FLY ASH UTILIZATION AS A TERTIARY TREATMENT PROCESS FOR THE REMOVAL OF PHOSPHORUS

By

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Bachelor of Arts

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1975

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
December, 1977

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PROCESS FOR THE REMOVAL OF PHOSPHORUS

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ACKNOWLEDGMENTS

I am greatly indebted to several people for their help, encouragement and support during the course of this work. Particular thanks to to Dr. Marcia Headstream for her continued enthusiasm and friendly council as major adviser. The members of my committee, Drs. Anthony Gaudy, Jr., and Don Kincannon have both been extremely helpful and supportive throughout. The special attention and support which I received from my husband was invaluable and also greatly appreciated.

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CHAPTER I

INTRODUCTION

Fly ash is the residual particulate material retrieved from stack gases after the combustion of pulverized coal. The major producers of fly ash are the electric power industries. Fly ash particles are suspended in the flue gases which leave the furnaces of coal fired power plants. These particles are considered to be an industrial aerosol and can cause major air pollution problems when discharged into the atmosphere. However, today most fly ash is collected from the flue gases by pollution control devices such as cyclone separators or electro-static precipitators.

The quantity of the fly ash produced continues to increase and it has been reported by Brackett (1) that by 1980 electric utilities in the United States will produce between 39 and 40 million tons of fly ash per year. With the production of such large quantities of this material there is an urgent need to find ecologically sound and productive uses for this combustion waste product.

Fly ash has been used effectively in wastewater treatment for the removal of refractory components and organic material and as a sludge conditioner and coagulant aid. Recently some experiments have been undertaken to investigate the potential utilization of fly ash for the removal of phosphorus from secondarily treated municipal wastewater effluents. The growing concern manifested over the rapidly deteriorating quality of the nation's fresh water resources as the result of excessive phosphorus loadings has provided the impetus for research to develop effective tertiary phosphorus removal techniques. If fly ash can be successfully utilized to lower the concentrations of phosphorus in wastewater effluents prior to discharge, the overall quality of the receiving body of water will be enhanced, the process of eutrophication will be hindered, and the water resource will become available for a wider range of beneficial uses. It is the purpose of this research to ascertain the phosphate removal capabilities of fly ash and to study its effectiveness in the tertiary treatment of wastewater for subsequent phosphorus removal and control.

CHAPTER II

LITERATURE REVIEW

Composition of Fly Ash

Fly ash is made up of a variety of inorganic compounds found in the earth's crust. The particle size, shape, density, color and chemical composition can vary widely in different samples of fly ash. It has been described by Stern (2) as an inhomogenous material composed of rough solid or hollow spherical particles. Brackett (1) has reported that fly ash particles can vary in size from less than one micron to approximately eighty microns.

Minnick (3) has reported a range of values for the weight percentage composition of fly ash which he gathered from a study of 20 different fly ashes. These values are presented in Table I. Brackett (1) has also pointed out that, chemically, more than 85% of most fly ashes consist of alumina, silica, iron oxide, lime and magnesia with the relative percentages of these constituents varying over a wide range.

Much has been learned about the chemical composition of fly ash through the analyses of water soluble fly ash extracts. Water quality parameters altered by the presence of fly ash as reported by Tenney and Echelberger (4) and Shannon and Fine (5), and Theis (6) include pH, and the concentrations of various cations and trace metals. Tenney and Echelberger (4) have reported reduced pH, increased hardness and

TABLE I

RANGES OF CHEMICAL COMPOSITION* AND SPECIFIC GRAVITY OF 20 FLY ASH SAMPLES

Silica, SiO_2	34.01 - 49.53
Alumina, Al_2O_3	17.50 - 30.39
Iron Oxide, Fe_2O_3	6.62 - 26.43
Carbon, C	.56 - 18.18
Calcium Oxide, CaO	.99 - 9.68
Magnesium Oxide, MgO	.55 - 1.63
Sulfur Trioxide, SO_3	.23 - 2.8
Apparent Specific Gravity	2.12 - 2.69

*Chemical composition is expressed as weight percent.

alkalinity and increased sulfates in lake water when they added fly ash. However in analyzing water soluble extracts obtained from the extraction of fly ash with distilled water, they observed increases in pH, hydroxide alkalinity, hardness and sulfates. Shannon and Fine, while studying cation solubilities of lignite fly ashes, also reported the release of cations such as calcium, sodium, magnesium and iron. Theis (6) has reported on potential trace metal contamination of water resources through the disposal of fly ash.

The chemical and physical properties of fly ash depend upon conditions within the producing plant and the nature of the coal itself (1) (7). The burning efficiency of any furnace will determine how much carbon is left in the ash. Carbon content has been reported by Johnson (8) to vary from 9-35% and can generally be found to be around 15%. Observations have also shown that any one coal will have an inherent as well as surface ash content (1)(7). The surface ash content is attributed to silts that are present in the coal when it is formed and which remain after combustion. It may also result from the rock or rock dust which is introduced in the mining process. Inherent ash content is structurally part of the coal and is the product of combustion which cannot be removed by mechanical means.

The resultant ash characteristics are also determined by the thoroughness of the pulverization of the coal. The standard size or degree of pulverization of the coal is gaged by a product fly ash of which 80-85% will pass a 200 mesh screen and 98% will pass a 50 mesh screen. This standard size guarantees against having an ash which will be too coarse to pass government specification and which will have a resultant high percentage of unburned carbon (1).

The type of ash collection device used in the production plant has also been reported to be an important factor in determining the quality of fly ash which is obtained (1)(7). The effect that any one collection device will have on an ash has a lot to do with the way in which the device operates. Three kinds of collectors typically used for fly ash collection are mechanical cyclones, electrostatic precipitators, and fabric filters. Brackett (1) and Stern (2) stated that the mechanical cyclone devices are useful for collection of ashes which have a high percentage of large dust particles. These devices spin the ash to the sides of the stack where they are skimmed off. Electrostatic precipitators have been shown to be more effective than the cyclone collectors in removing a wider range of particle sizes (2). These devices pass the fly ash particles through a voltage DC field to charge the particles and then through collecting plates with opposite polarity which attract the charged particles. Magill (7) has reported that although precipitators are in most cases very efficient, the fly ash may not in all cases be susceptible to accepting a charge. A chemical constituent inherent in the ash content of some fly ashes called halosite can prevent fly ash from accepting a charge and can therefore provide resistance to its collection. Brackett (1) has reported that a fabric bag filter may be of more use when handling a fly ash with a high halositic content.

Potential Uses of Fly Ash

While fly ash has been used in a variety of ways, the most widely known uses have been in the construction industry. Brackett (1) and Magill (7) have reported its use as an admix to help in the workability of concrete mixtures. Fly ash contains the important chemical constituents, silica and alumina, which are necessary in the manufacture of cement and concrete products. It has also been used in other constrution materials such as asphalt, masonry mortar and light weight aggregate.

Fly ash has also been used as a soil amender. It supplys the trace metals necessary for soil conditioning (9) and essential plant nutrients important for plant growth (10). Marten et al., (11) studied fly ash from 17 different power plants in nine states to determine the potential of using fly ash as a fertilizer. He was able to ascertain which plant nutrients contained in fly ash are available for uptake and utilization by plants.

Fly ash has been used fairly successfully in the treatment of polluted lake water. Higgins et al., (12) performed a series of experiments which attempted to determine optimum dosages of fly ash, lime, and/or gypsum for the removal of phosphate from eutrophic lake waters. He found that the phosphorus removal characteristics of the fly ash depended on the source and chemical composition of the fly ash selected. Using both jar test and <u>in situ</u> experiments, Higgins discovered that the phosphate removal capacity of his fly ash was relatively low, but that the concurrent addition of lime with the fly ash improved both total and soluble phosphorus removal. From this research he concluded that the phosphate concentration in a body of water could be more effectively controlled using lime rather than fly ash but that the addition of fly ash was necessary to improve clarification and to seal the sediments to prevent phosphate release.

Tenny and Echelberger (4) have observed the removal of phosphorus in lake water using fly ash, washed fly ash, and the aqueous extracts obtained from washing fly ash. They found that as the result of washing fly ash loses most of its phosphate removal capacity. The most effective phosphate removal was achieved by allowing the unwashed fly ash to interact directly with water containing phosphate. The major mechanism of phosphate removal is believed to be by chemical precipitation with calcium. Calcium ions (Ca^{++}) react with phosphate ions (PO_4^{-3}) in the presence of hydroxyl ion (OH^-) to form hydroxyapetite ($Ca_5(OH)(PO_4)_3$). If the phosphate is of the form HPO_4^{-2}, then the following reaction is thought to occur:

$$3HPO_4^{2-} + 5Ca^{2+} + 4OH^- \rightarrow Ca_5(OH)(PO_4)_3 + 3H_2O$$

This reaction has been found to occur primarily at pH values above nine. Hydroxyapetite below this pH is highly soluble.

It was suggested by Tenney and Echelberger (4) that concentration gradients and pH ranges favorable for phosphate precipitation are established in and around the surface of the fly ash particles when dry fly ash comes in contact with phosphate-containing water. The greatest degree of phosphate removal appears to be achieved at the surface of the fly ash rather than in the bulk solution. Their studies also indicated that fly ash would remove organic material from the eutrophic lake water and that adsorptive capacity increased with increased carbon content in the fly ash.

In wastewater treatment fly ash has been used in several different processes. The adsorption of refractory contaminants and COD from wastewater was investigated by Mancy (13), Eye and Basu (14), Deb et al., (15), Johnson (8) and Nelson and Guarino (16). Fly ash has also been used as a coagulant aid (17) and as a sludge conditioner (14). Gongoli and Thodos (18) and Guter (19) have used fly ash as an adsorbent to remove phosphorus and organic contaminants from wastewater.

Johnson (8) found that some fly ashes were effective in removing 66% of the soluble COD and 76% of the ABS (alkylbenzene sulfonate) present in the final effluent of secondarily treated wastewaters. This removal ability was correlated with the carbon content of the fly ash. Mancy et al., (13) also found that adsorption of ABS improved with an increasing carbon content in the fly ash regardless of contact time or fly ash dosage. The removal rate of akylbenzene sulfonate (ABS) by fly ash, was initially high and then declined rapidly over the course of the experiment. Researchers, therefore, concluded that contact times in excess of one hour were unnecessary. The total amount of ABS removed increased with increasing concentrations of fly ash, but as the total amount of fly ash increased the efficiency of removal decreased. Exact values of optimum detention time and dosage of fly ash were dependent on both the character of the adsorbate and the fly ash.

Deb et al., (15) has conducted studies to determine soluble COD removal by fly ash using secondary effluent from an extended aeration plant. He found that the majority of the soluble COD removal occurred within the first ten minutes of contact time with the fly ash. The COD removal was logarithmically related to time of mixing, initial COD concentration and the concentration of fly ash. Similar results were also obtained by Eye and Basu (14).

Phosphorus Removal From Wastewater

The use of fly ash for phosphorus removal from wastewaters is now being considered. Current methods of phosphorus removal from secondary wastewater streams include chemical precipitation, adsorption and the utilization of such processes as ion exchange and electrodialysis.

Chemical precipitation for phosphorus removal has been applied to both treated and untreated wastewater and has a long history of research by many investigators, Eberhardt and Nesbitt (20), Barth (21), Schmidt and McKinney (22), Ferguson et al., (23), and Spohr and Talts (24). Phosphorus is found in wastewater in three different chemical forms, ortho-phosphate, poly-phosphate, and organic phosphorus compounds. It has been reported that for the range of pH values found in municipal wastewater, the predominant form of phosphorus is HPO_4^{-2} (25). Hydrolysis of poly-phosphates and the decomposition of organic phosphate produce ortho-phosphate, and this form of phosphate is best suited for precipitation reactions. Three materials most commonly used for phosphorus precipitation are aluminum as alum, iron as ferric sulfate and ferrous sulfate, and calcium as lime.

Common adsorbents used in wastewater treatment are activated carbon, Fullers earth, alumina and silica gel. Adsorption may be either a chemical or physical process depending on the mechanism of molecular attachment at the particle surface. Chemical adsorption is characterized by a chemical bond whereas physical adsorption is characterized by weak bonds formed as the result of Van der Waals forces. Physical adsorption is responsible for the removal of refractory compounds from wastewater using granular activated carbon (26).

Adsorption as reported by Metcalf and Eddy (26) is a three step process in which adsorbate molecules (1) move through the film that surrounds the adsorbent (2) diffuse into the pores of the adsorbent if it is porous and (3) form bonds with the active surface of the adsorbent. The rate of adsorption is dependent on the rate of molecular movement or diffusion in the solution. Mixing, therefore, should enhance the rate of adsorption.

Equations which are used to describe adsorption isotherms have been developed by Freundlich (26). His equation is as follows:

$$X/M = kC^{1/n}$$

where X/M = amount adsorbed per unit weight of adsorbent

C = equilibrium concentration of adsorbate in solution after adsorption

k,n = empirical constants

The constants are obtained by plotting X/M versus C on double logarithmic paper.

Chemical precipitation techniques and adsorption as well as ion exchange and electrodialysis, although essentially effective in tertiary wastewater treatments for phosphorus removal, contain inherent problems which can ultimately limit their effective utilization. When chemical reagents are used for the removal of phosphorus as a precipitate, they often times have to be used in excess to bring about the proper chemical reactions. The excessive use of these chemicals could cause contamination of the wastewater by increasing the pH and the total dissolved solids concentration. A major drawback to the utilization of most adsorbents is regeneration. The process which is very necessary when adsorbents are used in wastewater treatment can be very costly. In order to make ion exchange resins practical for tertiary treatment reagents would also have to be employed for removal of organic as well as inorganic material from the spent resin. It has also been pointed out by Eliassen and Tchobanoglous (27) that carbonates and sulfates present in the wastewater will exhaust the resin capacity before adequate removal of phosphorus could take place. Chemical precipitation and membrane fouling occur when electrodialysis processes are used in wastewater treatment. Calcium carbonate in the wastewater precipitates on the membrane surface. In addition to this, colloidal and organic matter collect near or on the anion membranes which increase operating costs. In order to reduce these problems additional wastewater treatment must be provided.

The use of fly ash in tertiary treatment of wastewater for the removal of phosphorus is quite practical in comparison to some of the other current materials and methods that are used. Fly ash is a waste product and therefore is relatively inexpensive when compared to the cost of other materials. The two major mechanisms for phosphorus removal by fly ash are chemical precipitation and adsorption. Chemical precipitation with fly ash, as discussed previously, is thought to occur via precipitation with calcium. Therefore the calcium content of the ash would determine the phosphorus removal capacity.

Adsorption is also considered to be at least partially responsible for phosphorus removal by fly ash by several investigators (19)(8) and (28). Fly ash is an efficient adsorbent because of the large surface area resulting from the size and porosity of the particles. The adsorption capacity of fly ash for phosphorus has been found to increase with the carbon content of the fly ash (Tenney and Echelberger (4), Mancy et al., (13), Johnson (8)). Gongoli and Thodos (29) have used adsorption isotherms to demonstrate that phosphorus was being adsorbed by fly ash. In their studies they compare fly ash and alumina with respect to phosphate adsorption from wastewater. Fly ash was found to be more effective than alumina in phosphate removal and did not require regeneration.

Guter (19) investigated the potential of using fly ash to remove phosphate from secondary wastewater effluent. He found that fly ash in concentrations of 20 gm/l was able to lower an initial phosphate concentration of 6 mg/l to nearly zero. He also found that as the speed of mixing was increased phosphate removal also increased.

CHAPTER III

MATERIALS AND METHODS

Experimental Procedure

Fly ash was provided by the Comanche Steam Generation plant in Pueblo, Colorado. It is a product of coal mined in Wyoming that was burned in a tangential coal fired boiler. The fly ash was collected by a hot electrostatic precipitator. Chemical analysis of the fly ash itself was performed by the agronomy laboratory of Oklahoma State University.

Secondary effluent used was collected in a 13 liter container from the secondary clarifier at the Stillwater, Oklahoma trickling filter plant. This plant handles 4 MGD of sewage from a small community of about 30,000 people. The town itself contains no heavy industry and the sewage is thus primarily domestic. The effluent was used without additional pretreatment within an hour after collection in all experiments. Determinations of initial chemical and physical characteristics of the wastewater were made before addition of fly ash.

Initial studies involved chemical analyses of the fly ash. The properties studied included chemical composition, and analyses of water soluble extracts. Knowledge of chemical composition was necessary to establish the nature of the material, while analyses of the water soluble extracts gave an indication of the leachable or extractable components of the ash.

To determine the optimum fly ash dose for phosphorus removal in distilled water, a series of batch experiments were conducted using a 1 gm/l concentration of fly ash and various phosphate concentrations. The experiments were operated under both static and dynamic conditions to study the effects of mixing on the phosphate removal rate. Static experiments were ultimately discontinued because their utility in actual treatment processes was determined to be quite low after initial experiments. The fly ash dose as well as the phosphate concentration was varied until an optimum doseage of fly ash could be determined for a given phosphorus concentration. Other chemical parameters including hardness and pH were also measured in the course of these experiments.

To determine the optimum fly ash dose for maximum phosphorus removal from secondary effluent, additional experiments were performed using secondary wastewater effluent. Fly ash doses used for these experiments were estimated from the data gathered in the previous experiments. In addition to phosphate analyses, BOD, COD, hardness and pH were also measured to monitor any changes.

A third series of experiments in which the suspended solids were removed from the effluent prior to the addition of fly ash was performed. These experiments were conducted to observe any differences between these results and the results obtained while using effluent containing suspended solids.

In one series of experiments, lime was added to the fly ash-secondary effluent mixtures. In these studies the appropriate dose of fly ash was determined from the first series of experiments and the original hardness of the secondary effluent was doubled and tripled by the addition of lime.

In all experiments the optimum dose of fly ash was defined as that amount of fly ash which would remove phosphate to the limit of detection of the stannous chloride ortho-phosphate test within 15 minutes using mixed conditions. The 15 minute time interval was used to provide maximum contact between the aqueous phosphate solution and the fly ash particles.

Analytical Methods

Experiments were conducted in glass gallon jars using a three liter volume in all cases with multiple serial sample withdrawals. This volume was used to minimize any concentration changes due to sample withdrawal. One liter volumes were used in experiments where repeated sampling did not take place. All experiments were run in duplicate.

In static experiments the fly ash was added to the solution and allowed to settle. Dynamic conditions were maintained by continuous stirring with magnetic stirrers. Samples were withdrawn by pipette at appropriate intervals and filtered. All glassware including filtration apparatus was acid washed. Samples were filtered through .45μm membrane filters.

The various phosphate concentrations used in phosphate removal determinations were made using reagent grade potassium phosphate (KH_2PO_4) and distilled water. Phosphate was measured using the stannous chloride method as described in <u>Standard Methods</u> (30). All samples were filtered using membrane filters and a Bausch and Lomb Spectronic 20 was used in the colormetric analyses.

Biochemical Oxygen Demand tests (BOD) and Chemical Oxygen Demand analyses were made according to the methods described in <u>Standard Methods</u> (30). Dissolved Oxygen determinations for the BOD test were made using the Azide Modification Method (30).

Total hardness determinations were initially done using the EDTA titrametric procedure (30). However, the Hach method was later used (31). Four separate analyses showed good agreement between the two methods. Calcium and magnesium hardness were determined using the EDTA titrametric method (30). Sulfates were also measured using the Hach Chemical Method (31).

Alkalinity determinations were made on unfiltered samples to avoid changes in dissolved gases which could be induced by filtration. The procedures described in <u>Standard Methods</u> for alkalinity were utilized. The pH was measured on filtered samples using a Beckman Expandomatic SS-2 pH meter.

CHAPTER IV

RESULTS

Experimental results presented in this chapter include the chemical properties of fly ash, the analyses of the water soluble extracts of fly ash, and the results obtained from the various phosphate removal studies conducted. The raw data collected from the experiments conducted can be found in the Appendix.

Chemical analyses were performed on three separate fly ash samples and the results of all analyses are presented in Table II as percent by weight. The pH of the three samples was found to be 11.2 in all cases. Table III gives chemical analyses data provided by the production plant from a different batch of fly ash than that which was used in these experiments. However, it is from the same source. These values should be similar, but not necessarily identical to expected values for the fly ash used in these experiments. Some of the values are comparable to those cited by Minnick (3) (Table I) from the analysis of 20 different fly ashes, and for comparison purposes, Minnick's values are presented again in Table III.

Data from the chemical analyses of the water soluble extracts of fly ash obtained under both static and dynamic conditions are shown in Figures 1 and 2. Figure 1 shows the concentration of total hardness leached from one gram of fly ash in one liter of distilled water under both static and mixed conditions in a nine hour period. Each sample was

TABLE II

RESULTS FROM ANALYSES OF THREE FLY ASH SAMPLES EXPRESSED AS PERCENT COMPOSITION BY WEIGHT

Constituent	Percent Composition		
	1	2	3
Fe	2.21	2.30	2.50
Zn	0.051	0.047	0.053
Mn	0.182	0.183	0.197
K	0.23	0.19	0.15
P	0.35	0.325	0.343
$CaCO_3$	42.8	41.9	40.6

TABLE III

CHEMICAL COMPOSITION OF CHEROKEE PLANT FLY ASH

	Minnick (3)	Cherokee Plant Fly Ash
Silica, SiO_2	34.01-49.53	31.5
Alumina, Al_2O_3	17.50-30.39	18.5
Iron Oxide, Fe_2O_3	6.62-26.43	7.0
Carbon, C	.56-18.18	
Calcium Oxide, CaO	.99- 9.68	28.0
Magnesium Oxide, MgO	.55- 1.63	4.82
Sulfur trioxide, SO_3	.23- 2.8	5.47
Sodium Oxide, Na_2O		1.47
Potassium Oxide, K_2O		.34
Apparent specific gravity	2.12- 2.69	3.57

Figure 1. Total Hardness in mg/l Leached From 1 gm/l of Fly Ash Under Static and Mixed Conditions.

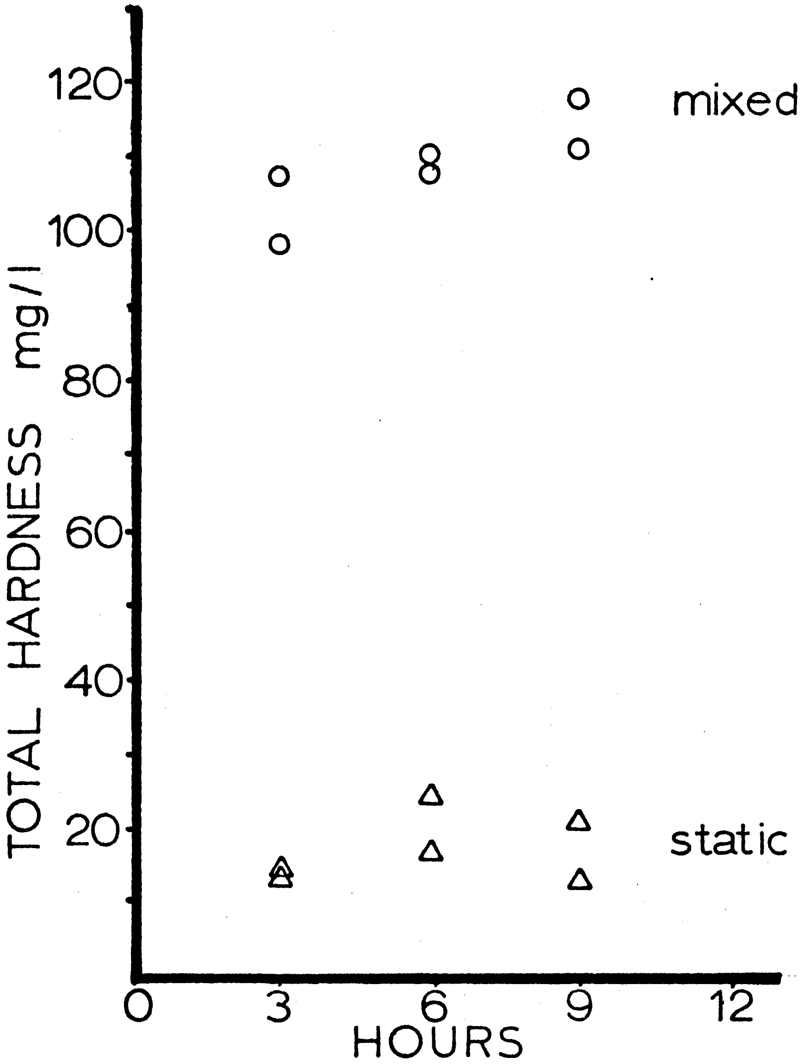
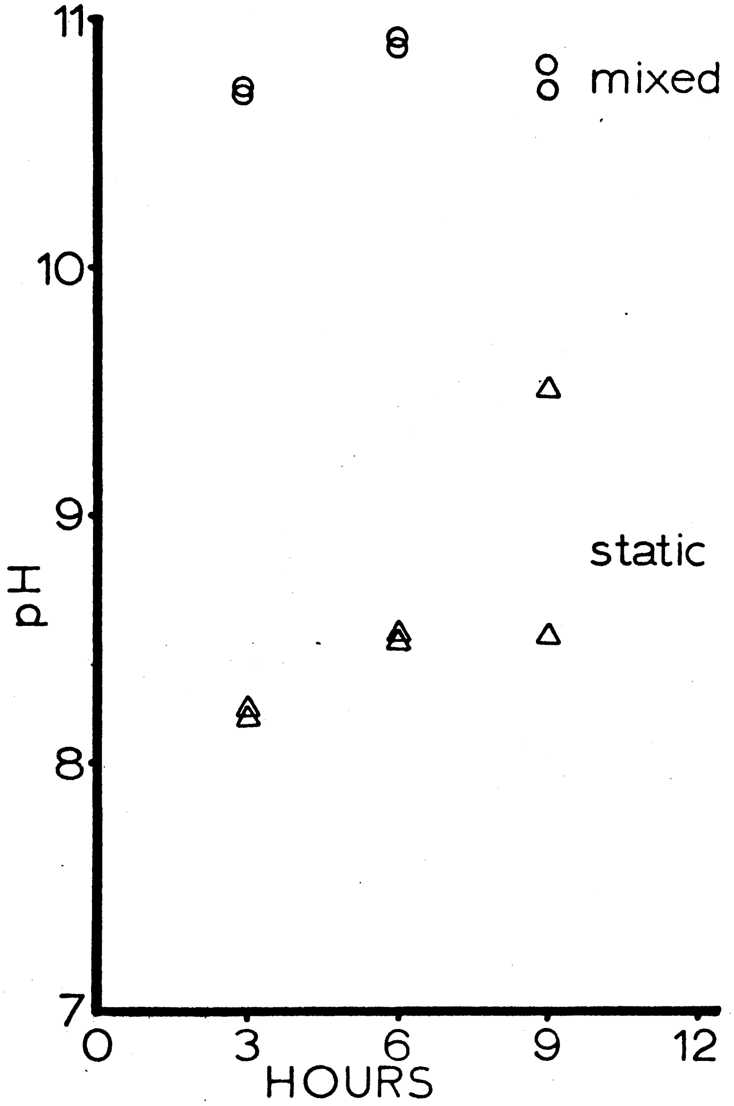

TOTAL HARDNESS mg/l
120
100
80
60
40
20
0
3
6
9
12
HOURS
mixed
static

Figure 2. Changes in pH Resulting From the Addition of Fly Ash to Distilled Water Using Static and Mixed Conditions.



11
10
9
8
7
pH
0
3
6
9
12
HOURS
mixed
static

done in duplicate. Figure 2 shows the resultant changes in pH accompanying the leaching process. Phosphate was analyzed for but not found in any of the soluble extracts.

Phosphorus uptake data obtained by the addition of one gram of fly ash to solutions containing various concentrations of phosphate under mixed and static conditions are shown in Figure 3. Phosphate concentrations in this experiment ranged from 5 mg/l to 50 mg/l.

From Figure 3, it appears that the majority of phosphorus uptake occurred within the first three hours. This time period was then used for additional phosphate uptake experiments in which percent phosphate removal by one gram/liter of fly ash during a three hour experimental period was determined using initial phosphate concentrations of 5-50 mg/l. The results of these experiments are shown in Figure 4.

In subsequent experiments both the phosphate concentration and the amount of fly ash were systematically varied. Static tests were discontinued because their utility as a treatment process was deemed quite low after the initial experiments. Fly ash dose was varied for a particular phosphate concentration until an optimum dose was determined. The optimum dose in these experiments was defined as the amount of fly ash which would reduce phosphate concentrations to undetectable levels. This actual result of zero phosphate remaining was not attained for all initial phosphate concentrations but an approximation of the correct dose of fly ash required for complete removal could be made by extrapolation of the data obtained. Figure 5 shows that two or more g/l of fly ash will completely remove an initial phosphate concentration of 5 mg/l in 1.5 hours.

Analyses for total hardness made in conjunction with phosphate

Figure 3. Phosphorus Uptake by Fly Ash Versus Time for Solutions Containing 5, 15, 20, 30 and 50 mg/l P as PO_4.

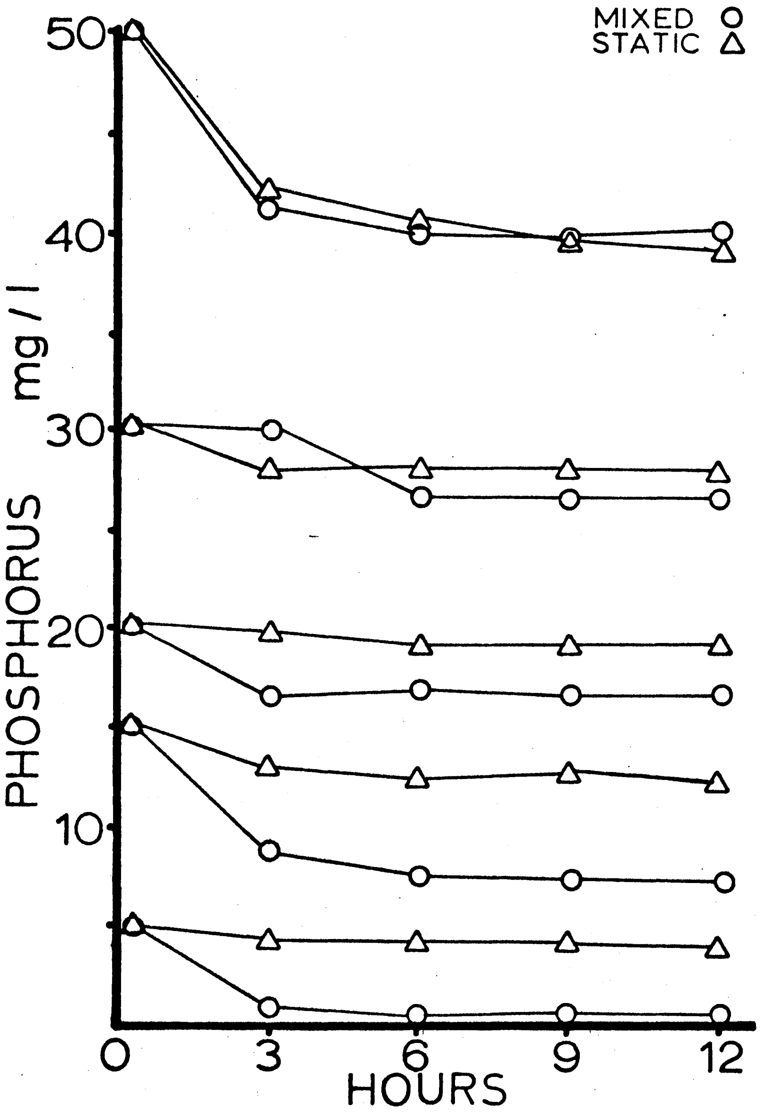

MIXED ○
STATIC △
50
40
30
20
10
0
3
6
9
12
PHOSPHORUS mg / l
HOURS

Figure 4. Percent Phosphorus Removed in Three Hours by 1 gm/l Fly Ash for Solutions Containing 5, 15, 20, 30 and 50 mg/l P as PO_4.

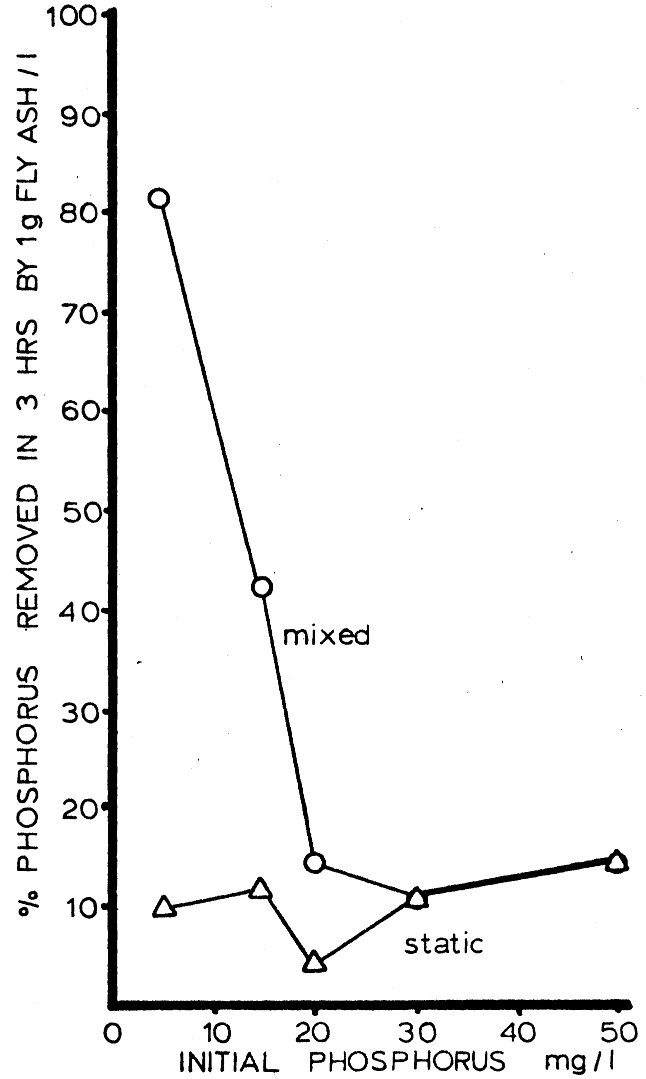
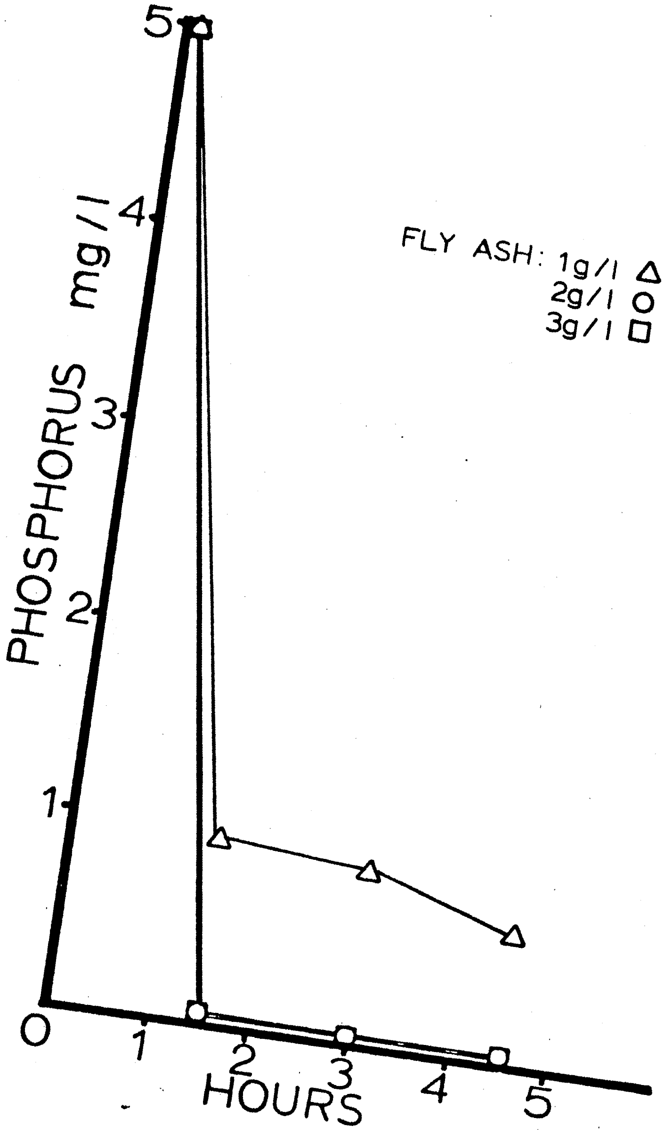

% PHOSPHORUS REMOVED IN 3 HRS BY 1g FLY ASH / l
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
INITIAL PHOSPHORUS mg / l
mixed
static

Figure 5. Phosphorus Removal Versus Time Using 1, 2 and 3 gm/l Fly Ash. Initial Phosphorus Concentration of 5 mg/l P as PO_4.


PHOSPHORUS mg/l
0
1
2
3
4
5
HOURS
FLY ASH: 1g/l △
2g/l ○
3g/l □

removal determinations are shown in Figure 6. Numbers adjacent to data points are indicative of pH values.

To determine immediate uptake in a 5 mg/l phosphate solution, the fly ash dose was increased to 3, 5, and 7 g/l. Measurements were taken immediately (less than 5 minutes) and at 0.5 and 1.5 hour intervals. The data obtained from these analyses are presented in Figure 7. Numbers adjacent to data points indicate pH. A fly ash dose of 3 g/l was adequate for immediate removal of nearly 90% of the phosphate from a 5 mg/l solution and for complete removal in 1.5 hours. Figure 8 shows the variations in hardness observed in these experiments.

Phosphate removal and pH and hardness in solutions having phosphate concentrations of 10 mg/l and fly ash doses of 3, 5, and 7 g/l are shown in Figures 9 and 10 respectively. Concentrations of fly ash between 5 and 7 g/l are adequate for virtually complete phosphate removal within 0.5 hours. Phosphate removal and hardness and pH in solutions having an initial phosphate concentration of 20 mg/l and fly ash concentrations of 7, 10, and 15 g/l are shown in Figures 11 and 12. Total immediate removal of phosphate was obtained using fly ash concentrations in the range of 10-15 mg/l.

A comparison of phosphate removal by fly ash in distilled water solutions of phosphate and in wastewater effluent was done using phosphate concentrations of 8.6 mg/l and 5.6 mg/l in the distilled water solutions. These concentrations were equivalent to those present in the actual secondary effluent. Results of the experiments using phosphate concentrations of 8.6 mg/l in distilled water are shown in Figures 13 and 14. Figure 13 represents phosphate removal whereas Figure 14 indicates the results of concurrent hardness and pH

Figure 6. Increases in Total Hardness and pH Versus Time for 1, 2 and 3 g/l Fly Ash and 5 mg/l P as PO_4.

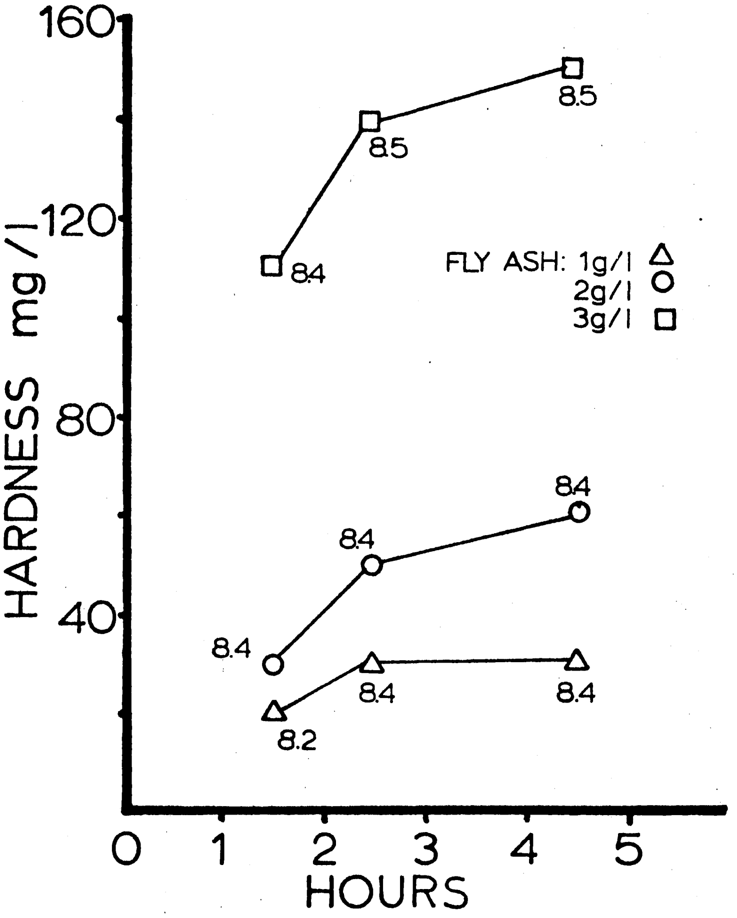

160
120
80
40
HARDNESS mg/l
0
1
2
3
4
5
HOURS
FLY ASH: 1g/l △
2g/l ○
3g/l □
8.4
8.5
8.5
8.4
8.4
8.4
8.4
8.4
8.4
8.2

Figure 7. Removal of 5 mg/l P as PO_4 by 3, 5 and 7 g/l Fly Ash Versus Time.

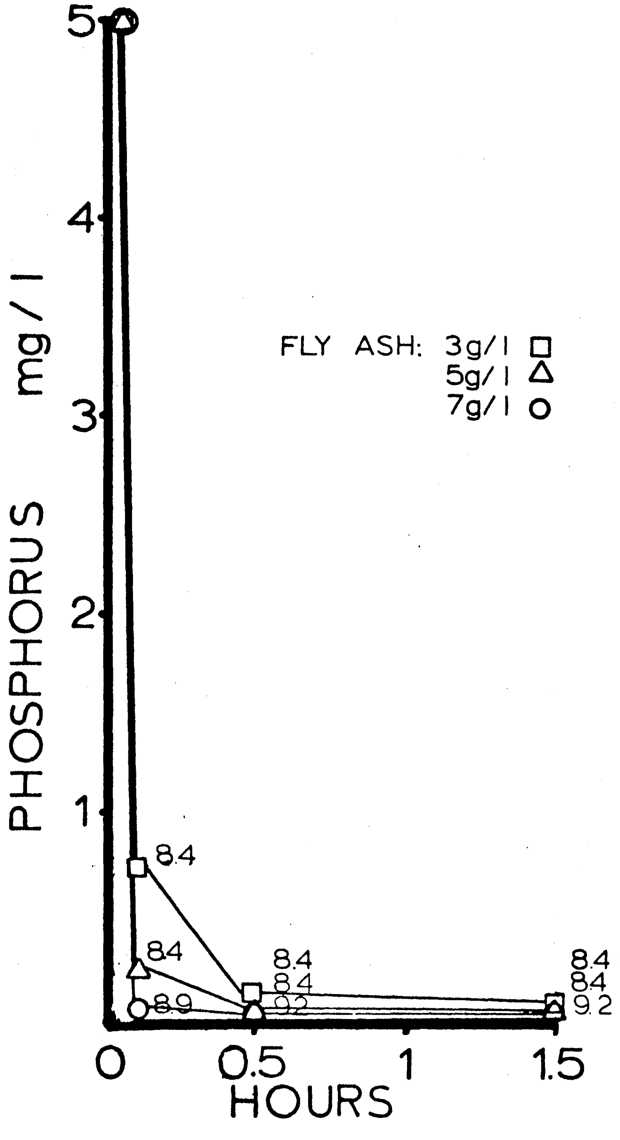

PHOSPHORUS mg / l
5
4
3
2
1
0
0.5
1
1.5
HOURS
FLY ASH: 3g/l □
5g/l △
7g/l ○
8.4
8.4
8.9
8.4
8.4
9.2
8.4
8.4
9.2

Figure 8. Variations in Total Hardness Accompanying the Removal of 5 mg/l P as PO_4 by 3, 5 and 7 g/l Fly Ash.

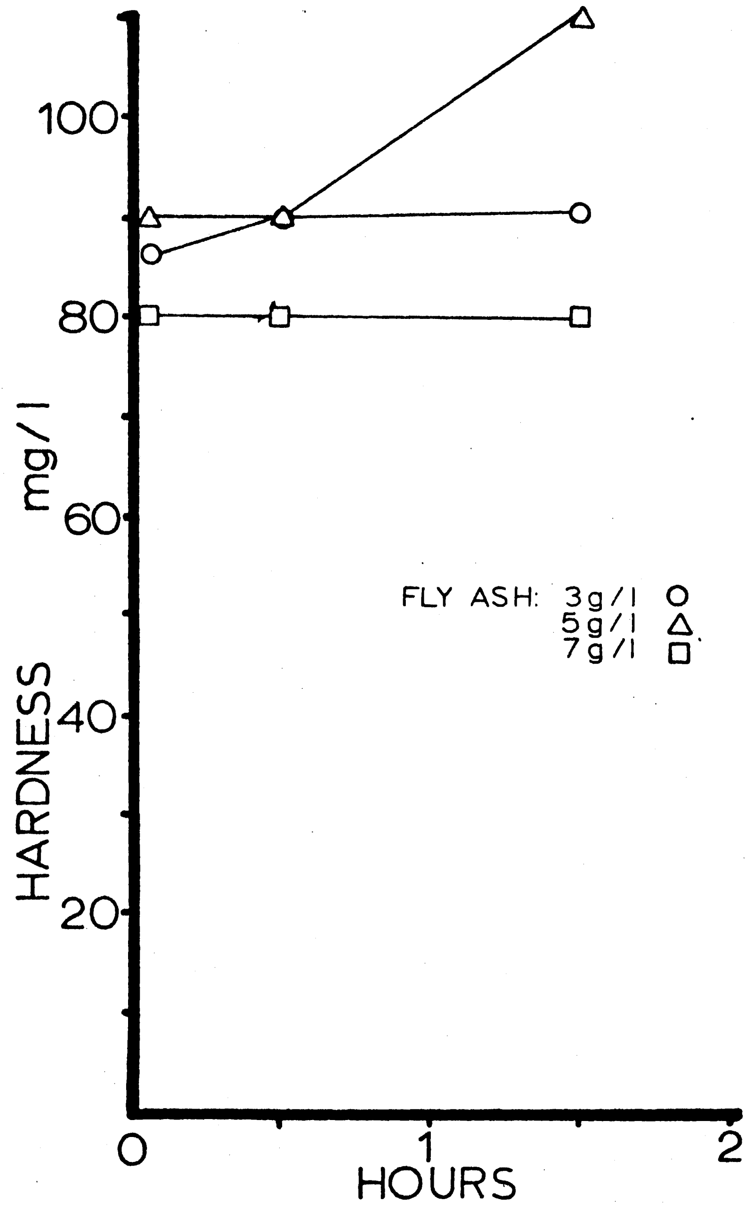
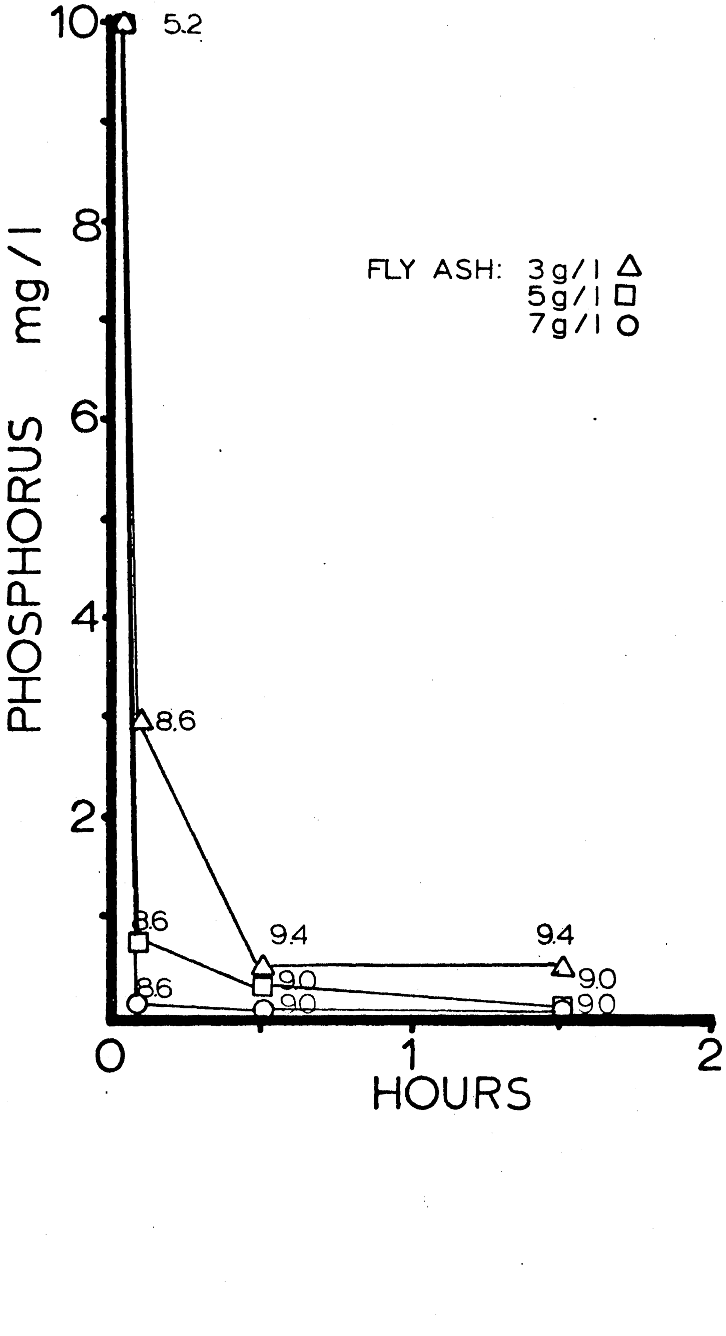

HARDNESS mg/l
100
80
60
40
20
0
1
2
HOURS
FLY ASH: 3g/l ○
5g/l △
7g/l □

Figure 9. Removal of 10 mg/l P as PO_4 by 3, 5 and 7 g/l of Fly Ash Versus Time.



PHOSPHORUS mg/l
10
8
6
4
2
0
1
2
HOURS
FLY ASH: 3g/l △
5g/l □
7g/l ○
5.2
8.6
8.6
8.6
9.4
9.0
9.0
9.4
9.0
9.0

Figure 10. Variations in Total Hardness Accompanying the Removal of 10 mg/l P as PO_4 by 3, 5 and 7 g/l Fly Ash.

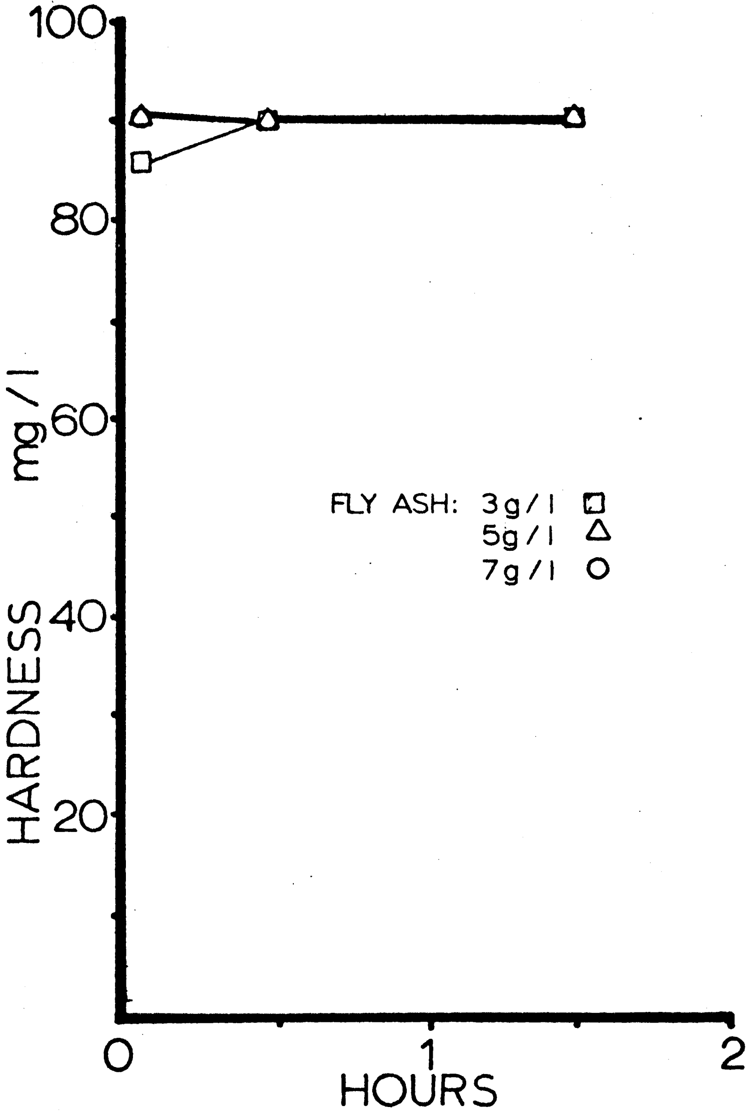

100
80
60
40
20
HARDNESS mg/l
0
1
2
HOURS
FLY ASH: 3g/l □
5g/l △
7g/l ○

Figure 11. Removal of 20 mg/l P as PO_4 by 7, 10 and 15 g/l Fly Ash Versus Time.

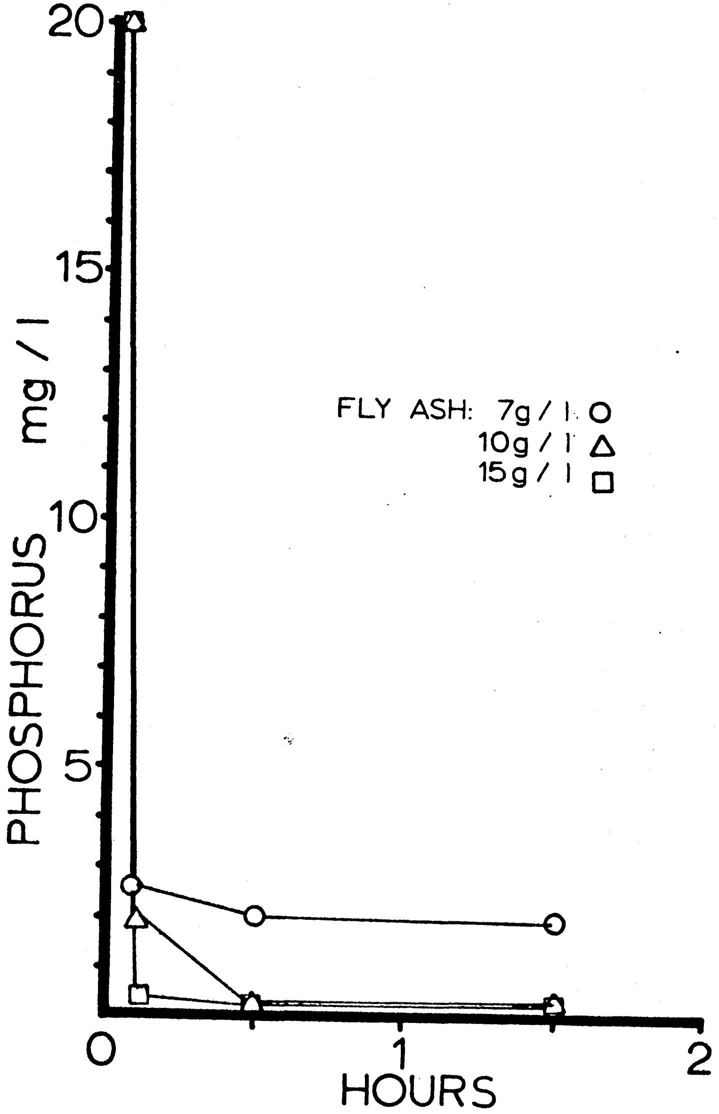

20
15
10
5
0
1
2
HOURS
PHOSPHORUS mg / l
FLY ASH: 7g / l ○
10g / l △
15g / l □

Figure 12. Variations in Total Hardness and pH Accompanying the Removal of 20 mg/l P as PO_4 by 7, 10 and 15 g/l Fly Ash.

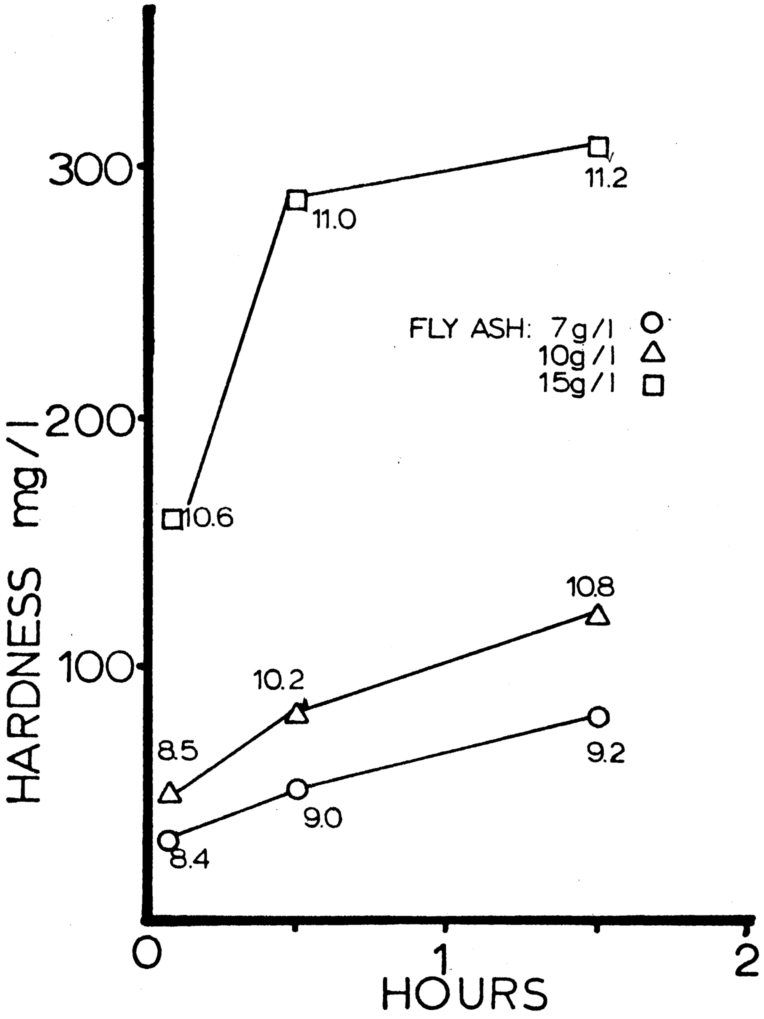

300
200
100
0
1
2
HARDNESS mg/l
HOURS
FLY ASH: 7g/l ○
10g/l △
15g/l □
11.2
11.0
10.6
10.8
10.2
8.5
9.2
9.0
8.4

Figure 13. Percent Phosphorus Removed From a Distilled Water Solution Containing 8.6 mg/l P as PO_4 by 7 and 10 g/l Fly Ash Plotted Versus Time.

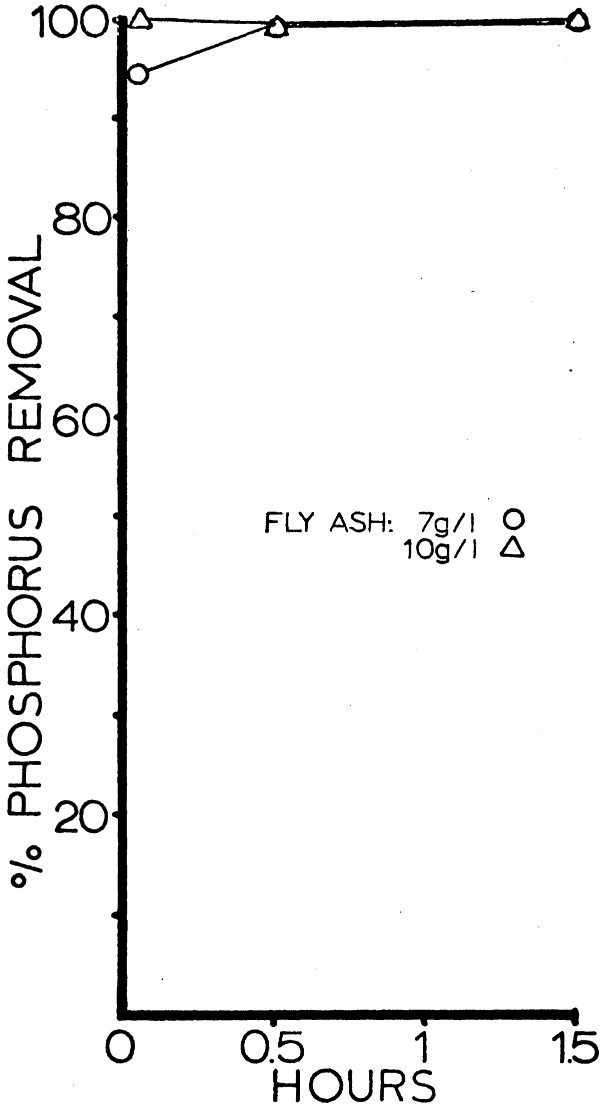
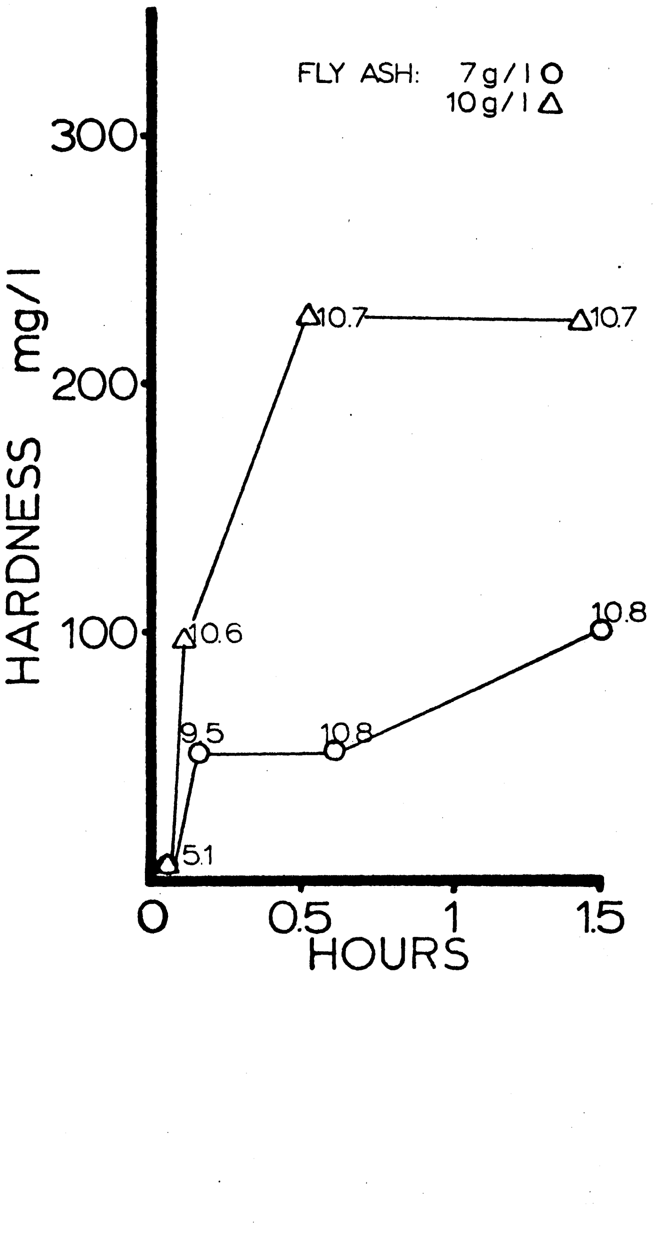

100
80
60
40
20
% PHOSPHORUS REMOVAL
0
0.5
1
1.5
HOURS
FLY ASH: 7g/l ○
10g/l △

Figure 14. Variations in Total Hardness and pH Accompanying the Removal of 8.6 mg/l P as PO_4 by 7 and 10 g/l Fly Ash.


FLY ASH: 7g/l ○
10g/l △
HARDNESS mg/l
300
200
100
10.7
10.7
10.6
10.8
9.5
10.8
5.1
0
0.5
1
1.5
HOURS

determinations. The numbers adjacent to the data points represent the pH values obtained. Results of phosphate removal by fly ash from actual wastewater effluent are shown in Figure 15 with the data from the corresponding hardness and pH analyses being presented in Figure 16. It can be seen from Figure 13 that 10 g/l of fly ash was sufficient to immediately remove nearly 100% of the phosphorus present in distilled water solutions. However the same amount of fly ash (10 g/l) was only capable of removing 42% of the initial phosphate concentration from actual effluent. In the distilled water solutions there was no hardness initially present (Figure 14) while the actual effluent had an initial hardness value of 175 mg/l (Figure 16). The pH of the distilled water solution was initially 5.1 (Figure 14) while the actual effluent had a pH of 7.6 (Figure 15). Hardness increased with an increasing fly ash dose in the distilled water solutions, (Figure 14) but was unchanged in the actual effluent, (Figure 16). The pH did not change significantly after the first measurement in either the effluent or distilled water solution.

In addition to phosphate analyses, BOD and COD removal were determined for the wastewater effluent containing 8.6 mg/l phosphate. Figure 17 is indicative of BOD removal by fly ash whereas Figure 18 shows the changes in the concentration of COD over the course of the experiment. Figure 17 shows that approximately 50% of the BOD was removed from the secondary effluent by both the 7 g/l and the 10 g/l fly ash doses after a 1.5 hour contact period. Figure 18 shows that less than 10% of the initial COD present in the actual effluent was removed by either the 7 or the 10 g/l dose of fly ash.

Results of the experiments involving phosphate removal, hardness

Figure 15. Percent Phosphorus Removed From Secondary Wastewater Effluent Containing 8.6 mg/l P as PO_4 by 7 and 10 g/l Fly Ash Plotted Versus Time.

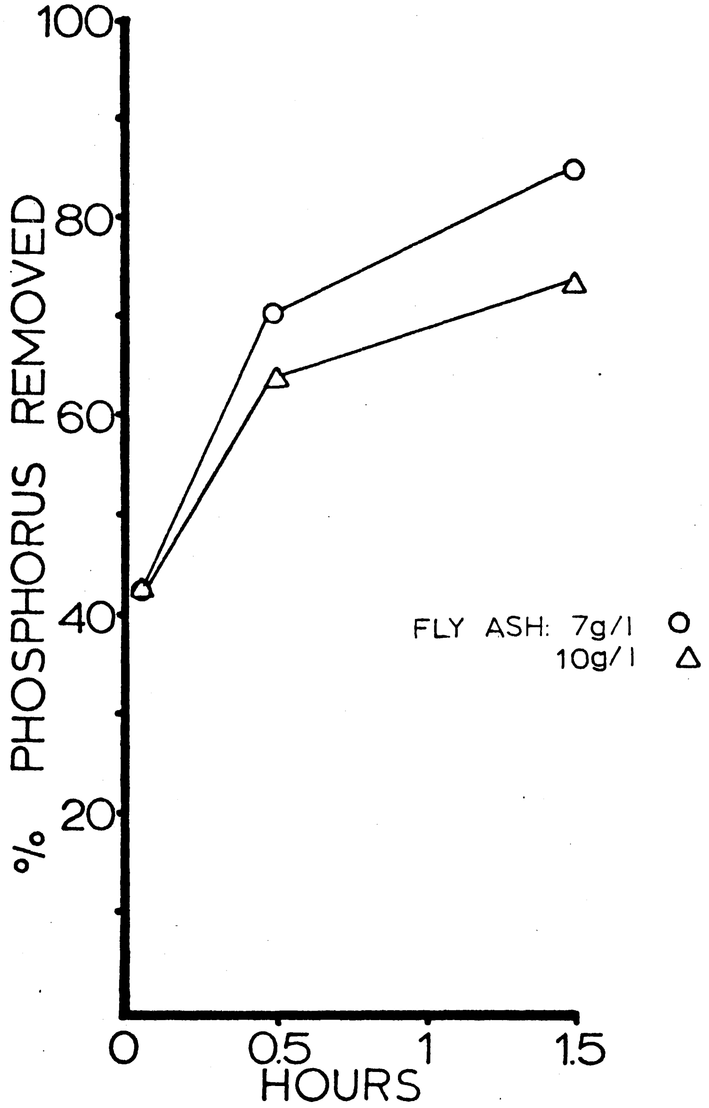

100
80
60
40
20
% PHOSPHORUS REMOVED
0
0.5
1
1.5
HOURS
FLY ASH: 7g/l ○
10g/l △

Figure 16. Changes in Total Hardness Resulting From Phosphorus Removal by Fly Ash From Secondary Effluent Containing 8.6 mg/l P as PO_4

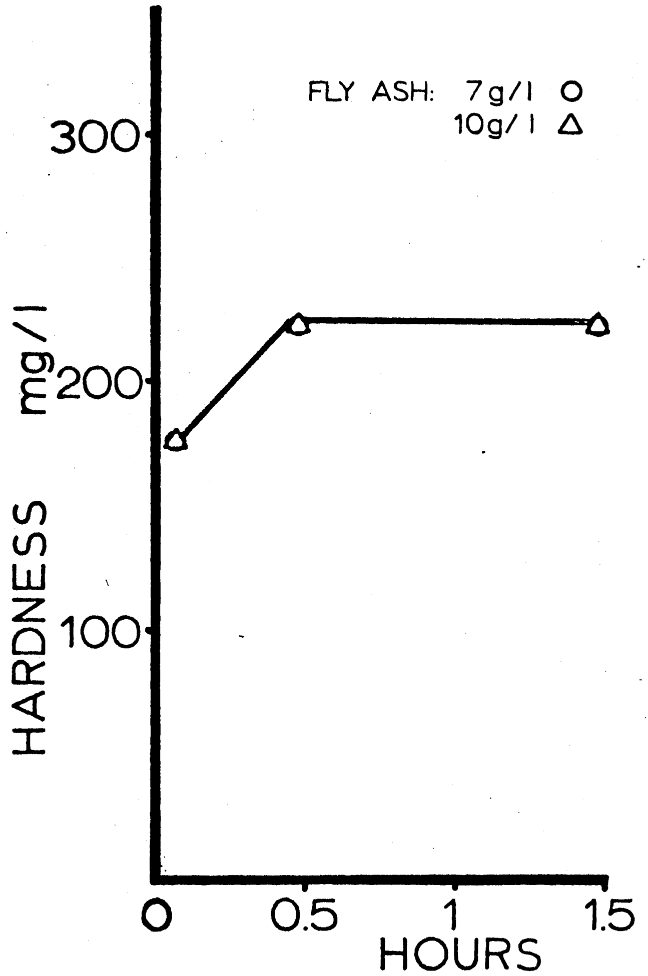

FLY ASH: 7g/l ○
10g/l △
HARDNESS mg/l
300
200
100
0
0.5
1
1.5
HOURS

Figure 17. Percent BOD Removed From Secondary Effluent Containing 8.6 mg/l P as PO_4 by 7 and 10 g/l Fly Ash Plotted Versus Time. The Initial BOD of the Effluent was 28.5 mg/l.

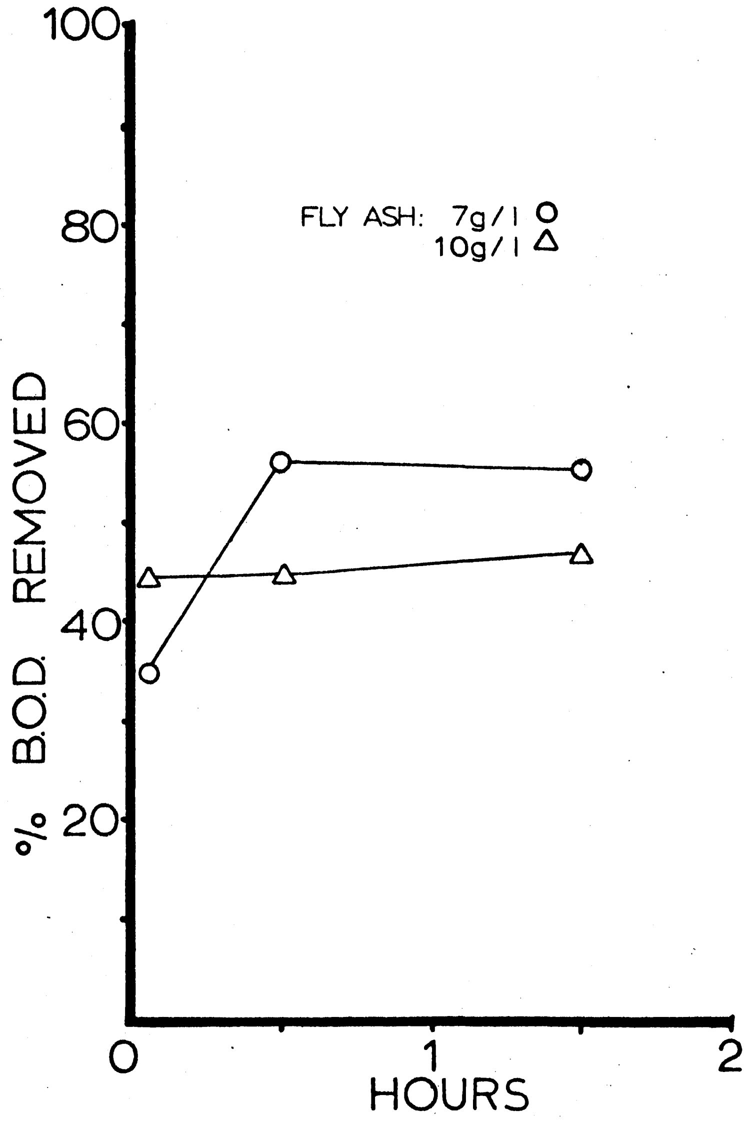
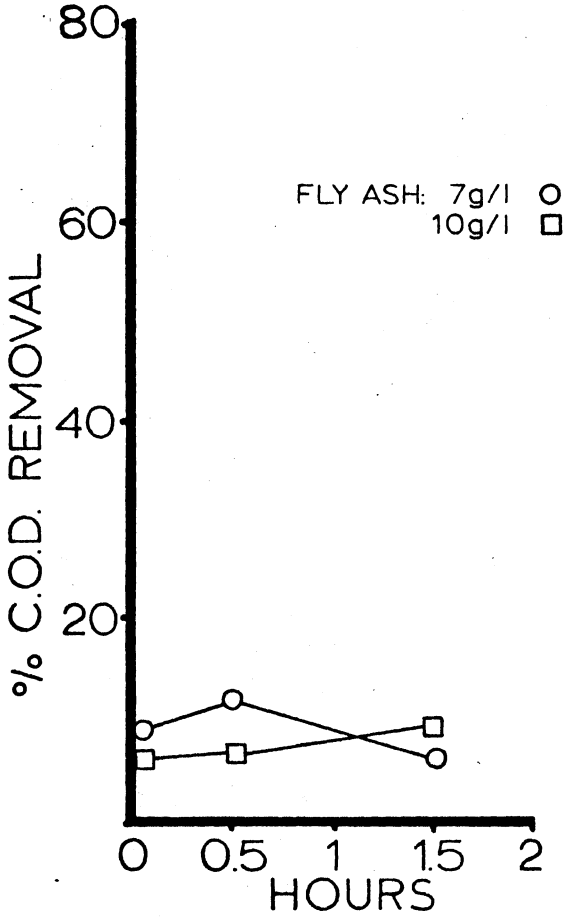

100
80
60
40
20
% B.O.D. REMOVED
0
1
2
HOURS
FLY ASH: 7g/l ○
10g/l △

Figure 18. Percent COD Removed From Secondary Effluent Containing 8.6 mg/l P as PO_4 by 7 and 10 g/l Fly Ash Plotted Versus Time. The Initial COD of the Effluent was 188 mg/l.


80
60
40
20
% C.O.D. REMOVAL
0
0.5
1
1.5
2
HOURS
FLY ASH: 7g/l ○
10g/l □

determination and COD removal from wastewater effluent having a phosphate concentration of 5.6 mg/l are shown in Figures 19, 20, and 21 respectively. Figures 19 and 20 are most appropriately compared to Figures 22 and 23 which contain the data collected from phosphate removal and hardness determinations from a distilled water solution containing 5 mg/l phosphate. These are identical to Figures 7 and 8 but are presented again to facilitate comparison. For a 98% immediate removal of phosphorus in actual effluent, 25 grams per liter of fly ash was necessary (Figure 19), while approximately the same degree of removal was accomplished with only 5 g/l of fly ash in the distilled water solutions (Figure 22). Figure 23 shows that the hardness of the effluent was initially 180 mg/l and immediately increased to a maximum of 250 mg/l upon addition of fly ash for all doses of fly ash. The final amount of hardness was not dependent upon fly ash dose. The pH of the effluent was initially 7.3 and upon addition of fly ash increased to a maximum of 9.0. The final pH was also not dependent on the fly ash dose. Immediate COD removal (Figure 21) was similar for all fly ash doses tested but after 1.5 hours contact time, the largest fly ash dose (25 gm/l) had removed approximately 33% of the initial 60 mg/l COD.

The effect of suspended solids on phosphate removal by fly ash is shown in Figure 24. The results presented were collected from an experiment in which 10 g/l of fly ash were added to sewage effluent containing 4.1 mg/l phosphate and suspended solids and to the same effluent from which the suspended solids had been removed.

Phosphate removal from actual effluent was also examined using lime and various mixtures of lime and fly ash to determine the effect of the increased calcium concentration on the phosphate removal

Figure 19. Percent Phosphorus Removed by 15, 20 and 25 g/l Fly Ash From Secondary Effluent Containing 5.6 mg/l P as PO_4 Plotted Versus Time.

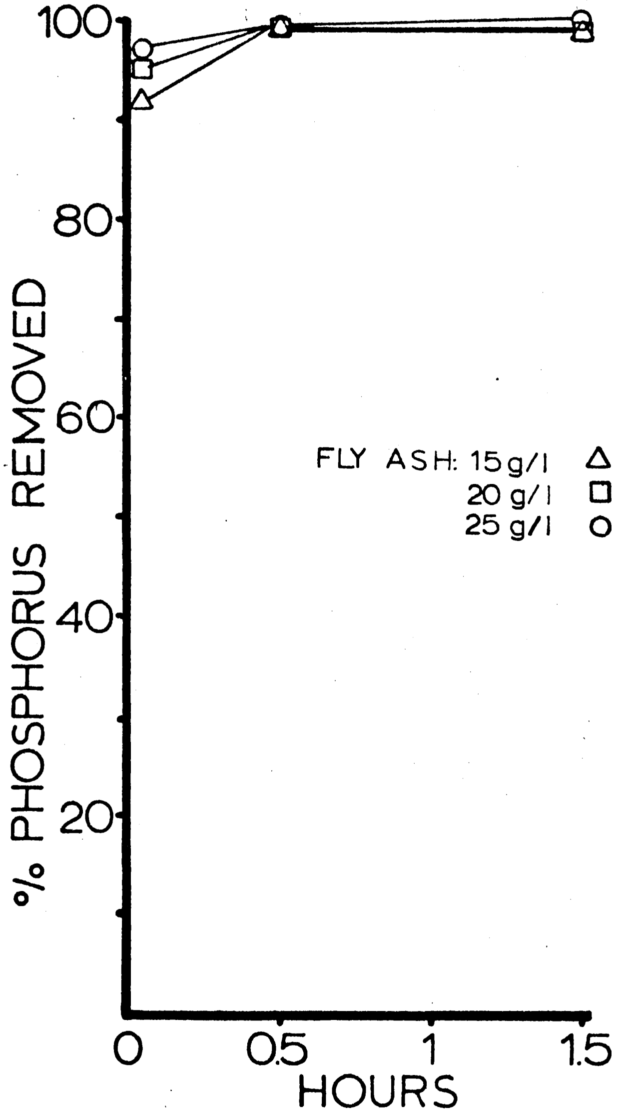

100
80
60
40
20
% PHOSPHORUS REMOVED
0
0.5
1
1.5
HOURS
FLY ASH: 15 g/l △
20 g/l □
25 g/l ○

Figure 20. Changes in Total Hardness Resulting From Phosphorus Removal by Fly Ash From Secondary Effluent Containing 5.6 mg/l P as PO_4.

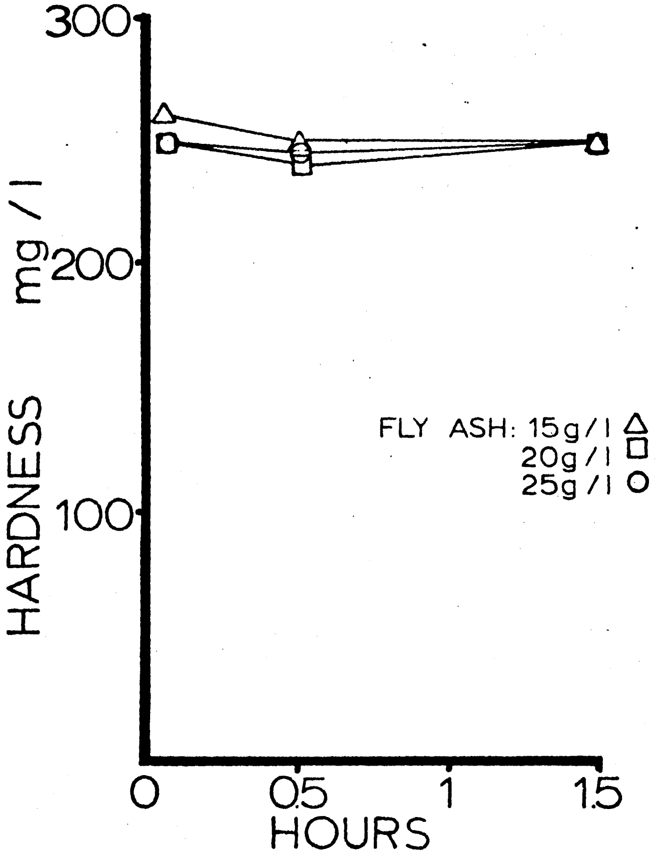

300
200
100
HARDNESS mg / l
0
0.5
1
1.5
HOURS
FLY ASH: 15g / l △
20g / l □
25g / l ○

Figure 21. Variations in Soluble COD Accompanying Phosphorus Removal by Fly Ash From Secondary Effluent Containing 5.6 mg/l P as PO_4. The Initial COD of the Effluent is 60 mg/l.

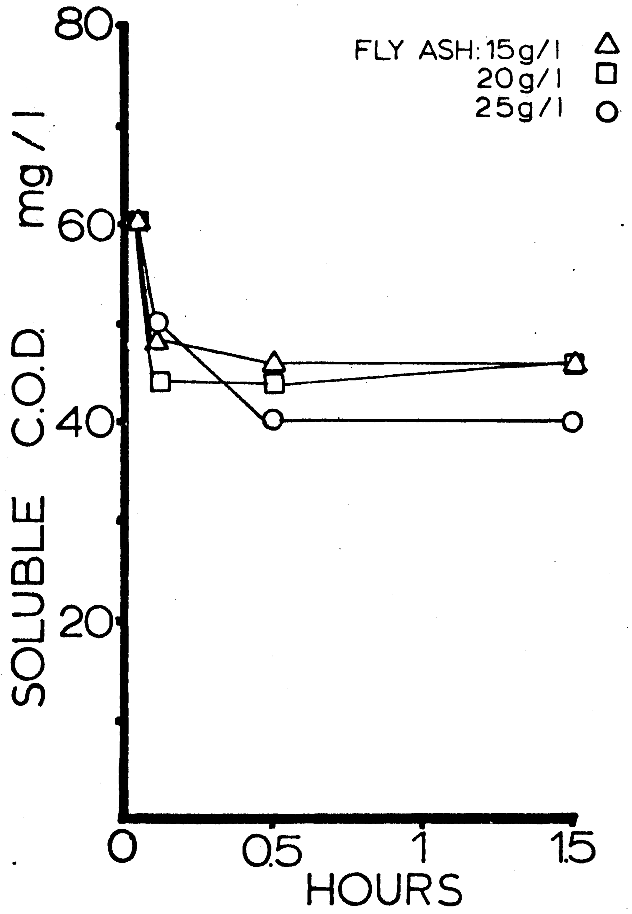
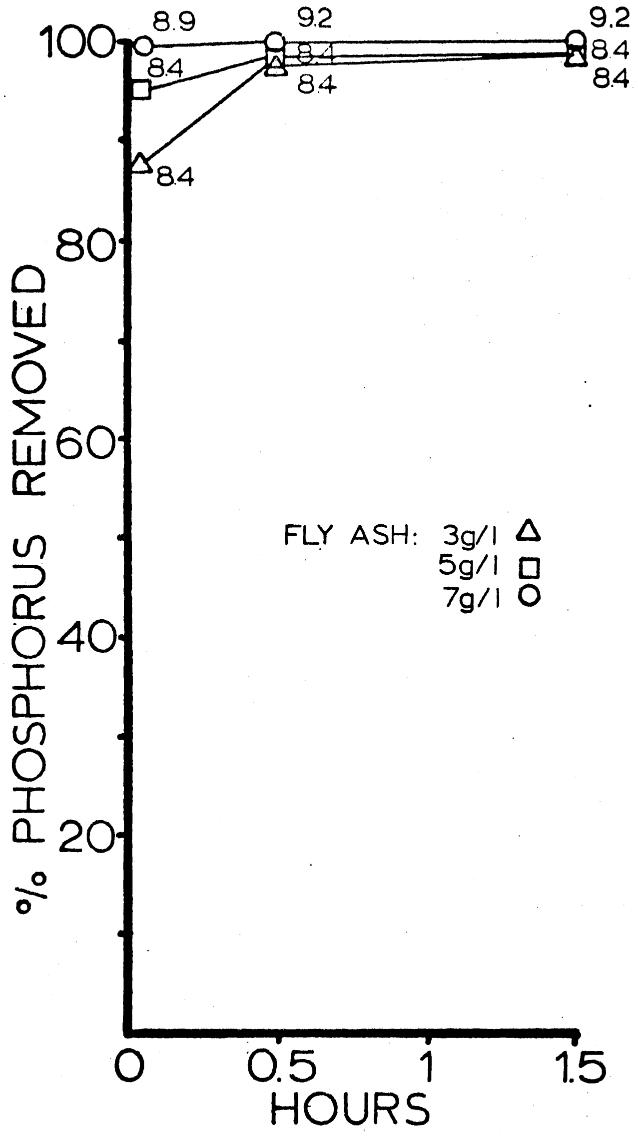

FLY ASH: 15g/l △
20g/l □
25g/l ○
SOLUBLE C.O.D. mg/l
80
60
40
20
0
0.5
1
1.5
HOURS

Figure 22. Percent Phosphorus Removed by 3, 5 and 7 g/l Fly Ash From a Distilled Water Solution Containing 5 mg/l P as PO_4 Plotted Versus Time.



% PHOSPHORUS REMOVED
100
80
60
40
20
0
0.5
1
1.5
HOURS
8.9
9.2
9.2
8.4
8.4
8.4
8.4
8.4
8.4
FLY ASH: 3g/l △
5g/l □
7g/l ○

Figure 23. Changes in Total Hardness Accompanying Phosphorus Removal by Fly Ash From a Distilled Water Solution Containing 5 mg/l P as PO_4.

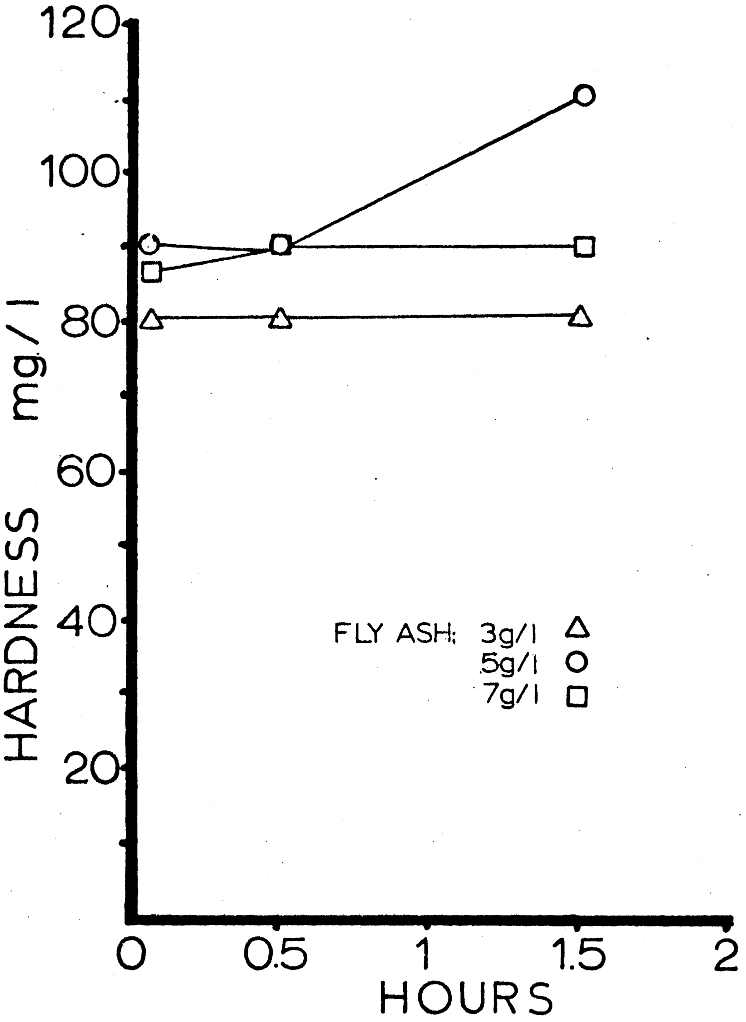
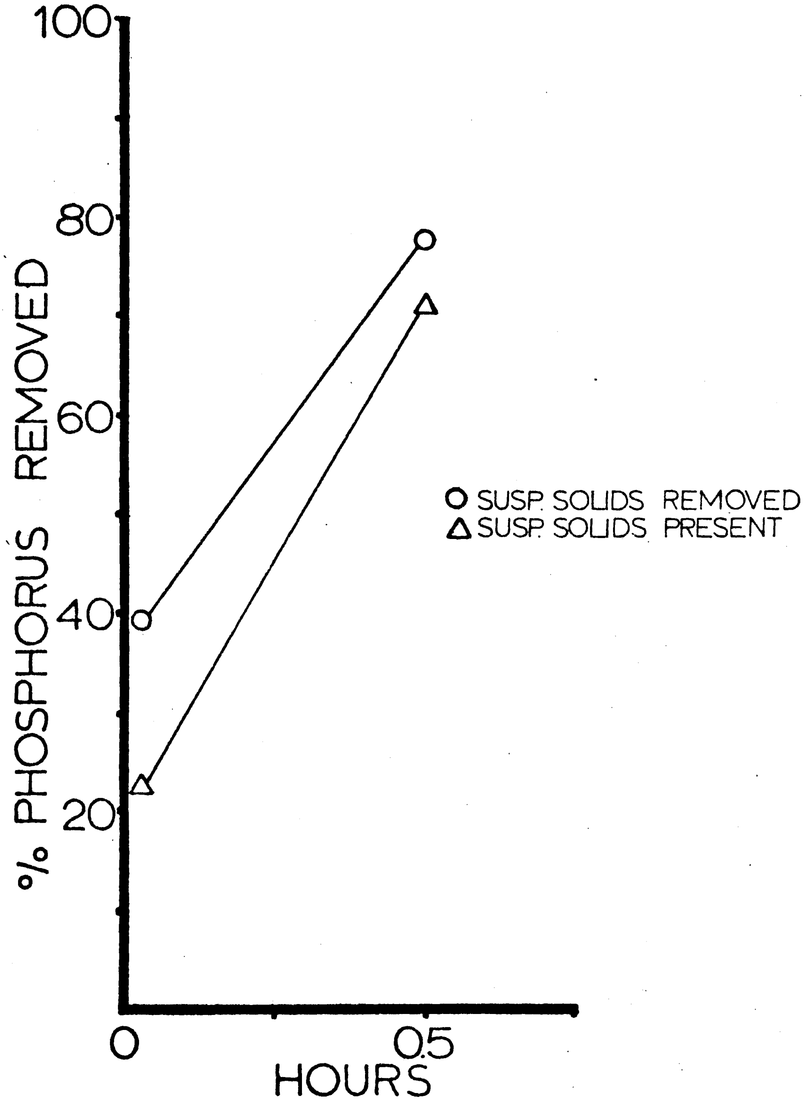

120
100
80
60
40
20
HARDNESS mg/l
0
0.5
1
1.5
2
HOURS
FLY ASH: 3g/l △
5g/l ○
7g/l □

Figure 24. The Effect of Suspended Solids on Phosphorus Removal by Fly Ash. Percent Phosphorus Removed Versus Time. 10 g of Fly Ash Per Liter Was Used.


100
80
60
40
20
% PHOSPHORUS REMOVED
0
0.5
HOURS
○ SUSP. SOLIDS REMOVED
△ SUSP. SOLIDS PRESENT

efficiency. Secondary effluent containing an initial phosphate concentration of 5.8 mg/l was subjected to three treatments which were as follows: (1) 10 g/l of fly ash, (2) 180 mg/l lime plus fly ash, (3) 360 mg/l lime plus fly ash. Two lime doses were used alone as a control for the experiment and these were 180 mg/l lime and 360 mg/l lime. Analyses for phosphate were made immediately and 0.5 hours after the addition of the fly ash, lime, or fly ash/lime mixture. The results obtained from this series of experiments are presented in Figure 25. Lime when added with the fly ash produced an acceleration of phosphorus uptake as shown by the higher values for immediate removal (Figure 25). However, after 0.5 hours effluent with fly ash only reached the same level of phosphate removal as the lime-fly ash mixtures.

Adsorption isotherms from this research are shown in Figure 26. Phosphate removed per gram of fly ash added for three different concentrations of phosphate (5, 10, and 20 mg/l) is plotted versus the equilibrium concentration of phosphate at 1.5 hours.

Figure 25. Percent Phosphorus as Phosphate Removed Versus Time by Fly Ash, Lime and Fly Ash-Lime Mixtures. 10 g/l Fly Ash Used Alone and in Fly Ash-Lime Mixture.

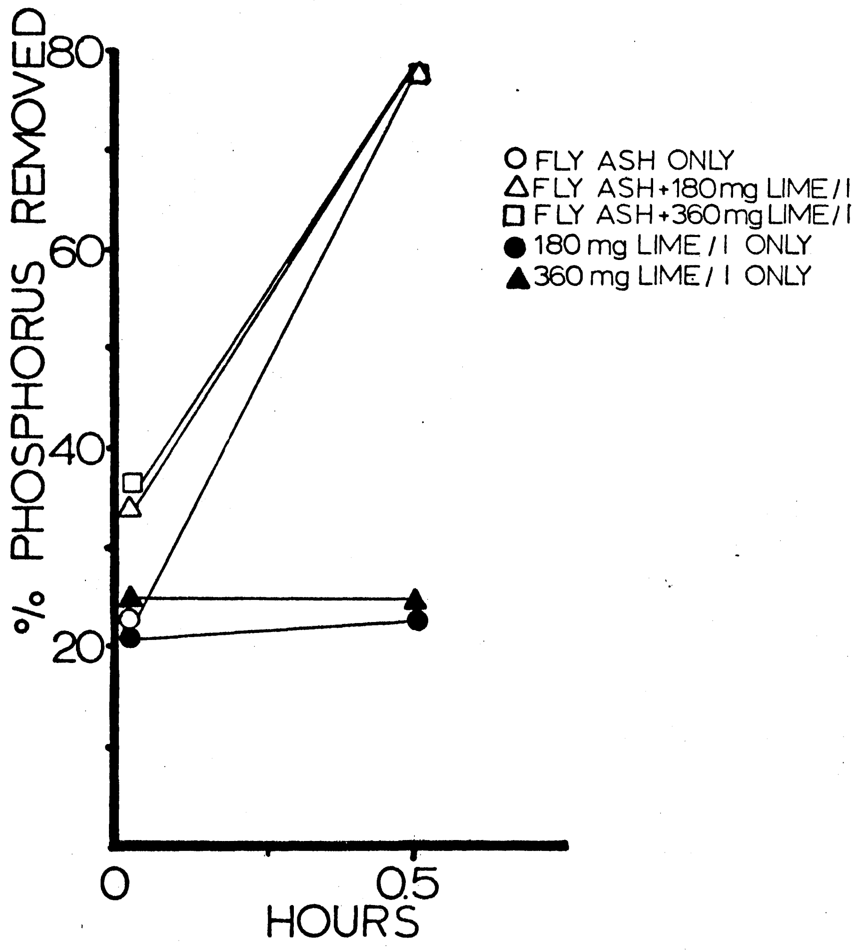
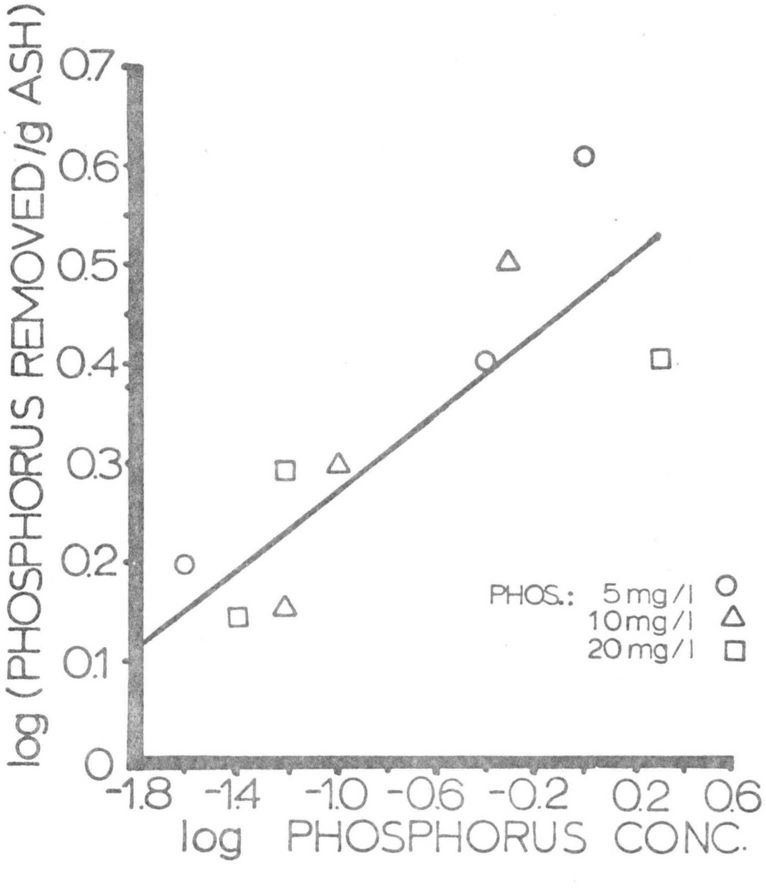

% PHOSPHORUS REMOVED
80
60
40
20
0
0.5
HOURS
○ FLY ASH ONLY
△ FLY ASH+180mg LIME/l
□ FLY ASH+360mg LIME/l
● 180 mg LIME/l ONLY
▲ 360 mg LIME/l ONLY

Figure 26. Adsorption Isotherm: Log Phosphorus Removal/g Fly Ash Versus Log Phosphorus Concentration. The Line Drawn is a Least Squares Linear Regression. $Y = .21X+.49$, $r^2 = .70$.


log (PHOSPHORUS REMOVED/g ASH)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-1.8
-1.4
-1.0
-0.6
-0.2
0.2
0.6
log PHOSPHORUS CONC.
PHOS.: 5 mg/l ○
10 mg/l △
20 mg/l □

CHAPTER V

DISCUSSION

The most important chemical constituent of fly ash with respect to phosphorus removal is calcium. The calcium content of the three fly ash samples analyzed in this experimental work ranged from 16.24% by weight to 17.12% by weight. This was comparable to the 20% by weight calcium content reported by the production plant on a different batch of fly ash that was, however, obtained from the same source. None of these values are comparable to the range of 0.72% to 6.91% by weight which was obtained by Minnick in his analyses of 20 different fly ash samples. However this difference in calcium content could be expected. Minnick in his analyses utilized eastern fly ash whereas the fly ash used in this research was obtained from a western state. Previous researchers have found that fly ash generated in the western part of the United States has a much higher calcium content than fly ash generated in the eastern part of the United States (32) and this research supports that finding.

If the chemical precipitation of phosphorus with calcium is going to occur in solution rather than at the ash particle surface, then the leachable or water soluble calcium content of the fly ash becomes significant. Figure 1 shows the total hardness expressed as calcium carbonate that was leached from a 1 gm solution of fly ash in distilled water over a nine hour experimental period under both static and mixed conditions. Total hardness was equal to calcium hardness in that no magnesium hardness was found when analyzed. The maximum amount of calcium leached under mixed conditions was 4.87% by weight (121.8 mg/l as $CaCO_3$) and under static conditions the maximum for a nine hour period was 0.8% by weight (20.8 mg/l as $CaCO_3$). It is obvious that by providing for more surface area contact of the ash with the leaching solution through mixing, greater amounts of calcium become water soluble. This data also shows that only a small percentage of the total calcium content of the fly ash is water soluble under the conditions utilized in this experimental work. It should therefore be noted that the total calcium content of fly ash which is usually the number reported for fly ash composition is not indicative of the amount that is available for phosphate precipitation in solution.

pH, in addition to total hardness is increased through the addition of fly ash to aqueous solutions. The maximum pH obtained in the mixed systems was 10.8 whereas the maximum pH obtained in the static systems was 9.5.

Several experiments using various concentrations of phosphorus were conducted to determine the amount of phosphate removal that could be achieved by 1 gm of fly ash. Initial data shown in Figure 3 indicated that the maximum removal occurred within three hours of the twelve hour experimental period. A three hour time period was then used to determine phosphate removal by 1 gm/l fly ash in aqueous solutions of phosphate ranging in concentration from 5-50 mg/l (Figure 4). As the phosphate concentration increased above 30 mg/l, there was a rapid decline in the percent removal achieved by 1 gm of fly ash in the mixed systems. Static conditions showed less consistent results possibly because fly ash was added and allowed to settle through the solution, and removal of phosphate could be dependent on how the fly ash particles settled. At phosphate concentrations of 30-50 mg/l, the amount of phosphate removed by 1 gm/l of fly ash was the same in both mixed and unmixed systems.

Phosphate removal from distilled water by fly ash appears to occur immediately upon the addition of the fly ash to a mixed system (Figures 7, 9 and 11). This phenomena of immediate removal is of value if fly ash is to be used as a tertiary treatment process for phosphate removal in that mixing and/or contact time can be kept at a minimum.

The data presented in Figure 25 were collected from a series of experiments designed to compare phosphate removal by fly ash with phosphate removal by lime and mixtures of lime and fly ash. It was thought that if chemical precipitation was the mechanism, an increase in the calcium content would increase phosphate removal. Adding lime concurrently with fly ash increased immediate phosphate removal but total removal at the end of a 0.5 hour period was identical for fly ash and the two lime-fly ash mixtures used.

Adsorption isotherms drawn from data collected in this research, Figure 26, suggest that adsorption may be taking place. The behavior of the solutions was consistent with reported values for phosphorus adsorption. The scatter observed on the graph is probably the result of the short time interval chosen, 1.5 hours. This time interval was probably not long enough for complete adsorption equilibrium to be established, in some cases, but these data are consistent and representative of the process taking place. The 1.5 hour time constraint is the result of trying to keep most of the experiments within a time interval which might be appropriate for the actual operation of a treatment plant. After some consideration 1.5 hours was chosen as an upper limit for contact time in an operational plant.

The results of this research with respect to phosphate removal from secondary effluent by fly ash show that fly ash can be used successfully as a phosphorus removal technique although the doses of fly ash required for phosphate removal from effluent are considerably higher than for comparable removal from distilled water solutions of phosphate. The higher dose is possibly necessitated by the many other interactions, such as competition for adsorption sites, that may take place between the fly ash and dissolved and suspended matter contained within the effluent. In an application of adsorption processes to sewage treatment, Weber (28) reported that adsorbent mixtures containing many compounds may increase the total adsorptive capacity even though components within the effluent may depress some adsorption interactions. A greater diversity of adsorptive sites in adsorbent mixtures will increase the total adsorptive capacity. Metcalf and Eddy (26) reported that the amount of inhibition of adsorption by competing mixtures in the adsorbate is related to the size of the molecules being adsorbed, their adsorptive affinities and the relative concentrations. Therefore the differences observed between amount of phosphorus removed from secondary effluent and that removed from distilled water solutions (Figures 13, 15, 19 and 22) may have been the result of competition for adsorbent sites by other components in the effluent such as matter exerting BOD, COD and suspended solids. Figures 17, 18, and 21 indicate that some soluble BOD and COD removal are obtained concurrently with phosphate removal. The inhibitory effect of suspended solids upon the phosphate removal efficiency can be seen in Figure 24. After suspended solids were removed by filtration from an effluent sample, rapid phosphorus uptake was observed immediately upon fly ash addition.

As mentioned previously the addition of lime in conjunction with fly ash had little effect on phosphate removal from secondary effluent. The amount of phosphorus immediately removed from effluent containing lime was greater than in solutions with only fly ash. However, total ultimate removal was unchanged.

Using fly ash for the tertiary removal of phosphate from wastewater might not be practical in some cases because of transportation costs and handling problems. As shown in Figure 19 to achieve 98% removal of 5.6 mg/l phosphorus concentration in actual secondary effluent 25 grams of fly ash per liter was required. This would be equivalent to approximately 6.0 tons of ash per million gallons of wastewater treated. With such large amounts of fly ash required, use might be limited to areas which would not require long distance transportation, or massive stockpiling of either the unused or spent fly ash. Situations such as this might be found in industrial complexes which combine power generating and wastewater treatment facilities. The economic feasibility of such endeavors would be very dependent upon cheap and reliable transportation facilities and could be determined only after suitable studies had been conducted. In addition, the construction of wastewater treatment facilities utilizing fly ash for phosphorus removal would also need an assured and constant source of fly ash and possibly also large stockpiles to insure uninterrupted operation. Many such factors would need to be taken into consideration during the design of treatment plants utilizing fly ash.

CHAPTER VI

CONCLUSIONS

From this investigation of the utility of fly ash in tertiary wastewater treatment for the removal of phosphorus there are several important conclusions.

1) When fly ash was added to distilled water under mixed and unmixed conditions, the hardness was shown to increase as well as the pH but mixed solutions showed greater increases in both pH and hardness.

2) In general, both pH and hardness were found to increase upon addition of fly ash to either sewage effluent or to distilled water solutions of phosphorus.

3) Mixing increased the amount of phosphorus which was removed from distilled water solutions by one gram per liter of fly ash until phosphorus concentrations became very high (greater than 20 mg/l) and then static and mixed conditions showed the same amount of removal.

4) Static experiments in which fly ash was added to phosphorus solutions and allowed to settle through the solution showed very low rates of phosphorus removal and were discontinued because their utility as a treatment process was deemed quite low.

5) Fly ash removed considerable amounts of phosphorus from distilled water solutions as well as from secondary effluent. However, optimum doses for the removal of phosphorus from distilled water would not adequately predict the phosphorus removal rates from secondary

effluent.

6) Fly ash treatment of secondary effluent resulted in considerable phosphorus removal and BOD and COD removal as well.

7) The majority of phosphorus removal took place within the first 15 minutes for both distilled water solutions and actual secondary effluent.

8) The removal of suspended solids from secondary effluent before addition of fly ash resulted in more rapid initial removal of phosphorus, but similar ultimate amounts.

9) The addition of lime to fly ash resulted in more rapid initial removal of phosphorus, but also did not increase ultimate removal.

10) Adsorption was shown to be partially responsible for phosphorus removal from secondary effluent.

11) The feasibility of fly ash treatment for phosphorus removal from secondary effluent has been confirmed, but the actual use of the process will be dependent upon economic factors.

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APPENDIX

DATA COLLECTED FROM EXPERIMENTAL RESEARCH

TABLE IV

CHEMICAL COMPOSITION AND pH OF WATER SOLUBLE EXTRACTS OBTAINED FROM 1 gm/l FLY ASH USING STATIC AND MIXED CONDITIONS

Time	Phenophthalein Alkalinity mg/l as $CaCO_3$	Total Alkalinity mg/l as $CaCO_3$	Total Hardness mg/l as $CaCO_3$	Sulfate mg/l	pH
<u>3 hrs</u>					
static	60.0	66.0	15.6	5.0	8.2
	60.0	66.0	13.92	5.0	8.2
mixed	78.3	83.5	111.36	12.0	10.7
	66.0	73.08	102.66	12.0	10.7
<u>6 hrs</u>					
static	60.0	66.0	24.36	5.0	8.5
	60.0	66.0	17.40	5.0	8.5
mixed	80.04	90.0	11.36	12.0	10.9
	78.3	87.0	114.84	12.0	10.9
<u>9 hrs</u>					
static	66.0	70.0	20.8	5.0	9.5
	60.0	66.0	13.92	5.0	8.5
mixed	80.04	90.08	114.84	12.0	10.7
	83.52	88.0	121.8	12.0	10.8

initial pH = 6.57

TABLE V

PHOSPHORUS REMOVAL BY 1 gm/l FLY ASH UNDER STATIC AND MIXED CONDITIONS

Replicate	Time (hours)	P as PO_4 mg/l Mixed	Static
		Initial Phosphorus Concentration 5 mg/l P as PO_4	
#1	0	5.0	5.0
	3	.9	4.5
	6	.35	4.27
	9	.17	4.0
	12	.14	4.0
#2	0	5.0	5.0
	3	.70	4.2
	6	.40	4.0
	9	.23	4.0
	12	.17	3.9
		Initial Phosphorus Concentration 15 mg/l P as PO_4	
#1	0	15.0	15.0
	3	8.38	13.0
	6	7.75	12.5
	9	7.5	12.5
	12	7.0	12.0
#2	0	15.0	15.0
	3	9.0	13.0
	6	7.5	12.5
	9	7.5	12.5
	12	7.0	12.0
		Initial Phosphorus Concentration 20 mg/l P as PO_4	
#1	0	20.0	20.0
	3	17.0	19.0
	6	17.0	18.0
	9	17.0	18.0
	12	17.0	18.0

TABLE V (Continued)

Replicate	Time (hours)	P as PO_4 mg/l Mixed	Static
#2	0	20.0	20.0
	3	17.0	20.0
	6	16.0	19.0
	9	16.0	19.0
	12	16.0	19.0
	Initial Phosphorus Concentration 30 mg/l P as PO_4		
#1	0	30.0	30.0
	3	30.0	27.0
	6	26.0	27.0
	9	26.0	27.0
	12	25.0	27.0
#2	0	30.0	30.0
	3	30.0	26.0
	6	25.0	26.0
	9	25.0	26.0
	12	25.0	26.0
	Initial Phosphorus Concentration 50 mg/l P as PO_4		
#1	0	50.0	50.0
	3	43.25	43.75
	6	40.63	42.13
	9	40.1	40.5
	12	40.0	39.0
#2	0	50.0	50.0
	3	42.5	43.0
	6	40.5	40.5
	9	40.0	39.0
	12	40.0	39.0

TABLE VI

DATA COLLECTED FROM DETERMINATION OF OPTIMUM FLY ASH DOSE FOR A SPECIFIED PHOSPHORUS CONCENTRATION

Replicate	Time hours	Fly Ash g/l	P as PO_4 mg/l	Total Hardness mg/l as $CaCO_3$	pH
		Initial Phosphorus Concentration 5 mg/l P as PO_4			
#1	0	1	5.0	0	5.9
	1.5	1	.9	20	8.2
	3.0	1	.85	30	8.4
	4.5	1	.64	30	8.4
#2	0	1	5.0	0	5.9
	1.5	1	.9	20	8.2
	3.0	1	.6	30	8.4
	4.5	1	.48	30	8.5
#1	0	2	5.0	0	5.9
	1.5	2	.01	30	8.4
	3.0	2	.06	50	8.4
	4.5	2	.06	60	8.4
#2	0	2	5.0	0	5.9
	1.5	2	.03	30	8.4
	3.0	2	.01	70	8.4
	4.5	2	0	70	8.4
#1	0	3	5.0	0	5.9
	1.5	3	.03	110	8.4
	3.0	3	.03	140	8.4
	4.5	3	0	150	8.4
#2	0	3	5.0	0	5.9
	1.5	3	.03	110	8.4
	3.0	3	.03	120	8.5
	4.5	3	0	150	8.5
		Initial Phosphorus Concentration 5 mg/l P as PO_4			
#1	0	3	5.0	0	5.6
	immed.	3	.64	80	8.4
	.5	3	.14	80	8.4
	1.5	3	.01	80	8.4

TABLE VI (Continued)

Replicate	Time hours	Fly Ash g/l	P as PO_4 mg/l	Total Hardness mg/l as $CaCO_3$	pH
#2	0	3	5.0	0	5.6
	immed.	3	.58	80	8.4
	.5	3	.04	80	8.4
	1.5	3	0	80	8.4
#1	0	5	5.0	0	5.6
	immed.	5	.21	90	8.3
	.5	5	.1	90	9.0
	1.5	5	0	110	9.0
#2	0	5	5.0	0	5.6
	immed.	5	0	90	8.6
	.5	5	0	90	9.3
	1.5	5	0	110	9.3
#1	0	7	5.0	0	5.6
	immed.	7	0	86	8.9
	.5	7	0	90	9.2
	1.5	7	0	90	9.4
#2	0	7	5.0	0	5.6
	immed.	7	0	80	9.0
	.5	7	0	90	9.2
	1.5	7	0	90	9.2
Initial Phosphorus Concentration 10 mg/l P as PO_4					
#1	0	3	10.0	0	5.2
	immed.	3	3.0	86	8.6
	.5	3	.5	90	9.4
	1.5	3	.5	90	9.4
#2	0	3	10.0	0	5.2
	immed.	3	3.0	87	8.9
	.5	3	.7	92	9.0
	1.5	3	.5	92	9.4
#1	0	5	10.0	0	5.2
	immed.	5	.76	90	8.6
	.5	5	.36	90	9.0
	1.5	5	.09	90	9.2
#2	0	5	10.0	0	5.2
	immed.	5	.56	90	8.6
	.5	5	.26	100	9.0
	1.5	5	.1	110	9.0

TABLE VI (Continued)

Replicate	Time hours	Fly Ash g/l	P as PO_4 mg/l	Total Hardness mg/l as $CaCO_3$	pH
#1	0	7	10.0	0	5.2
	immed.	7	.22	90	8.6
	.5	7	.06	86	9.0
	1.5	7	.06	92	9.0
#2	0	7	10.0	0	5.2
	immed.	7	.30	90	8.4
	.5	7	.07	90	9.0
	1.5	7	.07	92	9.2
			Initial Phosphorus Concentration 20 mg/l P as PO_4		
#1	0	7	20.0	0	5.0
	immed.	7	3.5	25	8.4
	.5	7	2.0	50	9.0
	1.5	7	2.0	80	9.2
#2	0	7	20.0	0	5.0
	immed.	7	6.2	25	8.4
	.5	7	2.8	56	9.0
	1.5	7	2.4	86	9.2
#1	0	10	20.0	0	5.0
	immed.	10	1.95	40	8.5
	.5	10	.36	80	10.2
	1.5	10	.06	120	10.8
#2	0	10	20.0	0	5.0
	immed.	10	1.90	40	8.5
	.5	10	.12	80	10.2
	1.5	10	.04	120	10.8
#1	0	15	20.0	0	5.0
	immed.	15	.2	150	10.6
	.5	15	.06	290	11.0
	1.5	15	.04	310	11.2
#2	0	15	20.0	0	5.0
	immed.	15	.06	180	10.6
	.5	15	.04	290	11.0
	1.5	15	0	310	11.2

TABLE VII

DATA COLLECTED FOR PHOSPHORUS REMOVAL BY FLY ASH FROM A DISTILLED WATER SOLUTION WITH 8.6 mg/l P as PO_4

Replicate	Time hours	Fly Ash g/l	P as PO_4 mg/l	Total Hardness mg/l as $CaCO_3$	pH
#1	0	7	8.6	0	5.1
	immed.	7	.55	70	9.5
	.5	7	.04	70	10.8
	1.5	7	.018	120	10.8
#2	0	7	8.6	0	5.1
	immed.	7	3.2	40	7.8
	.5	7	.26	50	9.4
	1.5	7	.05	90	10.6

TABLE VIII

DATA COLLECTED FOR PHOSPHORUS REMOVAL BY FLY ASH FROM SECONDARY EFFLUENT CONTAINING 8.6 mg/l P as PO_4

Replicate	Time hours	Fly Ash g/l	P as PO_4 mg/l	Total Hardness mg/l as $CaCO_3$	pH	COD mg/l	BOD mg/l
#1	0	7	8.6	175	7.6	188	28.5
	immed.	7	5.0	210	8.4	172	18.7
	.5	7	2.6	210	8.4	166	12.5
	1.5	7	1.35	210	8.8	174	12.75
#2	0	7	8.6	175	7.6	188	28.5
	immed.	7	3.2	210	8.6	172	18.7
	.5	7	2.1	210	8.8	170	13.5
	1.5	7	1.80	210	8.8	174	12.0
#1	0	10	8.6	175	7.6	188	28.5
	immed.	10	5.0	210	8.4	176	16.0
	.5	10	3.10	210	8.5	174	16.0
	1.5	10	3.30	210	8.8	172	15.0
#2	0	10	8.6	175	7.6	188	28.5
	immed.	10	5.0	210	8.4	172	17.0
	.5	10	3.10	210	8.8	176	14.7
	1.5	10	2.35	210	8.8	172	14.5

TABLE IX

DATA COLLECTED FOR PHOSPHORUS REMOVAL BY FLY ASH FROM SECONDARY EFFLUENT CONTAINING 5.6 mg/l P as PO_4

Replicate	Time hours	Fly Ash g/l	P as PO_4 mg/l	Total Hardness mg/l as $CaCO_3$	pH	COD mg/l
#1	0	15	5.6	180	7.3	60
	immed.	15	.5	252	9.0	44
	.5	15	.06	250	9.0	36
	1.5	15	.012	250	9.0	36
#2	0	15	5.6	180	7.3	60
	immed.	15	.6	252	9.0	52
	.5	15	.18	250	9.0	56
	1.5	15	.012	250	9.0	56
#1	0	20	5.6	180	7.3	60
	immed.	20	.26	250	9.0	52
	.5	20	.02	250	9.0	36
	1.5	20	0	240	9.0	40
#2	0	20	5.6	180	7.3	60
	immed.	20	.1	250	9.0	36
	.5	20	.02	240	9.0	52
	1.5	20	0	240	9.0	52
#1	0	25	5.6	100	7.3	60
	immed.	25	.1	250	9.0	52
	.5	25	.01	250	9.0	48
	1.5	25	0	250	9.0	48
#2	0	25	5.6	100	7.3	60
	immed.	25	.12	250	9.0	48
	.5	25	.01	250	9.0	32
	1.5	25	0	250	9.0	32

TABLE X

REMOVAL OF PHOSPHORUS BY FLY ASH FROM SECONDARY EFFLUENT - SUSPENDED SOLIDS PRESENT

Replicate	Time hours	Grams of Fly Ash per Liter	Phosphorus mg/l
#1	0	10	4.1
	immed.	10	3.20
	0.5	10	1.20
#2	0	10	4.1
	immed.	10	3.55
	0.5	10	1.20

TABLE XI

REMOVAL OF PHOSPHORUS BY FLY ASH FROM SECONDARY EFFLUENT. SUSPENDED SOLIDS REMOVED

Replicate	Time hours	Grams of Fly Ash per Liter	Phosphorus mg/l
#1	0	10	4.1
	immed.	10	2.5
	0.5	10	.95
#2	0	10	4.1
	immed.	10	2.45
	0.5	10	.90

TABLE XII

REMOVAL OF PHOSPHORUS IN SECONDARY EFFLUENT BY LIME AND FLY ASH. INITIAL HARDNESS OF THE EFFLUENT = 180 mg/l

Replicate	Time hours	Fly Ash g/l	Phosphorus mg/l
		Fly Ash	
#1	0	10	5.8
	immed.	10	4.5
	0.5	10	1.25
#2	0	10	5.8
	immed.	10	4.2
	0.5	10	1.0
		Fly Ash With 180 mg lime/liter	
#1	0	10	5.8
	immed.	10	3.85
	0.5	10	1.25
#2	0	10	5.8
	immed.	10	3.6
	0.5	10	1.30
		Fly Ash With 360 mg lime/liter	
#1	0	10	5.8
	immed.	10	3.7
	0.5	10	1.30
#2	0	10	5.8
	immed.	10	3.6
	0.5	10	1.30
		180 mg lime per liter only	
#1	0	10	5.8
	immed.	10	4.6
	0.5	10	4.5
#2	0	10	5.8
	immed.	10	4.5
	0.5	10	4.5

TABLE XII (Continued)

Replicate	Time hours	Fly Ash g/l	Phosphorus mg/l
	360 mg of lime only		
#1	0	10	5.8
	immed.	10	4.4
	0.5	10	4.4
#2	0	10	5.8
	immed.	10	4.4
	0.5	10	4.4

VITA

2

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