

Bulletin 32:
REMOVAL OF SELECTED CONTAMINANTS
FROM WATER BY SORPTION OF COAL

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PREFACE

Conventional water and wastewater treatment practices have little or no effect on an increasing number of both inorganic and complex synthetic organic wastes which presently contaminate our nation's watercourses. Among the inorganics particular concern in recent years has been directed toward phosphorus containing compounds, since it is widely thought that phosphorus is the nutrient which limits the growth of large quantities of algae in lakes and other bodies of water. Concern regarding organic pollutants has been directed toward synthetic organic pesticides which in the past decade have become recognized as significant water pollutants.

In order to protect the water resources of our nation new technologies for water and wastewater treatment must be developed. One of the more promising processes to be discovered in recent years is the use of activated carbon as an adsorbent for organic pollutants. The technical feasibility of this process has been fully demonstrated. Economic considerations, however, are frequently unfavorable owing to the high cost of the activated carbon. More recently a number of processes have been suggested which utilize the properties of coal as an adsorbent, flocculent, filter aid and filter media for the purpose of facilitating treatment of a variety of wastewaters. In evaluating these processes, there is a real need for quantitative data which describe the extent of uptake of a wide variety of contaminants on coal.

The research reported in this bulletin enables the evaluation of the sorption of selected pesticides and phosphorus containing compounds by a variety of grades of coal. The rate at which the uptake reaction proceeds is reported, and the optimum environmental conditions for sorption are noted. Information of this type helps to facilitate the proper evaluation of the various coal processes which are presently being proposed. In particular the extent to which sorption on coal may be substituted for sorption on activated carbon is discussed.

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INTRODUCTION

Current methods used for the treatment of domestic and industrial wastes are largely biological in nature. These methods are effective in eliminating biologically degradable material, but in many cases do not prevent the release of inorganic nutrients such as nitrogen and phosphorus and of persistent organic materials to receiving watercourses. Both of these types of contaminants are of increasing importance to those responsible for water quality control aspects of water resources management and new technologies leading to their removal in treatment processes must be developed.

Eutrophication of lakes and other bodies of water has created much concern over the past several years. Waters of eutrophic lakes contain large quantities of algae and have little or no dissolved oxygen in the hypolimnion. The recreational value of such waters is greatly reduced. Large amounts of nitrogen and phosphorus are present in eutrophic waters and constitute the major cause of the problem. Once these nutrients are introduced into the receiving waters the natural rate of eutrophication is greatly increased. Not until the nutrients are removed from waste discharges can the growth of large plant quantities be eliminated and the oxygen level required for other forms of life be restored in the receiving waters.

It is widely thought that phosphorus is the limiting nutrient in many bodies of water, and its removal from these waters will cause a substantial decrease in the plant life present. Phosphorus is abundant in domestic wastewater and its concentration is increasing due to the use of large quantities of synthetic detergents and the employment of garbage grinders and other modern conveniences. Removal or limitation of soluble phosphorus in wastewater effluents is thus a key factor in alleviating the aesthetic and economic problems associated with excessive algal growth.

Among the organic contaminants which pose the greatest problem in water quality control, none have created as much concern in recent years as have pesticides. The survival of today's burgeoning world population is almost totally dependent upon efficient and fruitful agricultural production. It has been only with the development of synthetic organic pesticides that man has been able to compete successfully with the insects and weeds endangering his food supply. Paradoxically, in some instances, the very tools of advanced technology that are concomitant with increased agricultural production, and that effectively combat starvation, may themselves actually become sources of environmental pollution.

The economic value and world-wide importance of chemical pesticides as agricultural production tools are unquestioned. However, residues of pesticides and other exogenously applied chemicals in foodstuffs are of concern to everyone everywhere. They are essential to food production and manufacture, yet without knowledge of their behavior in the environment, certain of the persistent pesticides could become dangerous to the public health and the ecological balance of nature.

The concern of the sanitary engineer with these exotic compounds is with the effects they may have on the environment, particularly in natural watercourses. Certain pesticides, such as the chlorinated hydrocarbons, persist for long periods of time in an aquatic environment due to their resistance to chemical and biological degradation. These compounds also exhibit chronic toxicity, being easily stored in the fatty tissues of animals. Thus, very dilute concentrations of long-lived pesticides can in time be lethal to animals exposed to them.

If dangerous or potentially dangerous concentrations of pesticides exist in water utilized for human consumption, methods must be developed to remove them easily and economically. Activated carbon is very effective in adsorbing organic compounds from dilute solution. The high cost of this adsorbent, however, often prohibits its use in large-scale treatment processes.

In recent years consideration has been given to utilizing the properties of coal as an adsorbent, flocculent, filter aid, and filter media for facilitating the treatment of a variety of waters and wastewater. Coal is relatively low in cost and thus is an attractive filter media if the removal of dissolved material by sorption can be accomplished concurrently with the elimination of suspended solids by filtration. Although coal is a poorer sorbent than is activated carbon, it is considerably more economical and can be incinerated after exposure to a wastewater stream.

The purpose of this research is to evaluate the extent of uptake of selected phosphorus containing compounds and synthetic organic pesticides by coal in both batch and continuous flow operations. The kinetics of the uptake process as well as the capacity of the coal for the sorbate at equilibrium are reported. A range of coal grades are included in the investigation. Information of this type enables the evaluation of the potential of coal contact processes for removal of these important pollutants.

REVIEW OF LITERATURE

While the current literature contains very few reports related to the effectiveness of coal in treatment processes, there is much information available that is relevant to this study. Among the topics discussed in this chapter are the properties of the selected sorbates, the chemical and physical considerations related to the sorption process, and the use, properties and reported studies of uptake of various contaminants utilizing either carbon or coal.

Properties of Selected Sorbates

Three synthetic organic pesticides and several phosphorus containing compounds were chosen for study. The pesticides were lindane, a representative chlorinated hydrocarbon insecticide, parathion, a typical organic phosphorus insecticide and chloroisopropyl carbamate, an important organic herbicide. The phosphate compounds utilized included potassium dihydrogen phosphate, sodium hexametaphosphate and sodium pyrophosphate.

Lindane

Lindane is an insecticide containing 99 per cent gamma isomer of benzene hexachloride. Its technical name is 1,2,3,4,5,6 hexachlorocyclohexane. Lindane was first synthesized by Michael Faraday in 1825. The development of lindane took place almost simultaneously in England and France during World War II. It is prepared by the chlorination of benzene in the presence of ultra-violet light.

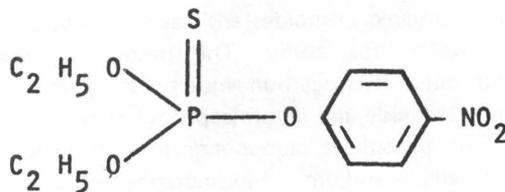
The gamma isomer of benzene hexachloride melts at 112.5°C with a slightly musty odor. It has a vapor pressure of 0.14 millimeters of mercury at 40°C. Reported water solubilities of lindane range from five to ten parts per million. Lindane is used for medical purposes in the treatment of scabies, pediculosis corporis and pubis (1).

Poisoning due to lindane may occur by ingestion, inhalation or by percutaneous adsorption. The acute symptoms are headache, nausea, vomiting, diarrhea, tremors, weakness, convulsions, and circulatory collapse. Hepatic damage has occurred in experimental animals exposed to repeated

doses of lindane. It is estimated that the fatal dose is 150 milligrams of lindane per kilogram of body weight. It has been found that lindane may be absorbed through the skin, and that it appears to be more toxic to younger animals. Residue tolerances of 10 parts per million in animal fat have been established. Mammals rapidly excrete the compound and its residual effects are much shorter than those of DDT, which can be stored in animal fat (1).

Parathion

Parathion is an organic phosphorus insecticide which was first developed in 1944 in Germany by Schrader. The technical name for parathion is O, O-diethyl O-p-nitrophenyl phosphorothioate, and it has the following structure:



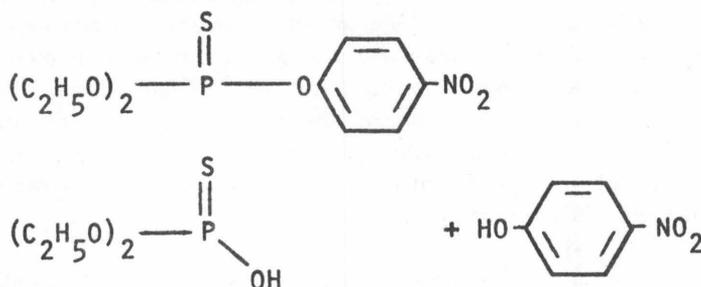
In its pure form, parathion is a colorless liquid with a melting point of 6°C and a boiling point of approximately 160°C. Its specific gravity is about 1.25 and its solubility in water has been reported as being approximately 24 mg/liter.

The organic phosphorous insecticides owe their toxicity to their ability to phosphorylate cholinesterase. The enzyme cholinesterase acts to hydrolyze the excess acetylcholine produced in the body. Acetylcholine may be thought of as an electrical transmitter which permits the passage of nerve impulses throughout the body. Without cholinesterase present to hydrolyze excess acetylcholine, the nerve pathways become uncontrollable, thus resulting in severe damage or death to the organism.

Experiments have been conducted using animals to determine toxic concentrations of parathion. According to Metcalf (2), the LD₅₀ of female rabbits, subjected to a single dose, was 45 mg/kg of body weight. DeOng (3) listed the LD₅₀ of rats as 15 mg/kg of body weight. The LD₅₀ is defined as the concentration that will cause death to 50 per cent of a controlled population of the organisms tested.

Parathion is subject to a replacement reaction in which the sulfur atom is replaced by an oxygen atom. This replacement results in the formation of parathion's oxygen analogue, para-oxon. Para-oxon is up to 10 times more toxic, and 100 times more soluble in water than is parathion. The hydrolysis of para-oxon in water takes place approximately eight times faster than parathion (4). It appears that the toxic effect of parathion in many instances is due to this conversion of parathion to para-oxon within the host organism.

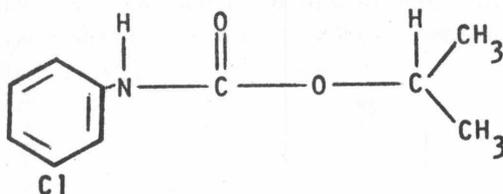
One very important characteristic of parathion is its tendency to hydrolyze in alkaline solutions. In alkaline solutions, parathion will hydrolyze to form two nontoxic compounds.



This reaction takes place very rapidly at high pH values and the reaction rate decreases with decreasing pH. Frear (5) noted that 50 per cent hydrolysis will take place in water solution, above a pH of 12, after about eight hours. This hydrolysis reaction is of major importance when considering the persistence of parathion in an aquatic environment (2).

Chloroisopropyl Carbamate

Chloro-isopropyl carbamate, usually abbreviated as CIPC, is an organic herbicide first developed in 1947 by Columbia-Southern Chemical Corporation (6). The scientific nomenclature for CIPC is isopropyl-N-(3-Chlorophenyl) carbamate. Its structural formula is given below:



In its pure form, CIPC is a white crystalline powder with a melting point of 38°C and a boiling point of 247°C , at which it decomposes. Its specific gravity at 30°C is 1.180 and its solubility in water has been reported as 108 ppm at 20°C (6).

CIPC is a mitotic poison which acts as a herbicide by preventing cell division (7). It is not absorbed by the leaves and is dependent on absorption through the root system. It is effective mainly in controlling germinating grasses and is used for weed control in cotton, soybeans, spinach and certain other field crops. It is applied either as a liquid emulsion or in granular form.

Data has been collected on the toxicity of CIPC to animals (6). The oral LD_{50} for rats lies between 5 to 7.5 grams per kilogram of body weight. The oral LD_{50} for rabbits is approximately 5 grams per kilogram of body weight. The LD_{50} is defined as that concentration which will cause death to 50 per cent of a controlled population of the organisms tested. Preliminary carcinogenic tests indicate that CIPC given orally in moderately toxic doses over a period of 18 months did not cause the development of benign or malignant tumors in any organs of rats.

Being an ester, CIPC is slowly hydrolyzed in acidic or basic conditions to yield m-chloro-aniline, carbon dioxide, and isopropyl alcohol. CIPC is subject to degradation in the presence of strong oxidizing agents but is not readily acted upon by mild organic intermediates and solvents.

Schwartz (8) conducted research on the resistance of CIPC to microbial degradation. He found that under the conditions normally found in water supplies, CIPC is strongly resistant to chemical attack and that very little CIPC would be adsorbed by suspended mineral solids in surface waters. He further concluded that significant concentrations of the intact herbicide or its metabolic intermediates could persist for weeks or months in a natural waste environment despite microbial action. Since CIPC possesses a relatively short life in the soil compared to other pesticides such as dieldrin and DDT, one might expect that once such pesticides reach a water supply they would persist for extremely long periods of time. Schwartz concluded by stating that the indications were that the self-purification capacity of natural water environments is not sufficient to eliminate these toxic substances.

Phosphorus Containing Compounds

The chemistry of phosphorus is exceedingly complex due to the many oxidation states of the element. This leads to a multiplicity of phosphorus compounds. Orthophosphoric acid, H_3PO_4 , and its salts are probably the best known phosphorus compounds. Orthophosphoric acid is formed by the hydration of phosphorus pentoxide, P_4O_{10} , but other phosphoric acids can be formed by the same means. Among these acids are pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, and metaphosphoric acid, HPO_3 . H_3PO_4 and $\text{H}_4\text{P}_2\text{O}_7$ exist as discrete molecules unlike HPO_3 , which is polymeric.

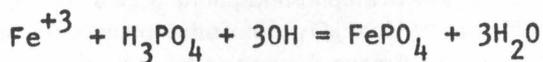
Pyrophosphates are used for water softening and as complexing agents in electroplating baths. Metaphosphates have been used extensively as sequestering agents. Polymeric metaphosphates of the form $(\text{NaPO}_3)_n$ have been widely used for water softening. $\text{Na}_3\text{P}_3\text{O}_9$ is particularly effective for sequestering the calcium ion. The complex formed with the calcium ion is such that it is nearly impossible to precipitate calcium with such reagents as carbonate (9).

It has been shown (10) that at pH 4, a ferric hydroxide gel strongly adsorbed phosphate ions. However, a large portion of the phosphate was released when the pH was raised to 9 using calcium bicarbonate. The orthophosphate ion is a relatively good complexing agent, especially with iron (11).

Einsele (12) found that under oxidizing conditions, phosphate precipitated in the presence of iron as insoluble ferric phosphate and that soluble phosphate is liberated upon reduction. Large amounts of phosphate are bound as insoluble ferric phosphate in the surface of oxidized muds in lakes and other bodies of water. Increases in the concentrations of dissolved substances, including phosphorus, occurring after exhaustion of the oxygen content in the hypolimnion of several European lakes are noted by Mortimer (13). Inorganic iron is practically insoluble in oxygenated neutral or alkaline waters and high iron concentrations are only maintained in the absence of oxygen.

Stumm (14) has shown that the solubility of phosphorus in equilibrium with insoluble ferric phosphate varies with pH. In neutral or alkaline pH ranges, FePO_4 is appreciably soluble. Under these conditions, the ratio of the phosphate to OH in the ferric phosphate precipitate will vary though the total number of negative charges will remain constant to allow for electroneutrality.

In alkalimetric titrations Stumm found that an equimolar addition of phosphoric acid to a ferric ion solution did not produce any appreciable increase in the amount of NaOH required to reach the equivalence point. This is explained by assuming that the reaction between the ferric ion and phosphoric acid leads to the deprotonation of phosphoric acid according to the reaction:



Sawyer (15) and others have shown that lime is valuable in removing phosphates by the formation of the very insoluble tricalcium phosphate at high pH values. Several investigators (16,17,18,19) have shown that, in lakes, the concentration of phosphorus is limited by the solubility of iron, aluminum or calcium phosphates and by the pH value of the system. Of particular importance, is the interaction phosphates, iron, and oxygen in natural bodies of water. Tucker (19) argues that, in the presence of oxygen, ferrous ions are oxidized to the ferric state leading to the formation of the insoluble precipitate ferric phosphate, FePO_4 . By this mechanism, phosphates are precipitated to the bottom sediments. During periods of stagnation in the lake, the oxygen concentration is lowered. In this low oxygen environment, the ferric phosphate, FePO_4 , is reduced to ferrous phosphate which is soluble. Mortimer (13) has shown that phosphate can be adsorbed on ferric hydroxide, Fe_2O_3 or on ferric hydroxide organic complexes in lake bottom muds providing that oxygen is present in the overlying water.

Yee (20) has investigated the removal of mixed phosphates on activated alumina. He found that activated alumina selectively removes orthophosphate (OP), pyrophosphate (PP), tripolyphosphate (TPP), and hexametaphosphate (HTP). The capacity for the polyphosphate was found to be approximately three times the capacity for orthophosphate. An equivalence ratio of calcium to phosphate (as PO_4^{3-}) of 1:1 was needed to obtain phosphate removal. Removals of 99 per cent were reported as long as this calcium to phosphate ration was maintained. Phosphate removal was insignificant without calcium in the system.

At pH greater than 5.5, there was an additional hydroxide ion consumption indicating that the affinity of Fe^{+3} for OH becomes larger than the affinity of Fe^{+3} for PO_4^{3-} .

It was noted that if the molar ratio of the ferric ion to orthophosphate exceeded one, then a "mixed" ferric hydroxophosphate ("basic ferric

phosphate") was precipitated. At very high ratios, a constant minimum level of residual soluble phosphate was reached. This agrees with the fact that soluble ferric phosphate complexes are in equilibrium with the solid phosphates.

Galal-Gorchev and Stumm (21) found that precipitates obtained from the Fe^{+3} and PO_4^- reaction in the pH range 1.5 to 2.6 had a Fe to P ratio of unity. This indicated that there is no OH^- in the structure of the precipitate. The color of the precipitate was white and not yellow as is normally encountered when OH^- is present in the precipitate.

According to Banerjee (23) the reaction of phosphoric acid and ferric ions leads to the formation of two complex ions. These are $\text{Fe}(\text{HPO}_4)^+$ and $\text{Fe}(\text{HPO}_4)_2^-$, and they are present in solution in the ratio 2:1. Lanford and Kiehl (22) have also verified the formation of $\text{Fe}(\text{HPO}_4)^+$.

The Sorption Process

Sorption may be defined as the condition in which molecules of a gas or liquid adhere to the surface of a solid by either physical or chemical forces. Physical adsorption is relatively non-specific and is due to weak forces of attraction between molecules. These attractive forces are usually considered to be due to van der Waal forces and are electrostatic in nature. Physical adsorption is generally quite reversible, that is, only a small amount of energy is required to break the bond between the sorbent and the sorbed molecule.

Chemical sorption, or chemisorption, is the result of much stronger forces of attraction which may be compared to the forces which bond the molecules of chemical compounds together. Chemical sorption is characterized by its high heat of adsorption and may be considered irreversible unless sufficient energy is added to sever the chemical bond between the sorbing media and the sorbed molecules. Chemical sorption, due to the nature of its bonding characteristics, is usually confined to the formation of a monolayer on the surface of the adsorbent.

Kinetic studies were conducted to determine the optimum contact period required to achieve equilibrium in a batch type sorption process and enable evaluation of the rate-limiting step in the process. Previous investigations (24) (25) have indicated that the rate-limiting step for removal of organic solutes from dilute aqueous solution by porous activated carbon in agitated nonflow systems is one of intraparticle transport of the solute in the

pores and the capillaries of the sorbent. For systems in which intraparticle transport is the rate-limiting step, a plot of the quantity of solute removed per unit weight of adsorbent versus the square-root of time should yield a linear relationship.

Sorption data from batch equilibrium studies is usually represented in the form of a sorption isotherm. A sorption isotherm expresses graphically a relationship between the quantity of material sorbed per unit weight of sorbent and the concentration of solute remaining in solution at equilibrium.

An empirical equation was developed by Freundlich to express sorption data. This equation is usually expressed as:

$$\frac{x}{m} = K C_e^{1/n}$$

where

$\frac{x}{m}$ = weight of substance adsorbed per unit weight of sorbent

C_e = concentration of solute remaining in solution at equilibrium

K, n = constants

Taking the logarithms of both sides yields the equation

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e$$

Therefore if the data is plotted on log paper, a straight line should result if the sorption data follows the Freundlich equation.

Another equation that is sometimes used to represent sorption data is the theoretically derived Langmuir isotherm. This equation was developed using the following assumptions: (1) the sorbed layer consists of a complete monomolecular film, (2) the sorption process consists of molecules condensing and evaporating from the surface of the solid, and (3) equilibrium is reached when the rate of condensation equals the rate of evaporation. The Langmuir equation takes the form

$$\frac{x}{m} = \frac{K C_e}{1 + K_1 C_e}$$

where K and K_1 are constants with theoretical significance but are usually obtained through experimental methods. The Langmuir equation was originally derived to explain the sorption of gases on solids and has not been found to be particularly useful in expressing data for the sorption of trace organics from solution.

Although the Freundlich equation has no theoretical basis, it has been found to be more adaptable to sorption data than the theoretically derived Langmuir equation. This is due to the fact that most physical adsorption processes do not comply with the first assumption on which the Langmuir equation is based. A complete monolayer is not usually formed in the sorption of solutes from dilute liquid solution.

Sorption of Trace Contaminants by Coal and Activated Carbon

A majority of the current investigations concerning sorption of trace organics from solution have been conducted using activated carbon as the adsorbing media. Recently, however, coal has been suggested as a possible alternative sorbent due to its similarity to activated carbon and because of the economic advantages offered by the use of coal as the sorbing media. Both activated carbon and coal owe their sorptive capabilities to their high ratio of surface area to volume. Although activated carbon has a much higher ultimate adsorptive capacity due to its higher surface area to volume ratio, the capillaries of the coal particle are much larger and therefore the rate of sorption on coal should be faster than the rate of sorption on activated carbon.

Studying the kinetics of adsorption on granular activated carbon, Morris and Weber (26) showed that uptake of various organics in dilute solution proceeds slowly for high molecular weight compounds such as tetradecyclobenzenesulfonate, and equilibrium is reached only after several weeks of contact time. It was noted that the rate of uptake was faster for removal of organic compounds from dilute solutions which implies that the sorption process favors the removal of trace quantities. The size and configuration of the compounds studied also affected the rate of sorption. The rate of sorption decreased with increasing molecular weight. Molecules with highly branched structures were removed much more slowly than those molecules of identical molecular weight but with a configuration that permits coiling of the molecule. It was also shown that the rate of sorption decreased as the diameter of the activated carbon particles increased.

In a later report, Morris and Weber (24) studied the rates of sorption of various pesticides in contact with granular activated carbon. It was found that the rate of uptake is relatively independent of the type of pesticide used and that the rate of removal of the pesticides favors sorption from dilute solutions. Weber and Gould (25) conducted similar studies and found that the rate limiting step of sorption of pesticides on granular activated carbon in agitated non-flow systems is one of intraparticle transport of the solute in the pores and capillaries of the adsorbent.

Schwartz (27) conducted kinetic studies of the adsorption of CIPC on activated carbon. He found that granular activated carbon readily sorbs CIPC from aqueous solution. Approximately 24 hours were required to reach equilibrium but about 90 per cent of the total equilibrium adsorption was achieved in four hours. The ultimate capacity of the activated carbon for CIPC was estimated to be about 0.34 mg. of CIPC per mg. of carbon. The sorption of CIPC was independent of the hydrogen ion concentration over the pH range from 4.8 to 9.3 and the adsorption appeared to involve physical or real chemical bonding. Schwartz finally concluded that the initial rates of sorption of the CIPC-activated carbon system vary directly with the square root of time, indicating that the rate-limiting step is one of intraparticle transport of the sorbate in the pores and capillaries of the sorbent.

In an evaluation of the use of activated carbon, Johnson, *et. al.*, (28) determined that granular activated carbon was effective in removing chemical oxygen demand (COD) and alkylbenzenesulfonate (ABS) from a sand-filtered, municipal waste water secondary effluent. Studies were also conducted to determine the feasibility of using chemical regenerates to restore the sorptive capacity of activated carbon that had been exhausted by exposure to the sand-filtered secondary effluent. It was determined that the sorptive ability of the activated carbon tested was only partially restored and therefore the sorptive capability of the activated carbon was eventually destroyed. From an economic standpoint, the authors concluded that chemical-oxidant regeneration of activated carbon exhausted by tertiary treated waste water is not economically feasible.

Joyce and Sukenik (29) studied the ability of activated carbon to remove COD and ABS from secondary waste water effluent. Waste water containing initially 50 ppm. COD and 5 ppm. ABS was passed through a 20 foot column at a flow rate of 10 gallons per minute per square foot of cross-sectional bed area. The effluent contained 12 to 20 ppm. COD and less than 0.5 ppm. ABS. Thermal reactivation of the granular activated carbon restored its virgin sorptive properties. In a later study (30), a flow rate of 4

gpm, per square foot, was used in an effort to evaluate the effect of increased detention time on the removal of COD and ABS. The data indicated that the reduced flow rate did not appreciably affect the removal efficiency of the activated carbon. Flocculation with alum and settling of the secondary effluent prior to carbon adsorption increased the adsorption capacity of the carbon and resulted in much lower levels of COD than the levels obtained with the unflocculated effluent. In another experiment, primary waste water effluent was passed through a carbon bed with a depth of 20 feet. The mechanical problems associated with the suspended solids, and the unsatisfactory BOD and COD reduction obtained, led to the conclusion that carbon treatment of primary effluent by this system was not feasible.

Williamson, *et. al.* (31), undertook an investigation to determine whether inexpensive, commercially available materials hold promise in the treatment of waste waters, especially secondary effluents. Minerals, industrial by-products, proteinaceous materials, conventional water treatment agents, and others were tested. Activated carbon was used as a reference. None of the solids tested were able to remove contaminants in secondary effluents as economically as activated carbon. These solids can, however, be expected to contribute towards the advancement of waste treatment through removal of specific contaminants.

Many investigations indicate that contact with activated carbon is an effective method of sorbing various organic chemicals from solution. However, the major difficulty associated with this process is an economic one. A general conclusion that may be reached is that the spent activated carbon must in many cases be reactivated for the process to be economically feasible. This consideration of economic factors has led to the search for an adsorbent which may have similar characteristics to activated carbon without the high cost associated with such a process.

There is at least one instance in which coal contact process has been used to treat an industrial waste. Gutzeit and Enyart (32) describe a treatment plant used by the General American Transportation Corporation of Pennsylvania in connection with a tank car cleaning facility. The waste water is high in oils and aromatic hydrocarbons. The treatment facility used a coal contact process in conjunction with normal biological treatment to remove 99.8 per cent of phenol from solution.

An investigation into the use of coal for tertiary treatment of domestic waste water was conducted by Johnson and Kunka (33). A continuous flow process was utilized to determine the adsorption of COD and ABS from

solution using various types of American coal as the adsorbing media. A High-Volatile-C Bituminous coal was considered to be the most effective of the coals tested. Several coal types were found to be objectionable as they added COD to the effluent.

Coal filtration has been used as a final treatment step in a number of sewage treatment processes with favorable results. The Rand Corporation of Cleveland, Ohio, under sponsorship of the Office of Coal Research, U.S. Department of the Interior has made perhaps the most extensive studies of the physical and the chemical properties of coal as they effect its use in wastewater treatment (34). In their studies they have investigated the sorptive properties of coal, but have devoted only a small portion of the report to studies of sorption by coal of pesticides and other high molecular weight organic compounds. The Rand Corporation study noted that all American coals investigated exhibited the property of sorbing dissolved organic matter from sewage, the sorptive process apparently varying with the rank and source of the coal. No coal was found to contribute soluble oxygen demand to water.

Ultimate disposal of organic contaminants sorbed onto the solid phase from solution may be accomplished by incineration along with the coal which was used for treatment. Even if it is assumed that the heating value of this waste product is ignored, the process might be cheaper to install and operate than are conventional secondary treatment plants. If the heating values can be usefully recovered, substantial economics can be predicted (34).

Coal classified as high volatile "B" to subbituminous "C" inclusive proved to possess the best sorptive properties. High volatile "C" coal appeared to be the most desirable of the coals used in the Rand study. Although the column sorption method appeared to be effective in judging the potential maximum removals of trace organics by coal, it was not reliable for comparing the performance of different sorbents relative to each other. Both total area of the coal and time of exposure were controlling factors in governing extent of sorption. In the column test, with a fixed flow rate, time of exposure was determined by the column length; however, because of the variations in particle size distribution and in the particle shape, columns filled to the same height with different coals could contain substantially different areas of adsorbent.

The Rand study also gave attention to the removal of phosphate in a coal contact process. Uptake of orthophosphate ranged from 35 to 85 per

cent in continuous-flow column studies and varied with the grade of coal utilized. Orthophosphate removal decreased significantly with time in contrast to BOD and COD removals which remained relatively constant. This result suggested that phosphate removal may rely on a mechanism of reaction with some constituent of coal rather than on straight-forward adsorption.

Shannon (35) investigated the use of coal as an adsorbent for the treatment of waste waters. A Canadian coal (High-Volatile-C bituminous) was studied in batch and column applications for the sorption of the dissolved Chemical Oxygen Demand (COD) of a synthetic waste water. It was shown that the coal, unlike activated carbon, displayed selective adsorption for the components of the synthetic waste.

The use of graded anthracite is well known as an aid to sand filtration in water treatment. Because of its favorable density in comparison to that of sand, anthracite affords a means by which a desirable coarse-grained layer can be formed on the surface of a rapid sand filter. This layer remains on the surface in spite of frequent back-washing. It is chemically stable and is considered to be a permanent component of the filter. Some industries have maintained that the characteristic particle shape of anthracite permits improved performance of rapid sand filters used in the treatment of their own wastes. Little information is available, however, on the effect of such anthracite layers on removal of persistent organics.

Activated carbon is well known for its adsorbing properties. The similarity between activated carbon and coal in addition to the thirty-or-more fold difference in cost, immediately draws attention to the attractiveness of coal even if its sorbing properties only just approach those of activated carbon.

EXPERIMENTAL PROCEDURES

Both batch and column studies were conducted in the course of this research. The purpose of this section is to describe in detail the equipment used and the procedures that were followed in determining the ability of coal to sorb and subsequently remove the selected contaminants from solution.

Batch Tests

Kinetic uptake studies were conducted utilizing five types of coal as well as activated carbon. Kinetic studies were used to determine the effect of pH coal concentration, and solute concentration on the rate of sorption. Equilibrium studies were conducted to determine total sorptive capacities. The coals utilized in the course of the research were pulverized prior to being employed in the experimental work and may be described as follows:

1. High-Volatile Bituminous-A, Pittsburg Seam
2. High-Volatile Bituminous-C, Indiana No. 6 Seam
3. High-Volatile Bituminous-C, Peabody-Lynnville Seam
4. Medium-Volatile Bituminous, Cedar Grove Seam
5. Low-Volatile Bituminous, Pocahontas Keystone Mine

Each of these coals was provided by the Rand Development Corporation of Cleveland, Ohio. Sieve analysis revealed a mean particle diameter that range from 0.2 to 0.5 mm. The iron content of the coals was also determined in accordance with the procedure described in a later section of this chapter. The activated carbon was Grade 517, 20 by 40 mesh, provided by Witco Chemical Company.

In order to eliminate the problem of variable pH during the course of the batch tests, a phosphate buffer or a citrate-phosphate buffer was utilized except when the removal of phosphate was being measured. In the latter case a carbonate system was employed. The phosphate buffer was normally used in the kinetic and equilibrium studies where the pH required was 7.0 to 6.5. For pH values of 5.0 or 3.5, the citrate-phosphate buffer was employed.

The same general procedures were followed in both the kinetic and equilibrium studies. An appropriate quantity of sorbent was weighed out in 100 ml. nalgene bottles on the analytical balance. The buffer solution containing the required concentration of contaminant was added to the bottles in specified amounts, and the caps were tightly secured. The bottles were placed on the reciprocating shaker which was normally operated at a rate of 300 excursions per minute. After contact with the sorbent for the appropriate time period, the bottles were removed from the shaker. In order to separate the sorbent from the liquid portion, a membrane filter was utilized. The liquid portion was then stored in 100 ml. brown bottles to await the appropriate analysis, and the sorbent remaining on the membrane filter was discarded.

Column Studies

Column studies were conducted to observe the sorptive characteristics of the selected solutes on coal in a continuous flow process. These tests were run to enable prediction of the efficiency of contaminant removal by coal in an actual process situation.

A diagram of the system used in this operation is shown in Figure 1. Upflow operation of this type of column is advantageous in that it prevents plugging associated with bound pockets of air. The column consisted of glass tubes, 13/16 of an inch in diameter and 13 inches long. The inlet and outlet of the column contained glass wool to prevent the escape of any coal particles to the effluent.

In order to minimize the effect of variable pH on the results, an appropriate buffer was used. A ten liter solution containing the buffer and the desired concentration of contaminant was used as the continuous flow reservoir. After passing through the column at the desired flow rate, the flow continued on the outlet point. Here, the desired volumes of flow were collected in a graduated cylinder, placed in small brown glass bottles, and stored to await quantitative analysis of remaining solute concentration.

Pesticide Analysis

The same procedure was followed in both the batch and continuous flow studies to extract pesticide from solution. High grade hexane was used in the extraction procedure and an appropriate volume was added to the water

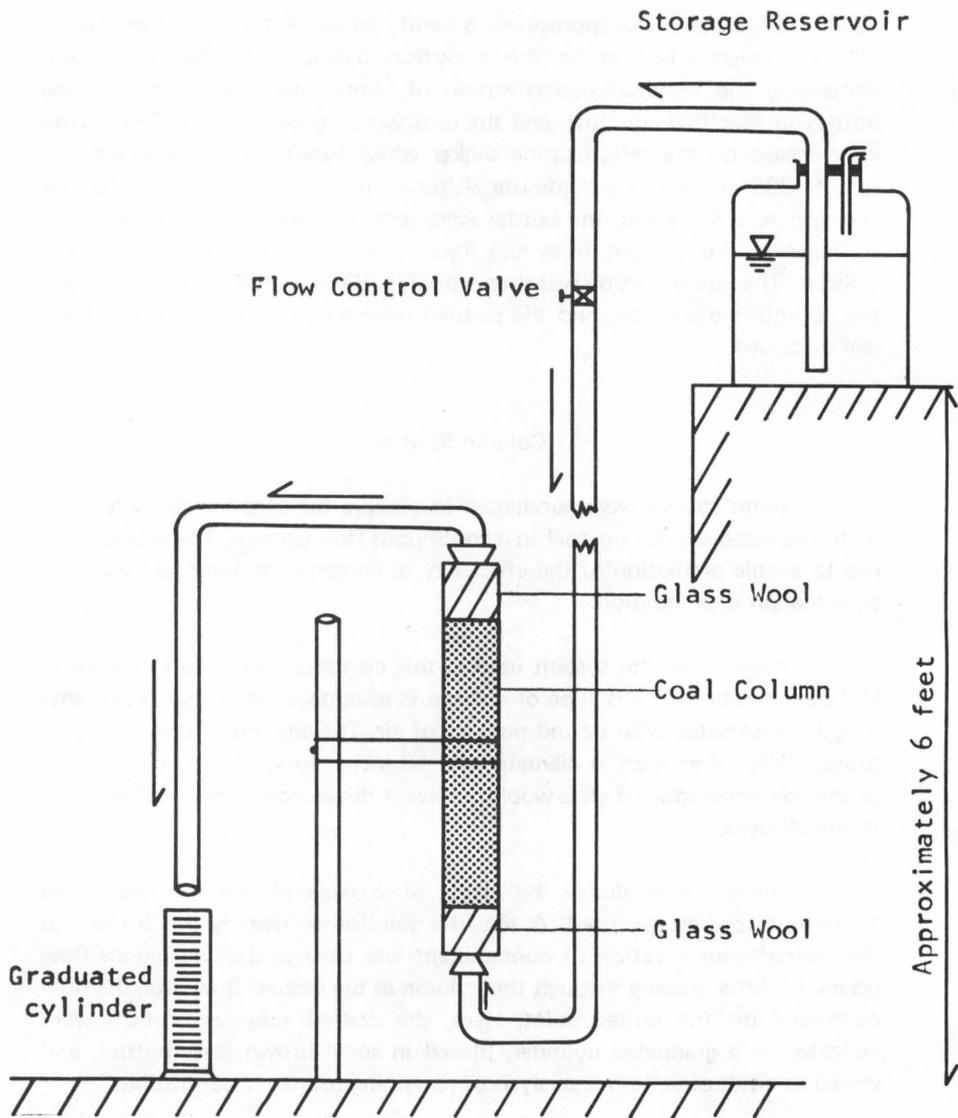


Figure 1. Continuous Flow Apparatus Used in This Research.

sample. Brown bottles containing the hexane and the water sample were agitated on the shaker for a period of one hour. This contact period was based on studies reported on pesticide extraction from water utilizing hexane (36). After extraction, the hexane-water mixture was poured into a 50 ml. burette and the water phase was drained and discarded while the hexane portion was transferred to brown bottles prior to injection into the gas chromatograph.

The greatest likelihood of experimental error associated with this research was in the extraction process and the subsequent analysis of pesticide concentration by the gas chromatograph. There is a definite advantage in using as small a hexane to water ratio as practical, but it is also important that the ratio be such that the concentration of pesticide in the hexane causes the response of the gas chromatograph to be in a recordable range. Therefore, the correct ratio of hexane to water must be chosen to accurately measure the pesticide which was extracted from the water sample. Due to the nature of the experiments conducted in this research, variable hexane to water ratios were used in the extraction procedure in order to obtain a chromatographic response in a range where the concentration of pesticide varied linearly with the area of the chromatogram.

A known concentration of each selected pesticide in hexane was required for determining a standard curve for measurement of pesticide concentration by the gas chromatograph. Since the range of detection of individual pesticides by the gas chromatograph varied with the pesticide, a wide range of standard solutions were prepared by successive dilution of the concentrated pesticides in hexane. A standard curve for each pesticide determination could be obtained by injecting appropriate quantities of the individual pesticide-hexane solution directly into the chromatograph.

In order to measure the concentration of pesticide extracted from the water samples, a Beckman GC-5 gas chromatograph was utilized. The basic units of the system are a gas cylinder with a constant pressure regulator, an oven for instant volatilization of liquid samples, the injection apparatus, the chromatography column, an electron capture detector and a separate recorder which amplifies the signal received from the detector. A schematic diagram of the chromatograph used in this research is shown in Figure 2.

The gas cylinder contains helium gas which continuously passes through the chromatographic column at a constant temperature and flow rate. A sample of from 0.3 to 10.0 microliters was injected into the sample port where it is flash evaporated to convert the components of the sample into a

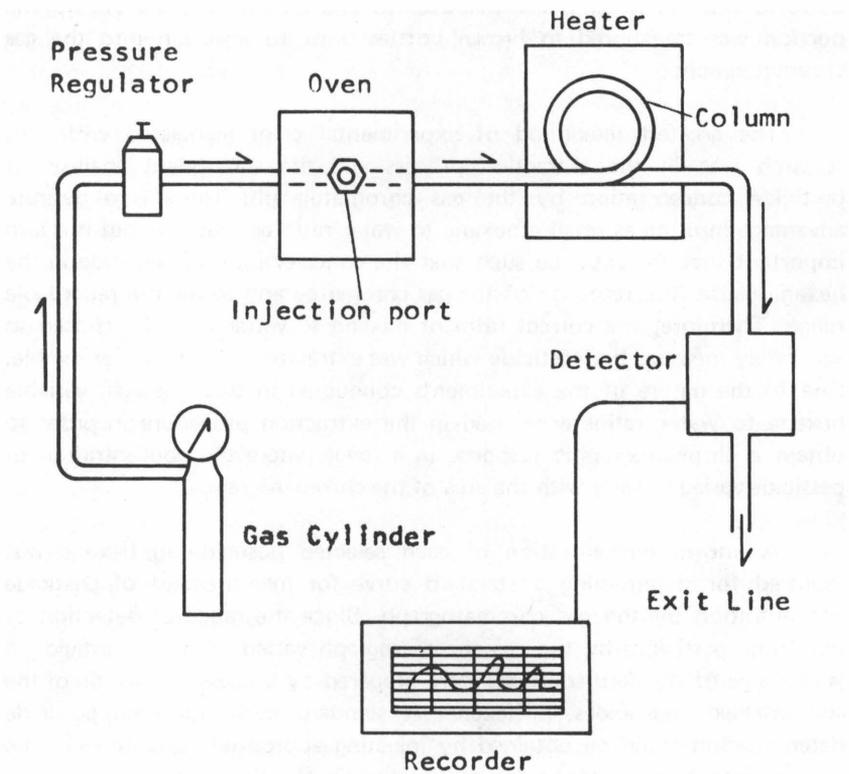


Figure 2. Schematic Diagram of the Gas Chromatograph.

gaseous state. The constantly flowing stream of carrier gas carries the gaseous constituents through the column. The gaseous constituents pass through the column at different rates so that they emerge from the column at different times. Their presence in the emerging carrier gas is detected and the response of the detector is amplified on the strip recorder. Each peak represents a specific chemical compound which has passed through the column. The time for each compound to emerge from the column is a characteristic of the compound and is known as its retention time. The area under the peak is proportional to the concentration of the compound in the sample.

The chromatographic column was a six-inch diameter spiral made of one-eighth inch stainless steel tubing. The length of the column was six feet. The column supporting material was a 80.100 mesh solid support known as GAS CHROM Q. The column was coated with a 10 per cent coating of a silicone substrate known as DC-200.

Since five different adsorbents were used in this research, various substances were extracted by the hexane along with the pesticides. These substances in several instances had a retention time similar to some pesticides and therefore they sometimes interfered with the measurement of the area under the pesticide peaks. In order to achieve separation of these contaminants from parathion in the column, the column temperature was varied between 190°C and 215°C. The detector was usually operated at 240°C. The gas flow rate ranged from 28 to 35 cubic centimeters per minute.

As previously mentioned, the area under the pesticide peak is proportional to the concentration of pesticide in the sample injected into the chromatograph. A standard curve was obtained by injecting various amounts of standard solution of pesticide in hexane. In order to determine the concentration pesticide in the hexane extract from the samples collected, a sample of the hexane extract was injected into the chromatograph and area under the pesticide peak was compared to the standard curve.

Phosphate and Iron Analysis

Phosphate determinations were accomplished with the use of Technicon Auto-Analyzer. The adapted method is a modification of the Fiske and Subbarow procedure which is based on the formation of phosphomolybdic acid and reduction by amino naphthol sulfonic acid. The only modification of the scheme recommended by Technicon employed in this work was the omission of the dialysis step. The purpose of this

modification was to obtain more sensitivity at the lower phosphate concentrations. This modification gave good sensitivity in the range from 0.5 mg/l to 40 mg/l PO_4^{\equiv} .

The 0.9% sodium chloride solution is required to maintain a high ionic strength in the dialysis step. This solution was included in the present experiments only to balance the flow since the flow scheme was set up with the dialysis step included. The reducing reagent solution was a 1.2% sodium bisulfite solution containing 400 mg/l of sodium sulfite and 200 mg/l of amino naphthol sulfonic acid. The acidic ammonium molybdate solution was 7.5 grams/liter of ammonium molybdate in a 9.8% sulfuric acid solution.

A stock orthophosphate solution was prepared by dissolving 1.4330 grams of potassium dihydrogen phosphate in 1.0 liter of distilled water. This gave a phosphate concentration of 1000 milligrams/liter. The desired concentrations were then obtained by diluting the stock solution.

Figure 3 shows the modified flow scheme that was used in the phosphate determinations. Samples of phosphate solutions were segmented with air and mixed with the sodium chloride solution. This mixture was then joined and mixed with the air segmented reducing solution. The acidic ammonium molybdate solution was introduced to the stream and further mixing took place. The reaction mixture was then sent through a $95^{\circ} \pm 1^{\circ}$ centigrade heating bath. A 40 foot length of time delay coil of 1.6 millimeter bore was used for this purpose. A blue color with optical density proportional to the phosphate concentration was produced during the three minutes required for the mixture to pass through the heating bath. A cooling coil was used to reduce the high temperature of the mixture coming from the heating bath.

Air bubbles were removed from the stream as it entered the 15 millimeter flow cell. Filters of 660 millimicrons were used in the colorimeter. The recorder plotted a response in percent transmittance which is proportional to the concentration of phosphate in the original sample. Standard solutions were run with each sample series to eliminate any error due to instrument or reagent changes. A standard curve from which sample phosphate concentrations were determined was obtained by plotting the log of the present transmittance against the phosphate concentrations of the standard solutions.

The total iron contained in the various coals used as sorbents was determined using an adaptation of the stannous chloride reduction and

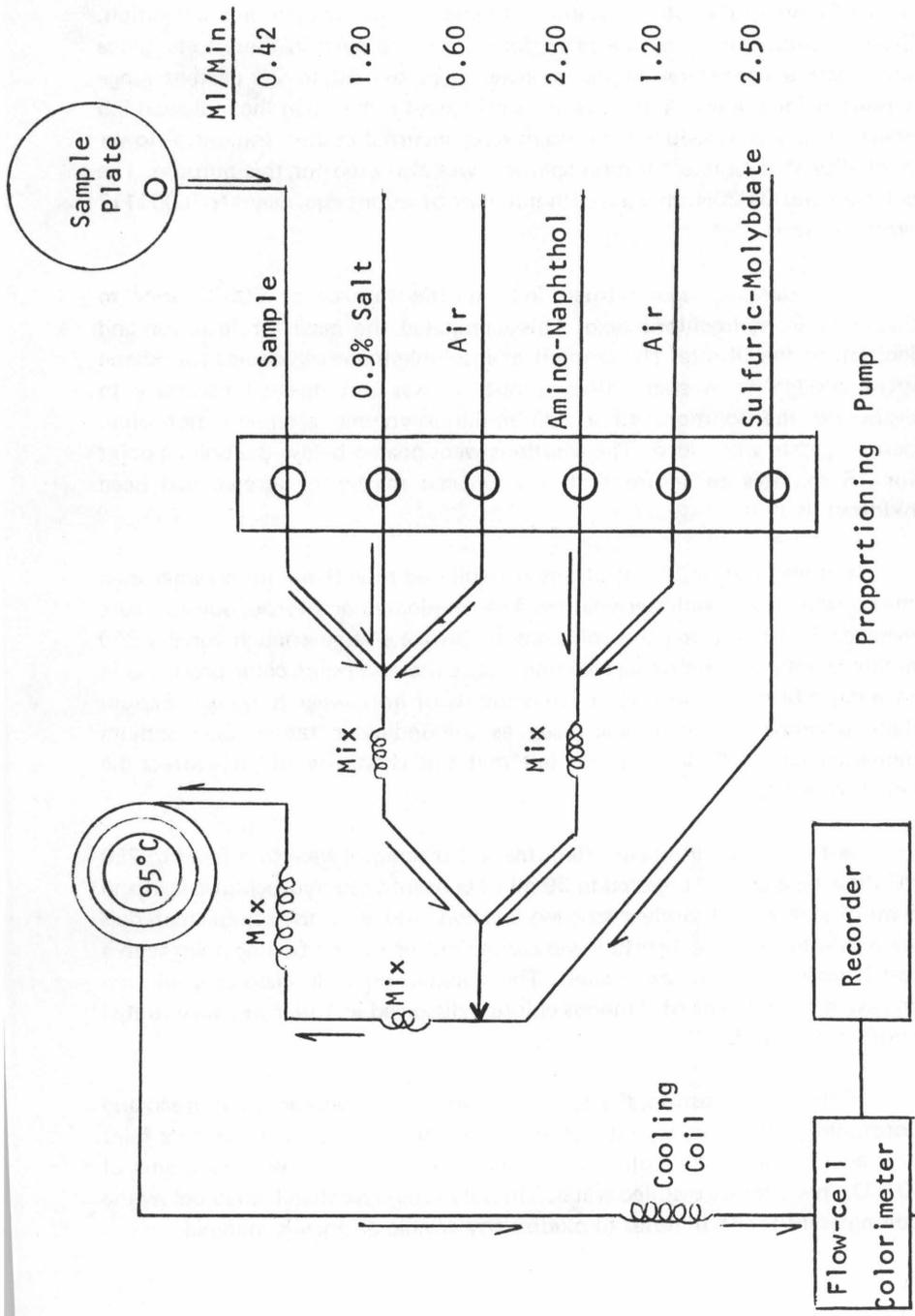


Figure 3. Flow Diagram for Orthophosphate Determination as used in this Research.

dichromate titration procedure as described by ASTM (37). This method uses diphenylamine sulfonate as an internal indicator for the dichromate titration. Several modifications of the procedure were employed in these tests. Since there was a concentration much lower than the 30 to 75 percent range suggested for the test, 1 gram samples were used rather than the indicated 0.5 grams. This was to reduce the percent error incurred in the titrations. A lower normality dichromate titrating solution was also used for this purpose. The solution was 0.020N, making each milliliter of titrant equivalent to 0.001117 grams of iron.

The samples were burned in a muffle furnace at 600°C prior to dissolving in hydrochloric acid. This eliminated the need for filtration and ignition of the filtrate. The amount of insoluble material was not considered great enough to warrant filtering out. It was not deemed necessary to evaporate the solutions to a 300 milliliter volume after the potassium permanganate was added. The solutions were heated below the boiling point for 15 minutes to insure that any organic matter or arsenic had been oxidized.

Before titration, the solutions were diluted to 200 milliliters rather than the suggested 300 milliliter volume. This eliminated any errors due to losses incurred in transferring the solutions to breakers large enough for the 300 milliliter volume. The smaller volume made the end point color produced in titrating a blank solution for trace amounts of iron easier to detect. Barium diphenylamine sulfonate was used as the indicator rather than sodium diphenylamine sulfonate. It was felt that this change would not affect the results of the tests.

After burning in the muffle furnace, the samples were transferred to 250 milliliter beakers and digested in 30 ml of concentrated hydrochloric acid and 5 ml of stannous chloride dissolving solution until all of the soluble materials were in solution. The digestion was carried out below the boiling point with a watch glass cover on the beakers. The stannous chloride dissolving solution consisted of 40 grams of stannous chloride dissolved in 1 liter of concentrated hydrochloric acid.

Following digestion, the covers and sides of the beakers were rinsed and potassium permanganate solution was added until the appearance of a faint permanent color. The potassium permanganate solution was 25 grams of KMnO_4 per liter of distilled water. The solutions were then heated below the boiling point for 15 minutes to oxidize any arsenic or organic material.

The sides of the beakers were rinsed and stannous chloride reducing solution was added to three drops in excess of the disappearance of the yellow ferric iron color. The solutions were then cooled in a 10°C refrigerator. The reducing solution consisted of 100 grams of stannous chloride dissolved in a liter of 1"1 hydrochloric acid. Following cooling, 15 milliliters of saturated mercuric chloride solution was added to oxidize the excess stannous chloride. The mixtures were cooled in the refrigerator for an additional 3 to 5 minutes.

Twenty milliliters of sulfuric-phosphoric acid solution and 5 drops of indicator solution were added to the mixtures followed by titration to a distinct violet end point with 0.02N potassium dichromate solution. The iron content was calculated as follows:

$$\text{Iron, percent} = \frac{(A - B) \times C}{D} \times 100$$

where

- A = Milliliters of $K_2Cr_2O_7$ required to titrate the sample
- B = milliliters of $K_2Cr_2O_7$ required to titrate the blank
- C = iron equivalence of $K_2Cr_2O_7$ in grams/milliliter
- D = weight of the ample in grams

The blank solution was prepared using the same amount of all reagents and was carried through all the steps of the procedure. This was done so that the trace iron quantities in the reagents would not be included in the iron content of the coal.

Three samples of each coal type were carried through the procedure and the iron content was calculated for each sample. The mean of the three values was taken as the iron content for that coal type. All of the values for each coal type were within $\pm 5.5\%$ of the mean.

EXPERIMENTAL RESULTS

The experiments conducted in this research were designed to determine the kinetic and equilibrium characteristics for the uptake of selected contaminants on coal. In some cases batch type kinetic and equilibrium studies were also conducted on activated carbon to compare results with those determined for coal. The column studies were performed to evaluate the use of coal in a continuous flow process such as a sorption column or a filter.

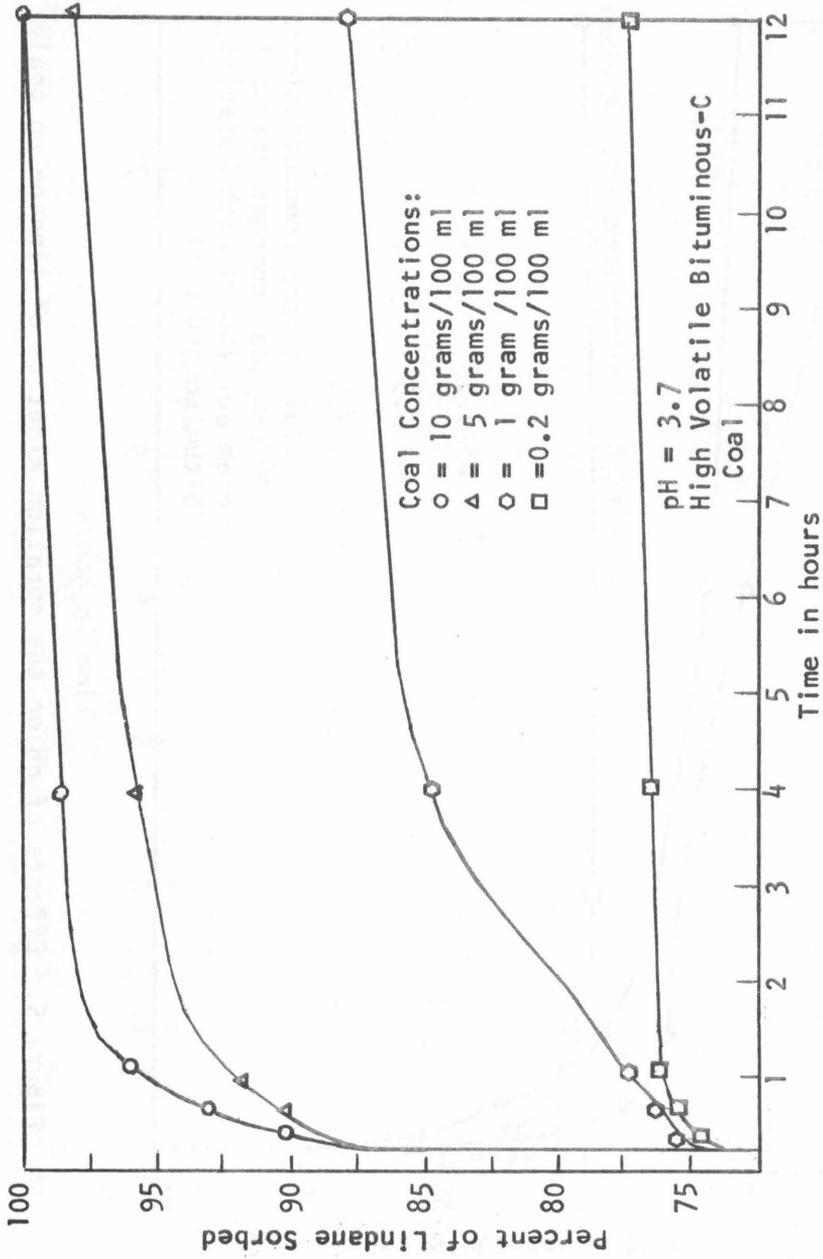
Lindane Sorption

The studies presented in this section are primarily of two types. Initially kinetic studies were made to determine the optimum agitation time and the rate of uptake of lindane by coal. The equilibrium tests were performed to measure the actual capacity of the coal for sorbing lindane under varying concentrations of coal and of pesticide.

Results of the kinetic studies indicated that the sorptive capacity of High Volatile Bituminous-C coal is largely reached within one hour, as evidenced by Figures 4 and 5. This relatively rapid uptake was demonstrated for all concentrations of coal and of pesticide used and for all pH ranges considered. As shown by Figure 5 the samples with the highest pH (9.3) exhibited the largest removal of pesticide while those with the lowest pH (5.5) exhibited the second highest lindane removal. The samples that tended toward a more neutral pH (7.5) showed the least effective pesticide removal. However, these results are not conclusive since the differences are small. Lindane is known to break down rather rapidly in solutions with a high pH. This degradation could have been responsible for the higher removals experienced with the alkaline system.

In the results of the equilibrium studies as shown in Figure 6, some indication is given that the coal does have a saturation point for sorption of lindane. This feature is shown by the near horizontal portion of the curve depicting the isotherm for the lower coal concentration. At this point the equilibrium concentration is increased while the amount of lindane sorbed per gram of coal remained relatively constant.

The efficiency of low concentrations of coal is noticeably greater than that of high concentrations in the removal of lindane at low equilibrium



27 Figure 4. Effects of variable concentrations of coal on the sorption kinetics of lindane on coal.

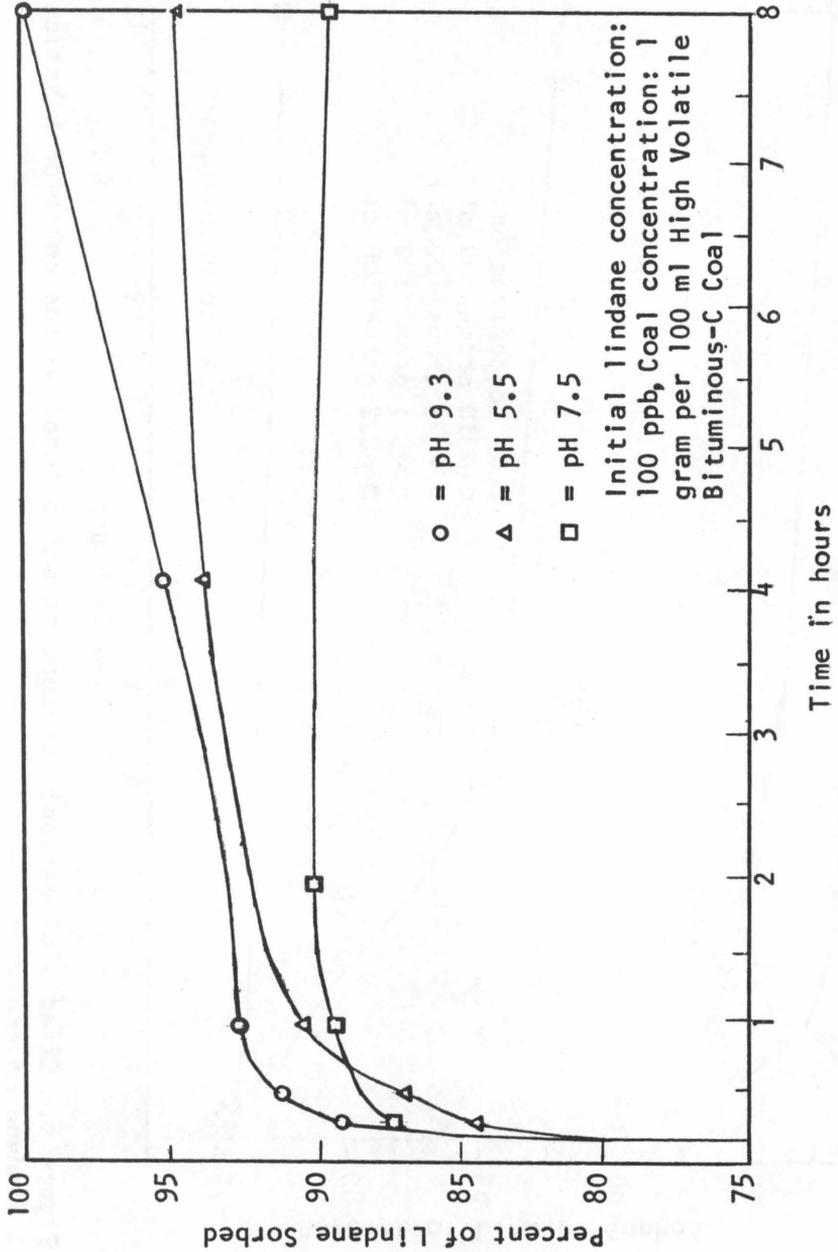


Figure 5. Effects of pH on the sorption kinetics of lindane on coal

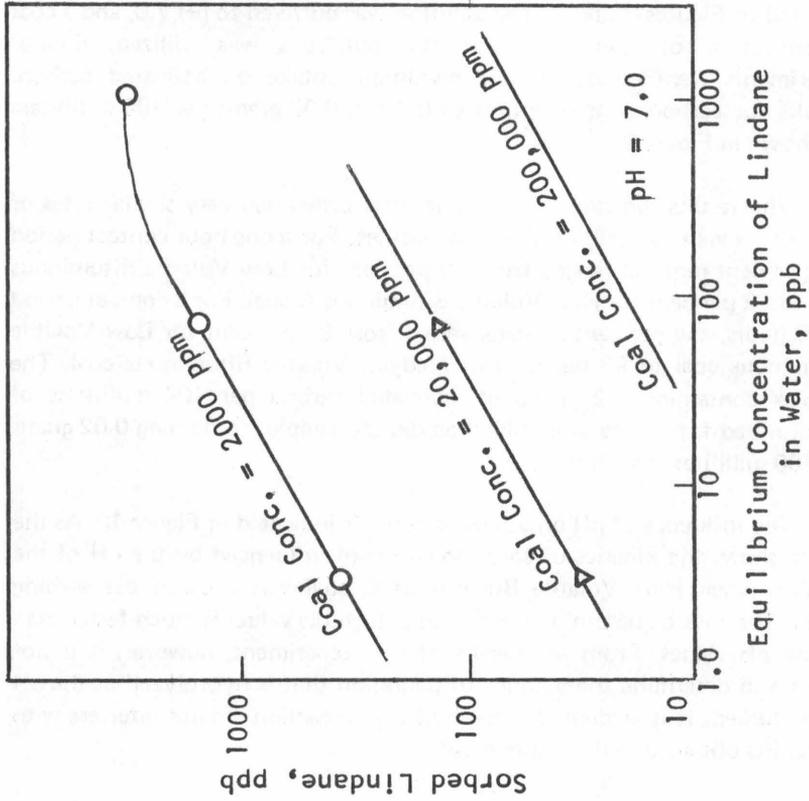


Figure 6. Sorption Isotherms for Lindane on High Volatile Bituminous-C Coal with Variable Coal Concentrations.

lindane concentrations. However, it must be noted from Figure 6 that the efficiency of the higher concentrations of coal appeared to increase with increasing equilibrium concentrations of lindane. The reason for this result may be due to approaching the water solubility of lindane.

Parathion Sorption

Kinetic studies for parathion uptake on four of the selected coals are depicted in Figures 7 and 8. The solution was buffered to pH 7.0, and a coal concentration of one gram per 100 milliliters was utilized. Similar experiments were conducted for parathion uptake on activated carbon. Results for carbon concentrations of 0.2 and 0.02 grams per 100 milliliters are shown in Figure 9.

The results indicate that all four coals tested had very similar rates of sorption as well as similar ultimate capacities. For a one hour contact period the per cent removal ranged from 90 per cent for Low Volatile Bituminous coal to 82 per cent for High Volatile Bituminous A coal. For a contact period of 10 hours, the per cent removal varied from 97 per cent for Low Volatile Bituminous coal to 93 per cent of Medium Volatile Bituminous coal. The samples containing 0.2 grams of activated carbon per 100 milliliters of solution had faster rate of uptake than did the samples containing 0.02 grams per 100 milliliters of solution.

The influence of pH on uptake kinetics is indicated in Figure 10. As the results show, the kinetics of sorption were not influenced by the pH of the solution when High Volatile Bituminous C coal was used as the sorbing media. The rate of parathion hydrolysis at high pH values is much faster than at low pH values. From the results of this experiment, however, it is not possible to determine the amount of parathion that is hydrolyzed at the pH levels studied. It is evident that the hydrolysis reaction did not interfere with the results obtained in this experiment.

Equilibrium batch studies of parathion sorption on coal and activated carbon were performed to determine if the data obtained could be expressed as either a Freundlich or a Langmuir isotherm. The results of these studies are shown in Figures 11 through 14. The six hour contact time was chosen because previous kinetic experiments showed that 90 per cent removal was achieved after this period. As the results indicate, both the Langmuir isotherm and the Freundlich isotherm yield approximately linear relationships for the equilibrium data.

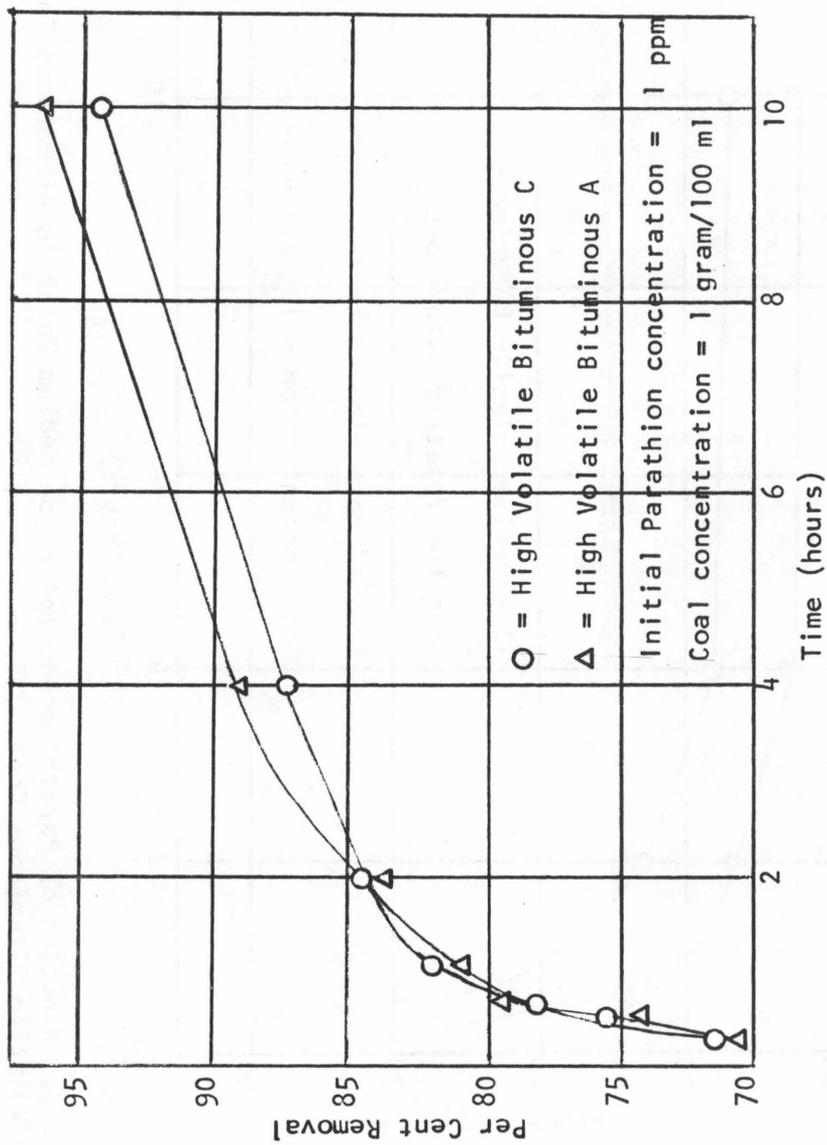


Figure 7. Kinetics of Parathion Adsorption for High Volatile Bituminous-C Coal and High Volatile Bituminous A Coal.

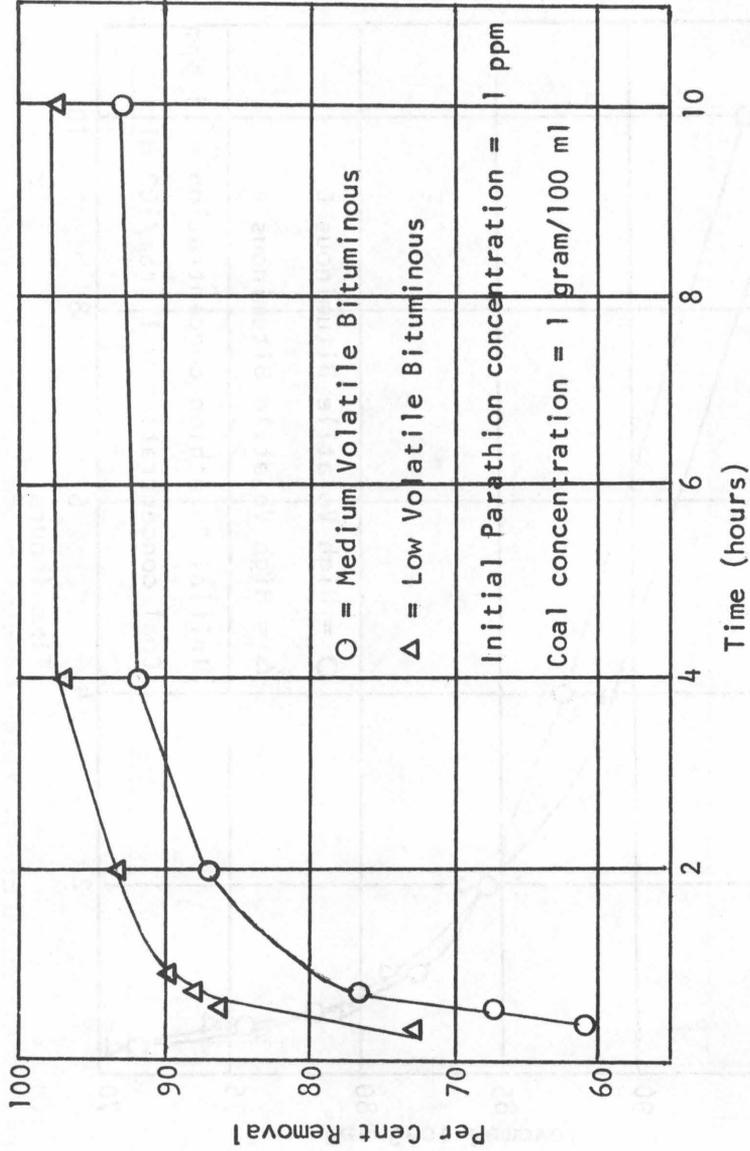
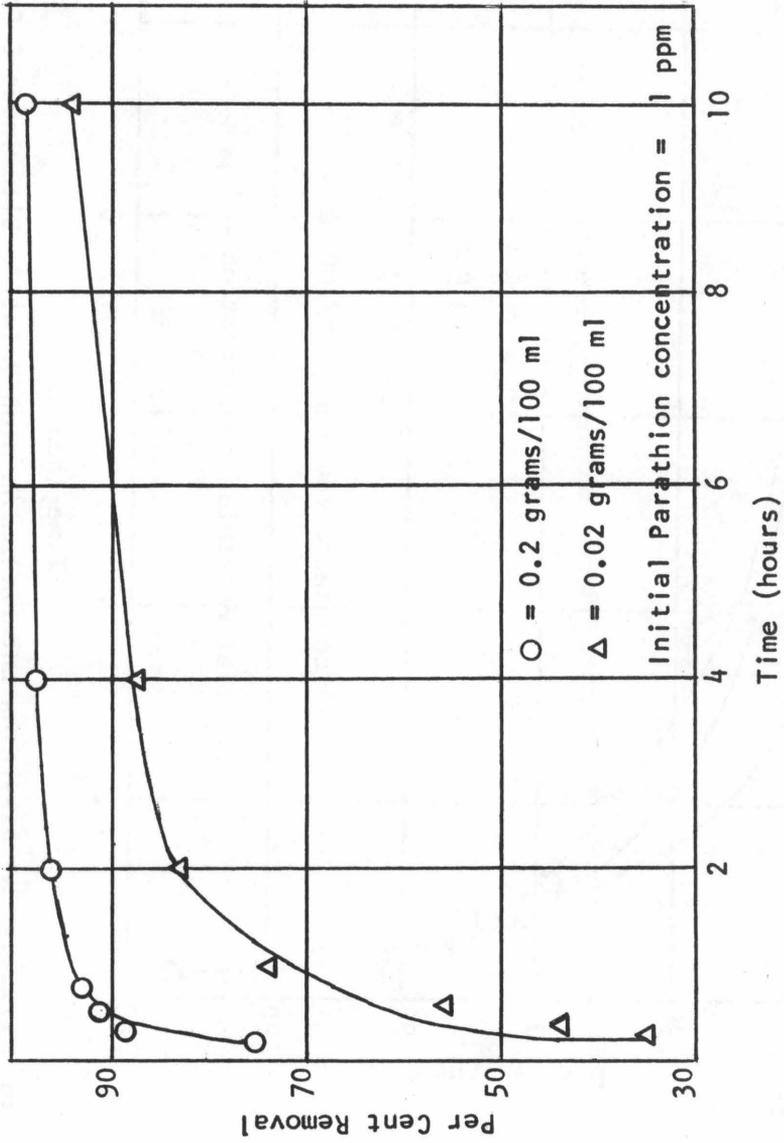


Figure 8. Kinetics of Parathion Adsorption on Medium Volatile Bituminous Coal and Low Volatile Bituminous Coal.



33 Figure 9. Kinetics of Parathion Adsorption on Activated Carbon.

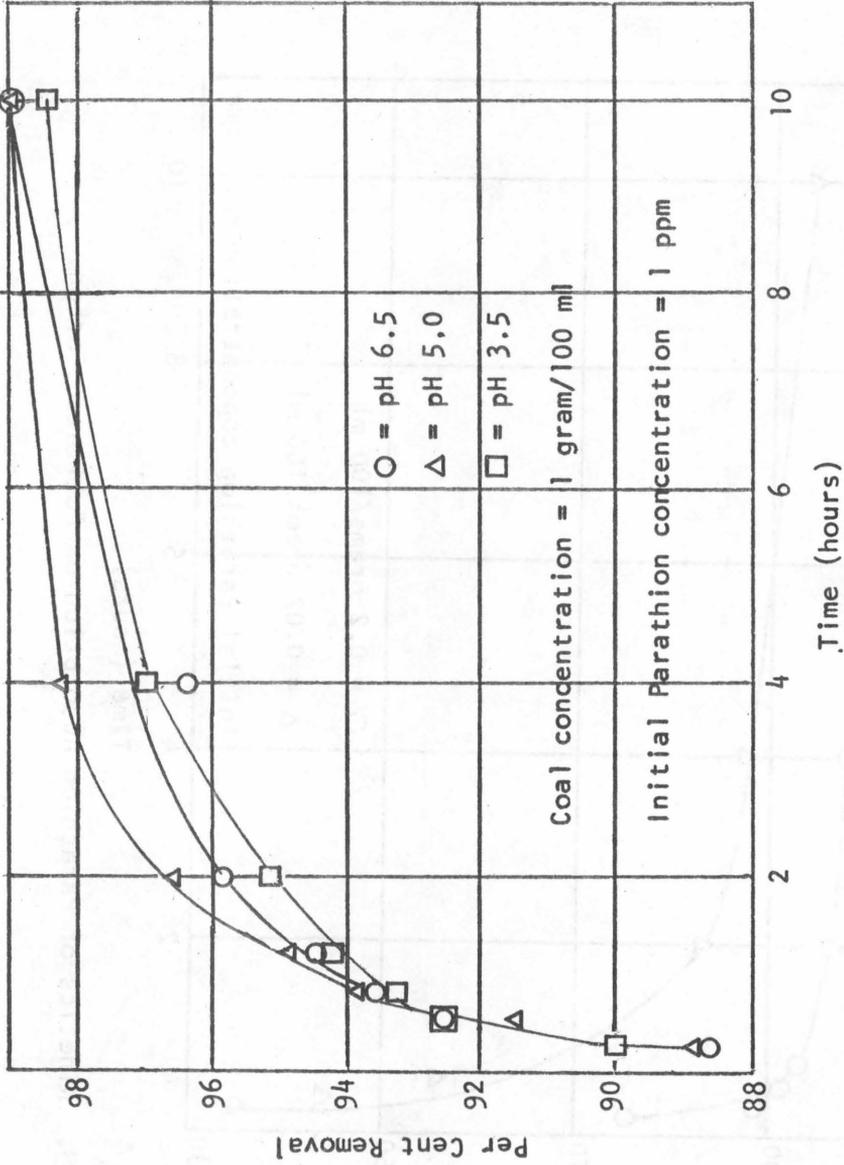


Figure 10. Kinetics of Parathion Adsorption on High Volatile Bituminous-C Coal with Variable pH,

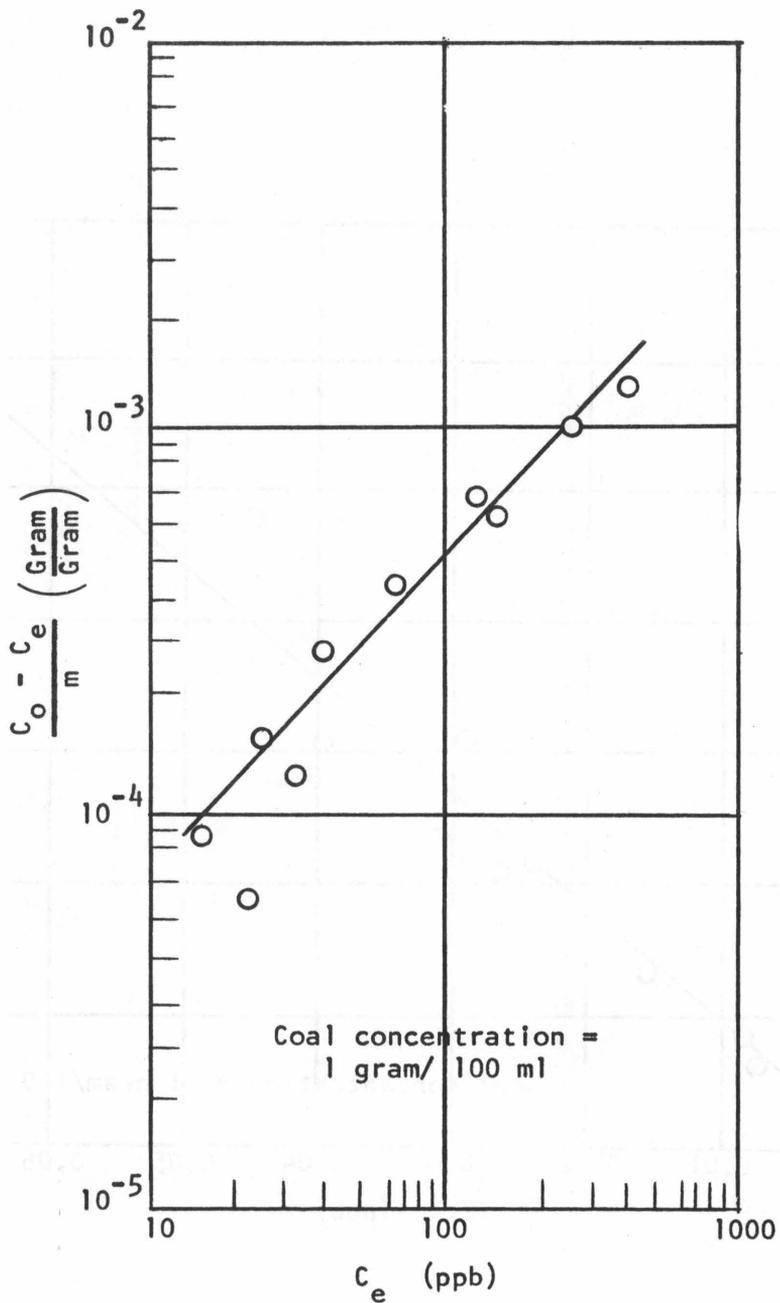


Figure 11. Freundlich Isotherm for Parathion Adsorption on High Volatile Bituminous-C Coal.

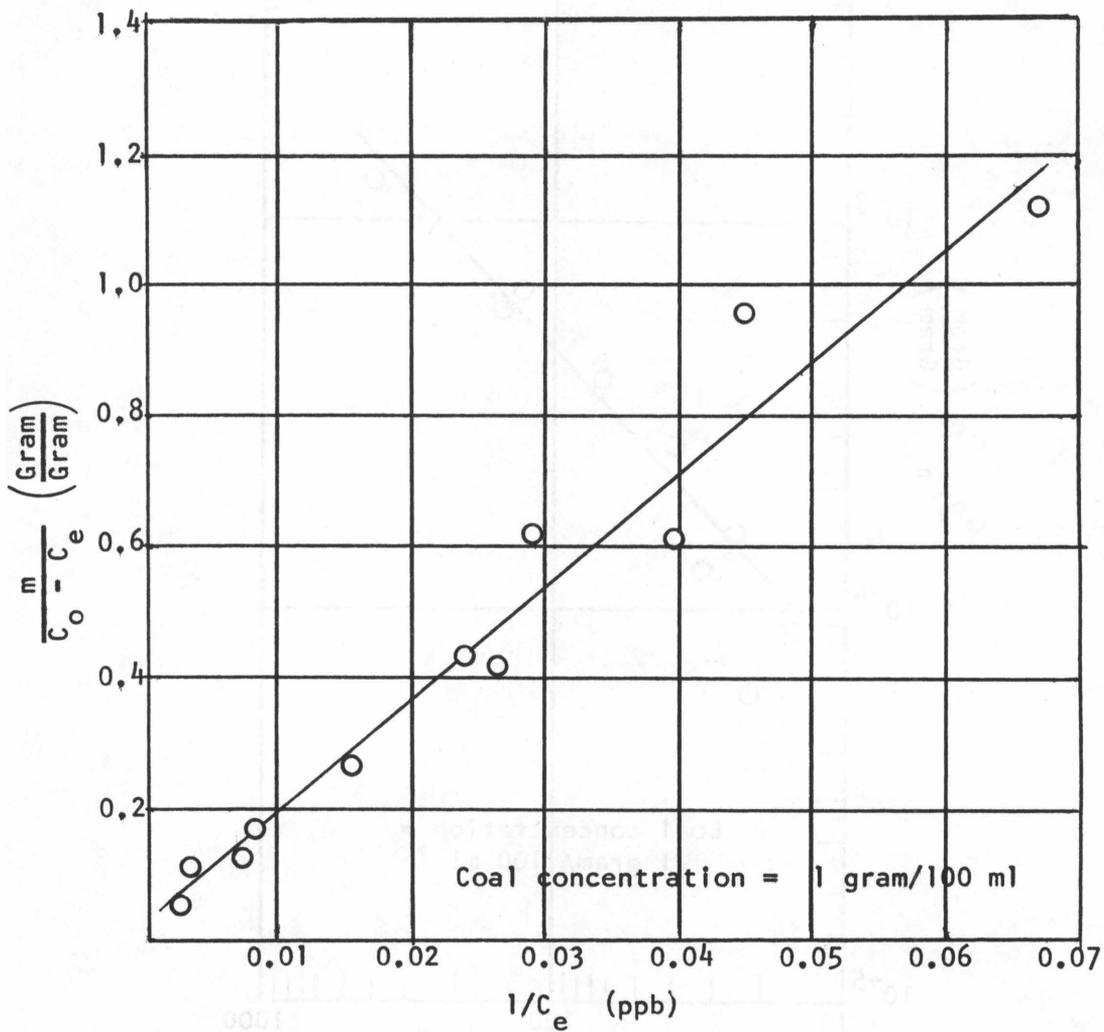


Figure 12. Langmuir Isotherm for Parathion Adsorption on High Volatile Bituminous-C Coal.

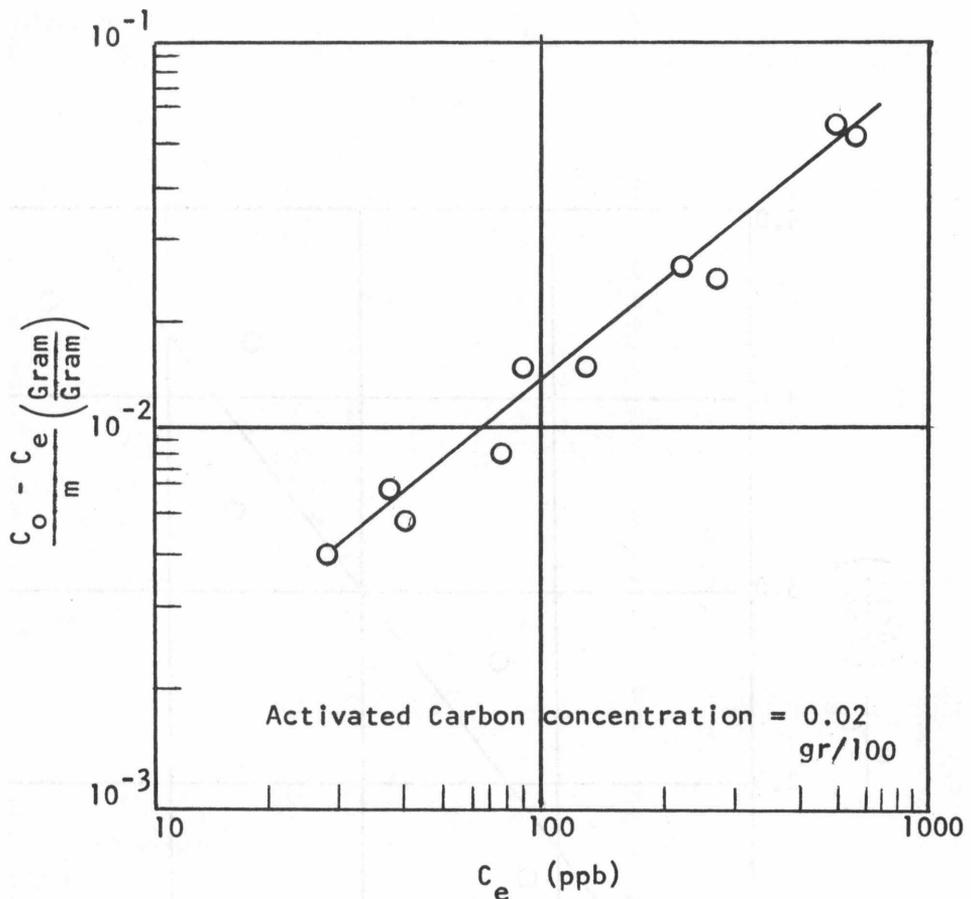


Figure 13. Freundlich Isotherm for Parathion Adsorption on Activated Carbon.

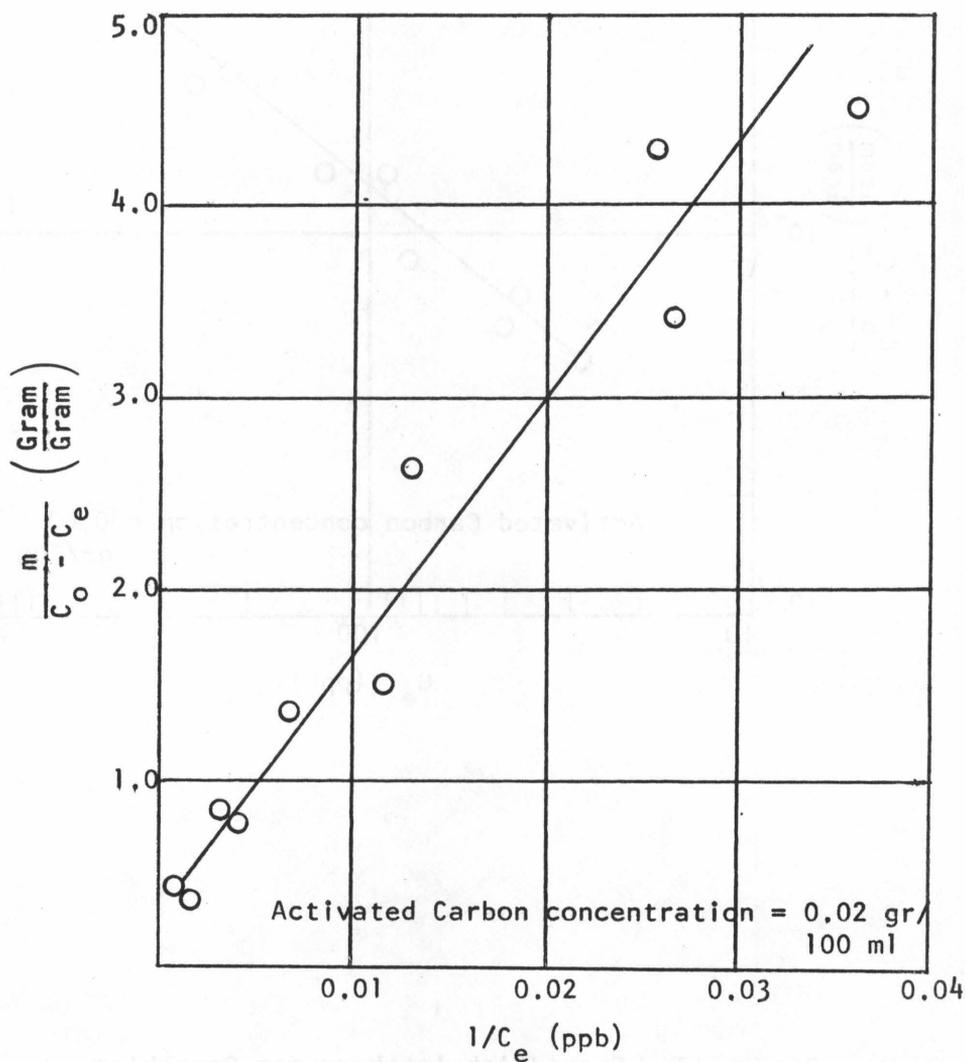


Figure 14. Langmuir Isotherm for Parathion Adsorption on Activated Carbon.

Experiments were also performed to determine the uptake capacity of coal for parathion in a continuous flow process. Breakthrough curves for two column runs are shown in Figures 15 and 16. In Column A a flow rate of 25 milliliters per minute was maintained resulting in a poorly defined breakthrough curve. For Column B the flow rate was decreased to 5 milliliters per minute and a better result was achieved.

Discussion: Medium Volatile Bituminous type coal was chosen for the continuous flow experiments. The Medium Volatile Bituminous coal offered an advantage in that it is the most coarse of the coal types available and therefore there were no problems associated with small particles of coal clogging the column and altering the flow rate during the course of the experiment.

Fifty per cent breakthrough was taken as the medium point on the breakthrough curve. This point is frequently used to characterize uptake in a column experiment of this type. The quantity of parathion adsorbed per unit weight of coal was 0.045 milligrams per gram for Column A and 0.035 milligrams per gram for Column B.

CIPC Sorption

Kinetic studies for CIPC uptake on four of the selected coals are shown in Figures 17 and 18. The solution was again buffered to pH 7.0 and a coal concentration of 2.0 grams per 100 milliliters was utilized. The influence of coal concentration on uptake kinetics is shown in Figure 19 for High Volatile Bituminous-C coal.

The results show that two hours were required for the solutions in contact with Low Volatile Bituminous coal and Medium Volatile Bituminous coal to reach equilibrium, while four hours were required for the other two coal types. This indicates that coals with low percentages of volatile matter tend to reach equilibrium more rapidly than coals with a higher volatile matter content.

For a one hour contact period the per cent removal of CIPC from solution ranged from 70 per cent for Low Volatile Bituminous coal to 81 per cent for High Volatile Bituminous-C coal. The ultimate sorptive capacities of the coals showed a wider variation. For a contact period of eight hours, the per cent removal varied from 90 per cent for High Volatile Bituminous-C coal to 75 per cent for Medium Volatile and Low Volatile Bituminous coals.

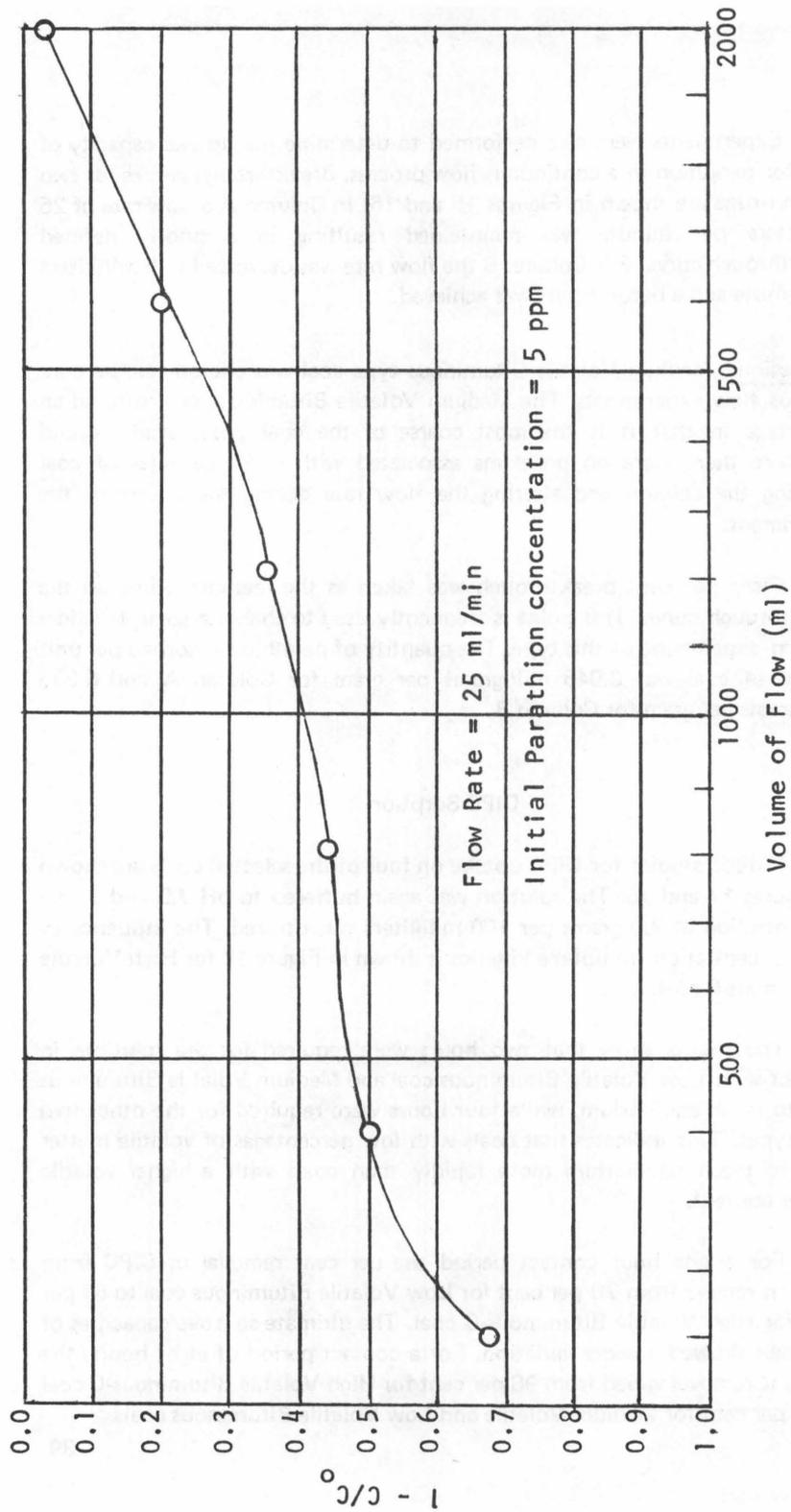


Figure 15. Parathion Breakthrough Curve for Column A.

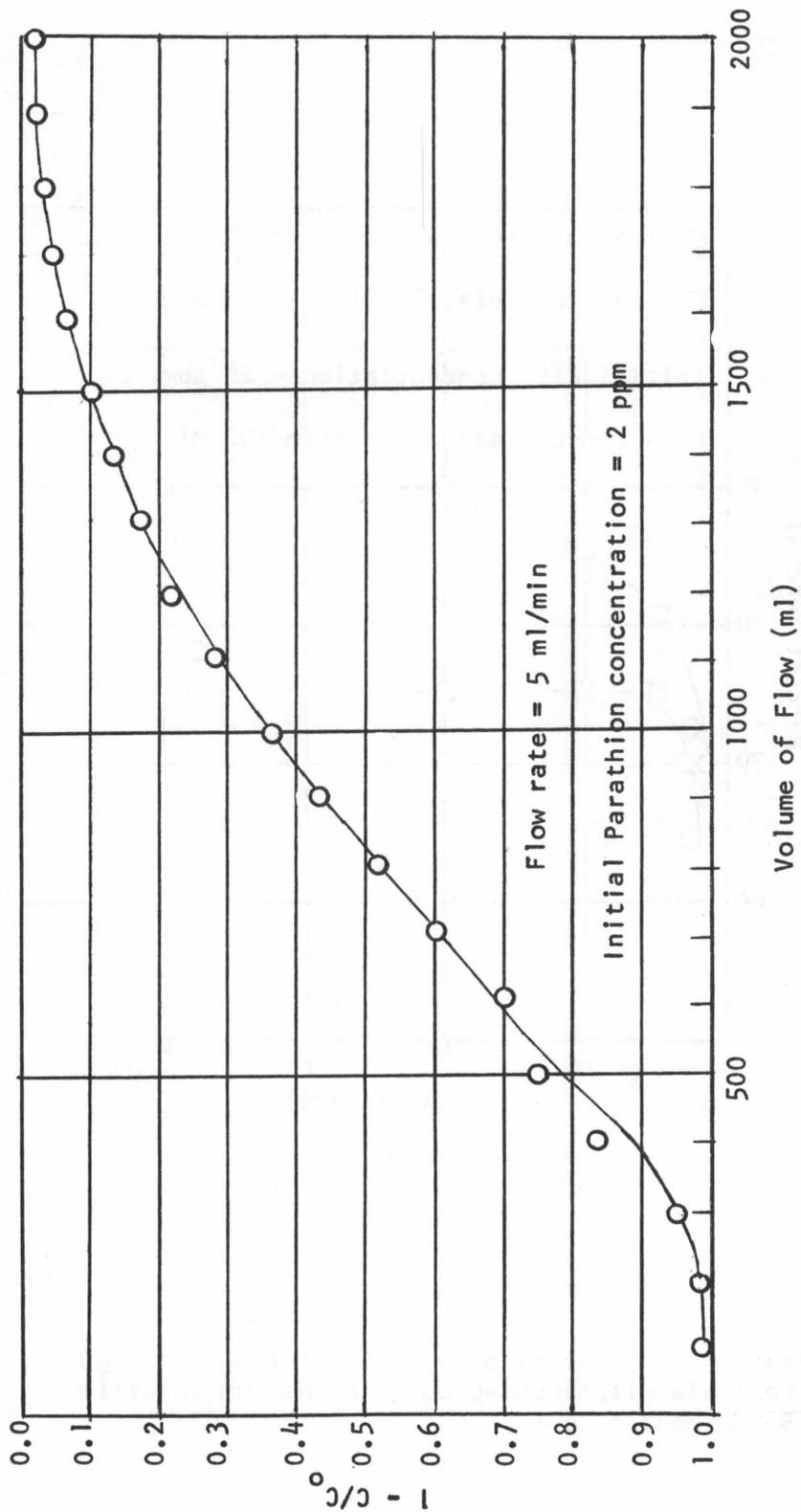


Figure 16. Parathion Breakthrough Curve for Column B

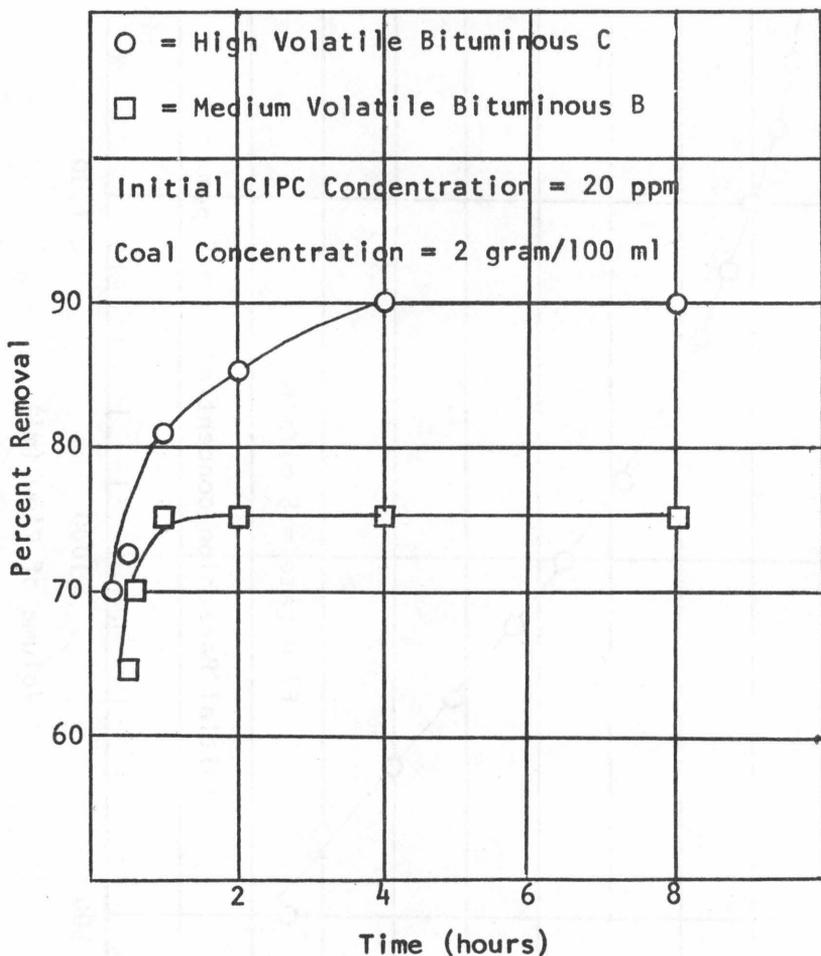


Figure 17. Kinetics of CIPC Adsorption for High Volatile Bituminous-C Coal and Medium Volatile Bituminous B Coal.

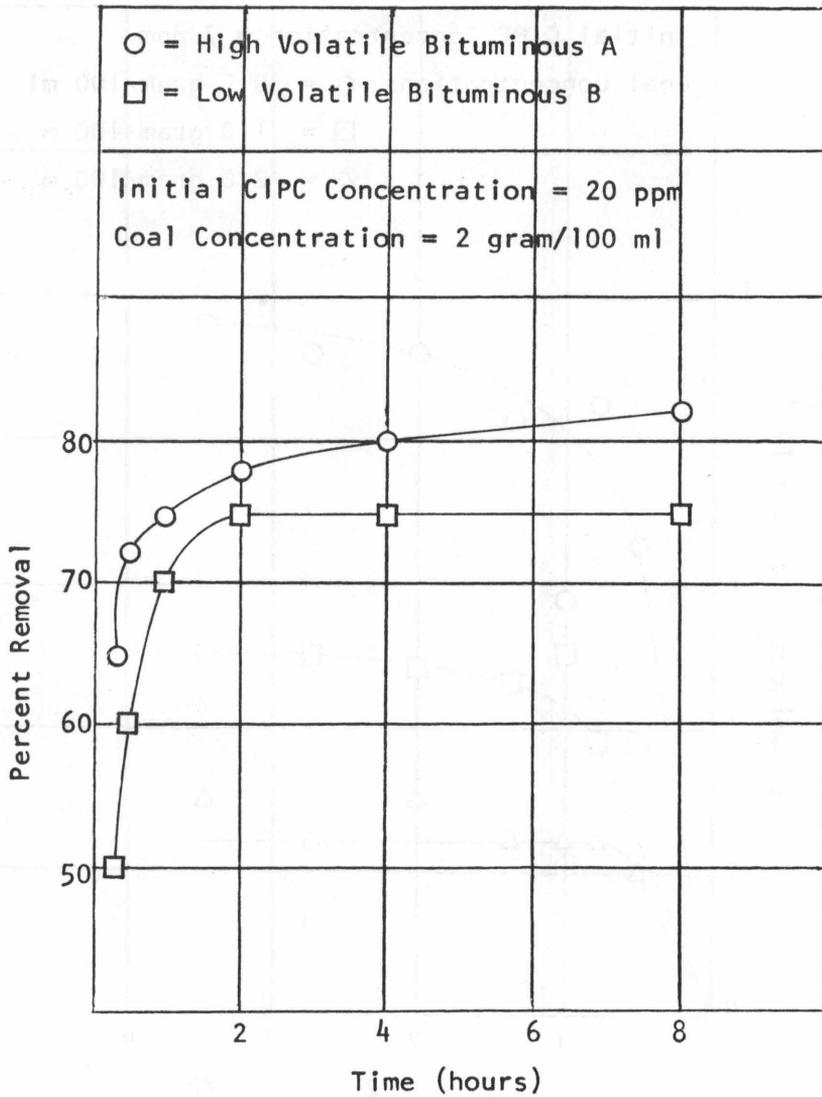


Figure 18. Kinetics of CIPC Adsorption for High Volatile Bituminous A Coal and Low Volatile Bituminous B Coal.

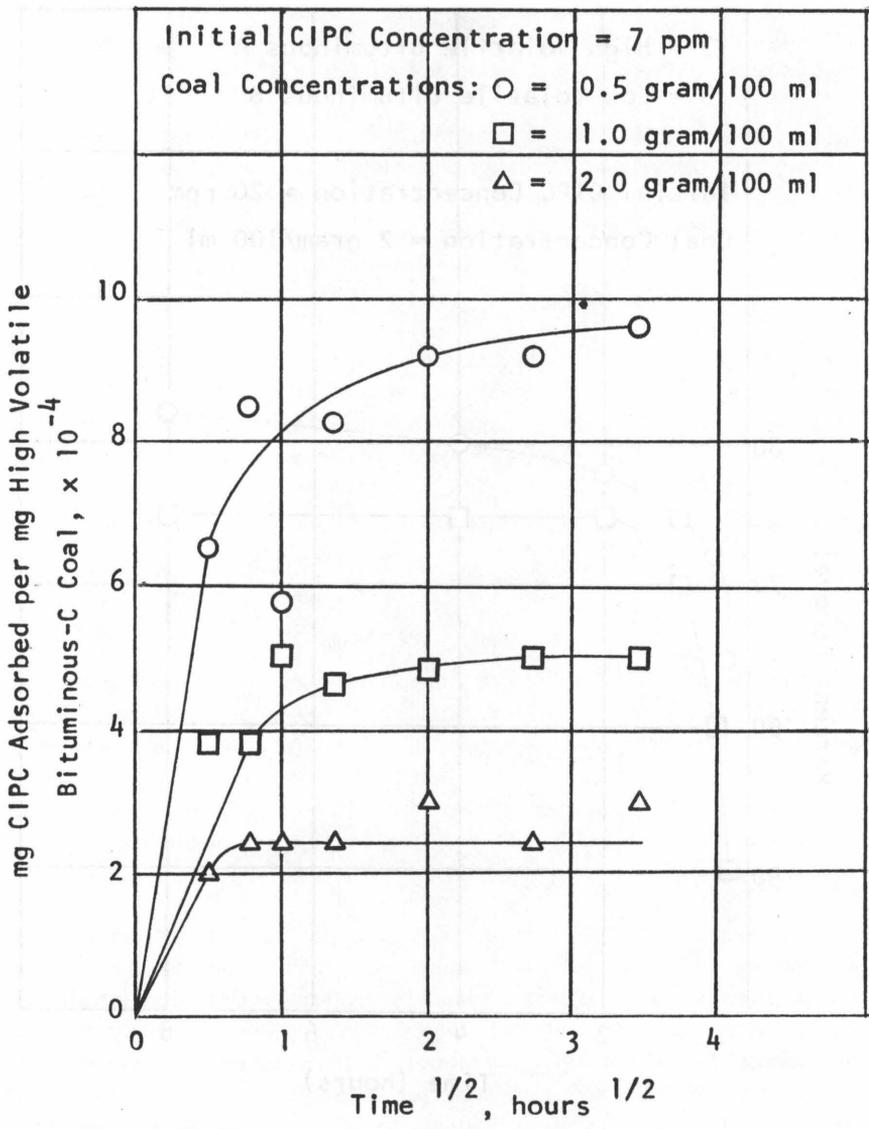


Figure 19. Rate of Adsorption of CIPC by High Volatile Bituminous-C Coal,

As noted in Figure 19, the milligrams of CIPC adsorbed per milligram High Volatile Bituminous-C coal for the coal concentrations of 0.5 gm/100 ml, 1.0 gm/100 ml and 2.0 gm/100 ml were, respectively, 9.4×10^{-4} and 2.4×10^{-4} . This is a linear relationship between coal concentration and CIPC adsorption per unit weight of coal. The concentrations of CIPC not adsorbed were, respectively, 2.3 ppm, 2.0 ppm and 2.2 ppm.

Continuous flow column studies were also conducted to determine CIPC removal in a coal contact process. Results of these studies are shown in Figures 20 through 23 and indicate the effect of coal type on the nature of the breakthrough curve. The system was operated at a flow rate of 20 milliliters per minute and the CIPC concentration in the influent was 10 mg/l.

Fifty per cent breakthrough, that is the medium point on the breakthrough curve, is frequently used to characterize uptake in a column experiment of this type. The quantities of CIPC adsorbed per unit weight of coal were 0.025 milligrams per gram for High Volatile A, 0.175 mg/gm for High Volatile Bituminous-C, 0.050 mg/gm for Medium Volatile Bituminous, and 0.025 mg/gm for Low Volatile Bituminous coal. The efficiencies of the coal types agree with the ranking achieved in the batch kinetic studies.

Phosphate Uptake

Initial studies on phosphate uptake were conducted to illustrate the extent of removal which could be expected in a coal contact process. Figure 24 shows the results of experiments aimed at establishing the coal dosage which would give measureable orthophosphate removal from a solution containing an initial phosphate concentration of 20 mg/l. A sodium bicarbonate buffer, although not ideal, was employed to maintain a pH value near neutrality.

It was noted that one gram of coal per 100 ml of sample was satisfactory coal concentration which was then employed for further investigations. The use of the 20 mg/l orthophosphate solution for kinetic studies was based on the fact that domestic sewage normally has an orthophosphate concentration of about 20 mg/l. Based on these data, a contact time of one hour was selected for all equilibrium studies. This period was sufficient to achieve approximately 80 per cent of the eventual phosphate removal at equilibrium.

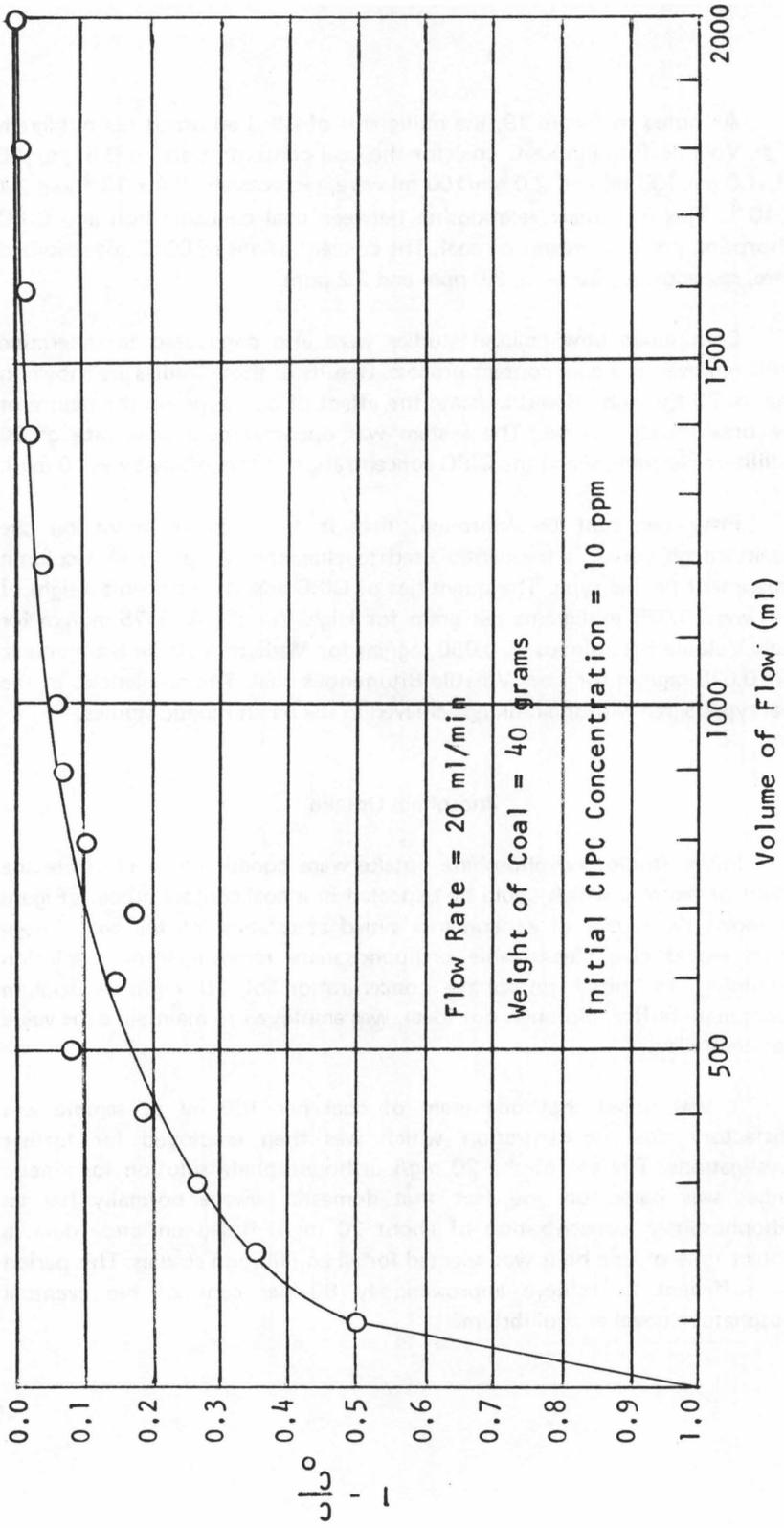


Figure 20, CIPC Breakthrough Curve for High Volatile Bituminous A Coal.

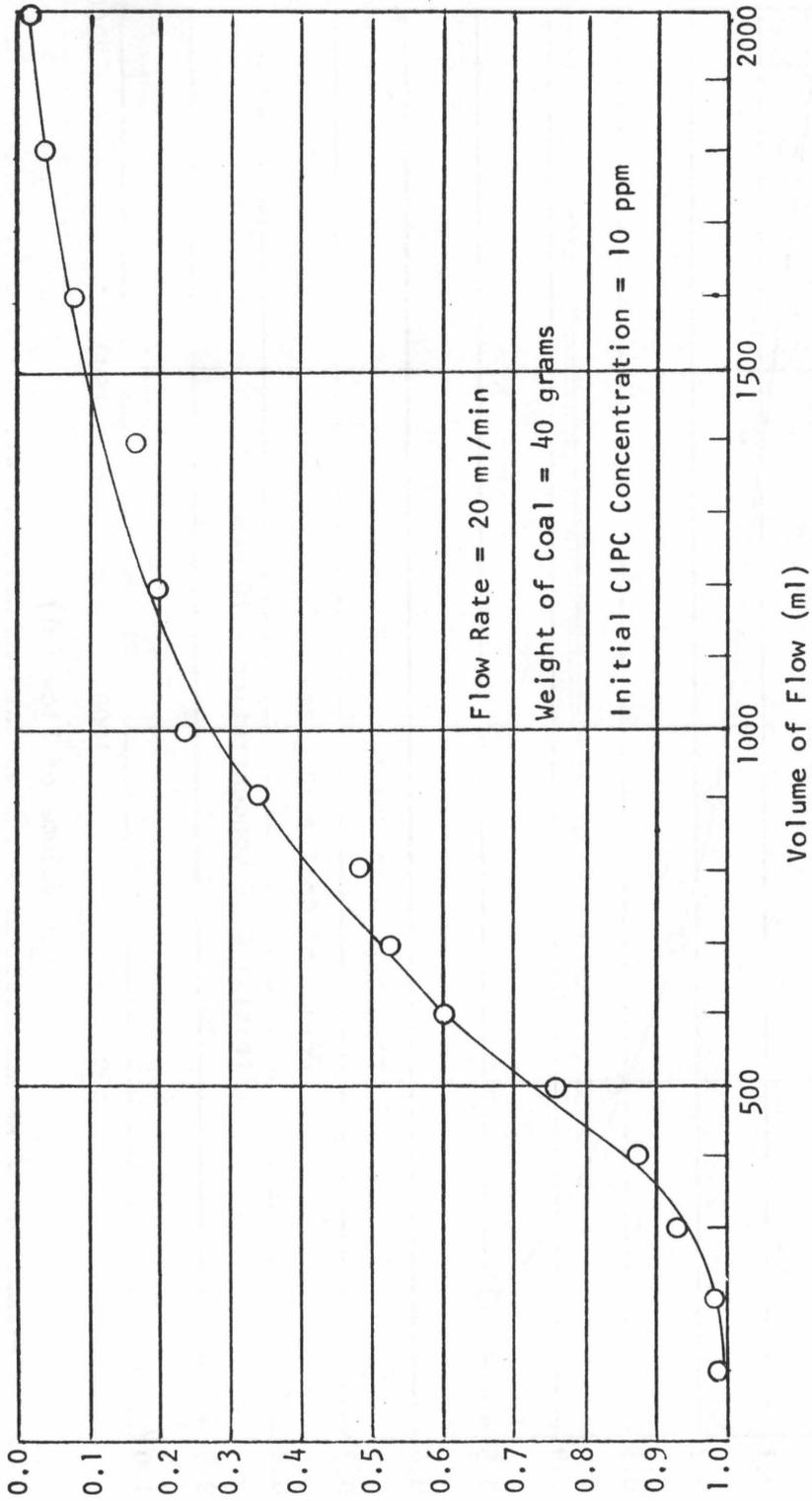


Figure 21. CIPC Breakthrough Curve for High Volatile Bituminous-C Coal.

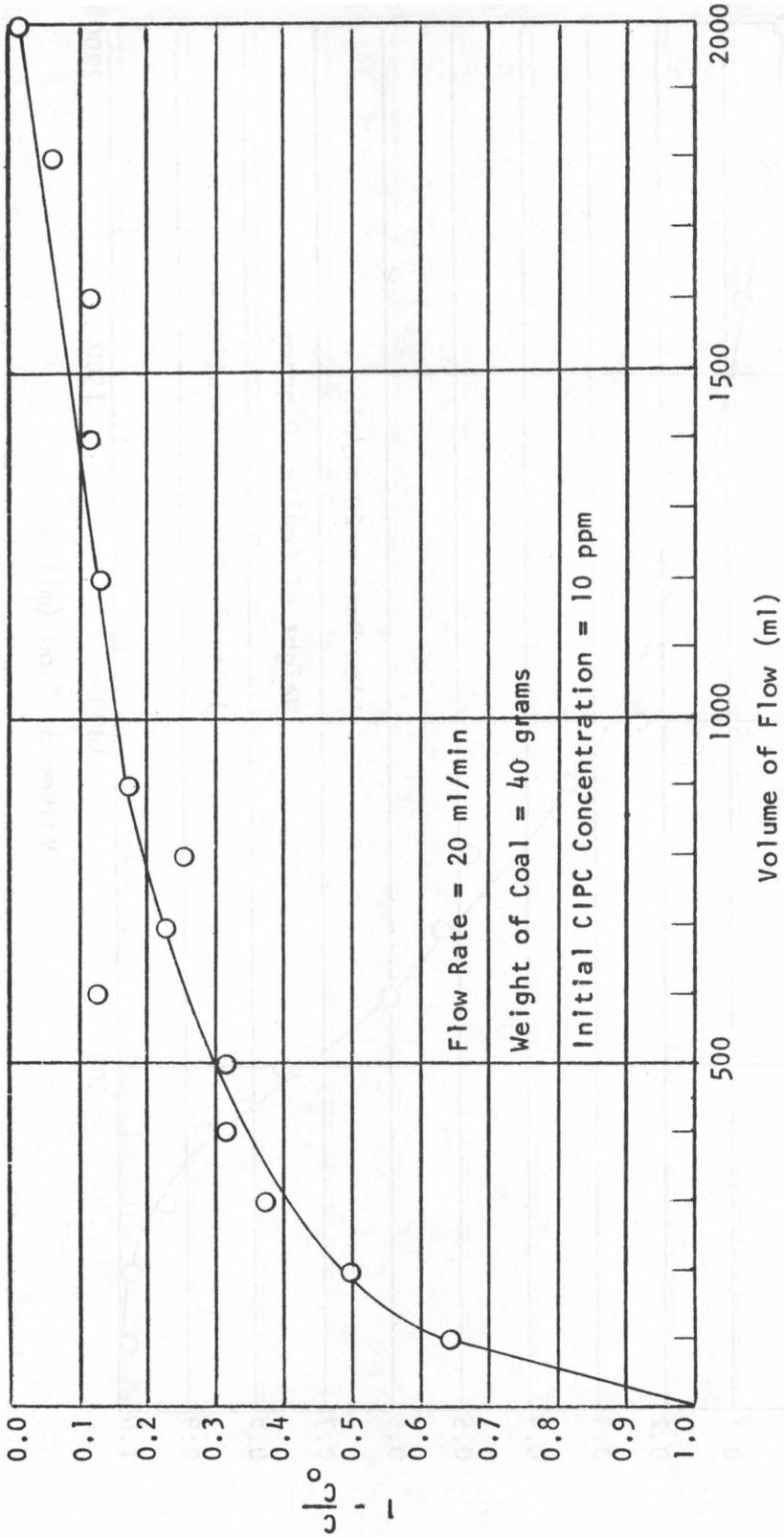


Figure 22, CIPC Breakthrough Curve for Medium Volatile Bituminous Coal.

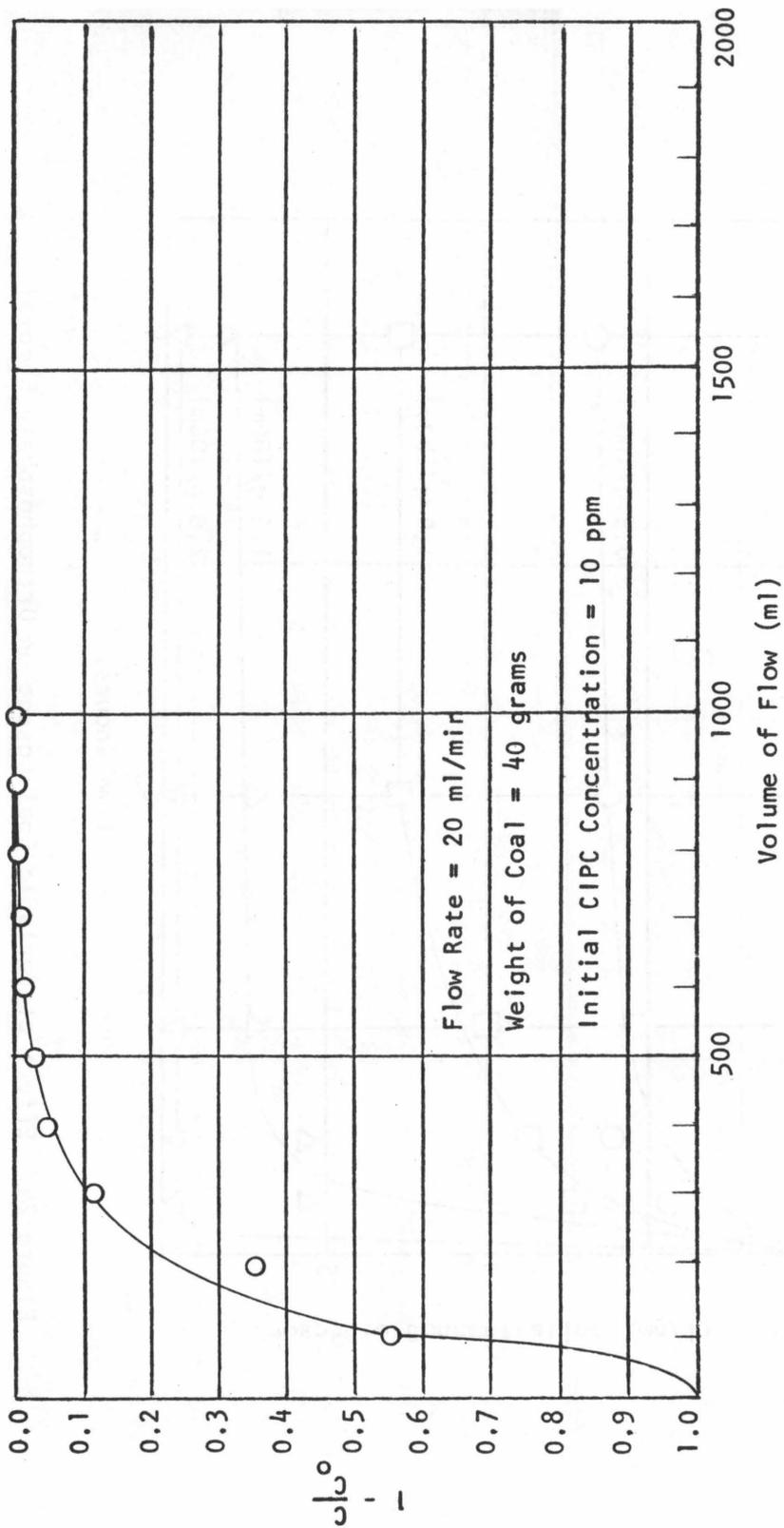


Figure 23. CIPC Breakthrough Curve for Low Volatile Bituminous Coal.

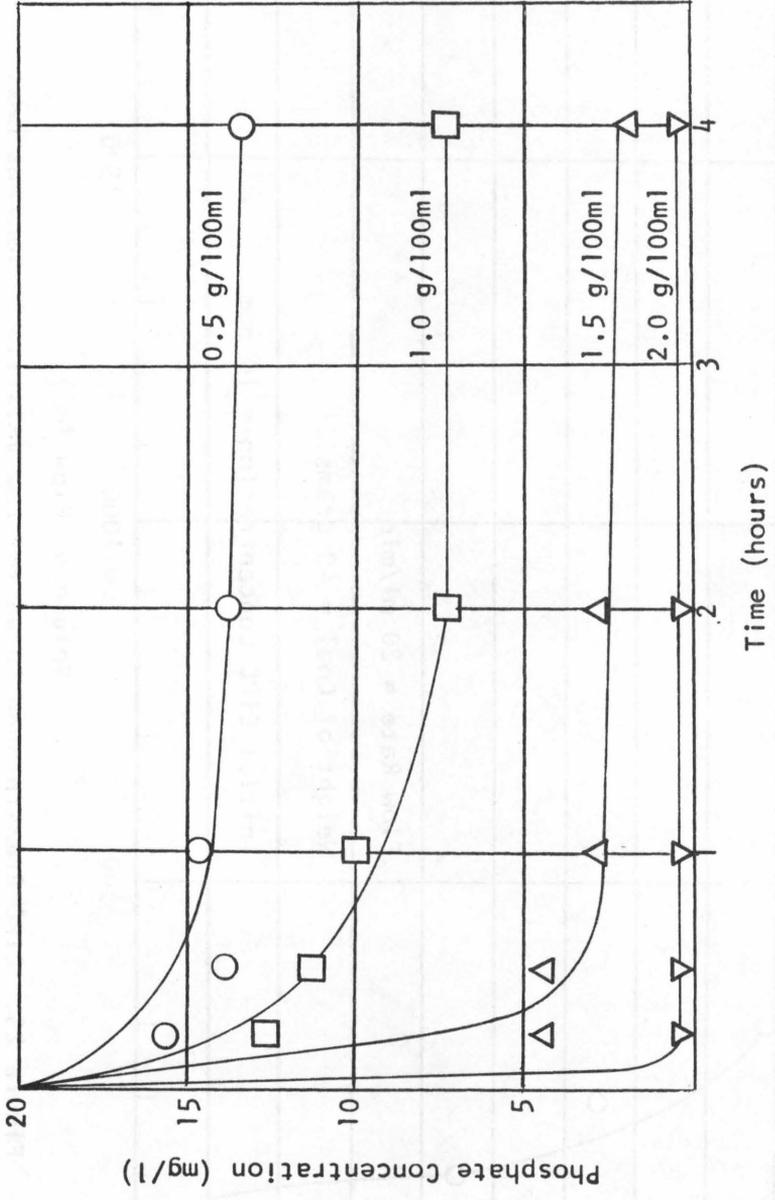


Figure 24. Effect of Variable Coal Dosage on Orthophosphate Removal.

The effect of varying pH on the kinetics of removal of orthophosphate is shown in Figures 25 through 28. As noted therein, phosphate sorption on coal varies considerably with pH. For High Volatile Bituminous-C grade coal maximum phosphate sorption occurs in the pH range five to six. For the other types of coal tested, maximum sorption occurred in the same range with the exception of Low Volatile Bituminous. This coal exhibited maximum sorption at about pH 4.

In general, those coals with the lower sorptive capacity reached equilibrium sooner than those with higher sorptive capacities. Equilibrium was also reached after a shorter time lapse at lower pH values in most of the tests that were conducted. The very slight phosphate removal from or release into solution at pH 2 indicates that the complex formed during sorption is quite soluble at this pH. It also indicates that some phosphorus compounds already contained in the coal are soluble at pH 2.

The effect of variable coal type on phosphate uptake at pH 4.0 is shown in Figure 29. Considerable differences in the sorptive capacities of the various coal types were noted. These differences are the result of both differences in the sizes of the coal particles, which were not standardized, as well as differences in the nature of the coals. The major differences, however, were attributed to the properties of the coals.

In addition to the experiments utilizing coal the removal of orthophosphate by activated carbon was also determined for comparative purposes. As expected activated carbon was almost totally ineffective in sorbing orthophosphate from solution. Lowering the pH of the solution did not change this result.

Two polyphosphates were also used in the batch kinetic studies. The substances selected for study were sodium metaphosphate and tetrasodium pyrophosphate decahydrate. Results of this work are shown in Figure 30. The two polyphosphates tested were both found to be removed to a significant degree by the coal. The metaphosphate removal closely resembled orthophosphate removal. The pyrophosphate was removed to a much greater extent than either the ortho or metaphosphates. The spontaneous hydrolysis reaction which converts the condensed phosphate forms to orthophosphate is relatively slow under normal conditions. The two standard polyphosphate solutions did not show enough spontaneous hydrolysis to orthophosphate to account for any but a small portion of the removal observed by this experiment.

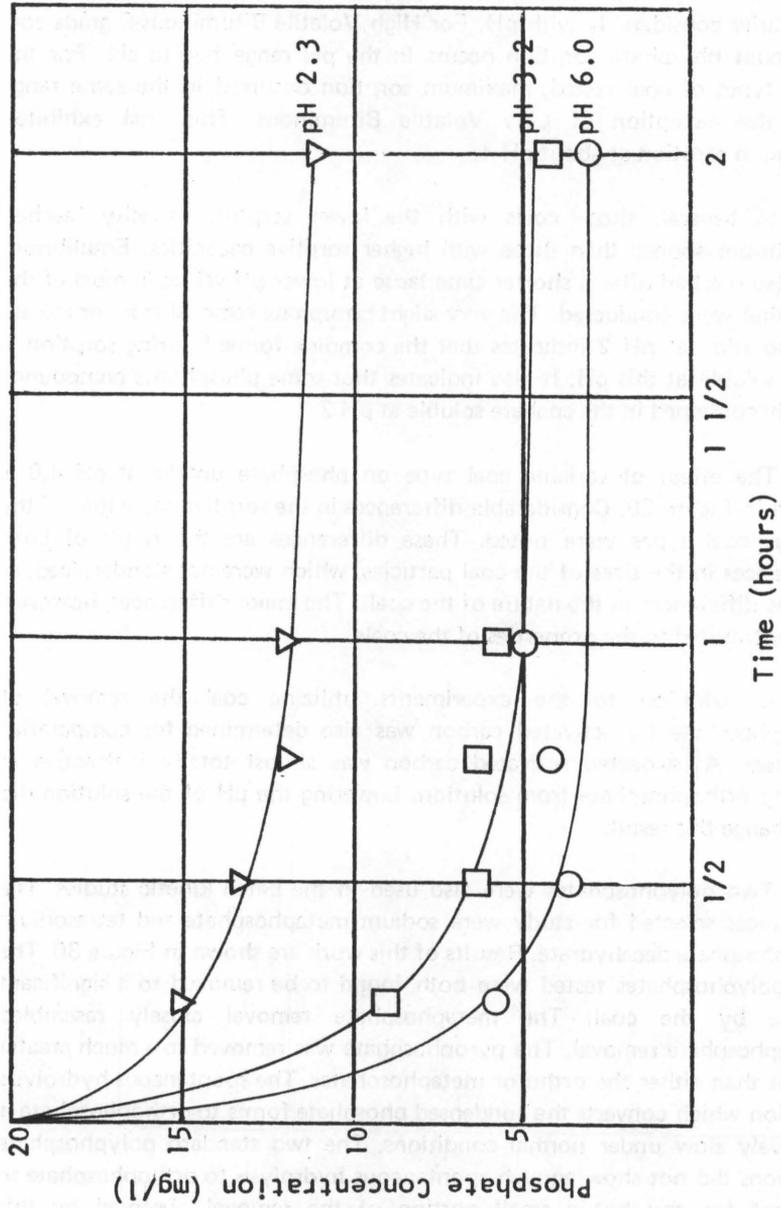
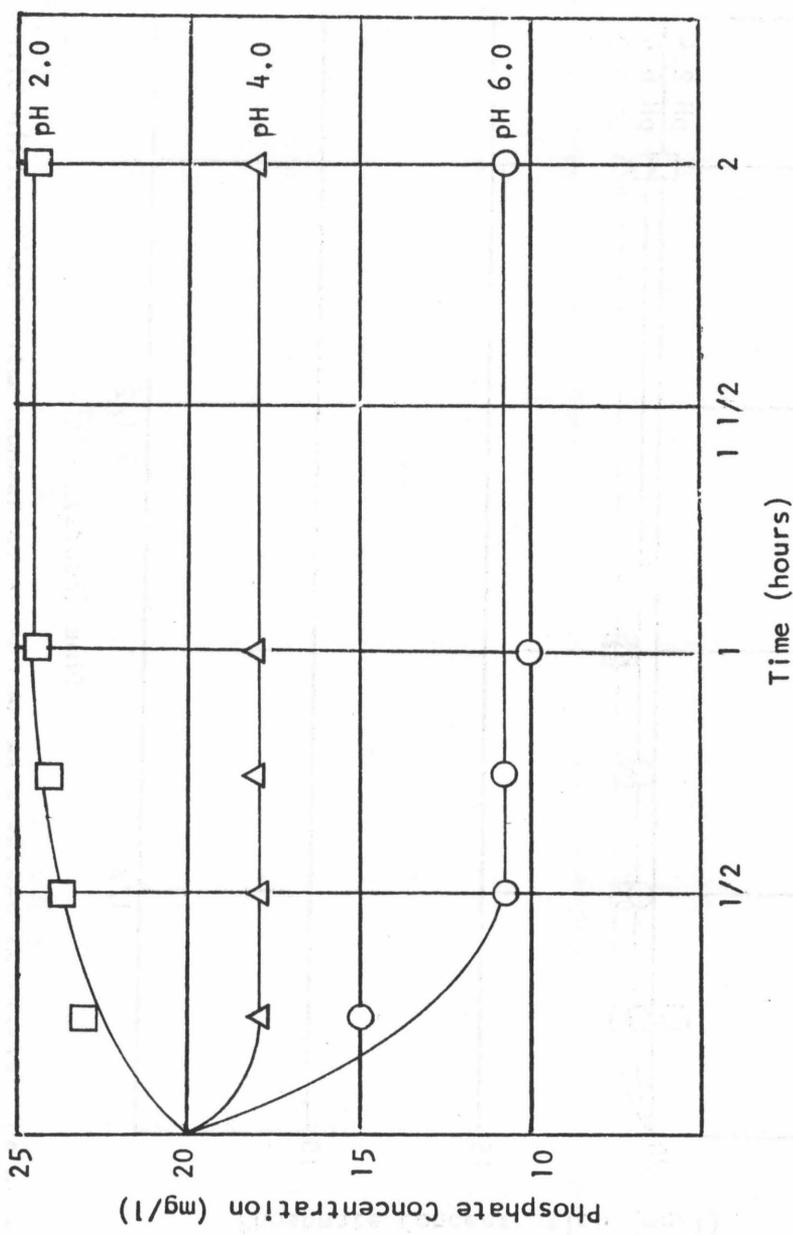


Figure 25. Effect of Variable pH on Phosphate Removal with High Volatile Bituminous-C Coal (Peabody - Lynnville).



53 Figure 26. Effect of Variable pH on Phosphate Removal with High Volatile Bituminous-A Coal.

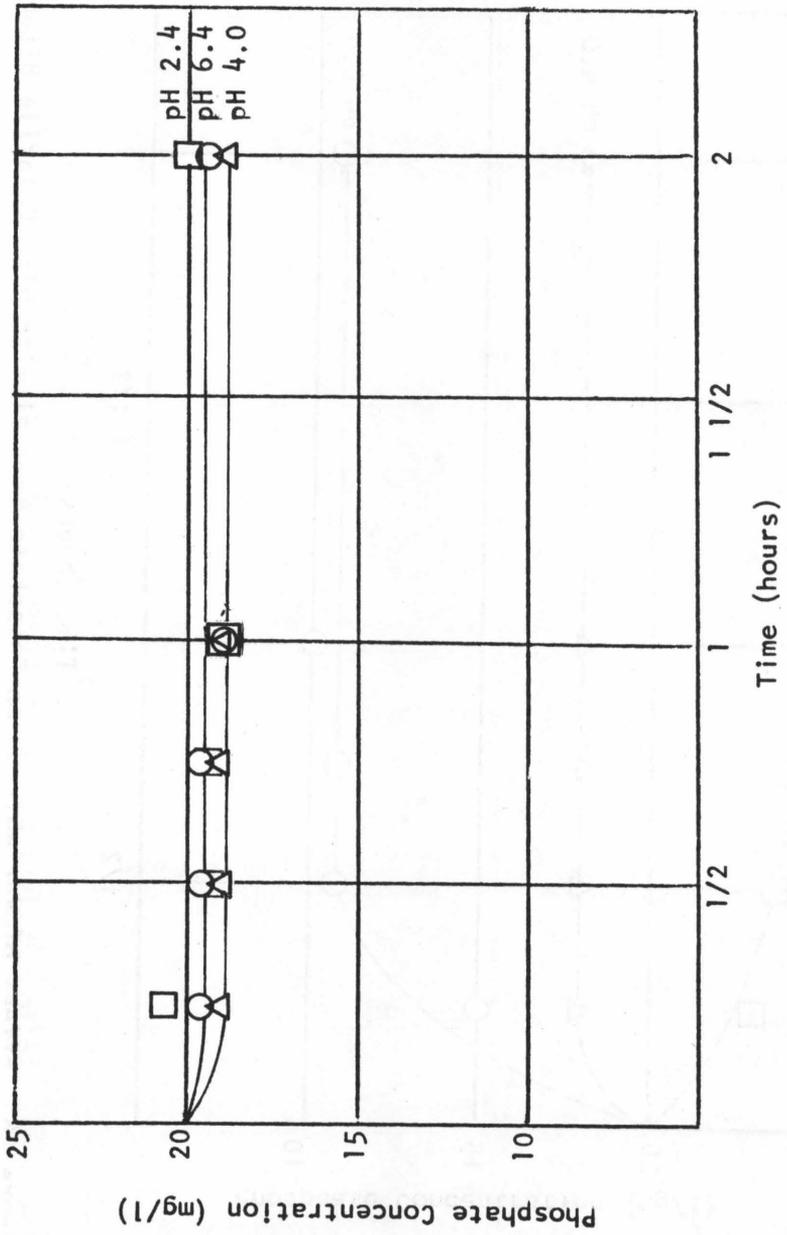
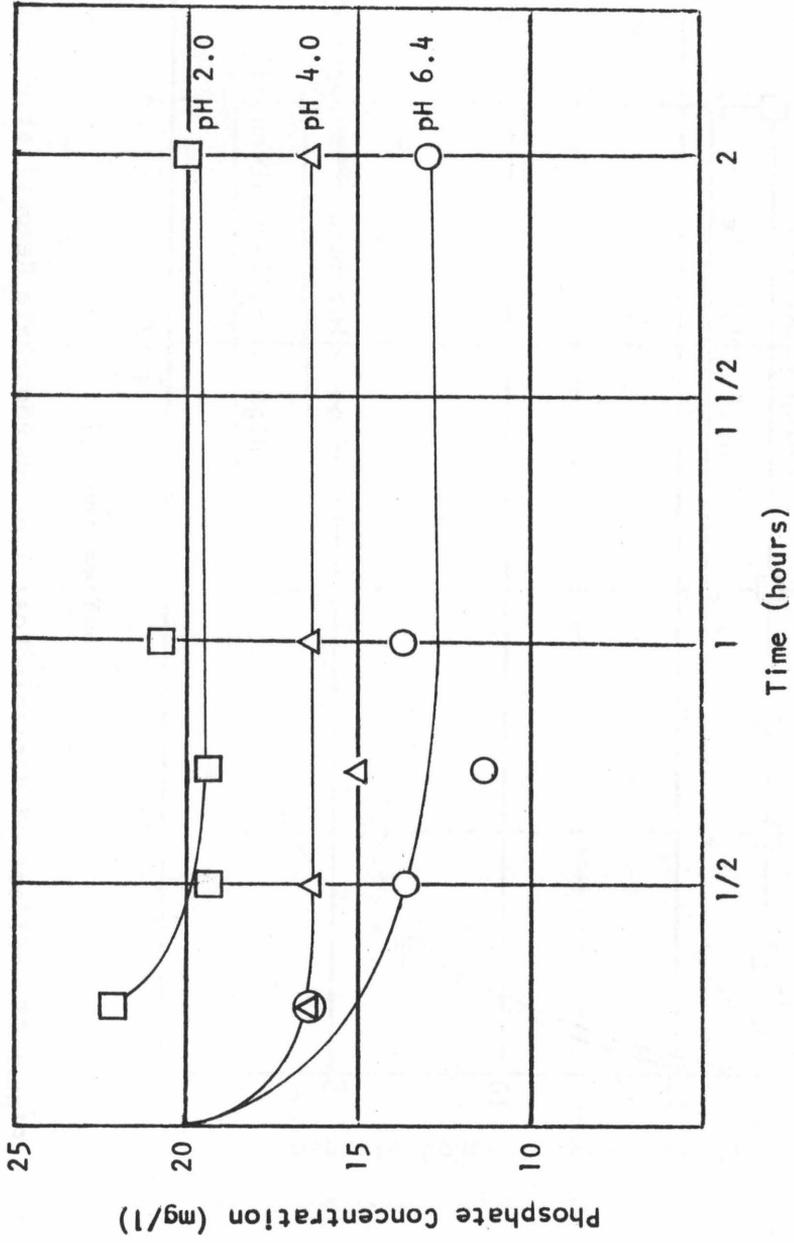


Figure 27. Effect of Variable pH on Phosphate Removal with Low Volatile Bituminous Coal.



59 Figure 28. Effect of Variable pH on Phosphate Removal with Medium Volatile Bituminous Coal.

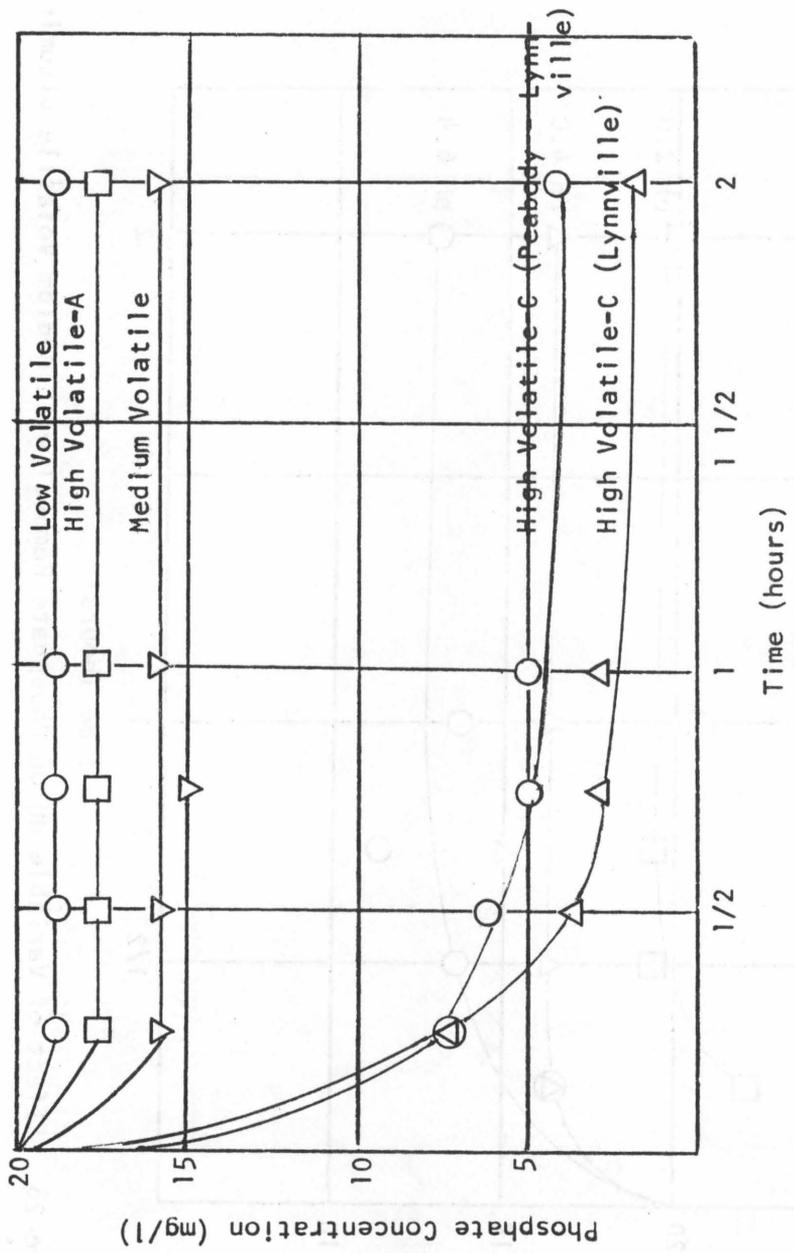


Figure 29. Effect of Variable Coal Type on Phosphate Removal at pH 4.0.

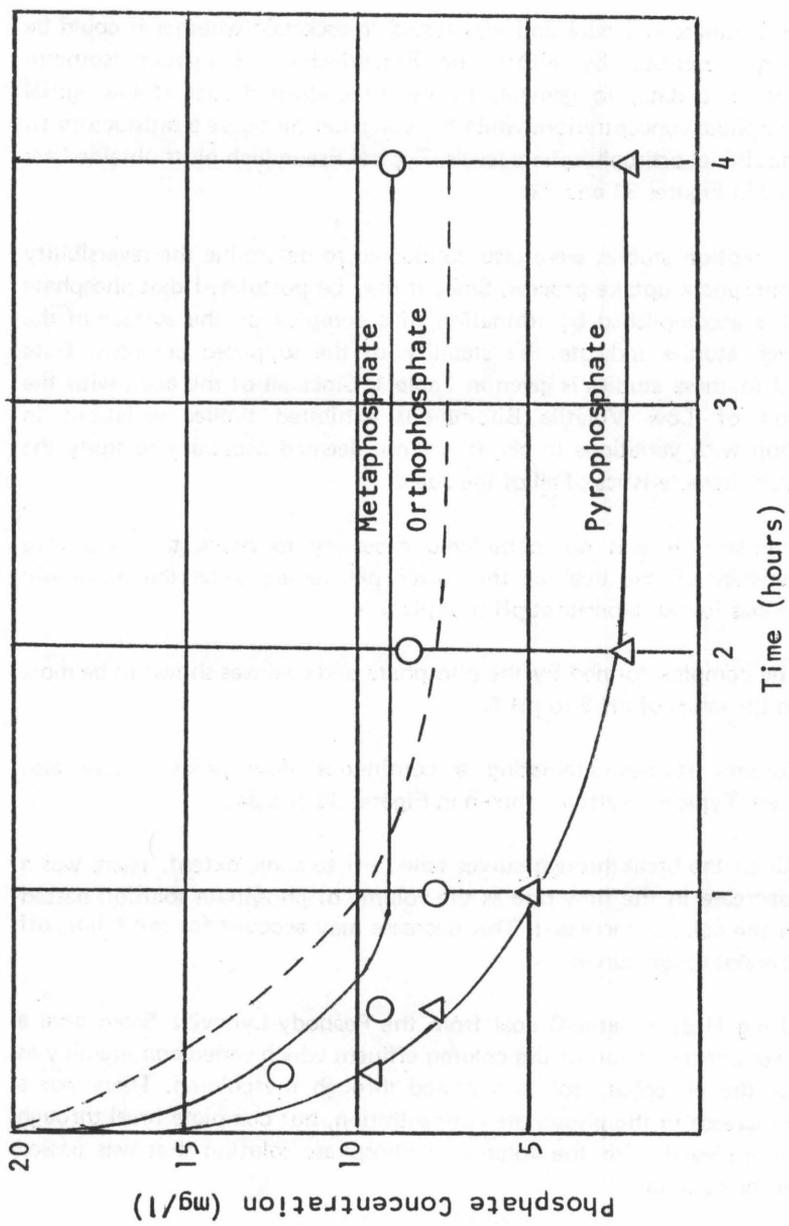


Figure 30. Kinetics of Polyphosphate Removal by 1.0g of Coal.

Data for phosphate uptake at equilibrium was obtained for High Volatile Bituminous-C coal and was tested to ascertain whether it could be adequately described by either the Freundlich or Langmuir isotherm equations. The data, in general, fit the Freundlich model at low initial orthophosphate concentrations while the Langmuir plot gave a satisfactory fit for higher initial orthophosphate levels. Typical Freundlich plots obtained are illustrated in Figures 31 and 32.

Desorption studies were also conducted to determine the reversibility of the phosphate uptake process. Since it may be postulated that phosphate removal is accomplished by formation of a complex on the surface of the coal, such studies indicate the stability of the supposed complex. Data obtained in these studies is given in Table 1. Since all of the coals with the exception of Low Volatile Bituminous exhibited similar variations in adsorption with variations in pH, it was not deemed necessary to study the desorptive characteristics of all of the coals.

Similarly, it was not considered necessary to check the desorptive characteristics of the coal at the lower pH values, since the maximum sorption was found to occur at pH 5 or pH 6.

The complex formed by the phosphate and coal was shown to be most stable in the range of pH 5 to pH 6.

Column studies simulating a continuous flow process were also conducted. Typical results are shown in Figures 33 and 34.

All of the breakthrough curves tailed off to some extent. There was a noted decrease in the flow rate as the volume of phosphate solution passed through the column increased. This decrease may account for the tailing off of the breakthrough curves.

Using High Volatile-C coal from the Peabody-Lynnville Seam gave a phosphate concentration in the column effluent which varied considerably as more of the phosphate solution passed through the column. There was a general increase in the phosphate concentration, but complete breakthrough was not achieved with the volume of phosphate solution that was passed through the column.

In an effort to determine the mechanism responsible for phosphate uptake a number of additional experiments were conducted. Attention was

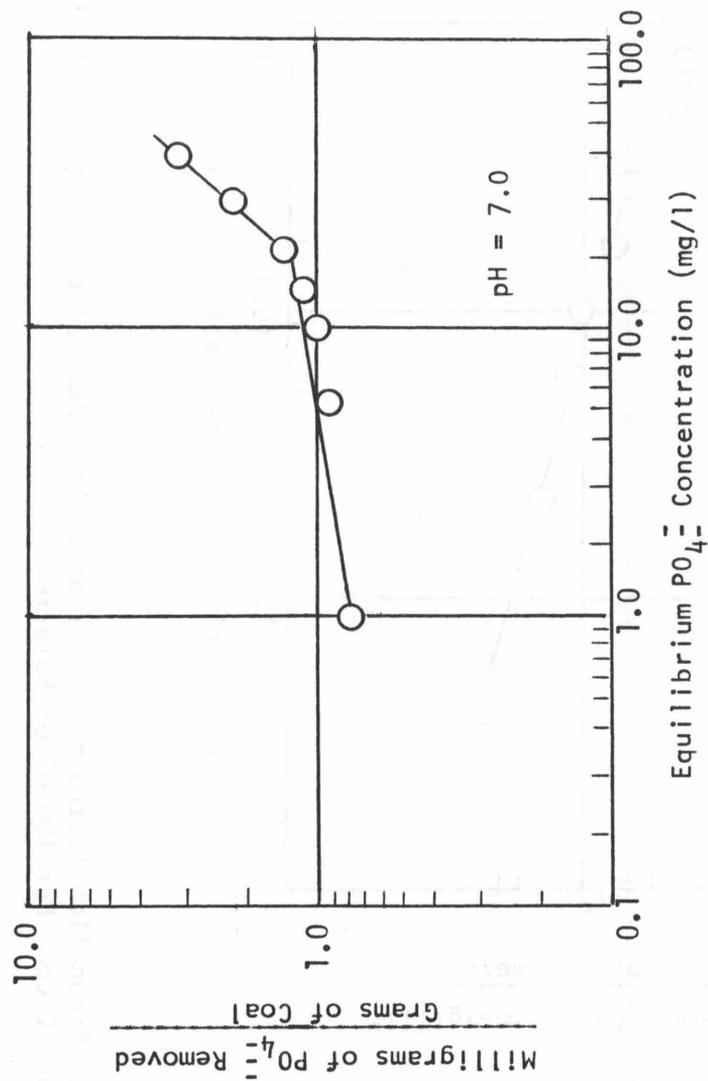


Figure 31. Freundlich Isotherm for Orthophosphate Removal by 0.5 Grams of High Volatile Bituminous-C Coal Per 100 ml of Solution.

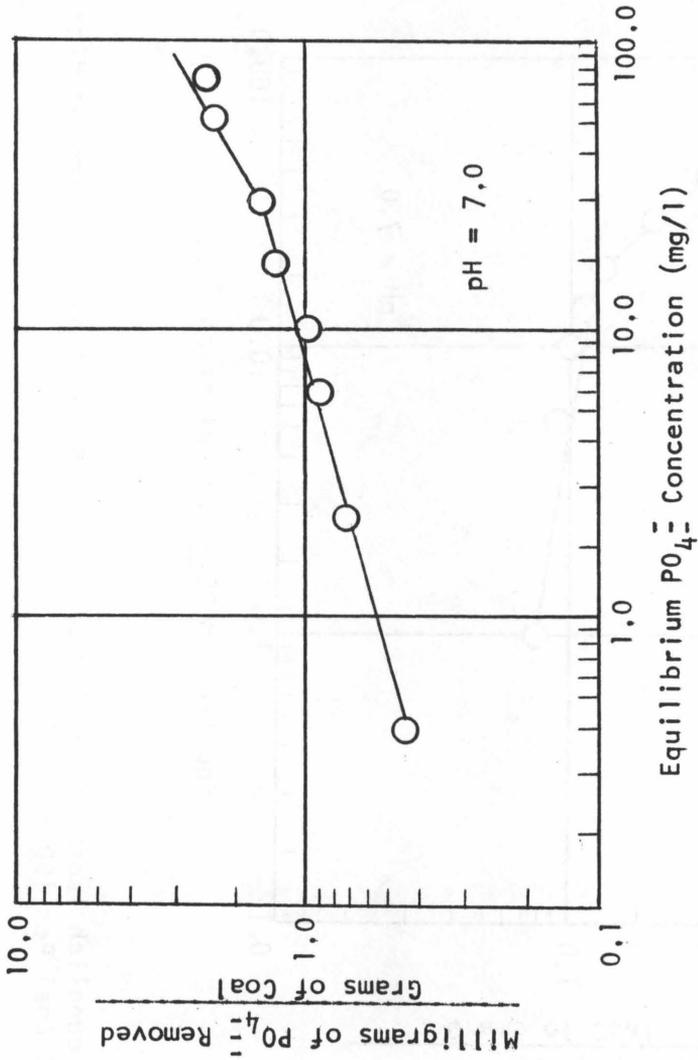


Figure 32, Freundlich Isotherm for Orthophosphate Removal by 1.0 Grams of High Volatile Bituminous-C Coal Per 100 ml of Solution.

TABLE 1

Desorption of Phosphate from High Volatile
Bituminous-C Coal in Aqueous Solution
At Variable pH

<u>pH</u>	<u>Contact Time</u>	<u>% Removal</u>	<u>% Desorption</u>
4.0	2 hr.	90	50
5.0	2 hr.	90	14
7.8	1 hr.	60	75
7.8	1 hr.	58.5	75

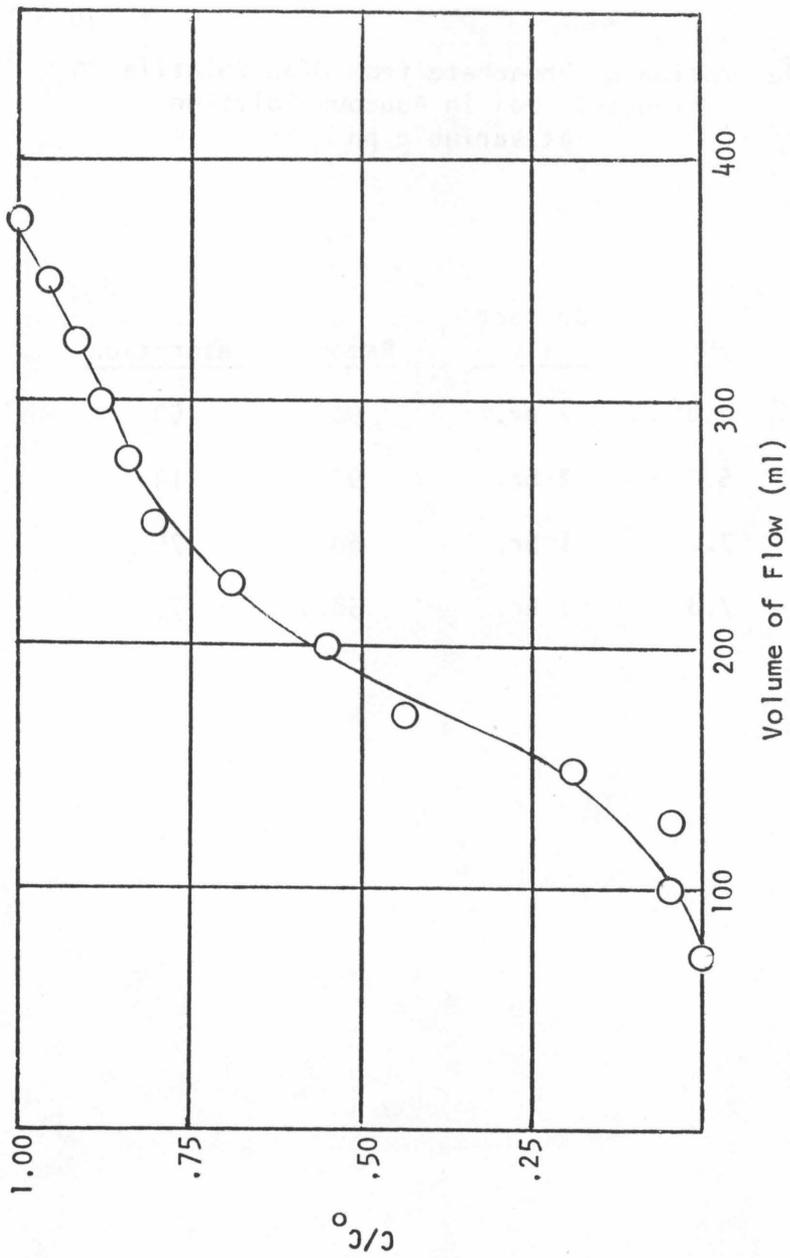


Figure 33. Breakthrough Curve for High Volatile Bituminous-C Coal (Lynnville).

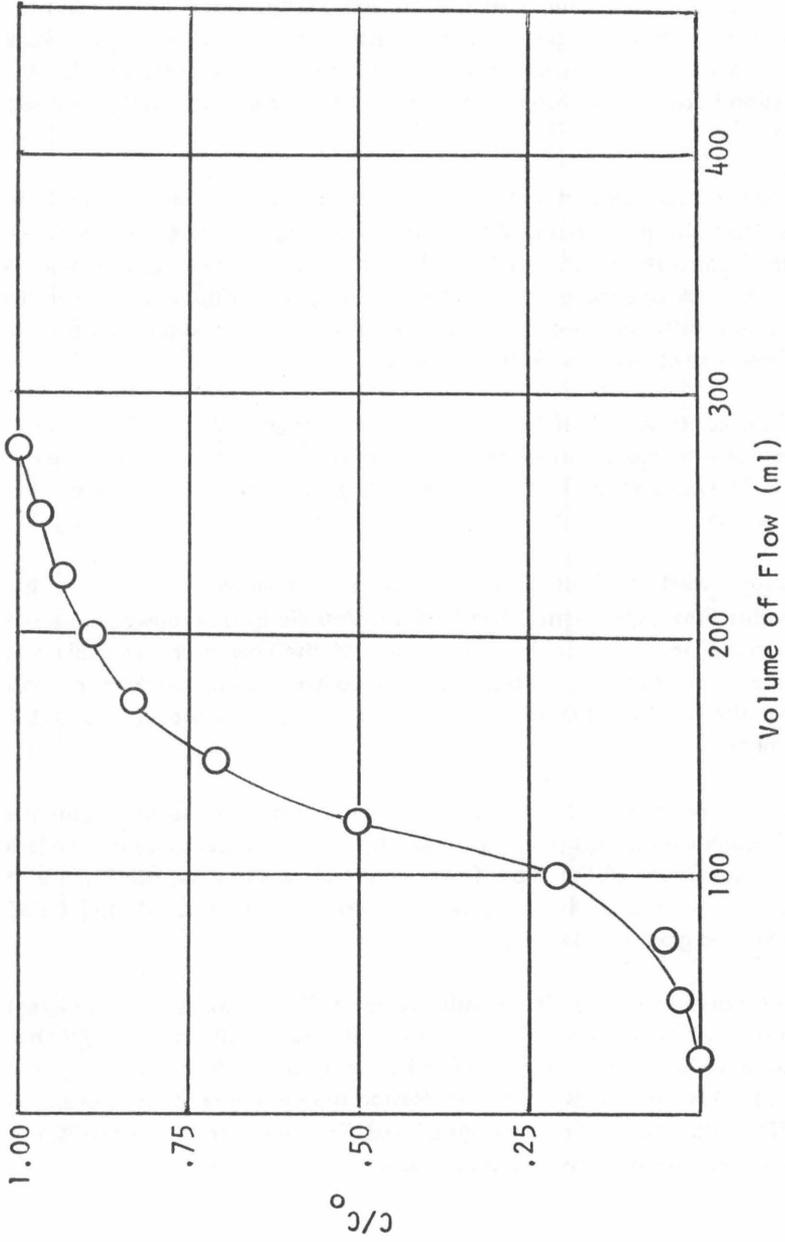


Figure 34. Breakthrough Curve for Medium Volatile Bituminous Coal.

centered on the iron content of the utilized coals in order to ascertain the role of iron in phosphate uptake. If the mechanism responsible for phosphate sorption is the formation of an iron-phosphate complex, there should be a correlation between the iron content of the coal and the extent of phosphate uptake.

The iron content of each of the selected coals is given in Table 2. In addition the phosphate removal as a typical batch-type sorption test is noted. A general correlation between iron content and phosphorus uptake may be noted. The lack of a more exact relationship may be attributed to the various coals having differing percentages of their total iron in a state such that an iron-phosphate complex is readily formed.

The contribution of iron to solution by High Volatile Bituminous-C coal was also measured under various conditions. Results are summarized in Table 3. The possibility of a ferric phosphate precipitation is clearly indicated by these data.

Discussion: Medium Volatile Bituminous type coal was chosen for the continuous flow experiments. The Medium Volatile Bituminous coal offered an advantage in that it is the most coarse of the coal types available and therefore there were no problems associated with small particles of coal clogging the column and altering the flow rate during the course of the experiment.

Fifty per cent breakthrough was taken as the medium point on the breakthrough curve. This point is frequently used to characterize uptake in a column experiment of this type. The quantity of parathion adsorbed per unit weight of coal was 0.045 milligrams per gram for Column A and 0.035 milligrams per gram for Column B.

As noted in Figure 19, the milligrams of CIPC adsorbed per milligram High Volatile Bituminous C coal for the coal concentrations of 0.5 gm/100 ml, 1.0 gm/100 ml, and 2.0 gm/100 ml were, respectively, 9.4×10^{-4} , 5.0×10^{-4} and 2.4×10^{-4} . This is a linear relationship between coal concentration and CIPC adsorption per unit weight of coal. The concentrations of CIPC not adsorbed were, respectively, 2.3 ppm, 2.0 ppm, and 2.2 ppm.

TABLE 2

Total Iron Content and Phosphate Uptake
for the Coal Types Used
in this Research

<u>Coal</u>	<u>Percent Iron</u>	<u>Percent Phosphorus Uptake*</u>
High Volatile-A	.468	12
High Volatile-C (Lynnville)	1.477	95
High Volatile-C (Peabody-Lynnville)	1.735	90
Medium Volatile	.344	20
Low Volatile	.444	10

*Assuming an initial phosphate concentration of 20 mg/l and a coal concentration of 1.0 grams per 100 milliliters.

TABLE 3

Iron Concentrations in Selected Samples

Initial Sample Composition	Coal Dosage g/100 ml	pH	Contact Time (hr)	Filtered?	Iron (mg/l)
Distilled H ₂ O	1.0	2.3	48	no	2.50
20 mg/l Orthophosphate	1.0	6.8	12	no	1.68
20 mg/l Metaphosphate	1.0	7.0	24	yes	1.04
20 mg/l Metaphosphate	1.0	7.0	24	no	4.00
20 mg/l Orthophosphate	1.0	3.0	15	yes	1.50
20 mg/l Orthophosphate	1.0	3.0	15	no	2.00

DISCUSSION OF RESULTS

The experimental work conducted during the course of this investigation helps to facilitate the assessment of various proposed waste treatment processes utilizing coal as a sorbing and filtering media. In such cases it is normally assumed that the spent filter media would be incinerated, thus extracting its thermal energy, and as a result significant economies would be realized. The cost of utilizing the coal in such a process would presumably be minimal since it would represent only a brief interlude on the coal's path from the mine to the point of consumption. The experimental research was specifically aimed at defining the extent to which trace micropollutants and phosphates would be removed in coal contact processes.

Three pesticides were selected as typical trace micropollutants. Lindane, a representative chlorinated hydrocarbon, has a water solubility of about ten parts per million. Parathion, typical of the organic phosphorus insecticides, is soluble in water to the extent of twenty-five parts per million. Chloroisopropyl carbamate selected to represent the organic herbicides has a reported water solubility of about 108 parts per million. Coal was shown in these experiments to be reasonably effective in removing the pesticides which were chosen for study. Kinetic studies all indicated a relatively rapid uptake with most of the removal occurring in the first few minutes and equilibrium being virtually achieved in one to two hours. This feature is particularly important in judging the suitability of a continuous flow system such as a filter or a sorption column for elimination of these contaminants from wastewater.

The suitability of substituting coal for activated carbon in water treatment was also considered. Pesticides of the type utilized in this study are typical micropollutants susceptible to removal by adsorption on activated carbon. Activated carbon was shown to be considerably more effective than the best coal in sorbing these compounds. Specifically, activated carbon was 10, 24 and 1000 times as effective as High Volatile Bituminous-C coal in removing lindane, parathion, and CIPC respectively. The coals varied considerably in their uptake efficiency indicating that these results are not general in nature, but must be determined for each coal and organic contaminant to be considered. The potential of coal in a water treatment process of this nature is clearly very limited.

In a wastewater treatment process wherein the influent is contaminated with considerable biologically non-gradable organics, there appears to be a

significant advantage in the use of coal in a moving bed filter or other unit of that type. In this process the suspended material would be removed by filtration and the biologically resistant dissolved material would be sorbed onto the coal. Such a plant would be capable of large removals of persistent organics, particularly if the type of coal was judiciously selected for maximum efficiency of removal of the organics present in the waste influent. It should be emphasized in this regard that the higher grade coals are, in general, not the best sorbents. This fact represents an added economic advantage to a coal process for treating wastewater contaminated with resistant organics. In such a system coal would be an ideal filter media since the combustion of the coal would also result in incineration of the collected contaminants as well as recovery of the fuel value of the coal itself.

The study of the kinetics of phosphate removal in a coal-water system gave some interesting and encouraging results. A near linear relationship was shown to exist between the amount of phosphate removal and the coal dosage. Each gram of coal was capable of removing about 10 mg/l of phosphate from a 100 ml solution initially containing 20 mg/l phosphate. In other words, 1.0 gram of coal per 100 milliliters of solution effected a 50 per cent reduction from an initial concentration of 20 mg/l in a batch system.

The fact that the activated carbon does not exhibit any ability to effect phosphate removal represents a real advantage in the use of coal. Unquestionably this uptake of phosphorus is the result of some contaminant in the coal rather than being due to a surface adsorption. The data obtained strongly suggests that phosphorus uptake in a coal contact process is due to interaction with iron on the surface of the coal. Thus if phosphorus removal is a prime objective of the treatment process, a coal with a relatively high content of iron should be selected for a moving bed filter.

The study of phosphate sorption on various coal types showed that the amount of phosphate sorbed varied considerably with variations in the coals. The Rand Development Corporation (34) found that of the coal types tested, High Volatile-C grade coal exhibited superior phosphate sorption properties. The same conclusion was reached in these studies. The High Volatile-A, Medium Volatile, and Low Volatile coals were capable of sorbing only about 5 mg/l phosphate per gram of coal from 100 ml of a 20 mg/l phosphate solution. At least 75% phosphate removals were obtained with High Volatile-C coal under similar conditions.

Considerable variation in phosphate sorption was also present with changes in pH. Minimum sorption occurred in the low pH range (pH 2) and

maximum sorption was found to occur at around pH 5 or 6. Above pH 6 there was a decrease in the amount of phosphate sorbed by the coal.

The amount of phosphate remaining in solution after a two hour contact period with High Volatile-C coal (Peabody-Lynville) at various pH values was found to approximately parallel the solubility of phosphorus in equilibrium with FePO_4 as given by Stumm (14). The other coal types used in this research with the exception of Low Volatile Bituminous exhibited similar tendencies. This result indicates that the mechanism by which phosphate is sorbed on coal is a reaction with ferric ions in the coal or released to solution by the coal to form ferric phosphate.

The range of least reversibility for the phosphate adsorption is pH 5 to pH 6. This corresponds to the range of maximum phosphate adsorption on coal. This further indicates that the mechanism of adsorption is the formation of ferric phosphate.

A direct correlation between the amount of phosphate sorbed and the iron content of the coal could not be established in this research. PO_4^{\ominus} and Fe^{+3} react to form FePO_4 in the ratio 1.7:1. Thus, only 1.18 mg of Fe^{+3} would be required to remove all of the phosphate from 100 ml of 20 mg/l phosphate solution. It is evident that only a very small portion of the iron contained in the coal is on a state where it can react with the phosphate to form FePO_4 . Apparently the different coal types contain different amounts of iron capable of reacting with the phosphate and this is the reason for the differences in the amount of phosphate adsorbed by the various coal types.

CONCLUSIONS

The following conclusions have been drawn from these studies conducted in this thesis:

1. Coal is an effective sorbent for lindane especially at relatively low concentrations of lindane. In dilute solutions, removals on the order of ninety per cent may be expected with a coal concentration of 10 grams per liter.
2. The sorptive capacity of coal for lindane is almost entirely reached within one hour of contact.
3. For parathion sorption on coal, the rate of uptake and the ultimate sorptive capacity of all the coal types tested were virtually the same. One gram of each of the coal types tested was capable of removing about 90 per cent of the parathion from 100 milliliters of a 1.0 mg/l parathion solution.
4. The pH of the system did not effect the kinetics of parathion sorption when High Volatile Bituminous-C coal was used as the sorbing media.
5. Both the Freundlich and Langmuir isotherms were reasonably suitable for expressing the batch equilibrium data for parathion sorption on coal.
6. Activated carbon was found to be 24 times more efficient than coal in removing parathion from dilute aqueous solutions.
7. Under continuous flow conditions, Medium Volatile Bituminous coal removed 0.045 milligrams of parathion per gram of coal at a flow rate of 25 ml/min and removed 0.035 milligrams of parathion per gram of coal at a flow rate of 5 ml/min.
8. For CIPC sorption on coal, the rate of uptake and the ultimate sorptive capacity of all the coal types tested were virtually the same, with only High Volatile Bituminous-C coal showing a significant difference. Two grams of High Volatile Bituminous-C coal were capable of removing about 90 per cent of the CIPC from 100 milliliters of a 20 ppm solution, while two grams each

of the three other coals were capable of about 80 per cent removal.

9. Under continuous flow conditions, High Volatile Bituminous-C coal is 3.5 times as efficient as Medium Volatile Bituminous coal and seven times as efficient as High Volatile Bituminous A and Low Volatile Bituminous coals in removing CIPC from dilute aqueous suspension.
10. A high-Volatile Bituminous-C coal was capable of effecting substantial removal of orthophosphate, pyrophosphate, and metaphosphate from aqueous solution. Of all coals tested this grade achieved superior phosphate removal.
11. In batch reaction, a coal dosage of 1.0 gram per 100 ml of orthophosphate solution was able to effect a 10 mg/l removal of orthophosphate provided the initial orthophosphate concentration is below 20 mg/l.
12. Optimum phosphate sorption on coal occurs between pH 5 and pH 6.
13. The mechanism of phosphate adsorption on coal appears to be the formation of ferric phosphate with the iron contained in the coal.

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