (lb)	Carbon loss (%)	System up-time (%)
1980-1981	0.217	0.615	1,857,176	11.5	70
1983	0.243	0.53	242,000	12	78
1984	0.226	0.36	250,000	18	40
1985	0.249	0.66	261,000	15.5	24
1986	0.195	0.67	260,000	17.3	99
1987	0.227	0.69	262,000	18	99
1988	0.255	0.75	237,000	16.9	95

Table 6.3 GAC transport and regeneration costs* - Jefferson Parish, La. (Data from Koffskey and Lykins, 1990; Lykins, 1987).

GAC transport		GAC regeneration	
Expense	Cost ($/lb)	Expense	Cost ($/lb)
GAC loss	0.015	GAC loss	0.052
Operating labor	0.003	Operating labor	0.014
Water	0.002	Water	0.007
Total	0.020	Electricity	0.059
		Maintenance labor	0.031
		maintenance material	0.017
		Laboratory	0.002
		Amortized unit cost	0.06
		Total	0.242

* Total cost = $0.262/lb ($0.577/kg)

A number of utilities, many of them with small water systems, have recently found volatile organic compounds (VOCs) in their groundwater sources. GAC is frequently considered for the removal of VOCs, but it has high unit costs associated with discarding spent GAC or installing on-site regeneration systems. Off-site or regional regeneration offers the possibility of minimizing these costs. In New England, three water utilities have been involved in a regional regeneration program: Connecticut Water Company's Kelseytown treatment plant, the Danvers, Mass., water treatment plant, and the Lowell, Mass., water treatment plant. Each of the participating utilities agreed to provide approximately 40,000 lb/year of carbon to be transferred to Manchester and regenerated.

Table 6.4 gives the unit costs for regional GAC regeneration for the three utilities, which clearly demonstrates the cost-effectiveness of regional reaction for these utilities. For example, the actual cost of regional regeneration for the Connecticut Water Company (CWC) was $0.662/lb versus complete virgin replacement at $1.007/lb and estimated on-site regeneration cost of $1.387/lb. Costs of regional regeneration are lower than those of replacement with virgin GAC. Estimated costs of on-site regeneration show that it is the highest cost alternative because of the considerably high unit costs associated with small regeneration facilities. The cost of regional regeneration for the CWC was considerably higher than that for the other two utilities. The main reasons for this were that (1) CWC experienced higher carbon losses and therefore used more makeup GAC, and (2) the transport distance between CWC and MWW was longer than between MWW and the other utilities. The higher carbon losses were probably related to the type of carbon used. CWC used a lignite-based adsorption media, whereas the carbon used by the Danvers and Lowell plants was a coal-based GAC. Since the lignite-based carbon is softer than coal-based

Table 6.4 Comparison of costs of regional regeneration with those of GAC replacement and on-site regeneration (1981) (Data from Adams *et al.*, 1986; Adams *et al.*, 1988).

Participating utilities	Regional regeneration cost ($/lb) Transport	Regeneration	Total	Virgin GAC replacement cost($/lb)[@]	Estimated cost of on-site regeneration[•]
Connecticut Water Co.	0.091	0.571	0.662	1.007	1.387
Danvers, Mass.	0.065	0.31	0.375	0.634	1.389
Lowell, Mass.	0.054	0.395	0.449	1.005	0.773

[@] Based on approximately 40,000 lb of GAC for each utilities.

[•] Based on cost equations developed from various field-scale GAC studies and other sources of information (Clark, 1983)

GAC, abrasion losses are suspected to be greater with this material. The total volumetric carbon loss was 23.5% for CWC, 15.3% for Lowell, and 11.5% for Danvers, respectively.

These examples have illustrated that on-site regenerations at Manchester and Jefferson Parish were considerably cheaper than replacing spent carbon with virgin carbon and, that regional regeneration proved to be cheaper than either replacement or estimated on-site regeneration for small utilities. The on-site regeneration alternatives were not cost-effective for small utilities.

6.3 A Cost Comparison between Thermal and Electrochemical Regenerations

In electrochemical regeneration, experimental equipment is easy to set up; it regenerates small amount of GAC. A major operation cost is the electricity consumption. For example, if loaded GAC is regenerated for five hours with a current of 50 mA (the average potential is 3.2 volts), a regeneration efficiency of 89% could be obtained. Process energy consumed is calculated as:

Electrical power = (voltage)x(current)x(time)

$$= (3.2)x(0.05)x(5) = 0.8\ W \cdot h = 0.8x10^{-3}\ kW \cdot h$$

For these 1.2g of GAC samples, the electricity consumption is then 0.67 W•h/g (0.67 kW•h/kg) of GAC. Since the GAC loading is 107 mg/g, the energy consumption can be converted to 6.79 W•h/g of phenol (RE = 89%) and 13.88 W•h/g of COD. This result is similar to that of Owen and Barry (1972) who have investigated the electrochemical regeneration of spent GAC which was used to remove soluble COD organics from secondary effluent of the Irvine Wastewater Treatment Plant (Irvine, CA). In their study,

power requirement for a 61.1% regeneration was 16 W•h/g.

If the same electrical power cost of $0.06/kW•h is assumed, the electrical expense in electrochemical regeneration is $0.04/kg of GAC. The best performing on-site thermal regeneration at the Manchester Water Works had an electrical power consumption of 0.205 kW•h/kg of GAC in its fluid bed furnace, which is much lower than that for electrochemical regeneration. However, the unit costs of power and fuel oil were $0.06/kg of GAC, which is higher than that for electrochemical regeneration. For the infrared furnace at Jefferson Parish, electricity consumption was 2.17 kW•h/kg and $0.13/kg of GAC, which is also higher than electrochemical regeneration. Thus, the energy consumption in electrochemical regeneration is slightly less than thermal regeneration. A summary of process energy costs (cost per kilogram of GAC) is presented in Table 6.5.

The labor cost represents about 29 and 19 percent of the total regeneration system expenditure in fluid bed and infrared furnaces, respectively. Owen and Barry (1972) calculated that labor cost for thermal regeneration is more than double that for electrochemical regeneration. In present, electrochemical regeneration labor fees cannot be estimated, but they are expected to be lower than in thermal regeneration.

In thermal regeneration, the RE is usually 95-100%, and the GAC loss is 10 to 15% for each regeneration cycle. If the GAC loss is considered, RE will be reduced to 85%. By way of contrast, the electrochemical regeneration has no GAC loss and can achieve 89% of RE in this particular example. If the same degree of restoration in adsorption capacity is assumed for thermal regeneration for consequent cycles, the GAC loss will still be 10-15% per cycle. Whereas, the electrochemical process lowered RE by 2% in subsequent regenerations. Thus, with respect to restoration capacity, electrochemical

Table 6.5 Costs of energy consumption between thermal and electrochemical regenerations.

Item	Fluid bed[@] ($/kg)	Infrared[*] ($/kg)	Electrochemical ($/kg)
Fuel oil	0.0492		
Electricity	0.011	0.13	0.04
Total	0.0602	0.13	0.04

[@] Costs based on fluid bed regeneration at Manchester Water Works.

[*] Costs based on infrared regeneration at Jefferson Parish, Water Treatment Plant.

regeneration is clearly more efficient than thermal regeneration. However, since the electrochemical process is merely in the stage of laboratory investigation, It is too early to establish the capital and maintenance costs of the process. Further research is needed for detailed economic assessment of the whole system. Nevertheless, electrochemical regeneration seems to be an attractive alternative for GAC regeneration. Because it regenerates a relatively small amount of GAC, it is especially suitable for small water and wastewater treatment utilities.

CHAPTER SEVEN

CONCLUSIONS AND RESEARCH RECOMMENDATIONS

7.1 Conclusions

1. Application of a current greatly enhances the desorption and oxidation of phenol adsorbed on GAC. Electrochemical regeneration achieves efficiencies up to 94 percent, while desorption without the aid of electricity is only about 5 percent. Phenol adsorption is quite irreversible while many other organics show reversible adsorption. Thus, electrochemical regeneration will likely be even more effective for GAC loaded with other organics.

2. Under the test conditions, the RE of cathodic regeneration is higher than that of anodic regeneration. Although it leaves a small amount of residual phenol in the electrolyte, cathodic regeneration can destroy such residuals using higher currents and/or longer regeneration times.

3. An increase in regeneration current and/or time increases the RE. The oxidation of phenol is more rapid under high currents, but the low current (combined with long regeneration times) could achieve high coulombic efficiency.

4. The electrolyte type, electrolyte concentration and GAC particle size also significantly affect the REs, while the effect of carbon loading is weak.

5. Multiple adsorption and regeneration steps indicate that the second and subsequent regenerations reduce the RE by an additional 2 percent per cycle.

6. Electrochemical regeneration appears to be less expensive than thermal regeneration. As electrochemical regeneration has no apparent GAC losses, it minimizes makeup carbon cost.

Thus, this laboratory study shows that electrochemical regeneration process is technologically feasible and likely more economic than thermal regeneration. Although this is inconclusive, it is an attractive alternative, specially for small water and wastewater treatment utilities where the GAC usage rates are not large.

7.2 Recommendations for Future Research

As a result of the regeneration capabilities and cost advantages of electrochemical regeneration demonstrated in this study, continuation of this research is highly worthwhile. It is necessary to establish the effect of many other variables on RE, such as: regeneration reactor configuration, electrode material, adsorbent (i.e. GACs other than F-400), various electrolytes and concentrations, various contaminants on the activated carbon, multiple layers of GAC on electrode, particle size, etc.

Since cathodic regeneration produced coloured electrolytes and there was some residual phenol in the electrolytes (while anodic regeneration did not), a detailed analysis of oxidation by-products in electrolytes is recommended. Also it is necessary to test the new evaluation method of regeneration efficiency.

Eventually, scale-up is essential to conduct a fair comparison with thermal regeneration. It will include the capital cost, operation and maintenance costs, and labour costs.

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Appendix A

1993 water quality results of the regional municipality of Ottawa-Carleton Ottawa river and Lemieux island/Britannia purification plants (source: the regional municipality of Ottawa-Carleton).

Parameter	Treated water		
	Min.	Max.	Average
Physical			
Temperature, °C	2.0	22.5	10.6
Colour, Hazen Units	3.0	7.0	3.3
Turbidity, N.T.U.	0.1	1.2	0.4
Chemical (mg/l)			
pH	6.8	9.9	8.3
Total Alkalinity, as $CaCO_3$	17.0	48.0	25.8
Total Hardness, as $CaCO_3$	26.0	72.0	51.7
Calcium Hardness, as $CaCO_3$	20.0	50.0	38.5
Magnesium Hardness, as $CaCO_3$	8.0	36.0	15.0
Spec-Cond. Micromhos/cm @ 25 °C	97.0	150.0	121.0
Suspended solids	N/A	N/A	N/A
Dissolved Solids	N/A	N/A	N/A
Total Solids	25.2	108.0	79.5

Note: N/A = not available.

APPENDIX B1

Phenol adsorption data

SET ONE

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	qe (mg/g)
1	p1	528.49	blank	298.56	
2	p2	478.43	1.3018	19.1	100.48
3	p3	478.39	1.3019	17.8	100.94
4	p4	474.9	1.2924	19	100.50
5	p5	475.42	1.2938	18.1	100.83
6	p6	477.76	1.3002	18.5	100.68
7	p7	473.83	1.2898	19.5	100.29
8	p8	475.58	1.2941	19.4	100.36
9	p9	477.5	1.2994	19.1	100.47
10	p10	474.87	1.2922	19.3	100.40
11	p11	475.26	1.2932	17.9	100.92
12	p12	477.75	1.3008	18	100.82
13	p13	478.08	1.3011	17	101.23
14	p14	478.58	0.4761	125	168.37
15	p15	476.19	0.4734	130	163.46
16	p16	477.13	0.4742	132	161.49
17	p17	476.75	0.4736	128	165.59
18	p18	477.05	0.8756	44.5	135.12
19	p19	478.13	0.8774	45	134.87
20	p20	475.19	blank	292.54	

Phenol concentration Co = 295.44 mg/l.

Start on Oct. 5, 1992. Initial pH = 6.85, D.O. = 8.4 mg/l.

End on Oct. 20, 1992. Final pH = 6.9, D.O. = 8.5 mg/l.

SET TWO

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	q (mg/g)
1	p24	518.22	1.3078	22.36	108.21
2	p27	518.27	1.3081	22.62	108.09
3	p52	518.44	1.3085	22.38	108.19
4	p28	518.24	1.308	21.70	108.46
6	p22	518.89	0.9081	56.47	136.55
7	p45	518.99	0.9084	55.09	137.32
5	p43	533.72	0.5861	115.35	164.00
8	p46	533.88	0.5863	115.80	163.58
9	p57	533.89	0.5864	113.30	165.83
10	p23	534.1	0.5867	114.26	164.94
11	p31	498.66	1.2583	21.18	108.69
12	p38	501	1.2644	21.73	108.45
13	p44	501.24	1.2648	22.72	108.08
14	p54	501.02	1.2644	21.51	108.55
15	p50	535.51	0.9372	55.41	137.15
16	p35	535.76	0.9376	54.14	137.88
17	p26	536.1	0.5889	114.15	165.04
18	p53	536.28	0.589	111.95	167.07
19	p47	536.27	0.589	117.06	162.41
20	p37	536.47	0.5892	114.35	164.88
21	p39	534.64	2.1443	3.83	72.71
22	p48	535.26	1.7518	9.11	87.49
23	p49	534.59	0.4016	155.80	185.88
24	p51	534.75	0.2699	194.40	200.19
25	p56	535.97	0.1548	223.00	250.82
26	p21	473.23	1.1946	22.39	108.17
27	p32	472.99	1.5483	8.96	87.52
29	p29	538.2	0.2721	195.33	198.01
30	p33	538.03	0.155	236.33	205.18
31	p41	471.73	blank	292.53	
32	p36	470.81	blank	298.36	

Phenol concentration Co = 295.55 mg/l.

Start on Nov. 20, 1992. Initial pH = 6.95, D.O = 9.62 mg/l.

End on Dec. 8, 1992. Final pH = 6.94, D.O. = 8.5 mg/l.

SET THREE

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	qe (mg/g)
1	p1	528.49	blank	293.33	
2	p5	475.42	1.2010	23.43	108.03
3	p6	477.76	1.2066	22.73	108.33
4	p7	473.83	1.1968	23.55	108.00
5	p8	475.58	1.2000	23.33	108.19
6	p9	477.5	1.2051	22.6	108.46
7	p10	474.87	1.1985	24.63	107.65
8	p11	475.26	0.8330	47.55	141.94
9	p12	477.75	0.8372	43.4	144.34
10	p13	478.08	0.8377	32.75	150.43
11	p14	478.58	0.5267	93.78	184.04
12	p15	476.19	0.5239	98.65	179.68
13	p16	477.13	0.5252	113.63	165.98
14	p17	476.75	0.5247	107.73	171.36
15	p18	477.05	0.5249	115.66	164.20
16	p19	478.13	0.5261	91.58	186.08
17	p20	475.19	blank	299.33	

Phenol concentration Co = 295.44 mg/l.

Start on Dec. 16, 1992. Initial pH = 6.93, D.O. = 8.5 mg/l.

End on Jan. 4, 1993. Final pH = 6.95, D.O. = 8.9 mg/l.

SET FOUR

No.	Bottle No.	Volume (ml)	Carbon (g)	Ce (mg/l)	qe (mg/g)
1	p24	518.22	1.3078	25.74	106.41
2	p27	518.27	1.3080	25.78	106.40
3	p52	518.44	1.3084	25.48	106.51
4	p28	518.24	1.3079	25.48	106.51
5	p22	518.89	1.3095	24.97	106.72
6	p45	518.99	1.3098	24.43	106.93
7	p43	533.72	1.3469	24.87	106.76
8	p46	533.88	1.3473	25.15	106.65
9	p57	533.89	1.3474	24.71	106.82
10	p23	534.1	1.3479	24.56	106.88
15	p50	535.51	1.3515	25	106.70
16	p35	535.76	1.3521	25.54	106.49
17	p26	536.1	1.3530	25.25	106.61
18	p53	536.28	1.3534	25.63	106.46
19	p47	536.27	0.5889	118.57	160.01
20	p37	536.47	0.5892	117.63	160.86
21	p39	534.64	0.5871	116.43	161.96
22	p48	535.26	0.5878	118.39	160.17
23	p49	534.59	0.5871	119.43	159.22
24	p51	534.75	0.5873	120.11	158.60
32			blank	87.15	
33			blank	89.42	

Phenol concentration Co = 294.29 mg/l.

Start on Jan. 13, 1993. Initial pH = 6.92, D.O. = 8.5 mg/l.

End on Jan. 18, 1993. Final pH = 6.95.

SET FIVE

No.	Bottle No.	Volume (ml)	Carbon (g)	Ce (mg/l)	qe (mg/g)
1	p31	498.66	1.2585	26.29	107.17
2	p38	501	1.2645	25.16	107.61
3	p44	501.24	1.2651	26.24	107.18
4	p54	501.02	1.2645	26.31	107.15
5	p21	473.23	0.8282	59.83	135.38
6	p32	472.99	0.8279	61.17	134.59
7	p42	538.7	0.5916	118.61	162.21
8	p29	538.2	0.5913	119.87	161.00
9	p33	538.03	0.5907	117.79	163.00
10	p56	535.97	0.5885	119.27	161.64
11	p55	475.08	1.1991	28.43	106.31
12	p58	477.38	1.2049	28.11	106.43
13	p30	474.57	blank	297.73	
14	p40	474.56	blank	295.77	

Phenol concentration Co = 296.75 mg/l.

Start on Jan. 18, 1993. Initial pH = 6.93.

End on Jan. 25, 1993. Final pH = 6.98.

SET SIX

No.	Bottle No.	Volume (ml)	Carbon (g)	Ce (mg/l)	qe (mg/g)
1	p1	528.49		297.66	
2	p2	478.43	1.2074	27.64	106.31
3	p3	478.39	1.2073	25.75	107.06
4	p4	474.9	1.1985	24.95	107.38
5	p5	475.42	1.2	25.45	107.16
6	p7	473.83	1.1958	26.94	106.59
7	p8	475.58	1.2003	25.7	107.07
8	p9	477.5	1.2051	24.65	107.49
9	p10	474.87	1.1982	25.03	107.37
10	p12	477.75	1.2059	24.36	107.59
11	p13	478.08	1.2067	24.36	107.60
12	p15	476.19	1.202	25.4	107.18
13	p16	477.13	1.204	24.92	107.40
14	p17	476.75	1.2032	25.83	107.03
15	p18	477.05	1.2039	24.43	107.59
16	p19	478.13	1.2066	25.12	107.32
17	p20	475.19		294.23	

Phenol concentration Co = 295.94 mg/l.

Start on Jan. 25, 1993, Initial pH = 6.93.

End on Feb. 1, 1993. Final pH = 6.95.

SET SEVEN

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	qe (mg/g)
1	p24	518.22	1.308	26.58	106.15
2	p27	518.27	1.3082	26.66	106.11
3	p52	518.44	1.3086	27.05	105.96
4	p28	518.24	1.3078	26.71	106.11
5	p22	518.89	0.9084	64.21	131.54
6	p45	518.99	0.9084	63.27	132.11
7	p43	533.72	0.5862	124.08	155.16
8	p46	533.88	0.5861	121.66	157.44
9	p57	533.89	0.5862	121.81	157.28
10	p23	534.1	0.5868	122.55	156.51
21	p39	534.64	1.3493	26.82	106.07
22	p48	535.26	1.3508	26.45	106.21
23	p49	534.59	1.3492	26.81	106.07
24	p51	534.75	1.3445	26.54	106.58
25	p55	475.08	0.8314	63.87	131.79
26	p58	477.38	0.8355	63.11	132.21
27	p30	474.57	1.198	27.15	105.91
28	p40	474.56	1.1979	26.83	106.04
29	p34	472.47	blank	292.66	
30	p41	471.73	blank	296.33	

Phenol concentration Co = 294.5 mg/l.

Start on Feb. 12, 1993. Initial pH = 6.97.

End on Feb. 18, 1993. Final pH = 7.04.

SET EIGHT

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	qe (mg/g)
1	p1	528.49	blank	296.10	
2	p2	478.43	1.2075	28.72	106.18
3	p3	478.39	1.2074	29.02	106.06
4	p4	474.9	1.1986	28.43	106.30
5	p5	475.42	1.2001	27.83	106.52
6	p6	477.76	0.5247	125.07	156.28
7	p7	473.83	0.5205	124.78	156.51
8	p8	475.58	0.5226	123.47	157.65
9	p9	477.5	0.5244	123.92	157.34
10	p10	474.87	1.1982	27.81	105.91
11	p11	475.26	1.1995	27.63	105.96
12	p12	477.75	1.2056	26.55	106.40
13	p14	478.58	1.2076	23.85	107.48
14	p20	475.19	blank	294.00	
15	p15	535.51	0.5881	120.14	159.27
16	p16	535.76	0.5885	119.33	159.97
17	p27	472.99	0.5186	118.67	160.87
18	p31	472.47	0.519	119.38	159.92
19	p32	471.73	0.5181	118.38	160.86
20	p33	470.81	0.5171	119.75	159.61

Phenol concentration Co = 296.71 mg/l.

Start on Feb. 19, 1993. Initial pH = 6.95.

End on Mar. 2, 1993. Final pH = 6.98.

SET NINE

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	qe (mg/g)
1	p24	518.22	1.6765	12.78	87.84
2	p27	518.27	1.6767	12.565	87.91
3	p52	518.44	1.3085	26.45	107.18
4	p28	518.24	1.308	26.39	107.20
5	p22	518.89	1.3095	26.28	107.26
6	p45	518.99	1.3099	26.59	107.12
7	p43	533.72	1.347	26.38	107.21
8	p46	533.88	1.3475	26.665	107.09
9	p57	533.89	1.3476	26.43	107.18
10	p23	534.1	1.3479	26.44	107.19
11	p44	501.24	1.2652	25.15	107.69
12	p54	501.02	1.2644	25.06	107.74
13	p50	535.51	0.9374	63.82	133.19
14	p35	535.76	0.9376	63.23	133.56
15	p26	536.1	0.5888	122.37	158.97
16	p53	536.28	0.5891	122.82	158.53
17	p47	536.27	0.4199	167.23	165.69
18	p37	536.47	0.4201	165.825	167.47
19	p29	538.2	0.2488	216.89	173.21
20	p33	538.03	0.2487	212.71	182.27
21	p31	498.66		295.73	
22	p38	501		298.20	

Phenol concentration Co = 296.96 mg/l.

Start on Mar. 9, 1993. Initial pH = 6.95.

End on Mar. 16, 1993. Final pH = 6.98.

SET TEN

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Ce (mg/l)	q (mg/g)
1	p1	528.49	blank	296.48	
2	p2	478.43	1.2074	27.65	106.67
3	p3	478.39	1.2074	26.89	106.97
4	p6	477.76	1.2057	27.10	106.89
5	p7	473.83	1.1958	27.59	106.70
6	p8	475.58	1.2005	27.59	106.67
7	p9	477.5	1.205	26.61	107.09
8	p10	474.87	1.1982	26.40	107.19
9	p11	475.26	1.1995	26.96	106.94
10	p12	477.75	1.206	22.43	108.71
11	p13	478.08	1.2065	24.73	107.83
12	p14	478.58	1.2077	25.64	107.48
13	p17	476.75	1.2035	26.33	107.17
14	p18	477.05	1.204	26.05	107.30
15	p55	475.08	1.1995	26.61	107.04
16	p58	477.38	1.2049	26.33	107.18
17	p30	474.23	1.1976	26.82	106.93
18	p40	474.56	1.1981	26.68	107.02
19	p20	475.19	blank	297.24	

Phenol concentration Co = 296.86 mg/l.

Start on April 9, 1993. Initial pH = 6.92.

End on April 17, 1993. Final pH = 6.9.

Appendix B2

GAC moisture content effect on loading

Remaining GAC loading data

No.	Volume (ml)	Carbon weight (g)	C_e (mg/l)	q_e (mg/g)
p10	474.87	1.1982	29.44	104.60
p11	475.26	1.1996	28.87	104.79
p12	477.75	0.5251	122.85	155.15
p13	478.08	0.5252	124.30	159.37

Previous GAC loading data (from set no. 9)

Average: $C_e = 26.18$ mg/l, $q_e = 107.29$ mg/g

$C_e = 122.6$ mg/l, $q_e = 158.75$ mg/g

Percentage increase in liquid phase concentration:

For GAC = 1.2g

$$\frac{29.16 - 26.18}{26.18} = 11.4\%$$

For GAC = 0.53g

$$\frac{123.58 - 122.6}{122.6} = 0.8\%$$

Percentage decrease in loading:

For GAC = 1.2g

$$\frac{107.29 - 104.7}{107.29} = 2.4\%$$

For GAC = 0.53g

$$\frac{158.75 - 157.26}{158.75} = 0.9\%$$

Appendix C
Kinetics Experiment Data

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Time (Min.)	Ce (mg/l)	Ce/Co	Time (day)
1	ps17	160.14	0.2965	20	187.72	0.633	0.01
2	ps18	160.04	0.2963	40	148.46	0.501	0.03
3	ps19	159.74	0.2957	61	130.64	0.441	0.04
4	ps20	159.96	0.2963	90	105.57	0.356	0.06
5	ps21	160.54	0.2973	120	97.65	0.330	0.08
6	ps22	159.85	0.2959	150	87.70	0.296	0.10
7	ps23	159.94	0.2963	180	79.32	0.268	0.13
8	ps24	160.89	0.2979	212	75.92	0.256	0.15
9	ps25	159.69	0.2956	240	75.92	0.256	0.17
10	ps26	159.53	0.2955	270	76.57	0.258	0.19
11	ps27	159.98	0.2962	300	73.33	0.247	0.21
12	ps58	159.35	0.2951	345	77.30	0.261	0.24
13	ps15	160.53	0.2972	360	73.65	0.249	0.25
14	ps28	159.64	0.2959	420	67.08	0.226	0.29
15	ps29	159.42	0.2953	480	67.23	0.227	0.33
16	ps67	159.55	0.2955	492	66.15	0.223	0.34
17	ps14	159.68	0.2959	570	61.75	0.208	0.40
18	ps31	160.48	0.2971	600	66.23	0.223	0.42
19	ps33	159.9	0.2961	720	65.61	0.221	0.50
20	ps34	159.24	0.2951	720	65.15	0.220	0.50
21	ps35	160.47	0.2973	780	61.29	0.207	0.54
22	ps36	159.39	0.2953	852	61.52	0.208	0.59
23	ps37	159.19	0.2948	960	61.52	0.208	0.67
24	ps38	159.44	0.2953	1088	61.37	0.207	0.76
25	ps39	159.14	0.2947	1205	60.98	0.206	0.84
26	ps40	158.85	0.2941	1320	56.97	0.192	0.92
27	ps41	159.46	0.2954	1455	59.47	0.201	1.01
28	ps42	160.62	0.2977	1685	57.49	0.194	1.17
29	ps43	160.32	0.2969	1920	58.59	0.198	1.33
30	ps44	160.65	0.2977	2198	55.07	0.186	1.53
31	ps45	159.19	0.2948	2400	57.63	0.194	1.67
32	ps46	161.29	0.2987	2640	54.78	0.185	1.83
33	ps47	160.27	0.297	2880	53.97	0.182	2.00

Con'd

No.	Bottle No.	Volume (ml)	Carbon Wt.(g)	Time (Min.)	Ce (mg/l)	Ce/Co	Time (day)
34	ps48	159.67	0.2958	2880	53.38	0.180	2.00
35	ps49	159.94	0.2961	3360	51.70	0.174	2.33
36	ps50	160.11	0.2966	3745	53.16	0.179	2.60
37	ps51	158.69	0.294	4320	51.55	0.174	3.00
38	ps52	159.63	0.2958	5040	51.70	0.174	3.50
39	ps53	159.33	0.2954	5760	50.75	0.171	4.00
40	ps54	158.88	0.2942	6514	50.53	0.171	4.52
41	ps55	161.23	0.2989	7210	50.89	0.172	5.01
42	ps56	159.49	0.2954	8047	49.22	0.166	5.59
43	ps57	159.76	0.2958	8640	50.09	0.169	6.00
44	ps32	159.68	0.2959	10080	51.55	0.174	7.00
45	ps59	160.03	0.2964	11520	51.63	0.174	8.00
46	ps60	158.69	0.2943	12600	50.23	0.170	8.75
47	ps61	159.6	0.2955	14400	50.53	0.171	10.00
48	ps62	160.89	0.2981	15840	49.22	0.166	11.00
49	ps63	159.9	0.2959	17280	47.77	0.161	12.00
50	ps64	159.07	0.2945	18720	50.28	0.170	13.00
51	ps65	161.02	0.2982	21600	49.29	0.166	15.00
52	ps66	158.94	0.2946	24480	50.82	0.172	17.00

Initial phenol concentration Co = 296.32 mg/L.

Start at Oct. 28, 1993.

Initial pH = 6.99, D.O. = 8.85.

Appendix D

Desorption isotherm data

No.	Adsorption					Desorption			Desorbed (%)
	Bottle No.	Volume (ml)	Carbon Wt. (g)	Ce1 (mg/l)	qe (mg/g)	Volume (ml)	Ced (mg/l)	qed (mg/g)	
1	p39	534.64	2.1443	3.83	72.707	534.64	3.3	71.885	1.13
2	p32	472.99	1.5483	8.96	87.517	472.99	6.2	85.623	2.16
2'	p48	535.26	1.7518	9.11	87.488	535.26	5.9	85.685	2.06
3	p6	477.76	1.2066	22.73	108.333	477.76	13.4	103.028	4.90
4	p11	475.26	0.833	47.5	141.968	475.26	20.2	130.443	8.12
5	p14	478.58	0.5267	102	176.576	478.58	20.9	157.585	10.75
6	p49	534.59	0.4016	155.80	185.884	534.59	20.4	158.728	14.61
7	p51	534.75	0.2699	194.40	200.193	534.75	19.4	161.756	19.20
8	p56	535.97	0.1548	223.00	250.820	478.39	16.1	201.064	19.84
9	p29	538.2	0.2721	195.33	198.010	478.43	20.7	161.613	18.38
10	p33	538.03	0.155	236.33	205.177	474.9	15.9	156.461	23.74

Adsorption tests:
Start on Nov. 20, 1992
Initial D.O. = 9.62, pH = 6.95
End on Dec. 8, 1992
Final D.O. = 8.5, pH = 6.94

Desorption tests (in a 1% NaCl solution):
Start on Dec. 8, 1992
End on Jan. 4, 1993

Appendix E1

Cathodic and anodic regeneration data

Carbon Wt.(g)	loading		Regeneration conditions				Residual phenol (mg/l)	Reloading		RE (%)
	Ce (mg/l)	q1 (mg/g)	Current (mA)	Time (hour)	GAC location			Ce2 (mg/l)	q2 (mg/g)	
1.3018	19.1	100.48	50	3	cathod	a batch	13.33	60.68	88.38	87.96
1.3019	17.8	100.94	50	3	anode	a batch	0	73.50	83.65	82.88
1.2924	19	100.50	50	3	cathode	a batch	14.99	66.46	86.24	85.81
1.2938	18.1	100.83	50	3	anode	a batch	0	82.31	80.42	79.76
1.3002	18.5	100.68	50	1.5 hr cathode + 1.5 hr anode		a batch	1.81	73.47	83.67	83.10
1.2898	19.5	100.29		1.5 hr anode + 1.5 hr cathode			1.81	101.22	73.45	73.24
1.2941	19.4	100.36	50	3	cathode	a batch	13.89	59.69	88.74	88.42
1.2994	19.1	100.47		3	anode		13.89	74.18	83.41	83.02
1.2929	18.57	101.21	50	3	cathode	a batch	20.3	56.68	88.06	87.01
1.299	17.18	101.73		3	anode		20.3	78.12	80.19	78.83
1.2913	18.55	101.23	50	1.5 hr cathode + 1.5 hr anode		a batch	3.6	66.22	84.57	83.54
1.2913	18.26	101.33		1.5 hr anode + 1.5 hr cathode			3.6	97.31	73.14	72.18
1.3476	26.43	107.18	50	5	anode	a batch		80.24	85.82	80.07
1.3479	26.44	107.19	50	5	cathode	a batch		58.46	94.46	88.13
1.1958	27.59	106.7	50	5	anode	a batch		91.16	82.19	77.03
1.2077	25.64	107.48	50	5	cathode	a batch		46.11	100.05	93.09

Appendix E2
Regeneration current and time experimental data

Bottle Volume (ml)	Carbon Wt.(g)	Loading		Regeneration conditions		Residual phenol (mg/l)	Reloading		RE (%)
		Ce1 (mg/l)	qe1 (mg/g)	Current (mA)	Time (hour)		Ce2 (mg/l)	qe2 (mg/l)	
518.22	1.3078	22.36	108.21	0	1.5	0	131.22	65.43	60.46
518.44	1.3085	22.38	108.19	0	2.5	0	132.05	65.09	60.16
533.72	0.5861	115.35	164.00	0	1.5	0	246.45	45.42	27.70
533.89	0.5864	113.3	165.83	0	2.5	0.1	248.54	43.51	26.24
476.19	0.5239	98.65	179.68	0	1.5	0	247.33	42.11	23.44
476.75	0.5247	107.73	171.36	0	2.5	0	247.33	42.10	24.56
535.76	1.3521	25.54	106.49	0	0	1.4	145.23	60.03	56.38
536.28	1.3534	25.63	106.46	0	0	-	141.53	61.50	57.77
534.75	0.5873	120.11	158.60	0	0	-	257.33	35.89	22.63
518.27	1.3081	22.62	108.09	10	1.5	0	121.50	69.27	64.08
473.23	1.1946	22.5	108.12	10	2.5	0	119.52	70.04	64.78
518.24	1.308	21.7	108.46	10	2.5	6.8	119.30	70.14	64.67
477.5	1.2051	22.6	108.46	10	5	26.83	86.60	82.29	75.87
475.42	1.201	23.4	108.04	10	7.5	22.5	69.30	89.06	82.44
474.87	1.1985	24.6	107.66	10	10	33.15	61.00	92.43	85.85
501.02	1.2645	26.31	107.15	10	10	-	58.50	94.08	87.80
475.08	1.1991	28.43	106.31	10	15	-	53.38	96.10	90.4
498.66	1.2585	26.29	107.16	10	20	-	47.34	98.50	91.92
478.43	1.2075	28.72	106.18	10	40	-	42.90	100.66	94.8

518.24	1.3079	25.48	106.51	30	5	49.92	56.17	95.32	89.49
474.9	1.1985	24.95	107.38	30	7.5	-	51.37	96.34	89.72
518.99	1.3098	24.43	106.93	30	10	34.32	50.78	97.46	91.14
477.75	1.2059	24.36	107.59	50	1.5	-	71.40	88.39	82.15
535.51	1.3515	25	106.70	50	2.5	45.7	68.60	90.40	84.72
518.27	1.3080	25.78	106.40	50	5	32.29	46.60	99.12	93.16
534.1	1.3479	26.44	107.19	50	5	33.3	58.46	94.47	88.13
501.02	1.2644	25.06	107.74	50	5	-	61.15	93.04	86.69
476.19	1.202	25.4	107.18	50	5	-	48.53	97.45	90.92
477.13	1.204	24.92	107.40	50	5	-	58.89	93.37	86.94
478.13	1.2066	25.12	107.31	50	5	-	62.46	91.95	85.68
478.58	1.2077	25.64	107.48	50	5	-	46.11	100.05	93.09
475.58	1.2005	27.59	106.67	50	7.5	13.5	48.34	99.13	92.93
478.39	1.2073	25.75	107.06	50	7.5	-	63.45	91.55	85.51
518.44	1.3084	25.48	106.51	50	10	6.5	46.13	99.30	93.23
474.87	1.1982	25.03	107.37	70	5	22.1	41.82	100.14	93.27
475.42	1.2	25.45	107.16	70	7.5	-	68.64	89.48	83.50
478.43	1.2074	27.64	106.31	70	10	-	47.96	97.69	91.89
474.87	1.2922	19.3	100.40	100	1.5	0	80.81	80.98	80.65
477.75	1.3008	18	100.82	100	2.5	5.26	54.31	90.66	89.93
518.22	1.3078	25.74	106.41	100	2.5	30.2	53.29	96.47	90.65
477.38	1.2049	28.11	106.44	100	5	6.4	46.54	98.81	92.84
475.58	1.2	23.3	108.21	100	5	-	47.70	97.73	90.32
501	1.2645	25.16	107.60	100	7.5	-	41.62	100.76	93.65
473.83	1.1968	23.5	108.02	100	10	0	55.20	94.66	87.63
501.24	1.2651	26.24	107.18	100	10	-	42.12	100.57	93.83

533.72	1.3469	24.87	106.76	150	2.5	11.2	45.08	99.72	93.41
473.83	1.1958	26.94	106.59	150	2.5	-	60.64	92.67	86.94
533.88	1.3473	25.15	106.65	200	2.5	0	66.64	91.18	85.49
475.58	1.2003	25.7	107.07	200	2.5	-	59.76	93.01	86.86
477.5	1.2051	24.65	107.49	250	2.5	-	61.46	92.34	85.90
533.89	1.3474	24.71	106.82	250	2.5	0	52.44	96.80	90.62
534.1	1.3479	24.56	106.88	300	2.5	0	63.35	92.48	86.53
Pre-electrochemical regeneration									
475.08	1.2929			50	1.5		19.57	100.29	
477.38	1.299			50	1.5		18.18	100.81	
474.56	1.2913			50	1.5		19.55	100.31	
474.56	1.2913			50	1.5		19.26	100.42	

Appendix E3

Electrolyte concentrations and types experimental data

Bottle volume (ml)	GAC weight (g)	Loading		Regeneration conditions		Reloading		RE (%)
		Ce1 (mg/l)	qe1 (mg/g)	Electrolyte	Concentration (%)	Ce2 (mg/l)	qe2 (mg/g)	
474.56	1.1979	26.83	106.04	NaCl	5	57.7	94.79	89.39
478.39	1.2074	29.02	106.06	NaCl	2	71.9	89.17	84.07
474.57	1.198	27.15	105.91	NaCl	2	68.89	90.35	85.31
534.64	1.3493	26.82	106.07	NaCl	0.5	59.25	94.19	88.80
534.75	1.3445	26.54	106.58	NaCl	0.5	58.33	94.91	89.05
535.26	1.3508	26.45	106.21	NaCl	0.1	74.67	88.08	82.93
474.9	1.1986	28.43	106.3	NaCl	0.05	64.23	90.79	85.41
474.23	1.1976	26.82	106.93	NaCl	0.001	104.83	76.72	71.75
474.56	1.1981	26.68	107.02	NaCl	0.01	90.2	82.54	77.13
518.44	1.3085	26.45	107.18	NaHCO3	1	124.72	67.97	63.42
478.43	1.2074	27.65	106.67	NaHCO3	1	123.18	69.50	65.15
518.89	1.3095	26.28	107.26	Na2SO4	1	43.88	100.01	93.24
518.99	1.3099	26.59	107.12	Na2SO4	1	69.97	89.66	83.70
478.39	1.2074	26.89	106.97	CH3COONa	1	66.54	91.94	85.95
533.88	1.3475	26.665	107.09	CH3COONa	1	73.83	88.13	82.29
475.08	1.1995	26.61	107.04	Tap water		91.91	81.85	76.47
477.38	1.2049	26.33	107.18	Tap water		89.88	82.69	77.15

Regeneration current = 50 mA, Regeneration time = 5 hours.

Appendix E4
GAC particle sizes and loadings experimental data

GAC particle sizes

Bottle		Carbon weight (g)	Loading		Regeneration conditions		Reloading		RE (%)
No.	Volume (ml)		Ce1 (mg/l)	qe1 (mg/g)	Current (mA)	Time (hour)	Ce2 (mg/l)	qe2 (mg/g)	
Particle size 30/40 mesh									
ps38	159.44	0.4025	29.45	106.61	50	5	41.20	101.95	95.63
ps50	160.11	0.4039	29.07	106.84	50	5	47.40	99.57	93.20
ps58	159.35	0.4021	28.7	106.95	50	5	45.27	100.39	93.86
Particle size 12/16 mesh									
p27	518.27	1.3082	26.66	106.11	50	5	86.57	83.99	79.16
p52	518.44	1.3086	27.05	105.96	50	5	84.08	84.98	80.20
p28	518.24	1.3078	26.71	106.11	50	5	69.50	90.78	85.55

GAC loadings

p24	518.22	1.6765	12.78	87.84	50	5	26.95	83.25	94.77
p27	518.27	1.6767	12.565	87.91	50	5	23.82	84.21	95.80
p50	535.51	0.9374	63.82	133.19	50	5	86.57	119.80	89.94
p35	535.76	0.9376	63.23	133.56	50	5	112.42	105.05	78.66
p26	536.1	0.5888	122.37	158.97	50	5	144.86	137.86	86.72
p53	536.28	0.5891	122.82	158.53	50	5	164.39	120.06	75.73
p47	536.27	0.4199	167.23	165.69	50	5	192.71	132.26	79.82
p37	536.47	0.4201	165.825	167.47	50	5	189.55	136.28	81.38
p29	538.2	0.2488	216.89	173.21	50	5	220.32	164.29	94.85
p33	538.03	0.2487	212.71	182.27	50	5	226.01	152.00	83.39

Appendix E5

Multiple cycles of loading and regeneration experimental data

Bottle		Carbon	Loading		Regeneration conditions		Relosding		RE	
No.	Volume (ml)	weight (g)	Ce1 (mg/l)	qe1 (mg/g)	Current (mA)	Time (hour)	Ce2 (mg/l)	qe2 (mg/g)	(%)	
p15	476.19	1.202	25.4	107.18	50	5	48.53	97.45	90.92	
p16	477.13	1.204	24.92	107.4	50	5	58.89	93.37	86.94	
p19	478.13	1.2066	25.12	107.31	50	5	62.46	91.95	85.68	1 cycle
					50	5	55.27	95.65	89.24	
					50	5	53.88	96.23	89.60	
					50	5	53.09	96.54	89.96	2 cycles
					50	5	63.43	92.52	86.32	
					50	5	82.52	84.98	79.12	
					50	5	82.41	85.02	79.23	3 cycles
					50	5	80.2	85.87	80.12	
					50	5	59.69	94.03	87.55	
					50	5	66.7	91.24	85.03	4 cycles
					50	5	70.32	90.43	84.37	
					50	5	69.07	90.95	84.69	
					50	5	81.25	86.12	80.25	5 cycles