"ADSORPTION OF HEAVY METALS AT LOW

CONCENTRATIONS USING GRANULAR COALS"

by

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B.Sc. (Eng.), University of Manitoba, 1972

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF APPLIED SCIENCE

in the

Department of Civil Engineering

We accept this thesis as conforming to the required
standard

The University of British Columbia

May, 1976

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ABSTRACT

The adsorption of low concentrations of heavy metals, such as zinc,

copper, lead and mercury, by various British Columbia coals was investigated.

Five British Columbia coals were used as adsorbents for the four

heavy metals described above. Batch tests were run on all five coals.

namely, Hat Creek Oxidised, Hat Creek Unoxidised, Cominco Oxidised, Cominao

Ash Waste and Cominco Production Coal. The optimum contact time for batch

tests was found to be 60 mins. Batch tests provided a quick comparison of

the adsorptive capacities of the five coals. Based on the batch tests data,

the best performing coal from each of the Hat Creek and Cominco groups, namely,

Hat Creek Oxidised and Cominco Ash Waste were chosen for further investiga-

tory work using column tests.

For the column tests, the influent concentrations were 2 mg/ℓ and

less for zinc, copper and lead. Column work with mercury was carried out

with influent concentrations of 5 µg/ℓ and less.

Column tests showed the following:-

a) Varying the cross-sectional area of the coal column from

.001 ft^2 to .002 ft^2 has no significant influence on the adsorptive

capacity. Both columns have diameters more than 10 times that of

the average coal particle.

b) The most crucial factor affecting adsorptive capacity is the

pH of the influent. There is a definite decrease in capacity with

decreasing pH.

c) The capacity decreases with increasing flow rate, but the

relationship is not linear. The decrease in capacity due to a

flow rate increase from 1 to 3 Igpm/ft^2 is much greater than the

decrease in capacity due to an increase from 3 to 5 Igpm/ft^2.

d) Comparing the adsorptive affinities of zinc, copper and lead, it is seen that lead displayed the greatest affinity with copper second and zinc third. At 10% breakthrough concentration, the capacities displayed by Cominco Ash Waste coal for lead, copper and zinc were in the ratio of 12:6:1. The influent pH and initial concentrations involved were 4.0 and 2 mg/ℓ respectively, and the flow rate was 1 Igpm/ft^2.

e) Using influents containing a mixture of zinc, copper and lead results in smaller individual capacities for Zn, Cu and Pb than would be achieved with single solute influents. But the total overall capacity of the coal for heavy metals is greater with mixed influents than with any single solute influent.

f) Tests with mercury influents show that deterioration of the concentration of the mercury solution occurs at concentration of 5 µg/ℓ and less.

g) Of the two coals chosen for column test work, Hat Creek Oxidised is the superior coal with regard to the adsorptive capacity of heavy metals. Tests run at an influent pH of 4.0 and influent concentrations of 2 mg/ℓ of each metal, showed the ratio of capacities of Hat Creek Oxidised: Darco activated carbon: Cominco Ash Waste for Zn to be 12.1 : 1.2 : 1.0, for Cu to be 11.9 : 1.7 : 1.0 and for Pb to be 3.8 : 0.7 : 1.0.

An attempt was made to correlate the column effluent pH with the effluent metal concentration. It was found that this correlation is more pronounced at lower influent pH values.

During the course of the column work, a growth of fungus was observed at the top of the coal columns. It is possible that adsorptive capacities were affected by this fungus.

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Chapter 1

INTRODUCTION

A lot of research has been done and an adequate amount of data compiled on the adsorption of organic pollutants by activated carbon. Advanced waste treatment plants such as the one at Lake Tahoe, California, for example, employ granular activated carbon to remove various types of organic constituents in the wastewaters with a good degree of success.

Weber and Morris[10] in their work with activated carbons and organic solutes reported high adsorption capacities for organics such as nitrochlorobenzene and high molecular weight sulfonated alkylbenzenes.

The Rand Corporation[12] conducted a study with a 10,000 gal/day pilot plant with 18/120 mesh coal as a consumable precoat filter for treating raw sewage and secondary effluent. They reported a 90% decrease in suspended solids and about 50% decrease in phosphates and C.O.D. when raw sewage or secondary effluent was treated with the coal filter.

Relatively speaking, there has not been much work done on coal as an adsorbent of inorganics such as the heavy metals. Hendren[3] reported good adsorption capacities for lead, copper and zinc using granular coals. The coals used were from British Columbia, namely, Hat Creek and Crowsnest coals. Of several size fractions tested, 28/48 mesh fraction was found to display good adsorption capacities as well as satisfactory hydraulic flow properties. The major portion of his work was done at influent waste concentrations of 10-100 mg/ℓ.

Sigworth and Smith[7] listed the adsorption potentials of various inorganic compounds by activated carbon. They attributed mercury and lead with high adsorption affinities. According to their list, copper and zinc were classified as having only a slight potential for adsorption by activated carbon.

British Columbia has vast coal reserves. The present production of

1

coal in British Columbia is about 7 million tons per year. It, therefore,

seems both logical and wise that the possible potential for using B.C. coals

as adsorbents for heavy metals, prior to its use as a fuel, should be well

investigated. Another good reason for doing such an investigation would be

an economic one. Although certain types of activated carbon may display fair

adsorption capacities for heavy metals, activated carbon is relatively expen-

sive at about $500/ton. The present price of coal is $15-$22 per ton. It

may well turn out that the cost of using a coal system to remove heavy metals

is cheaper than using an activated carbon system.

When making an economic comparison of the two systems, one must take

into account the percent recovery of usable coal size fractions from the raw

commercial coal as well as the individual adsorptive capacities on a unit

weight basis. The percent recovery of useful coal size fractions that can

serve as adsorbents in column operations will crucially determine the economics

of such a coal system.

The notion that coal adsorption may fare poorly at very low concen-

trations of influent heavy metal has been in the minds of many. To investigate

this aspect of coal use, the influent heavy metal concentrations used in this

research are all very low. For zinc, copper and lead, the influent concentra-

tions are in the range of 0.5 mg/ℓ to 2.0 mg/ℓ. In the case of mercury,

the influent concentration used for the column tests was 5 µg/ℓ. These

concentrations are in the range of permissable levels outlined by the Pollution

Control Branch for the above heavy metals in industrial effluents.

In this research, five different British Columbia coals were studied

under batch conditions. The effects of contact time, of pH, and of varying

initial concentrations were investigated. The batch tests provided a quick comparison of the performance of the five coals. One type of coal from each of the Hat Creek group and the Cominco group was chosen for further investigations under column operating conditions.

The column tests used a coal bed with a cross-sectional area of .001 ft^2 and a coal depth of 10 inches. During the column studies, the effects of varying cross-sectional area, influent pH, flow rate and influent concentration were also investigated. Although the laboratory scale column tests cannot supply data that are immediately useful for full scale design, they nonetheless give worthwhile information on relative adsorption capacities under flow-through column operation conditions. The column data can then be used to compare with other documented removal methods.

Chapter 2

GENERAL NOTES ON ADSORBENTS

AND

ADSORBATES USED IN THIS STUDY

2.1 Types of Coal

The adsorbents used in this research are all coals native to British Columbia. Five coals were used in the Batch Tests and two of these five were chosen for Column Tests. The five coals are:-

1. Hat Creek Oxidised is the coal picked up from the surface of the coal seams at Hat Creek.

2. Hat Creek Unoxidised is obtained from a mixture of core samples of the Hat Creek coal deposits. The core samples were from depths of 50' - 1,000' below the surface of the ground.

3. Cominco Oxidised is the coal that had been exposed to oxidation processes and consequently had lost its coking properties.

4. Cominco Ash Waste is the coal with a high percentage of inert ashes and non volatile matter. It is the waste product in a coal cleaning process.

5. Cominco Production is the coal that is produced for marketing.

The last three coals described above, namely, the Cominco coals were all supplied directly by Consolidated Mining and Smelting Company, Ltd. from Trail, British Columbia. They were received in a crushed form and were sealed in plastic bags.

The abbreviations used herein for the five coals are as follows;-

H.C. OX	- Hat Creek Oxidised
H.C. UN	- Hat Creek Unoxidised
CO:OX	- Cominco Oxidised
CO:ASH	- Cominco Ash Waste
CO:PROD	- Cominco Production

2.2. Coal Preparation

The coal was washed with tap water to get rid of dirt particles. After being dried in an oven, it was put through a Traylor Gyratory Crusher with ¼" opening (≈3½ mesh), and then put through a Massco Cone Crusher with an .0083" opening (≈65 mesh). It was subsequently dry-sieved using a mechanical shaker and 28/48 mesh screens. Wet sieving of the 28/48 coal particles was then done to remove the fines stuck to the 28/48 particles. Further removal of fines was accomplished by backwashing the coal in a plexiglass column. When almost all the fines were removed, the coal was dried at 103° C. for about 40 hours. It was then transferred into a bottle, flushed with nitrogen gas and kept sealed until use. After each sample extraction, the bottle was reflushed with nitrogen and resealed.

2.3 Percent Recovery of 28/48 Size Fraction from Raw Commercial Coal

Based on Hendren's findings[3] on the optimal particles size fraction with respect to adsorptive capacity as well as hydraulic flow, the 28/48 Tyler mesh size fraction was chosen for this entire research.

Following the coal crushing procedure outlined previously, about 13% of the initial raw coal weight was recovered in the 28/48 size range in the case of H.C. OX. The percent recovery figure in the 28/48 size range for CO:ASH was about 14%.

2.4 Optimizing the Coal Preparation Procedure for Increased Percent Recovery of 28/48 Size Fraction

A point to note is that a 65 mesh was used in the final crusher. This means most of the coal was crushed to a size finer than the 28/48 size range, and most of the coal therefore went right through the 48 screen.

Thus, the crushing procedure will prove crucial when the overall economics of the system are considered. There is no reason not to expect the percent recovery in the 28/48 size fraction to be increased tremendously from the figures stated above for the two coals if the following steps are taken:-

1.   Use the proper type of crusher or a series of crushers that will minimize the fraction of coal smaller than 48 mesh size.

2.   Use an optimal closed-circuit system that allows recrushing of coal particles bigger than 28 mesh size.

3.   Use the type of screen that will minimize further particle break-up.

4.   Use a method of removal of the remaining slime and fines that will not enhance further fracture of the coal particles.

Unfortunately, there will always be a certain percentage lost as slime and fines which are removed by wet sieving and backwashing processes. Slime is made up of fines smaller than .08 mm or 200 mesh size. Slime resists wetting action of the water and floats to the top.

2.5 Synthetic Wastewaters

The waste solutions were prepared synthetically in the laboratory. The materials used to make up a 1000 mg/ℓ stock solution of the heavy metal are listed in TABLE 2.1.

TABLE 2.1

SYNTHETIC WASTEWATERS

HEAVY METAL	MATERIALS USED TO MAKE 1000 mg/ℓ STOCK SOLUTION	
	SOLUTE	SOLVENT
Cu	Copper Oxide	Dilute Nitric Acid
Zn	Zinc Oxide	" " "
Pb	Lead Metal	" " "
Hg	Mercuric Chloride	Distilled Water

The materials used are the same as the ones used in Atomic Absorption stock solutions.

The prepared 1000 mg/ℓ stock solution was then used to make up dilutions of a desired concentration.

When the prepared waste solution was found to be too acidic, the pH was adjusted as required by addition of NaOH. Preliminary tests showed that NaOH does not interfere with the adsorption process.

Chapter 3

BATCH TESTS

3.1 Introduction

Emphasis was laid on initial concentrations of 2 mg/ℓ and less. Throughout the batch tests, all five coals were tested with 2 mg/ℓ initial concentrations of copper, lead and zinc, with the best two coals being further subjected to tests with initial concentrations of 1 mg/ℓ and 0.5 mg/ℓ, as well as with some higher concentrations. Copper tests were the exception where all five coals were subjected to tests with higher concentrations. Mercury tests were done in very low concentrations of 15 - 50 µg/ℓ for most of the batch tests.

An optimum practical contact time was investigated for two reasons: to save time, and to minimize particle break-up of the coal which is favoured with long periods of shaking.

It was suspected that the pH would play an important role in the adsorption process. The effects of pH on the adsorptive capacity of coal were investigated with zinc, copper and lead solutions.

From the batch tests data, a plot of capacity (mg adsorbed/ g of coal) versus equilibrium concentration (mg/ℓ) can be drawn. Such data display is called an "ADSORPTION ISOTHERM", which is simply a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. Commonly, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion.

The major portion of the batch tests involved determining the adsorption isotherms for the four heavy metals under study, (i.e., Zn, Cu, Pb and Hg) under various conditions of pH, initial concentration, type of

adsorbent and other parameters.

3.2 Batch Testing Procedure

A) For Copper, Lead and Zinc

1. The required amount of coal was placed in a 250 ml Erlenmeyer flask.

2. One hundred millilitres of the synthetic wastewater of known concentration was added to the flask.

3. The flask was closed with a rubber stopper and shaken with a wrist-action shaker for the required contact time. Shaking intensity was such that the wastewater was well agitated but not severe enough to move the coal around and break the particles.

4. The coal was filtered off and the clear filtrate was analysed by Atomic Adsorption Spectroscopy for the equilibrium concentration of metal ions. The analysis for copper, lead and zinc was in accordance with "Water Analysis by Atomic Adsorption - Varian Techtron".

B) For Mercury

The procedure is the same as for copper, zinc and lead described previously up to the point when the shaking is completed. The solvent testing is accomplished as follows:-

a) Instead of filtering, 50 ml of wastewater is simply decanted into a test tube. Decanting is done instead of filtration to avoid any mercury being adsorbed by the filter paper.

b) The decanted solution is placed in a cooler for about 1 hour.

c)   0.5 mℓ of concentrated H_2SO_4 is then added to the sample to allow overnight storage of the sample without volatilization of mercury.

d)   Before testing on the atomic absorption spectrophotometer, 0.5 mℓ of 6 percent potassium permanganate is added. The test tube is then shaken and allowed to sit for about 20 minutes.

e)   Three millilitres of sample is transferred to a testing flask and diluted up to 100 mℓ.

f)   0.5 mℓ of 10 percent hydroxylamine hydrochloride is added.

g)   Two millilitres of 10 percent $SnCl_2$ is added just before analysis by the cold vapour technique according to "Water Analysis by Atomic Absorption - Varian Techtron".

The above procedure gives rise to a detection limit of .05 µg/ℓ of mercury. Confidence decreases with levels below .05 µg/ℓ due to background interference.

3.3 Determination of Optimum Contact Time

Batch tests were done on H.C. OX and H.C. UN to determine the equilibrium concentration at various contact times. The pH of the solution was 2.0 and the results are shown in Figure 3.1(a).

The same kind of tests were done with the Cominco coals at a pH of 5.2. The data obtained for this series of tests are shown in Figure 3.1(b).

From the results, the following conclusions can be made:-

1.   Contact time of 60 mins. will achieve nearly all of the ultimate removal (i.e., 93 percent and greater of the ultimate removal).

2.   Acid or neutral conditions do not influence the optimum contact

FIG. 3.1 (a)
CONTACT TIME - EQUILIBRIUM CONCENTRATION
FOR COPPER
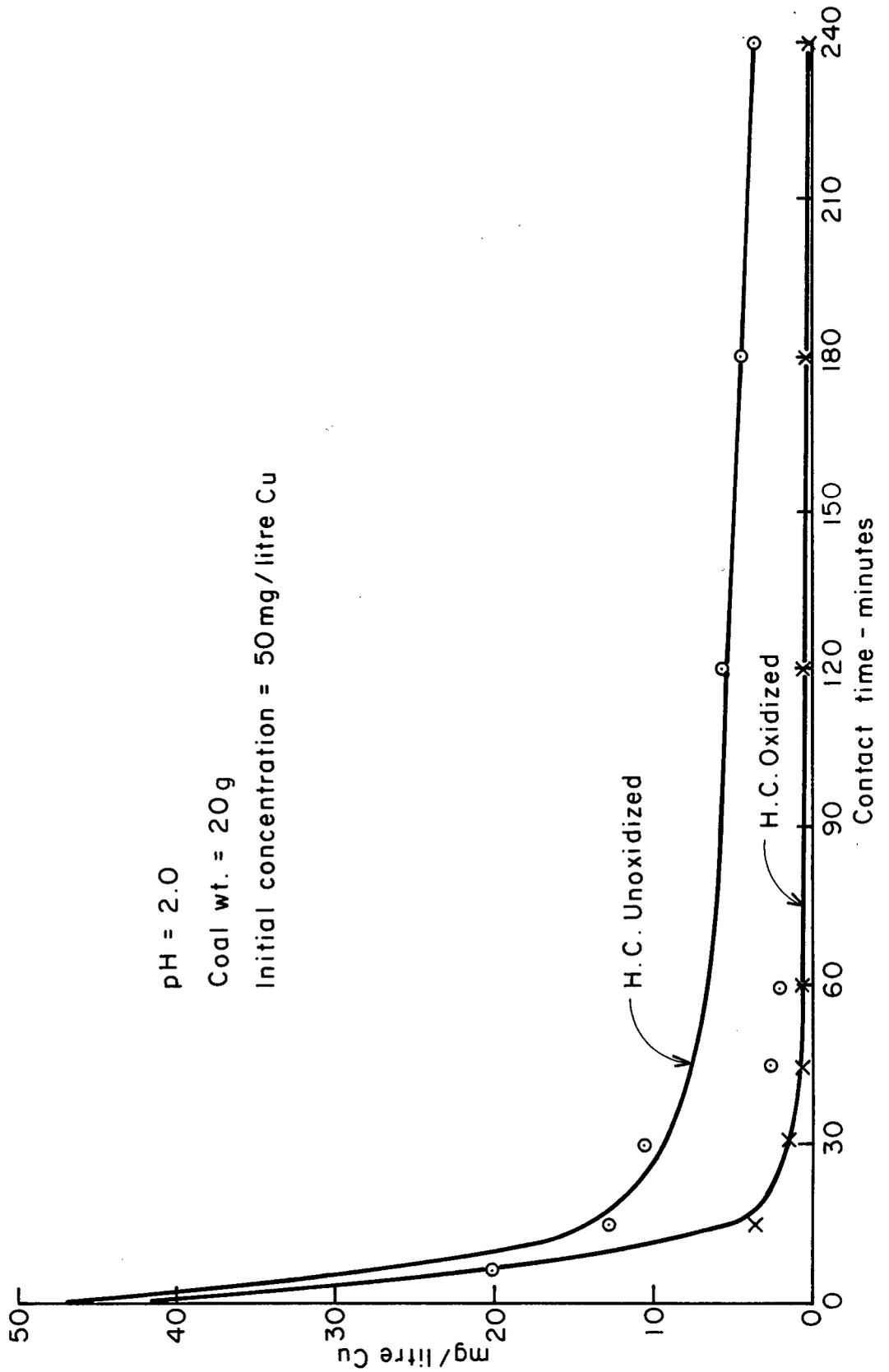
FIG. 3.1 (b)
CONTACT TIME – EQUILIBRIUM CONCENTRATION
FOR COPPER

pH = 5.2

Coal wt. 20g

Initial concentration = 50mg / litre Cu

Co : Production

Co : Ash

Co : Oxidized

mg / litre Cu

Contact Time – minutes
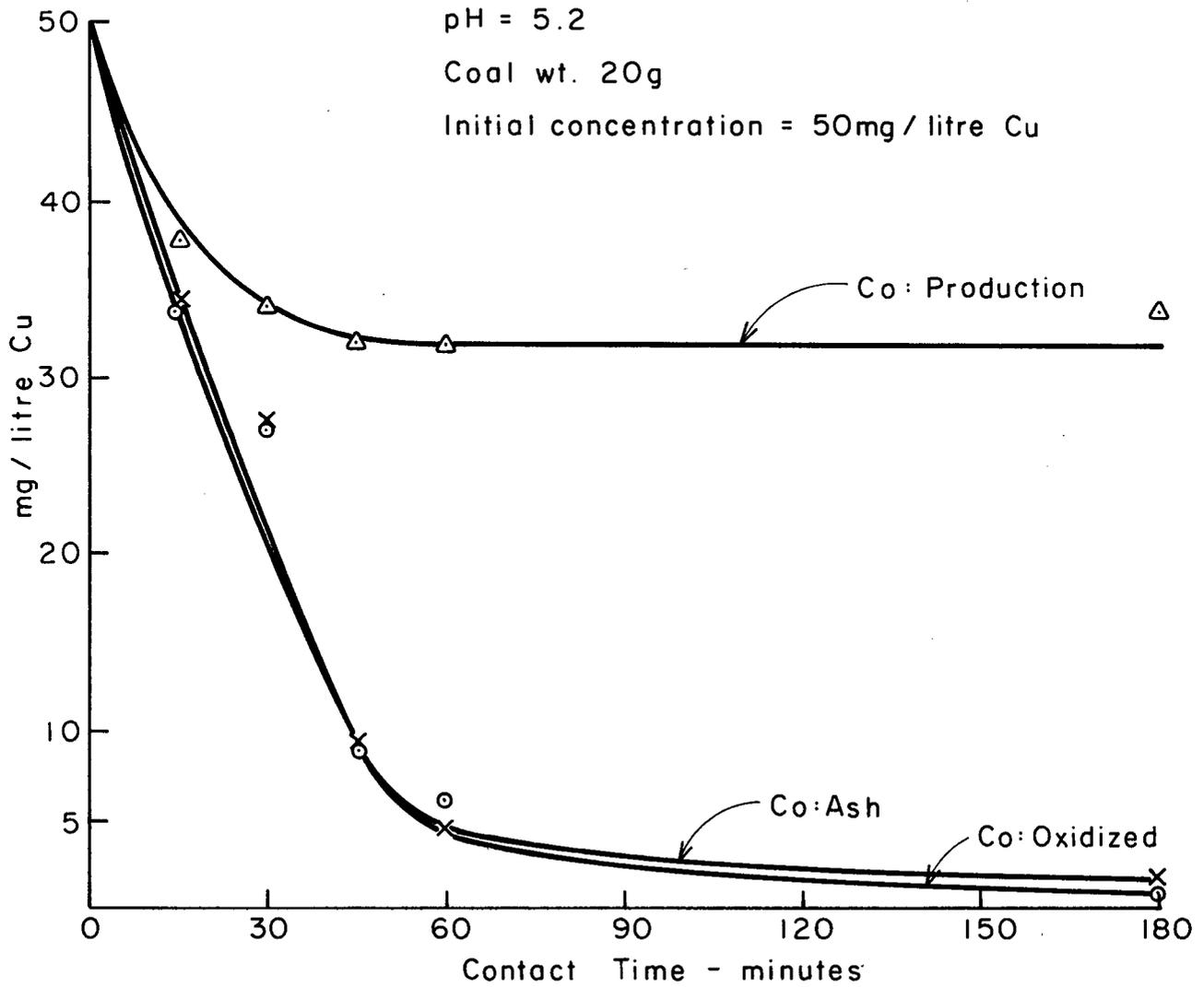
FIG. 3.1 (c)
CONTACT TIME - EQUILIBRIUM CONCENTRATION
FOR COPPER

pH = 5.3

Coal wt. = 4 g

Initial concentration = 10mg/litre Cu
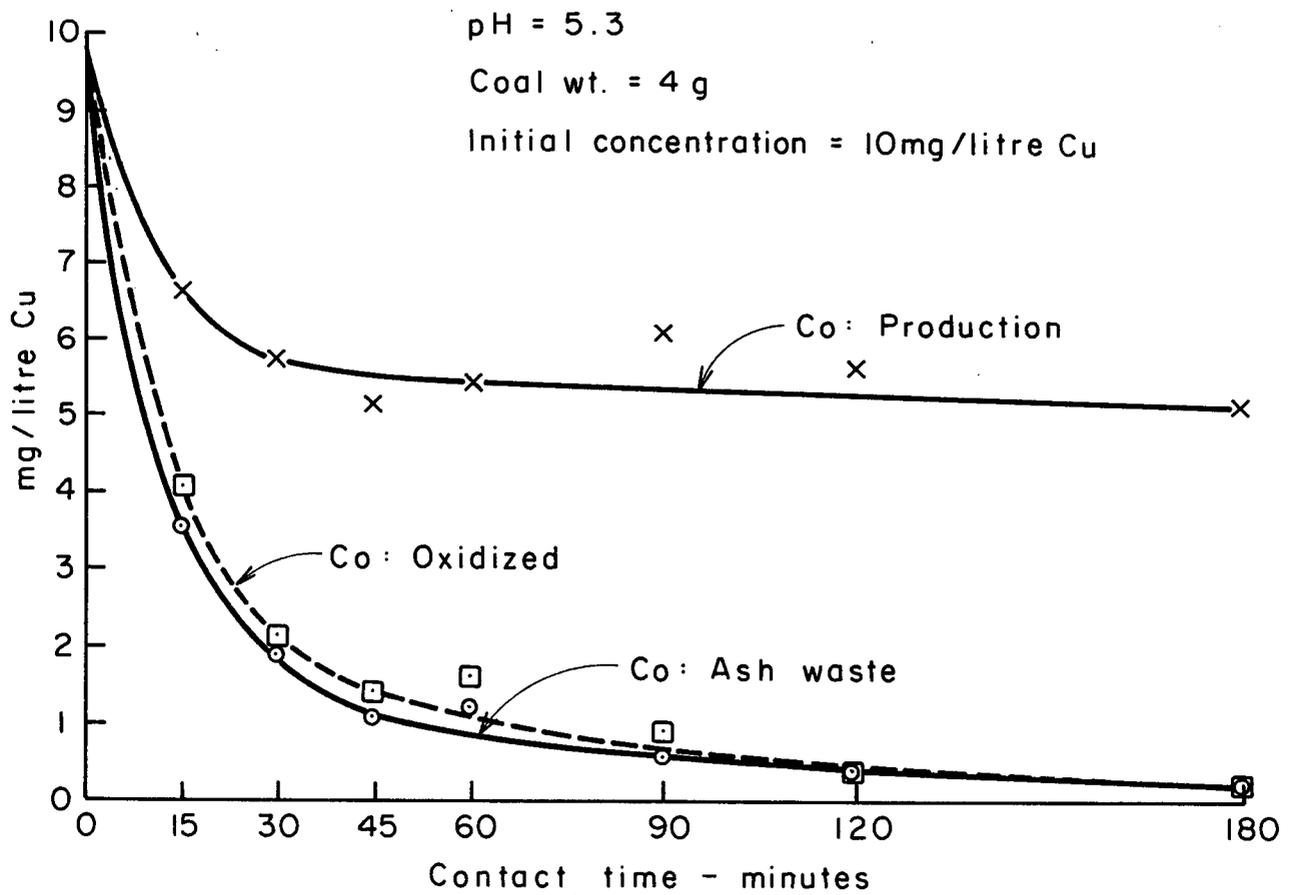
time. The equilibrium contact time curve levels out by the end of 60 mins.

The Cominco coals were next batch tested with copper at an initial concentration of 10 mg/ℓ instead of 50 mg/ℓ. The weight of coal was also proportionately decreased five times from 20 gm to 4 gm (Figure 3.1(c)). The results indicate that an optimum contact time of 60 minutes still holds at different concentrations and coal weights. This fact is further supported by results in Figure 3.2, where an optimum contact time of 1 hour is still valid at different combinations of coal weight and initial concentration.

Extending the contact time to 3 or 4 hours contributes very little to further removal and may even enhance particle break-up and consequent size reduction of the 28/48 coal.

3.4 Effects of pH on Adsorptive Capacity of Coal

Several batch tests were performed to investigate the effect of pH on the adsorption process.

Since H.C. OX had so far displayed a greater adsorptive capacity than the other coals, it was used for this set of batch tests. The concentration of waste was initially 2 mg/ℓ, the weight of coal was 1 gm and the contact time was 1 hour. Tests were performed at pH values of 1.5, 2.5, 4.0 and 5.8 for solutions containing each of copper, lead and zinc.

The results are shown in tabular form in Table 3.1. There is a definite relationship between pH and adsorptive capacity. At pH of 1.5 the capacity was nil for all three metals at these low concentrations. With the increase of pH there is a corresponding rise in capacity. In the case of lead, the coal had adsorbed the metal to well below the detection limit at a pH of 5.5.

TABLE 3.1

EFFECTS OF pH ON THE ADSORPTIVE CAPACITY OF COAL

Initial concentration = 2.0 mg/ℓ

Coal = H.C. OX

Coal Weight = 1 gm

Metal	pH	Equilibrium concentration after 1 hour (mg/ℓ)	mg Adsorbed / gm coal
Cu	1.5	2.00	0.000
	2.5	1.20	0.080
	4.0	0.30	0.170
	5.6	0.25	0.175
Zn	1.5	2.00	0.000
	2.5	1.62	0.038
	4.0	0.43	0.157
	6.2	0.30	0.170
Pb	1.5	2.00	0.000
	2.5	0.80	0.120
	4.0	0.00	0.200
	5.5	0.00	0.200

Following the trend of the results, the capacity should even be greater at a pH of 7 but, since the emphasis was on acidic wastes, no tests were done at higher pH values. It can be seen that the rate of change in adsorptive capacity per unit change in pH is different for each metal.

3.5 Effects of Initial Concentration Change & Coal Weight Change on Percent Removal

Table 3.2 shows the effect of changing coal weight and initial concentration in the same proportion on the percent removal achieved. With 20 gm of coal and 50 mg/ℓ Cu, 91 percent removal is achieved. By reducing both parameters to half (10 gm of coal and 25 mg/ℓ Cu) 87 percent removal is achieved and when the parameters are divided by 5 to 4 gm of coal and 10 mg/ℓ Cu, 92 percent removal is seen. Taking the noise and other inherent errors into consideration, it can be concluded that when coal weight and initial concentration are both changed in the same proportion, the percent removal stays about the same. The percent removals were calculated from values at contact time of 60 minutes. Figure 3.2 shows the results of varying one parameter by five times while keeping the other parameter fixed. The following points summarize the data:-

1. Starting off with 1 gm of Cominco Ash coal and 50 mg/ℓ Cu resulted in 19 percent removal at 1 hour contact time;

2. Increasing the amount of coal 5 times and using the same 50 mg/ℓ Cu solution resulted in 47 percent removal at 1 hour;

3. With a copper concentration of 10 mg/ℓ and the same coal weight, 73 percent removal was obtained in 1 hour - an increase in percent removal over that of case (1) by 54 percent. This is about double

FIG. 3.2
EFFECTS ON PERCENT REMOVAL WHEN CHANGING ONE PARAMETER WHILE KEEPING THE OTHER FIXED

1gm COAL

19 % Removal

5 gm COAL

47% Removal

pH = 5.2

Coal = Cominco Ash

Waste Element = Cu

1 gm COAL

73% Removal

Contact time – minutes
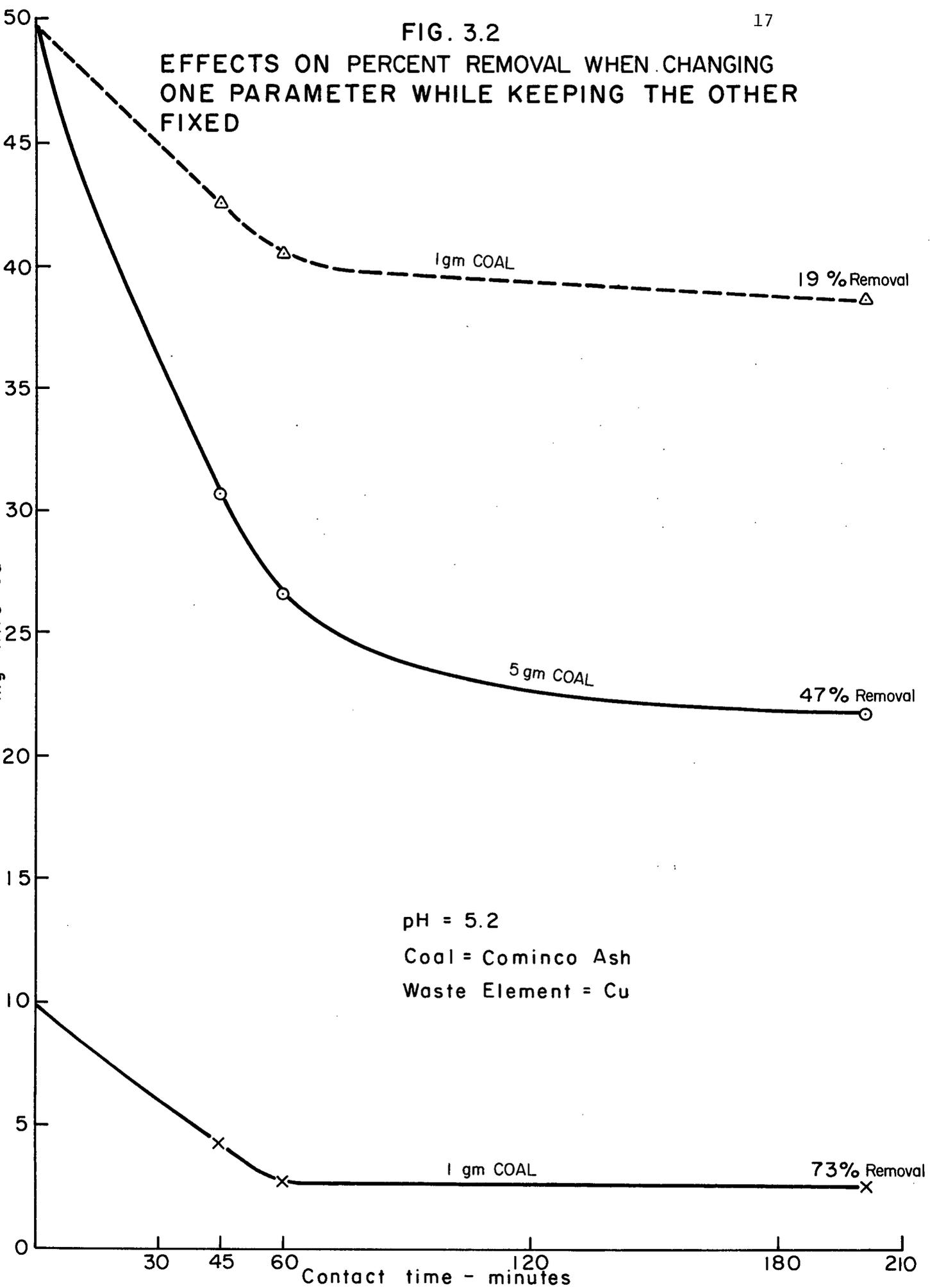
TABLE 3.2

EFFECT OF CHANGING COAL WEIGHT & INITIAL CONCENTRATION IN

THE SAME PROPORTION ON THE PERCENT

REMOVAL

Coal = Cominco Ash Waste

pH ≃ 5.2

Coal Weight (gm)	Initial Concentration (mg/ℓ Cu)	Equilibrium Concentration @ 1 hr (mg/ℓ Cu)	Percent Removal of Cu
20	50	4.5	91
10	25	3.3	87
4	10	0.8	92

the increase achieved by increasing the coal weight 5 times.

This increase in percent removal when the waste concentration is lowered promises a good polishing job by coal treatment at low concentrations. A possible explanation for this increase in percent removal on dilution could be the very slight increase in pH on dilution. At 50 mg/ℓ the pH was 5.2 and at 10 mg/ℓ the pH was approximately 5.3. Another possible explanation could be the change in the controlling or limiting phase of the reaction. At high solute concentrations, the available exchange sites might be limiting; while at lower solute concentrations, the boundary layer concentration gradient might be limiting.

3.6 Adsorption Isotherms for Copper

1.   Figure 3.3(a) shows adsorption isotherms for copper with all five types of coals. The initial concentrations of copper is 2 mg/ℓ and the coal weight is changed from 1.0 to 10.0 gm to give the data points on the isotherm. All five coals brought the concentration down to 0.3 mg/ℓ and less. The best performance is displayed by CO:OX and CO:ASH where the equilibrium concentration is brought down to 0.05 mg/ℓ. For a quick comparison with acti- vated carbon, some Darco Activated Carbon (Grade 12 x 20) was also tested. The resulting adsorption isotherm for activated carbon shows the copper concentra- tion being brought down to undetectable levels. Taking instrument noise into account, it could be interpreted that there is practically no difference between the batch removal efficiency of activated carbon and CO:ASH or CO:OXIDISED at low initial concentrations of copper.

2.   Figure 3.3(b) shows isotherm data for CO:ASH and H.C.OX coals with initial concentrations of 1.0 mg/ℓ and 0.5 mg/ℓ of copper. The coal weight was varied from 0.5 gm to 3.0 gm to give the points on the isotherm. The data shows that CO:ASH reduces the concentration to .01 mg/ℓ when treating a solution of 1.0 mg/ℓ, and to undetectable levels when treating a solution containing 0.5 mg/ℓ. It is further evident that CO:ASH provides higher removal efficiencies at these low solute concentrations than does H.C. OX.

3.   Figure 3.3(c) shows copper isotherms for all five coals, using coal weights of 0.5 gm and initial solute concentration ranging from 2 mg/ℓ to 300 mg/ℓ of copper. At higher concentrations, both of the Hat Creek coals have a greater capacity than any of the Cominco coals. The H.C. OX reaches a capacity of 6.0 mg Cu/gm coal at an equilibrium concentration of about 170 mg/ℓ Cu. CO:ASH and CO:OX seem to behave identically with regard to copper in both high

FIG. 3.3 (a)

COPPER ADSORPTION ISOTHERMS

pH = 5.3
Initial concentration = 2mg/litre Cu

×——×   H.C. Oxidized

△——△   H.C. Unoxidized

▢---▢   Co: Production

⊙——⊙   Co: Ash

■---■   Co: Oxidized

●——●   Activated Carbon

INITIAL CONCENTRATION:

0.5 mg/litre Cu { H.C. oxidized +--+
                  CO: ash ▲--▲

1.0 mg/litre Cu { H.C. oxidized ×—×
                  CO: ash △—△

pH = 5.5
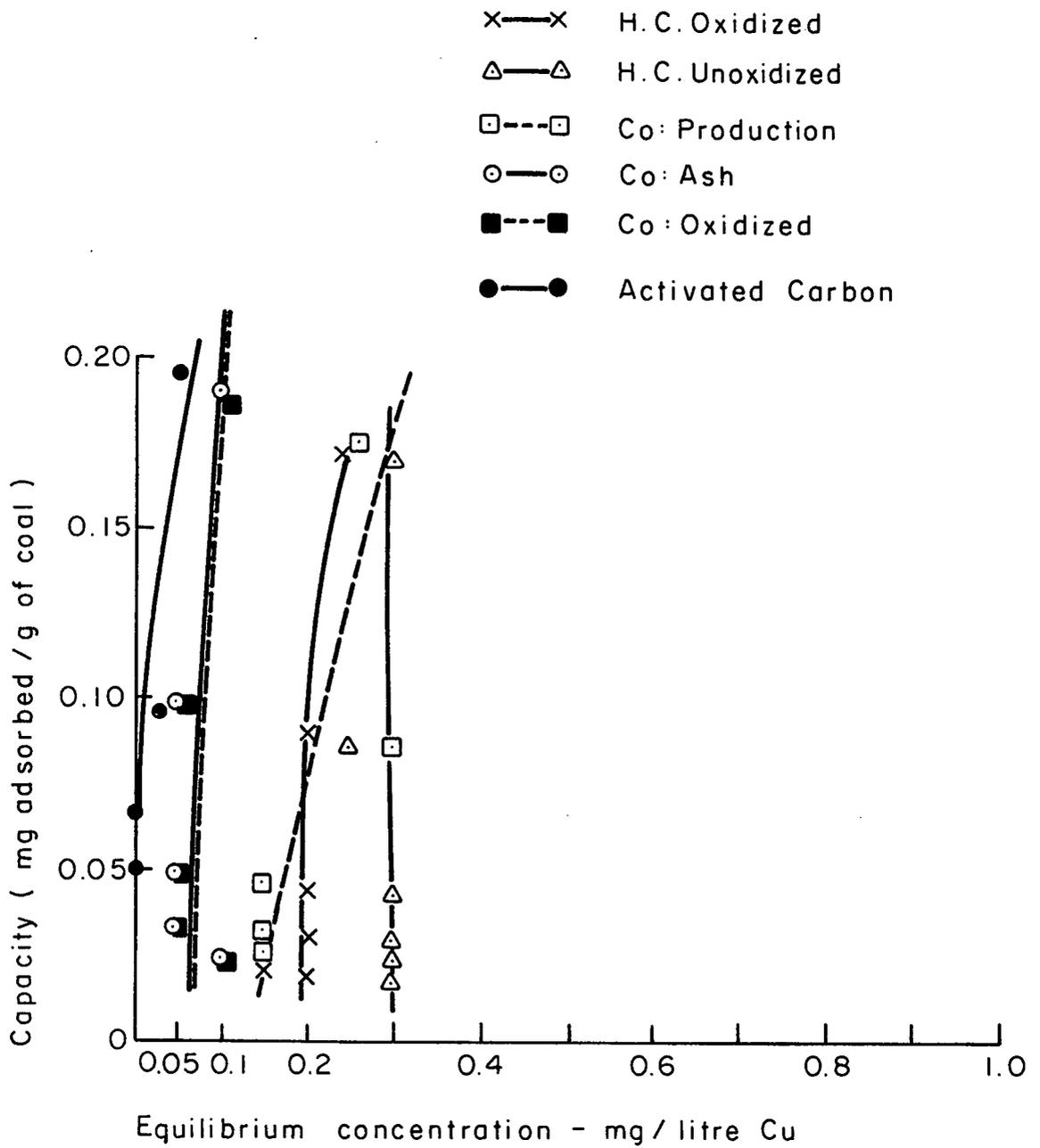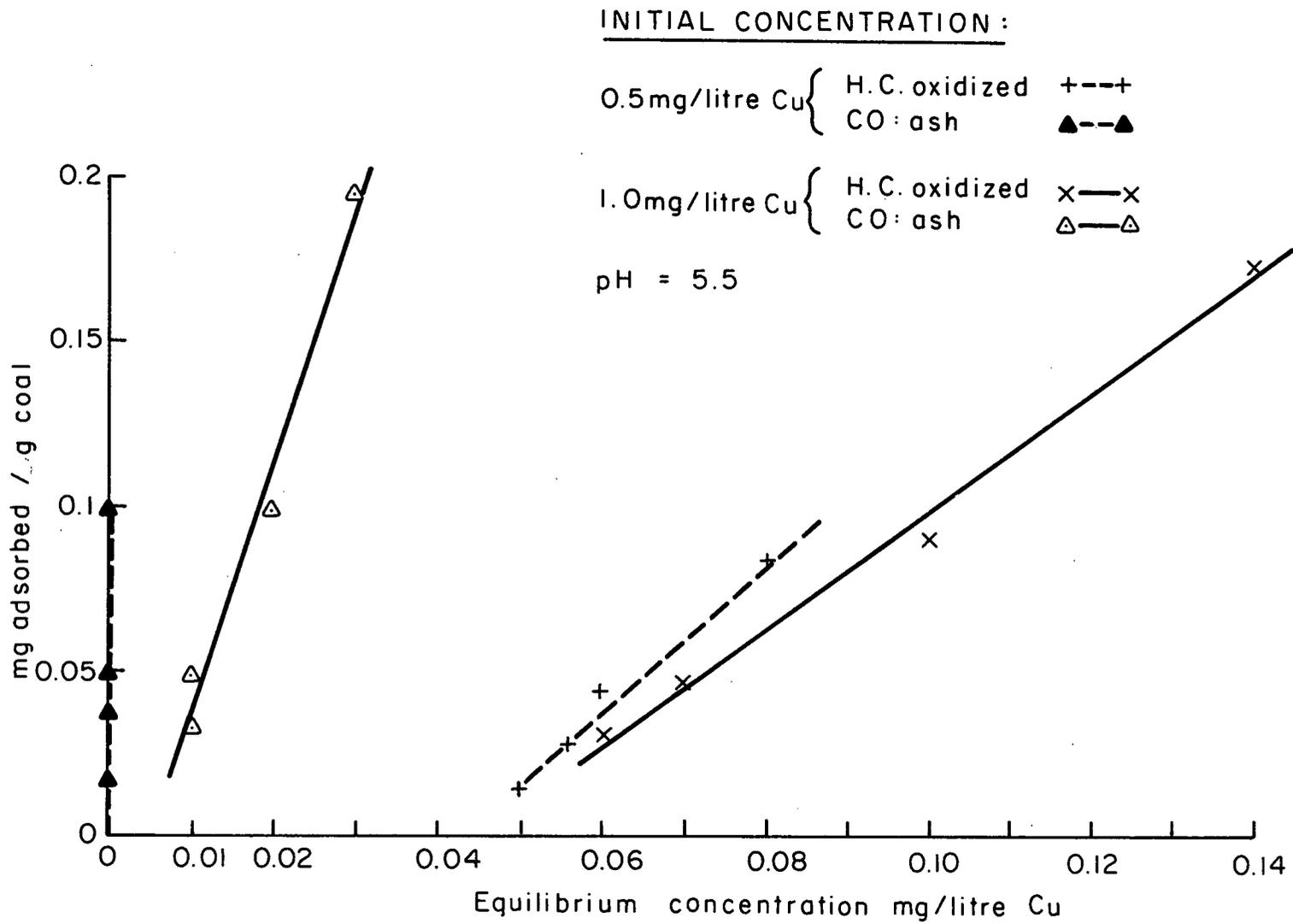
FIG. 3.3 (b)
COPPER ADSORPTION ISOTHERMS

mg adsorbed / g coal

Equilibrium concentration mg/litre Cu

FIG. 3.3(c)
COPPER ADSORPTION ISOTHERMS.

pH = 5.0 — 5.4
Coal weight = 0.5g

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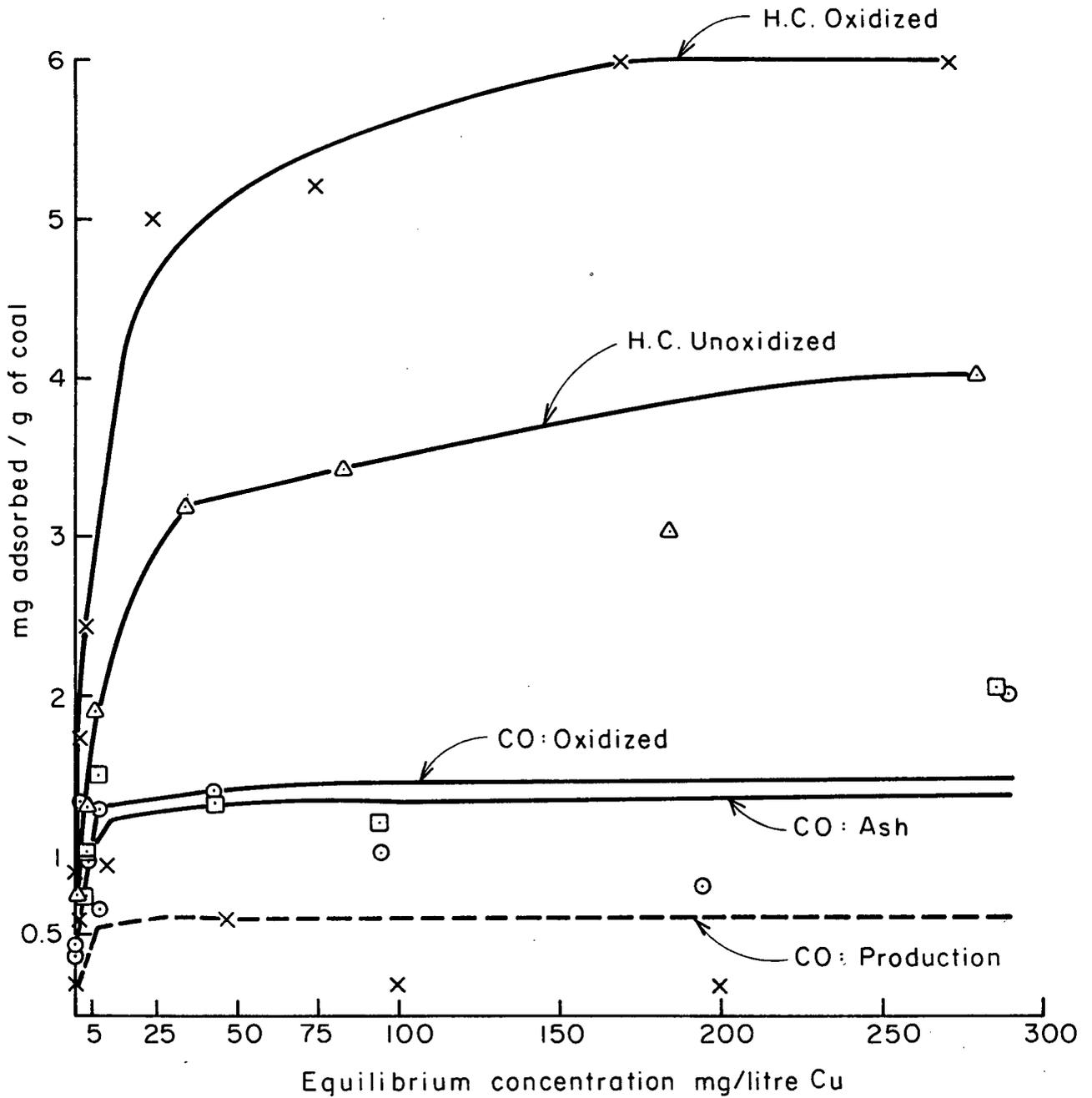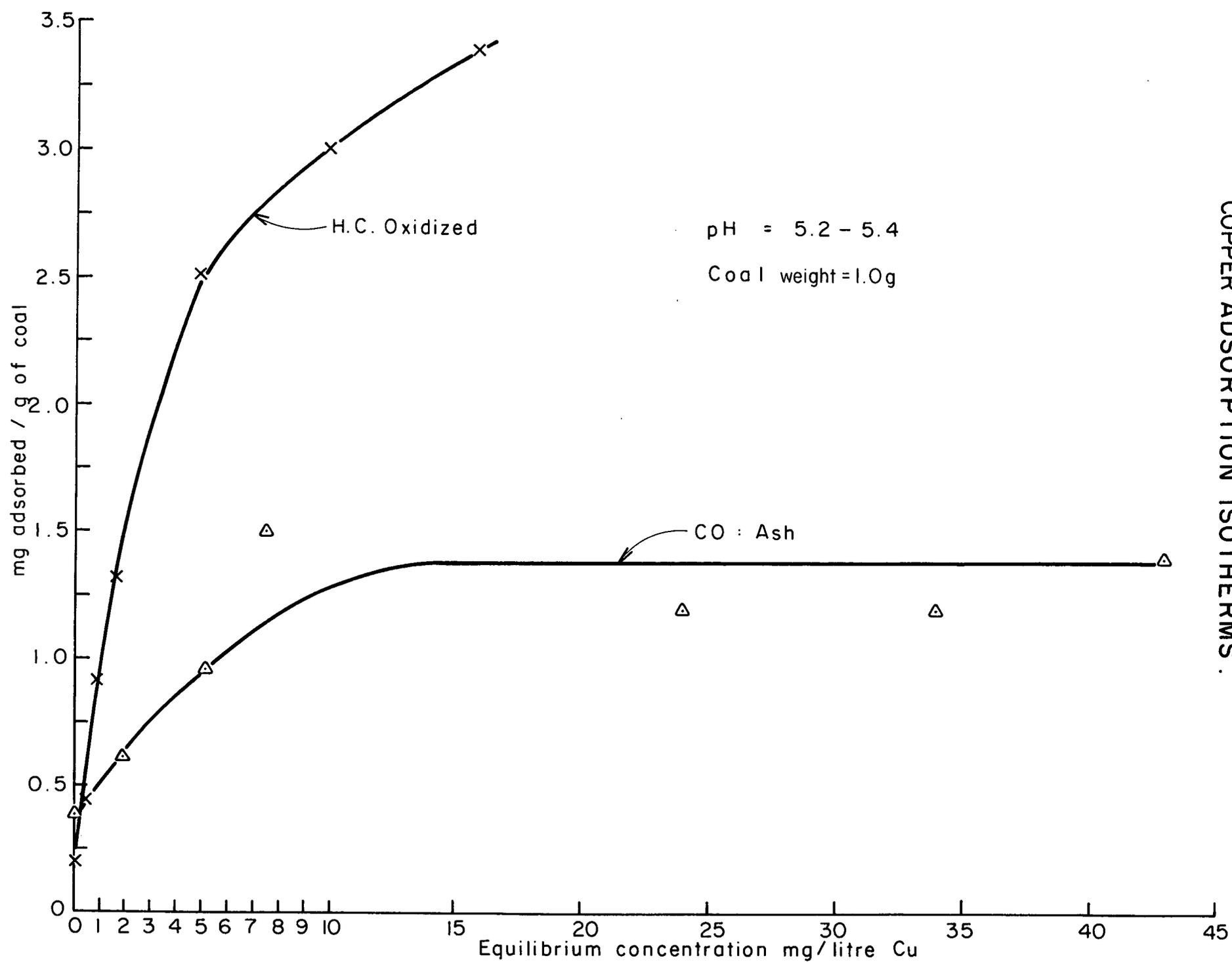
FIG. 3.3 (d)

COPPER ADSORPTION ISOTHERMS.

pH = 5.2 – 5.4

Coal weight = 1.0 g

H.C. Oxidized

CO : Ash

mg adsorbed / g of coal

Equilibrium concentration mg/litre Cu

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and low equilibrium concentrations.

4.   Figure 3.3(d) shows adsorption isotherms for H.C. OX and CO:ASH coals using coal weights of 1.0 gm and initial copper concentrations ranging from 2 mg/ℓ to 50 mg/ℓ.   H.C. OX performs better at higher concentrations while the CO:ASH has a greater capacity at copper concentrations of 2 mg/ℓ and less.   (Note the intersection of two isotherms at about 0.5 mg/ℓ equilibrium concentration).

Considering the copper isotherm results and a few other practical factors, CO:ASH and H.C. OX were chosen for tests with initial concentrations of 1.0 mg/ℓ and 0.5 mg/ℓ while varying the coal weight and also for tests with a fixed coal weight of 1 gm while varying the initial concentrations from 2 mg/ℓ – 50 mg/ℓ. This procedure is applied in zinc and lead tests also.

3.7 Adsorption Isotherms for Lead

1.   All five coals were tested using a solute concentration of 2 mg/ℓ of lead, while the coal weight was varied from 1.0 to 4.0 gm.   The pH was 5.2. All five coals reduced the solute concentration to undetectable levels in all the tests performed. This "super" performance may be explainable by either a very high affinity of the coals for lead, or the relatively high detection limit for lead. The detection limits for the elements of concern are shown below.

Element	Detection Limit by Atomic Absorption
Hg	.05 µg/ℓ for a 3 mℓ sample (cold vapour technique)
Zn	0.01 mg/ℓ (flame technique)
Cu	0.04 mg/ℓ (flame technique)
Pb	0.10 mg/ℓ (flame technique)
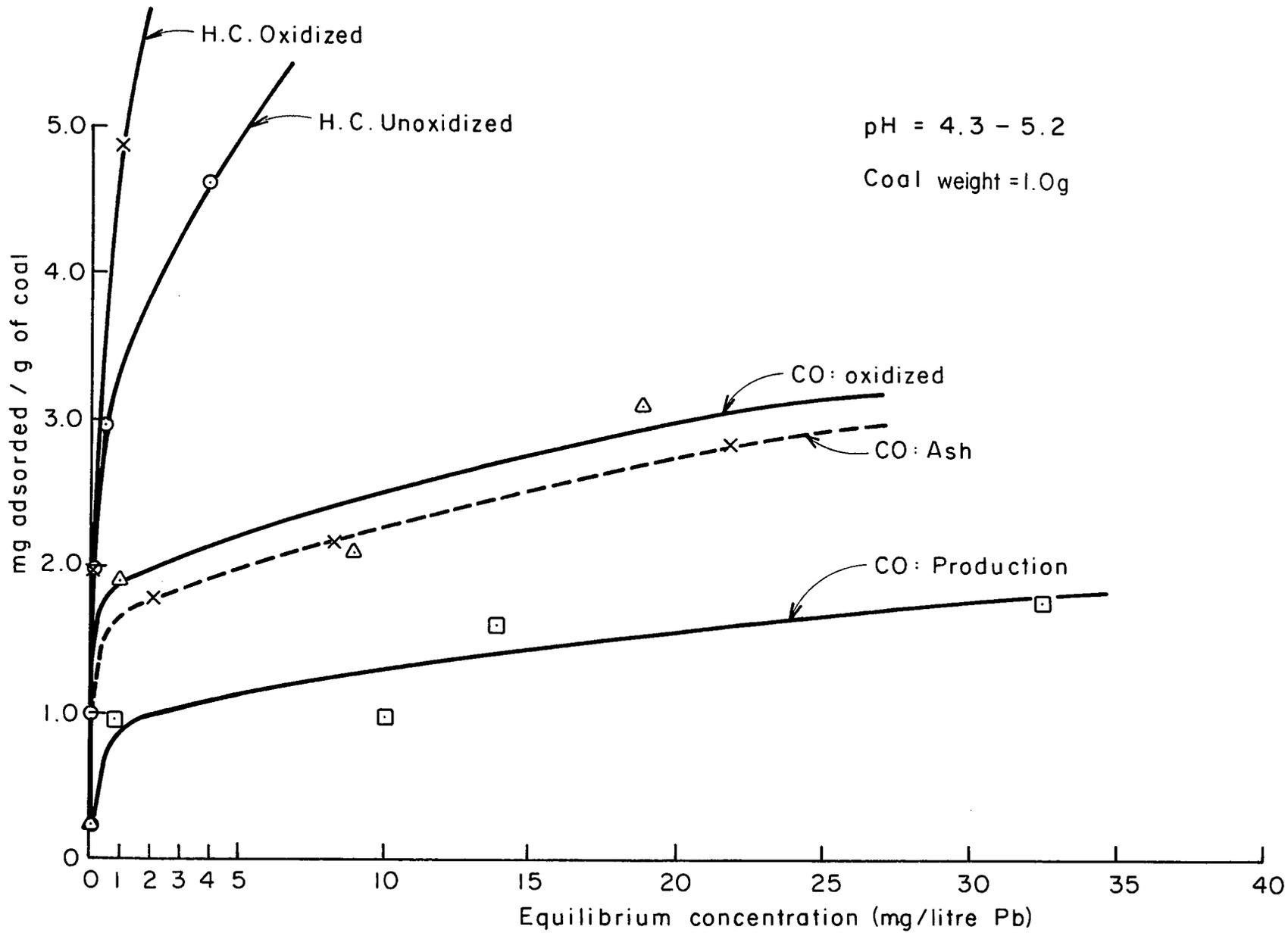
FIG. 3.4
LEAD ADSORPTION ISOTHERMS.

2. Figure 3.4 shows the adsorption isotherms of all five coals using an adsorbent weight of 1.0 gm and initial lead concentrations ranging from 2mg/ℓ to 50mg/ℓ. Hat Creek coals perform better than Cominco coals at higher concentrations. H.C. OX performed the best and achieved a capacity of 5 mg adsorbed/gm of coal at an equilibrium concentration of 1.2 mg/ℓ.

3.8 Adsorption Isotherms for Zinc

1. Figure 3.5(a) shows the adsorption isotherms for all five coals using an initial concentration of 2 mg/ℓ Zn with adsorbent weights being varied from 0.5 gm to 4.0 gm. The Hat Creek coals were found to be better performers in this concentration range, with the H.C. OX reducing the zinc concentration to 0.12 mg/ℓ (using 4 gm of coal). The Hat Creek coals have isotherms with practically no scatter whatsoever. This could mean that the Hat Creek coals have adsorption properties more homogeneously distributed throughout the coal mass than the Cominco coals.

2. Figure 3.5(b) shows the isotherms for H.C. OX and CO:ASH coals with initial solute concentrations of 1.0 mg/ℓ Zn and 0.5 mg/ℓ Zn. The coal weight was varied from 0.5 gm to 3.0 gm. The H.C. OX shows a greater capacity than CO:ASH at all equilibrium concentrations tested. With an initial concentration of 0.5 mg/ℓ, the H.C. OX reduced the concentration to 0.02 mg/ℓ. With an initial zinc concentration of 0.5 mg/ℓ, the isotherms for the two coals came closer to each other, indicating a smaller difference in capacity within this range of equilibrium concentrations.

3. Isotherms for H.C. OX and CO:ASH with initial zinc concentrations ranging from 2 mg/ℓ to 50 mg/ℓ are shown in Figure 3.5(c). The coal weight was fixed at 1.0 gm. H.C. OX performs better, showing a capacity of 2.13 mg adsorbed/gm coal at an equilibrium solute concentration of 28.7 mg/ℓ.
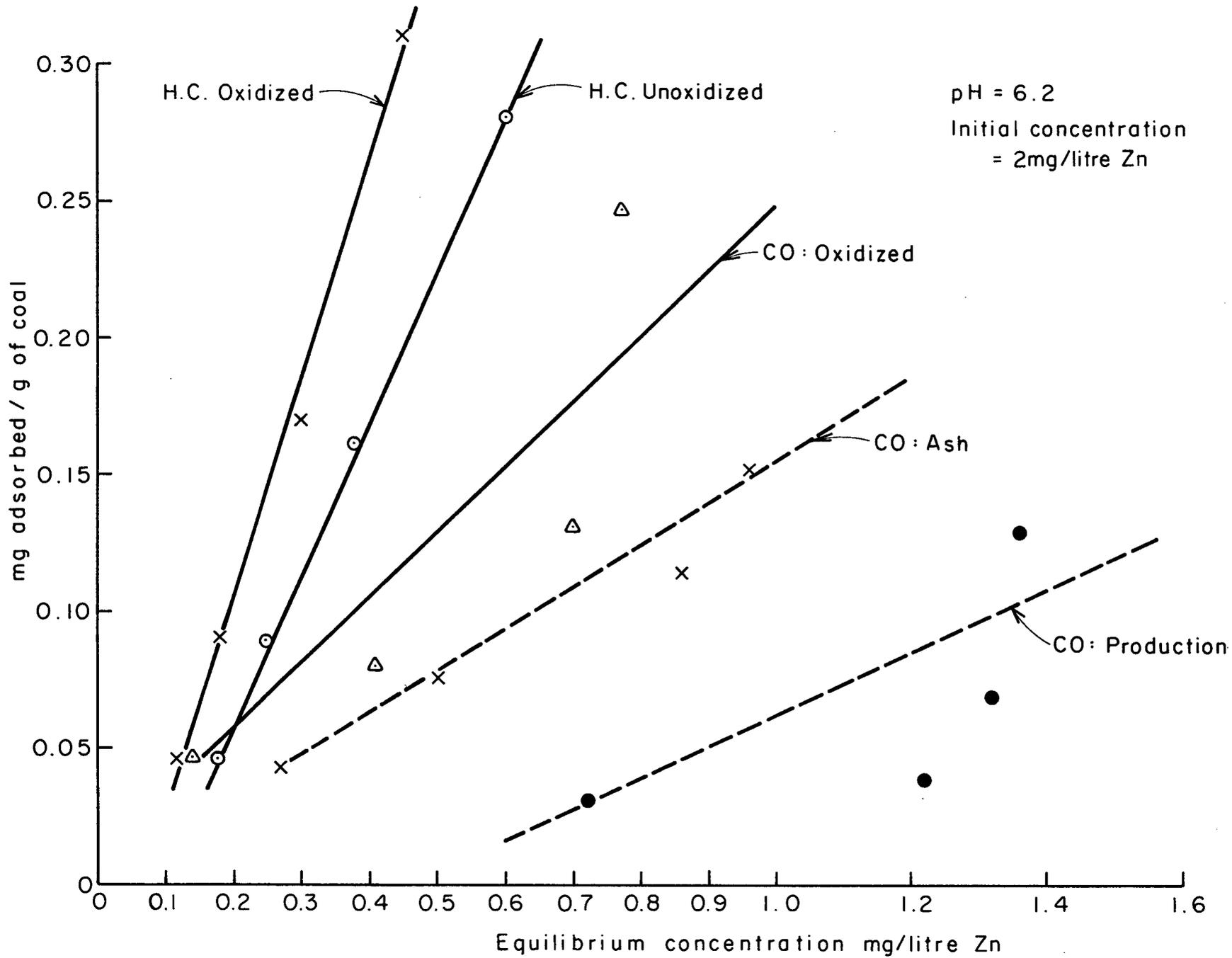
FIG. 3.5(a)

ZINC ADSORPTION ISOTHERMS.

FIG. 3.5(b)
ZINC ADSORPTION ISOTHERMS.

pH = 6.0
Initial concentration = 1mg/litre Zn
and 0.5mg/litre Zn

ZINC ADSORPTION ISOTHERMS.

FIG.3.5(c)

29
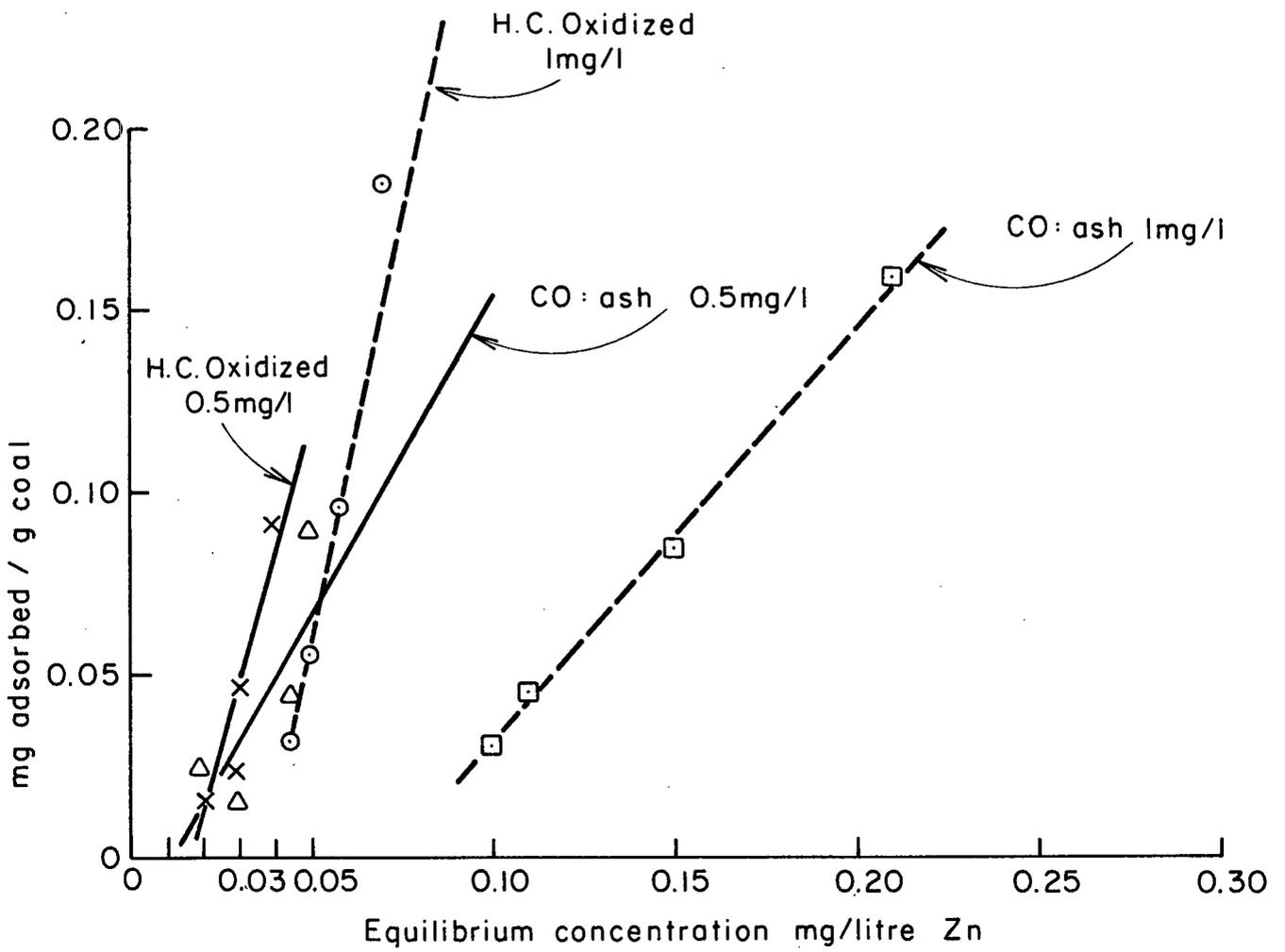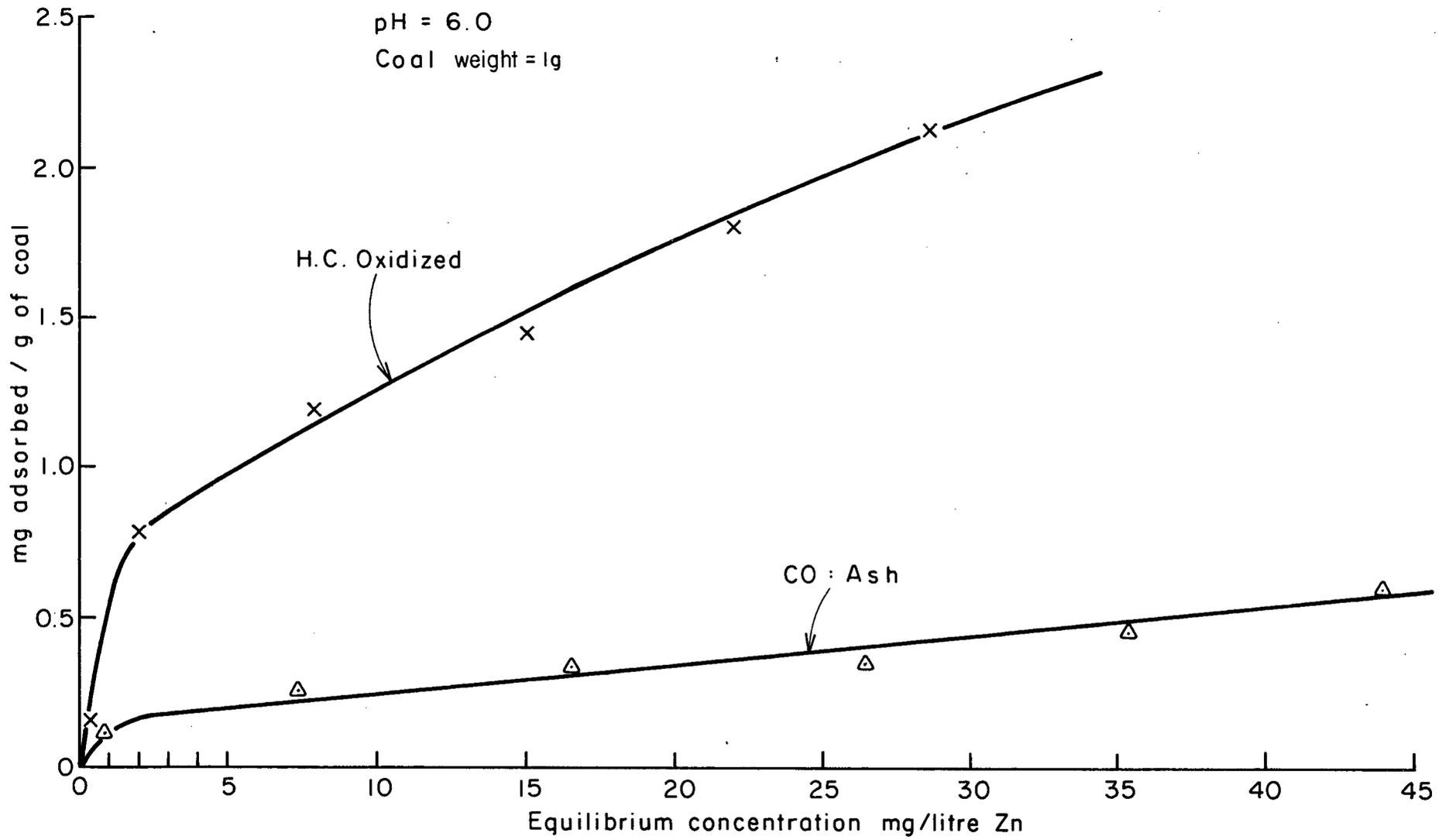
3.9 Adsorption Isotherms for Mercury

1.   In Figure 3.6(a) results are shown from a series of tests using initial solute concentrations of 50 $\mu g/\ell$ Hg, with coal weights varying from 1 gm to 4 gm. The isotherms show that the Hat Creek coals have higher adsorptive capacities than do the Cominco coals. The two Cominco coals have very similar isotherms, indicating very similar adsorptive properties.

2.   Figure 3.6(b) shows isotherm results for H.C. OX and CO:ASH with initial mercury concentrations of 15 $\mu g/\ell$ and 30 $\mu g/\ell$. The coal weight was varied from 0.5 gm to 3.0 gm. H.C. OX displays a greater capacity than CO:ASH at all equilibrium concentrations tested. With an initial concentration of 15 $\mu g/\ell$, H.C. OX produced an effluent containing 3 $\mu g/\ell$, indicating good percent removal even at this low initial concentration.

3.   The isotherms for H.C. OX and CO:ASH with initial concentrations ranging from 100 $\mu g/\ell$ to 2000 $\mu g/\ell$ (i.e., from .1 mg/ℓ to 2.0 mg/ℓ) are shown in Figure 3.6(c). The coal weight used was 1.0 gm. The slope of the H.C. OX isotherm is very much steeper than that of the CO:ASH isotherm indicating a significant capacity advantage using H.C. OX. It reached a capacity of 0.18 mg adsorbed/gm coal at an equilibrium mercury concentration of 0.21 mg/ℓ.

3.10 Batch Tests - Summary and Conclusions

1.   The optimum contact time for batch tests to achieve a high percentage of ultimate equilibrium concentration within a short practical period of time was found to be 1 hour.

2.   The adsorptive capacity of coal for copper, lead and zinc was found to increase as the pH was raised from 1.5 to 6.2. The rate of change in adsorptive capacity per unit change in pH is different for each metal.

FIG. 3.6 (a)

MERCURY ADSORPTION ISOTHERMS.

pH = 5.8
Initial concentration = 50 ug/l (0.050 mg/litre)
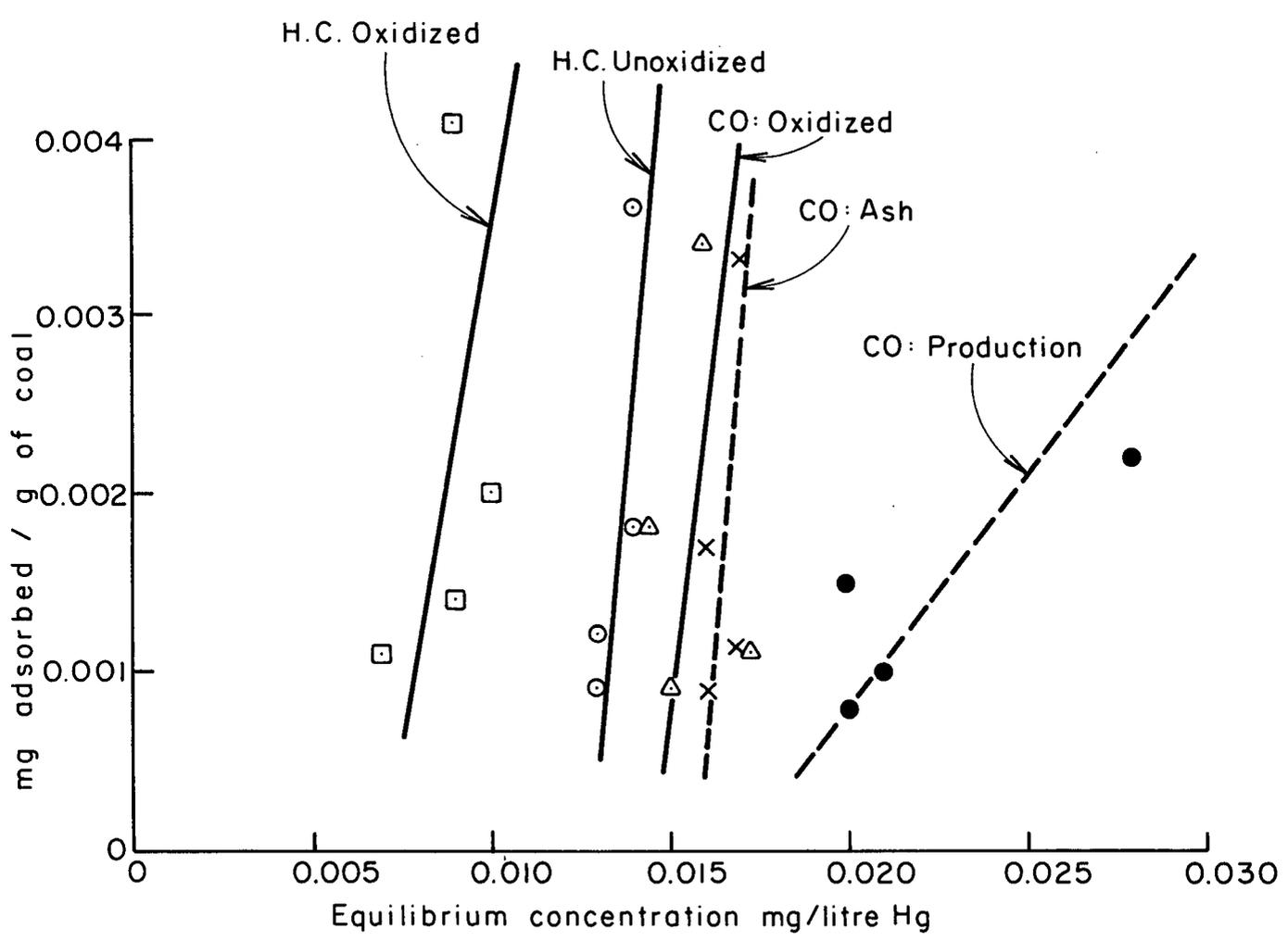
FIG. 3.6 (b)

MERCURY ADSORPTION ISOTHERMS.

pH = 5.8

Initial concentration = 15 ug/l and 30 ug/l of Hg
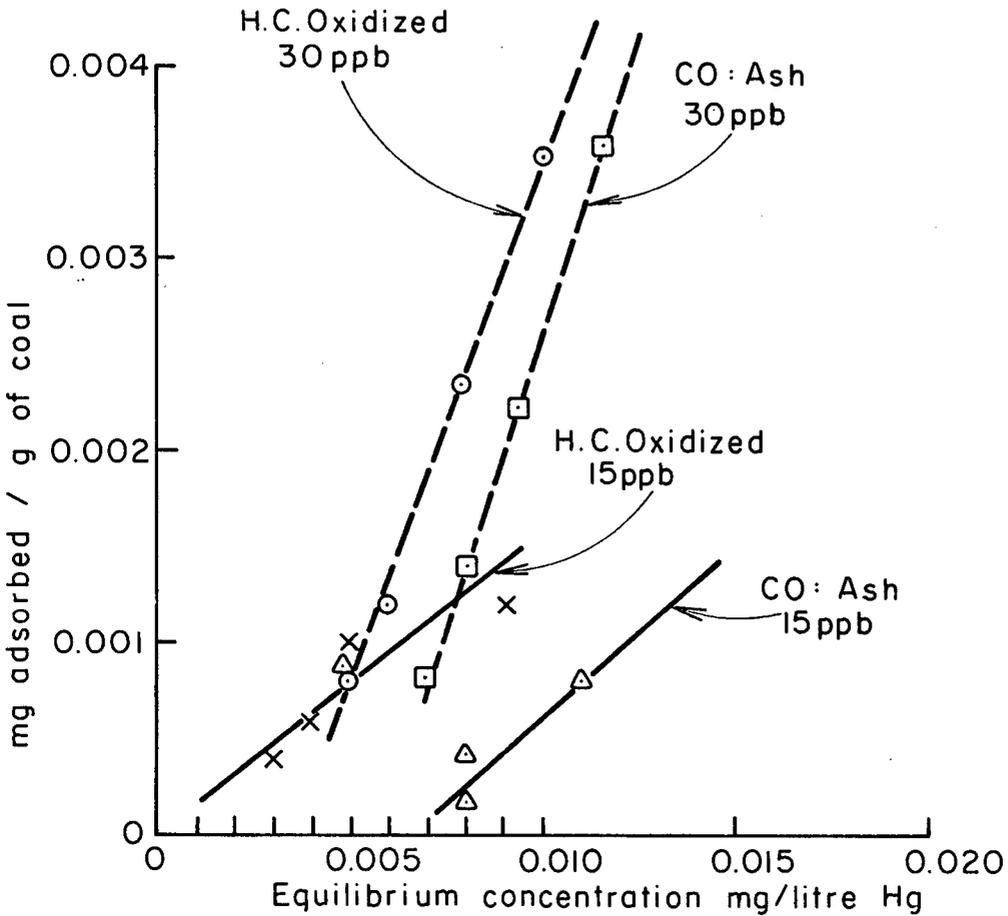
pH = 5.4 — 5.8

Coal weight = 1 g

Initial concentrations = 100 ug/l — 2,000 ug/l

MERCURY ADSORPTION ISOTHERMS.

FIG. 3.6(c)

H.C.Oxidized

CO : Ash

mg adsorbed / g of coal

Equilibrium concentration mg/litre Hg

33
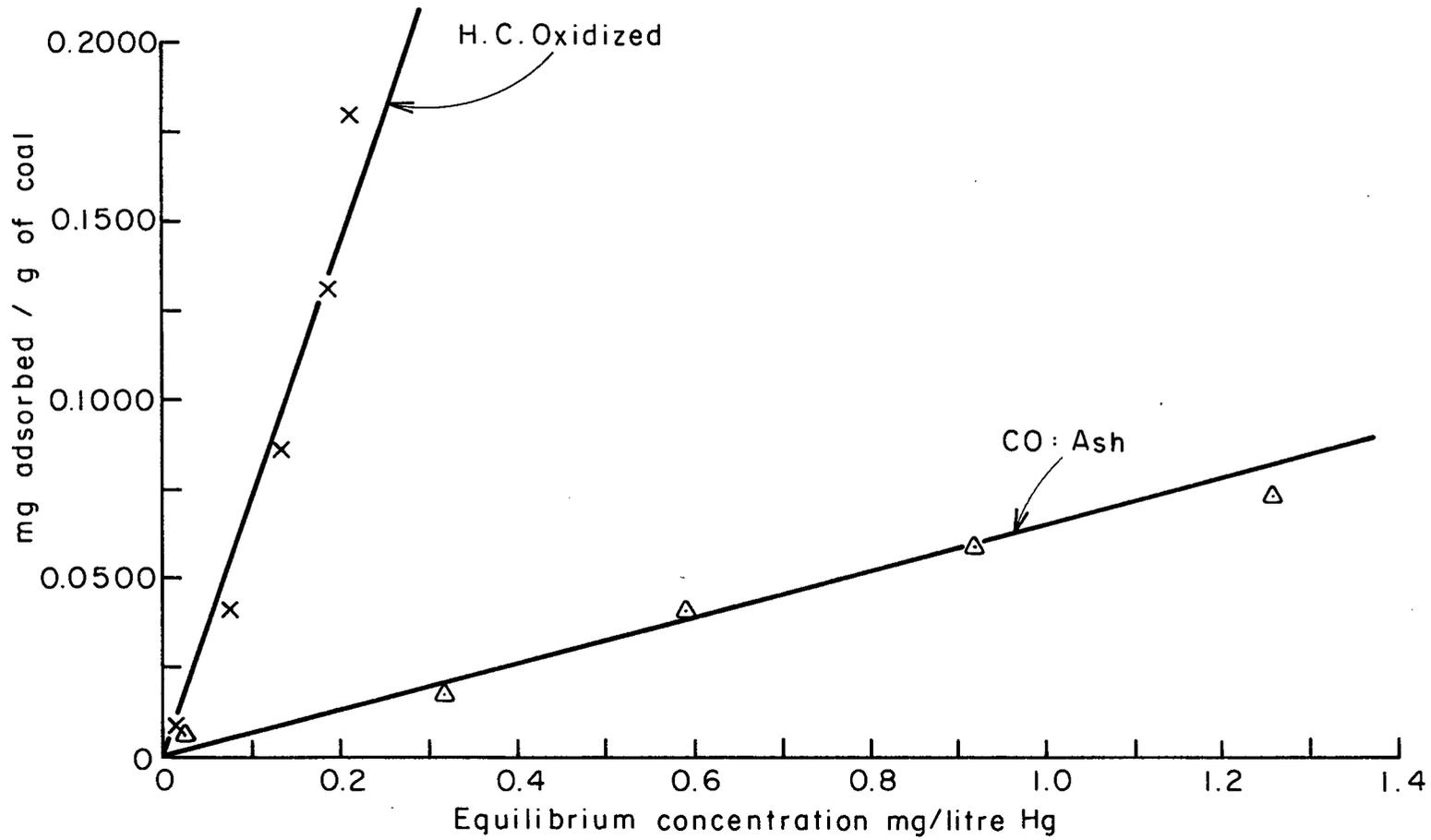
3.   When coal weight and initial metal concentration are both changed in the same proportion, the percent removal stays about the same.

4.   Diluting the waste resulted in a significantly greater increase in percent removal than would be obtained when the coal weight is increased instead by the same proportion.

5.   (a) Of the two Hat Creek coals, H.C. OX was the better performer with copper, zinc and mercury as the adsorbate. In the case of lead, H.C. OX has a greater capacity within the 2 mg/ℓ – 50 mg/ℓ equilibrium concentration range. No differentiation could be made when the equilibrium concentration was below 2 mg/ℓ Pb. Among the Cominco coals, CO:OX and CO:ASH displayed the same isotherm with 2 mg/ℓ Cu initial concentration. In almost all of the remaining experiments with lead, zinc and mercury, CO:OX appeared to be only marginally better than CO:ASH.

On the basis of these results, H.C. OX and CO:ASH were chosen as the best of each coal type for the column test phase of the project. CO:ASH was chosen because it performed almost as well as CO:OX, and it has a better production potential because of its greater availability.

(b) Table 3.3 shows the comparison of H.C. OX and CO:ASH with regard to their adsorptive capacities. Table 3.3 indicates adsorptive superiority of H.C. OX with lead, zinc and mercury. In the case of copper, H.C. OX has a greater adsorptive capacity in the higher initial concentration range (2.0 mg/ℓ – 50 mg/ℓ), while in the lower initial concentration range of 2.0 mg/ℓ and less the situation is reversed and CO:ASH proved to be the superior one.

(c) Table 3.4 shows a comparison of performance of a particular coal with each of the four heavy metals. Within the equilibrium concen-

tration range of .03 mg/ℓ to 30.0 mg/ℓ, lead has the greatest affinity for adsorption by both coals. Copper proved to have the second highest affinity, zinc third and mercury last with regard to adsorption by both coals.

TABLE 3.3

COMPARISON OF H.C. OX AND CO:ASH

Note: The coal with a better adsorption performance is printed in the relevant slot.

Element	Initial Concentrations of Wastewater			
	0.5 mg/ℓ	1.0 mg/ℓ	2.0 mg/ℓ	2.0 mg/ℓ – 50 mg/ℓ
Cu	CO:ASH	CO:ASH	CO:ASH	H.C. OX
Pb	← ←	UNDIFFERENTIABLE	→ →	H.C. OX
Zn	H.C. OX	H.C. OX	H.C. OX	H.C. OX
	15 μg/ℓ	30 μg/ℓ	50 μg/ℓ	100 μg/ℓ – 2000 μg/ℓ (.1 mg/ℓ – 2.0 mg/ℓ)
Hg	H.C. OX	H.C. OX	H.C. OX	H.C. OX

TABLE 3.4

Comparison of the Capacities of Two Coals For

Each of the Four Heavy Metals

Coal	Equilibrium Concentration (mg/ℓ)	Capacity (mg adsorbed/gm coal)			
		Pb	Cu	Hg	Zn
	.05	BDL*	.015	.035	.080
	.10	>.10	.10	.07	.25
	.50	3.20	.50	.35	.37
H.C. OX	1.0	4.80	.90	---	.55
	5.0	>5.0	2.50	---	.98
	10.0	>5.0	3.00	---	1.27
	30.0	>5.0	4.80	---	2.17
	.03	BDL*	.18	.003	.03
	.10	>.20	.20	.008	.032
	.50	1.50	.43	.035	.08
CO:ASH	1.0	1.68	.50	.065	.155
	5.0	1.98	.95	---	.20
	10.0	2.30	1.28	---	.25
	30.0	3.10	1.38	---	.45

NOTE:

1. * BDL means the equilibrium concentration is below detection
    limit and consequently the capacity cannot be determined.

2. Several blanks are shown in the Hg column due to the fact
    that Hg was not tested at these higher concentrations.

4.1 Introduction

Based on the results of the batch tests, H.C. OX from the Hat Creek group and CO:ASH from the Cominco group of coals were chosen for further investigatory work with continuous flow, fixed-bed columns.

On the basis of the data from the batch tests and from a few preliminary column tests at various values of the influent pH, the maximum adsorptive capacity of a particular column was suspected to occur at an influent pH near neutrality (6 to 7.5). Initial results indicated that at such a neutral pH, and under the laboratory conditions used in this research, it would take more than ten or eleven days for any sign of metal breakthrough to occur. To overcome this impracticality with regard to the time factor, the pH was reduced to 4.0, which gave rise to a breakthrough within a reasonable period of time. Then an extrapolation factor, derived from previous column test data was employed to give an estimate of the adsorptive capacity at an influent pH of $6.0 \sim 7.5$.

The influent metal concentrations were at 2 mg/ℓ and less for zinc, copper and lead, and less than 5 μg/ℓ for mercury. These figures are in the neighbourhood of permissable levels, set up by the Pollution Control Board of British Columbia, for discharge of these metals into various types of receiving waters.

The flow rates tested were between one and five Igpm/ft^2. These flow rates are representative of the ones used in rapid sand filtration and activated carbon adsorption systems.

The coal depth was maintained at ten inches for the following reasons: 1) to ensure that the depth is greater than the critical bed depth to prevent penetration of concentration in excess of breakthrough concentration at zero time;

2) to satisfy practical considerations that the breakthrough does not take too long a period of time. Excessively deep beds of coal will result in long periods of time for breakthroughs to occur. The depth of the coal bed is an important criterion whenever comparative work is done, since the contact time is primarily dependent on the bed depth for a given flow rate. Table 4.1 shows the corresponding contact times for the flow rates listed, based on an empty column and a coal-filled column of 10 inches.

TABLE 4.1

CONTACT TIMES FOR A 10-INCH COLUMN
AT GIVEN FLOW RATES

FLOW RATE		CONTACT TIME (Min)	
Igpm/ft^2	inches/min	Empty Column	Coal-filled Column
1	1.92	5.21	2.86
5	9.60	1.04	0.58

For the calculation of the actual contact time for a coal-filled column, the porosity of the coal column is necessary. From the literature on bed porosity, packing, etc. (11, pp.537), a graph, relating sphericity, type of packing and porosity, was used to estimate the porosity. With an assumed sphericity of the particles of 0.6 and a normal type of packing, the resultant porosity was estimated at 0.55.

Example Calculation for Actual Contact Time

$$1 \text{ Igpm/ft}^2 = 1.92 \text{ in/min}$$

Based on an empty column of 10 inches

$$\text{contact time} = 10 \text{ in} \times \frac{1}{1.92 \text{ in/min}}$$

$$= 5.21 \text{ min}$$

Using the porosity factor of 0.55,

the actual contact time of coal-filled column of 10 inches

$$= 5.21 \text{ min} \times 0.55$$

$$= 2.86 \text{ min}$$

The major portion of the column work (i.e., investigating the effects of pH, flow rate, etc.) was done with zinc as the adsorbate. Zinc was chosen because it is more sensitive on the atomic absorption spectrophotometer than copper or lead.

The general objective of the column tests was to obtain some figures for the capacities of the two coals tested for zinc, copper and lead at influent pH values of 4.0 and 5.7.

Tests for mercury were run with influents in the 5 μg/ℓ range, with an effluent pH of 7.5.

4.2 Column Testing Apparatus

From preliminary column tests, it was apparent that breakthrough would, generally, not occur before 24 hours had elapsed. This necessitated a holding tank of adequate size for the influent in order that the tank could be filled once in every 24 hours or so for practical convenience. Figure 4.1(a) and Figure 4.1(b) are schematic diagrams of the apparatus used. As the liquid passes through the coal column and out through the burette, the liquid level
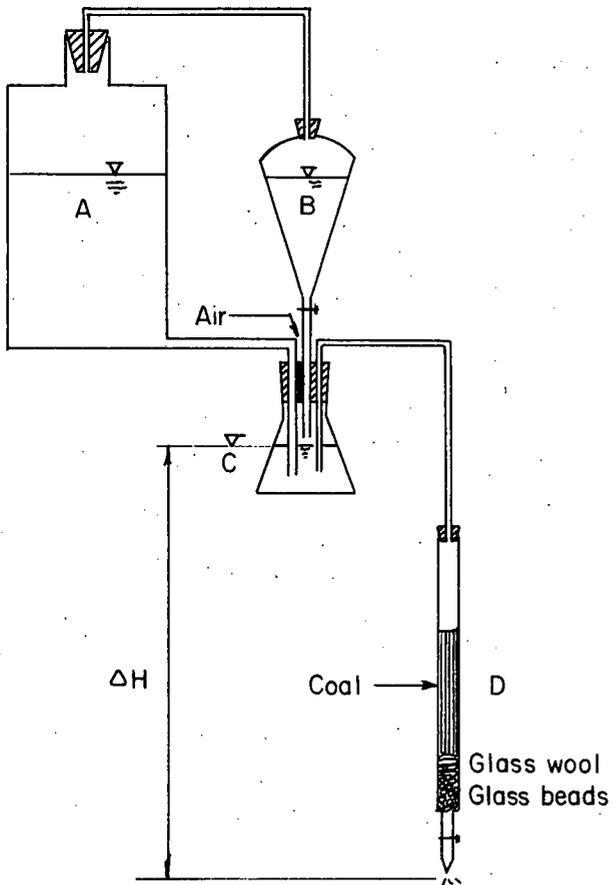
FIG. 4.I (a)
CONSTANT HYDRAULIC HEAD APPARATUS
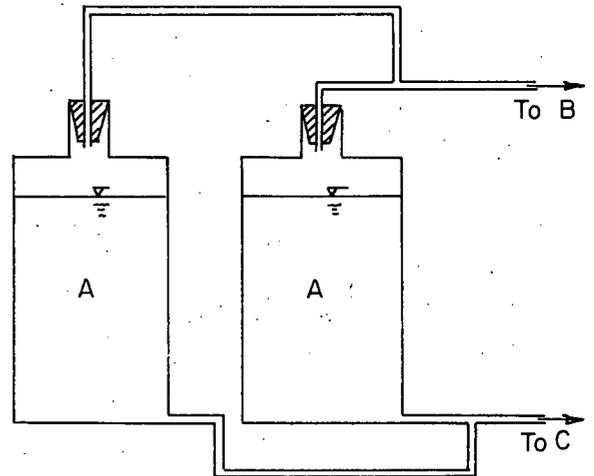
FIG. 4.I (b)
DOUBLE TANK FEED MODIFICATION

A   INFLUENT HOLDING TANK
B   SEPARATORY FUNNEL
C   ERLENMEYER FLASK
D   BURETTE

in C will fall. Just as the level falls below that of the opening of the tubing connected to B, air will enter through the hole in the stopper of C, as shown, and up through the tubing into B. This will reduce the partial vacuum in A and B and more liquid will fall into C until the partial vacuum in A and B above the liquid levels is in equilibrium with the hydraulic heads supported in A and B.

Thus, we have a constant head of ΔH as shown in Figure 4.1(a) to drive the liquid through the coal column. For the flow rate to remain constant after being set, it is essential that the hydraulic driving head remains constant.

The element B (separatory funnel) can be simply replaced by a straight tubing. Using a separatory funnel provides the system with additional influent storage volume.

Figure 4.1(b) shows the modified set-up that was used when running tests at 5 Igpm/ft^2 where a larger influent storage volume was necessary. Here, there are two tanks, instead of one, connected to the rest of the apparatus according to the same principles.

4.3 Column Testing Procedure

A) Copper, Lead and Zinc

The laboratory procedure consists of the following steps:-

1) The influent solution of a desired metal concentration is prepared and its pH adjusted to the desired value.

2) Enough coal to fill 10 inches of the burette is weighed out in a beaker.

3) Distilled water is added so that the coal in the beaker is completely submerged. The contents are then subjected to a slow boil for about five minutes in order to expel all the entrapped air and to

thoroughly wet the coal.

4)   The wetted coal is then transferred into the burette, which is packed at the bottom with glass wool and glass beads. During this transfer, the coal in the burette is carefully kept submerged to prevent any re-entrapment of air.

5)   The influent solution is introduced into the coal column, and the burette valve is adjusted to achieve the desired flow rate.

6)   The effluent is sampled at desired intervals.

7)   The pH of the effluent samples is measured.

8)   The metal concentration of the effluent samples is measured with an Atomic Absorption Spectrophotometer as in the Batch Testing Procedure.

For most of the tests, the system was kept running until the effluent concentration exceeded a level of twenty to thirty percent of the influent concentration.

B)   Mercury

The procedure is the same as for zinc, copper and lead, but the effluent samples are subjected to a pretreatment described below, before being tested on the Atomic Absorption Spectrophotometer.

This pretreatment consists of the following steps:-

1)   100 mℓ of the effluent is collected and cooled in a refrigerator for about 1 hour. Care must be taken that the container of the collected effluent has a perfect sealing cap that will prevent any volatilization of the mercury.

2)   1 mℓ of concentrated sulfuric acid is added to the cooled sample. This is done to fix the mercury in the solution better and thus to enable overnight storage.

3)   About 20 minutes before testing on the Atomic Absorption

Spectrophotometer, 1 ml of 6 percent potassium permanganate is

added. The container is then shaken and allowed to sit.

4)   The total contents of the container, 100 ml of effluent and

2 ml of reagents,are transferred to a testing flask.

5)   Then 0.5 ml of 10 percent $NH_2OH.HCl$ is added.

6)   Finally 2.0 ml of 10 percent $SnCl_2$ is added just before analysis

on the Atomic Absorption Spectrophotometer by the cold vapour

technique.

The above procedure enabled accurate detection down to a limit of

0.05 µg/l.

4.4 Breakthrough Curve Calculations

A typical breakthrough curve is shown in Figure 4.2. An arbitrary

breakthrough concentration of 0.5 mg/l was chosen. A horizontal line is drawn

through this 0.5 mg/l mark to intersect the curve and a vertical line is then

drawn through this intersection. After having determined the milligrams of zinc

adsorbed and the milligrams of zinc passed through, (refer to Figure 4.2) the

following two calculations can be done.

1) $\dfrac{\text{mg of Zn adsorbed}}{\text{gm of coal in column}}$ =   mg of Zn adsorbed per gm of coal.

2) $\dfrac{\text{mg of Zn passed out through effluent}}{\text{litres of treated effluent at breakthrough concentration}}$

=   Average effluent concentration in mg/l

4.5 Breakthrough Curves for Zinc

The batch tests showed that the adsorption isotherms for zinc had the

least scatter of the heavy metals tested. Due to this fact and the fact that

FIG.4.2
A TYPICAL BREAKTHROUGH CURVE
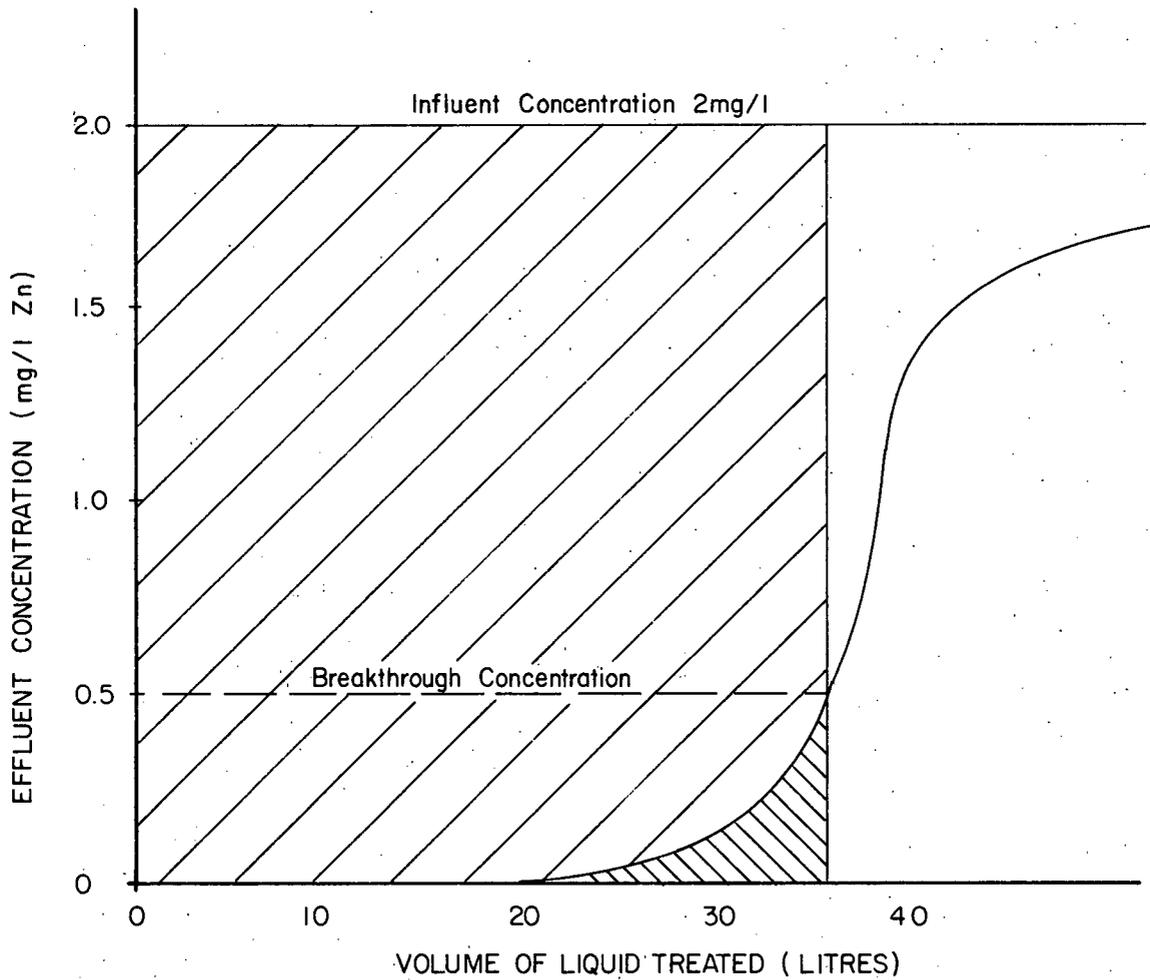
THIS AREA ABOVE THE CURVE REPRESENTS THE
WEIGHT OF ZINC IN MILLIGRAMS ADSORBED BY THE COAL

THIS AREA BELOW THE CURVE REPRESENTS THE WEIGHT OF
ZINC IN MILLIGRAMS PASSED OUT THROUGH THE EFFLUENT

zinc is more sensitive on the Atomic Absorption Spectrophotometer than lead or copper, zinc was chosen as the main impurity for column tests to investigate the effects of absorptive capacity caused by:-

    a)   Variations in cross-sectional area of the coal bed.

    b)   "   in influent pH.

    c)   "   in flow rate.

    d)   "   in influent metal concentration.

a)   Effect of Varying the Cross-Sectional Area of the Coal Bed

        After a few trial column tests with burettes of various diameters available in the laboratory, the choice of the cross-sectional area to be used was narrowed down between that of the 50 ml burette ($.001$ ft^2) and that of the 100 ml burette ($.002$ ft^2). Using the smaller area of $.001$ ft^2 would mean a practical convenience of having to use less coal per column and less total liquid to reach breakthrough. On the other hand, care must be taken not to go below the critical diameter and encourage wall effects, which will reduce the adsorptive capacity of the coal column.

        Figure 4.3 shows the breakthrough curves for the column tests performed using bed areas of $.001$ ft^2 and $.002$ ft^2.

        From TABLE 4.2, it is apparent that there is only a slight decrease in adsorptive capacity when the cross-sectional area was changed from 0.002 ft^2 to 0.001 ft^2. Therefore, it was decided to use the 50 ml burette with a 0.001 ft^2 for the rest of the study. It was suspected though, that wall effects would be experienced if a smaller diameter burette than the 50 ml burette were used.

Influent = 2.0 mg/l Zn
Influent pH = 5.7
Flow rate = 1 Igpm/ft.²
Bed depth = 10 inches
Coal = CO ASH

BED CROSS-SECTIONAL AREA   COAL WEIGHT

x———x   .002 ft.²   38 gm
o———o   .001 ft.²   20 gm

EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)
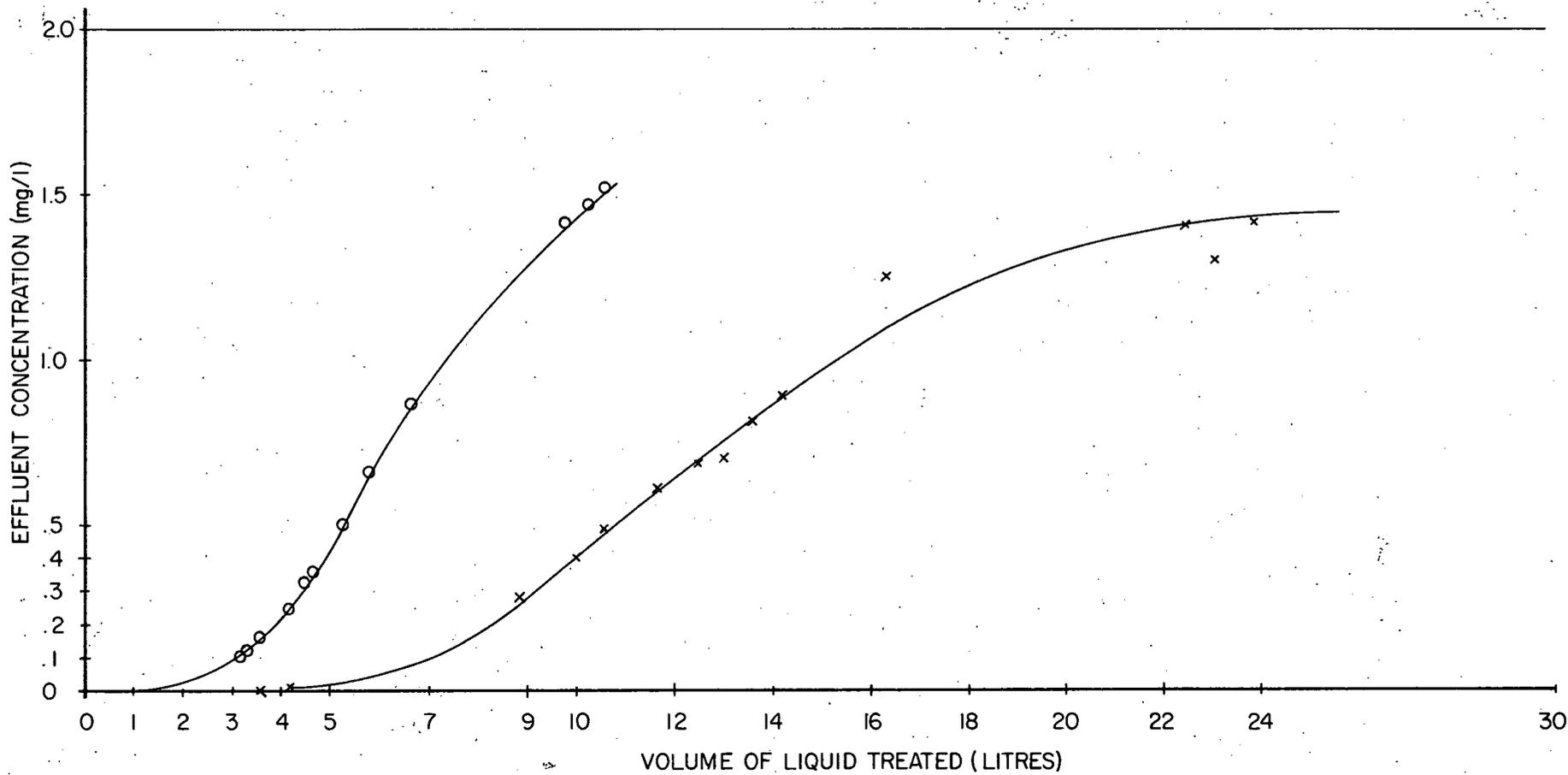
TABLE 4.2

EFFECT OF CHANGING CROSS-SECTIONAL AREA

OF THE COAL BED

Cross-sectional Area of Coal Bed (ft)	Capacity (mg/gm) at			Average Effluent Concentration (mg/) at		
	10%	25%	50%	10%	25%	50%
0.001	0.378	0.503	0.624	.046	.133	.310
0.002	0.438	0.540	0.692	.042	.113	.308

Note-   10%, 25%, 50% refers to the breakthrough concentration of 10% of

the influent, 25% of the influent and 50% of the influent. This

notation will be used henceforth in the TABLES.

b) Effect of Varying the Influent pH

Many other researchers have found that the pH of the influent plays a

critical role in determining the adsorptive capacity. The pH of a solution

from which adsorption occurs may, for one or more of a number of reasons,

influence the extent of adsorption. Because hydrogen and hydroxide ions are

adsorbed quite strongly, the adsorption of other ions is influenced by the pH

of the solution. Weber[9] found that, in general, adsorption of typical organic

pollutants from water is increased with decreasing pH. In many cases, this may

result from neutralisation of negative charges at the surface of the carbon

with increasing hydrogen-ion concentration, thereby reducing hindrance of

diffusion and making available more of the active surface of the carbon.

Figure 4.4 shows the breakthrough curves obtained at influent pH

values of 3.0, 4.0 and 5.7 for both H.C. OX and CO:ASH coals. There is a

definite decrease in adsorptive capacity with decreasing pH in both cases.

TABLE 4.3 summarises the results of Figure 4.4 in a tabular form. H.C. OX at

a breakthrough of 10 percent shows a capacity decrease of 84 percent when the

TABLE 4.3

EFFECT ON ZINC ADSORPTION OF VARYING THE INFLUENT pH

Breakthrough Conc. as Percent of Influent Conc.	Influent pH	Capacity (mg/gm)		Average Effluent Conc. (mg/ℓ)		Throughput* (litres)	
		H.C.OX	CO:ASH	H.C.OX	CO:ASH	H.C.OX	CO:ASH
10% = .2mg/ℓ	3	0.138	.013	.030	.252	0.85	0.10
	4	1.582	.074	.017	.070	10.33	0.72
	5.7	9.716	.370	.010	.027	63.47	3.72
25% = .5mg/ℓ	3	0.204	.014	.107	.194	1.41	0.13
	4	1.805	.105	.059	.110	12.00	1.15
	5.7	10.481	.491	.037	.126	69.33	5.22
50% = 1.0mg/ℓ	3	0.260	.018	.323	.344	1.95	0.22
	4	1.931	.146	.129	.345	13.33	1.68
	5.7	10.943	.627	.082	.310	74.00	7.40

*THROUGHPUT signifies the total volume of liquid that has passed through the column at any particular time.

Influent = 2mg/l Zn
Flow rate = 1 Igpm/ft.^{2}
Bed depth = 10 inches
Coal weight = H.C. OX = 13gm
CO:ASH = 20gm

FIG. 4.4
EFFECT OF VARYING THE INFLUENT pH

EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)

pH = 3.0
pH = 4.0
pH = 5.7
pH = 3.0
pH = 4.0
pH = 5.7

×——× H.C. OX
○—-—○ CO:ASH

49
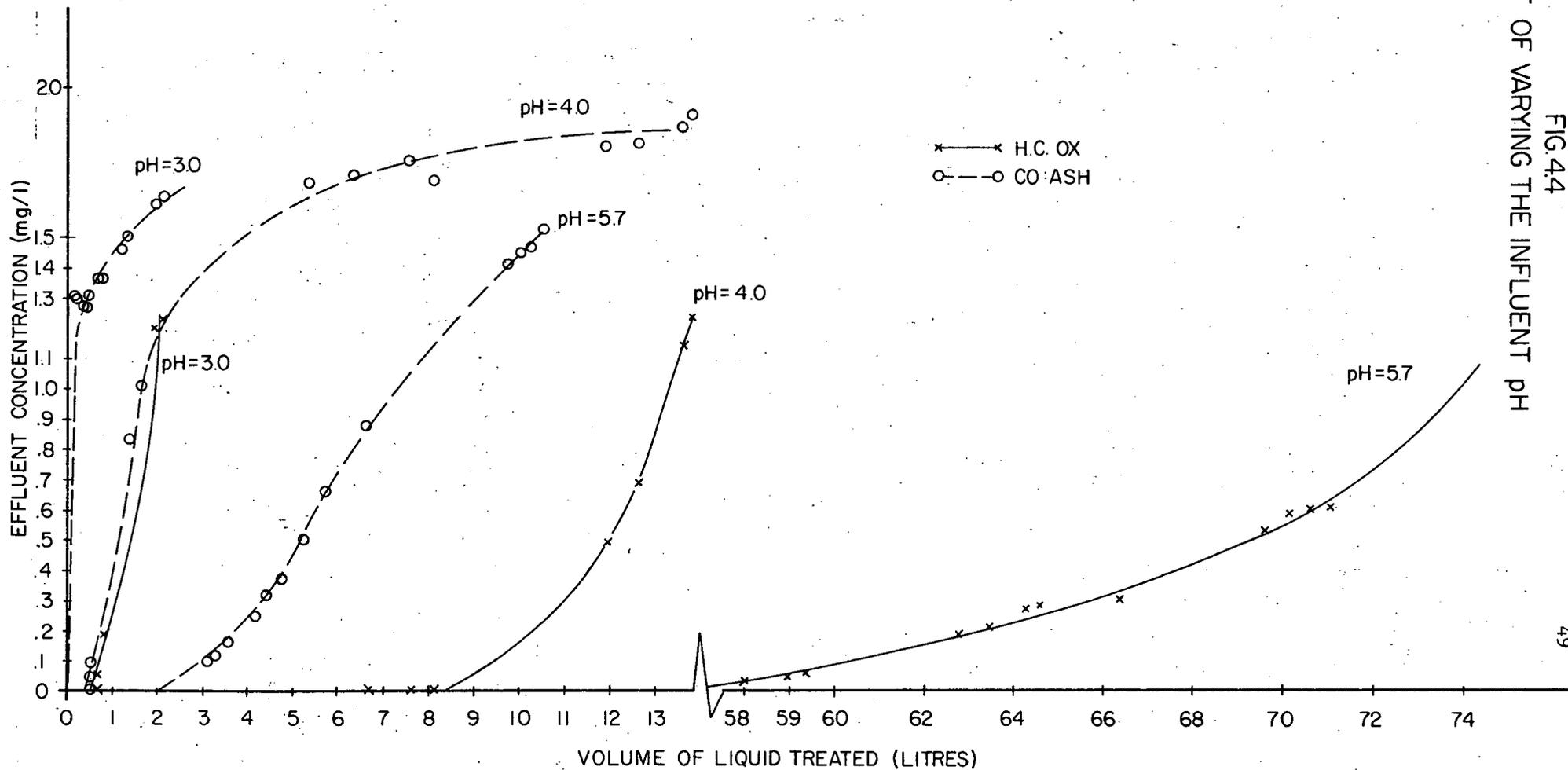
pH was depressed from 5.7 to 4.0. On further depressing the pH to 3.0, the decrease in capacity was 99 percent. Similarly, at breakthrough concentrations of 25 percent and 50 percent of influent concentration, the decrease in capacity was 83 percent and 82 percent, respectively, when the pH was depressed from 5.7 to 4.0. On further depression of pH to 3.0, the decrease in capacity was 98 percent and 98 percent, respectively. Thus, for H.C. OX under the test conditions stated in Figure 4.4, the average capacity decrease, over the range of 10 percent to 50 percent breakthrough concentrations, is 83 percent when the pH was depressed from 5.7 to 4.0, and 98 percent when further depressed to a pH of 3.0. Similarly, for CO:ASH at 10 percent, 25 percent and 50 percent breakthrough concentrations, the decrease in capacity on depression of pH from 5.7 to 4.0 is 80 percent, 79 percent and 77 percent, respectively. On further depression of pH to 3.0, the capacity decrease is 96 percent, 97 percent and 97 percent, respectively. Thus, for CO:ASH under the same test conditions the average capacity decrease is 79 percent when the pH is lowered from 5.7 to 4.0, and 97 percent when the pH is further depressed to 3.0.

The percent decreases in adsorption with decreasing pH for both types of coals are approximately the same. This decrease in adsorption with decreasing pH is contrary to what Weber[9] found. The reason for this discrepancy may be due to the fact that he was working with organic pollutants and activated carbon while in this study the combination is heavy metals and granular coal.

Since the hydrogen ion can also be adsorbed, it is suspected that the hydrogen ion is in competition with the heavy metal ion for the active sites on the coal surface. As the pH is depressed, the hydrogen ion concentration increases and more active sites are made unavailable to the heavy metal. Thus, the drop in capacity on lowering the pH may be partly due to this competition by the hydrogen ion. Another reason for this drop in capacity may be due to

a change in the complex formulation of the heavy metal with decreasing pH. The lower pH favors the awuo complex which may not be as readily adsorbed.

Hendrey[3] found the same decrease in adsorption with decreasing pH in his work on heavy metals with granular coal. Since the pH factor is so crucial to the favourable outcome of the adsorption system using granular coal, more research should be done in this area to find out the exact relationships between pH and adsorption. An important point to make note of is that some kind of pre-treatment may be necessary when treating acidic wastes with this type of system, in order that the pH of the wastes may be increased to ensure reasonable adsorption capacities.

c) Effect of Varying the Flow Rate

The effect of flow rate on the adsorptive capacity was investigated by varying the flow rate between 1-5 Igpm/ft^2, a range representative of flow rates employed in modern rapid sand filtration and activated carbon adsorption systems.

Due to the laboratory equipment available and other practical considerations, the exact flow rates used were 1.01 Igpm/ft^2, 3.04 Igpm/ft^2 and 5.06 Igpm/ft^2. Whenever flow rates of 1 Igpm/ft^2, 3 Igpm/ft^2 and 5 Igpm/ft^2 are mentioned in this thesis, the exact values are the ones mentioned above.

If the adsorption capacities of two columns, similar in all respects but the flow rate, are for all practical purposes the same, then the logical industrial benefit would be to use the higher flow rate and save the cost of building columns with larger diameters when treating higher volumes of wastewater. However, the possibility of saving operating cost by building a larger column must also be borne in mind.

Figure 4.5 and Figure 4.6 show the breakthrough curves at different flow rates obtained for CO:ASH and H.C. OX, respectively. TABLE 4.4 is a

TABLE 4.4

EFFECT ON ZINC ADSORPTION OF VARYING THE FLOW RATE

Breakthrough Conc. as Percent of Influent Conc.	Flow Rate (Igpm/ft^2)	Capacity (mg/gm)		Average Effluent Conc. (mg/ℓ)		Throughput (litres)	
		H.C.OX	CO:ASH	H.C.OX	CO:ASH	H.C.OX	CO:ASH
10%	1	9.716	.386	.008	.039	62.8	3.85
	3	5.402	.231	.032	.065	35.4	2.33
	5	5.571	.161	.019	.106	36.3	1.66
25%	1	10.481	.503	.040	.124	68.9	5.30
	3	7.080	.358	.123	.190	48.7	3.85
	5	6.696	.288	.087	.194	45.3	3.12
50%	1	—	.627	—	.289	—	7.33
	3	9.697	.536	.363	.429	76.0	6.76
	5	8.258	.491	.266	.493	61.2	6.45

a tabular summary of the above two figures. It shows the capacity, average effluent concentration and the corresponding throughput at 10 percent, 25 percent and 50 percent breakthrough concentrations.

At a breakthrough concentration of 10 percent, H.C. OX undergoes a 44 percent decrease in capacity when flow rate was changed from 1 to 3 $Igpm/ft^2$ and a 43 percent decrease when the flow rate was raised to 5 $Igpm/ft^2$. At the breakthrough concentration of 25 percent, it suffers a 32 percent capacity decrease at 3 $Igpm/ft^2$ and a 36 percent capacity decrease at 5 $Igpm/ft^2$. The data for 50 percent breakthrough concentration was not obtainable for 1 $Igpm/ft^2$ due to time considerations.

For CO:ASH, at 10 percent breakthrough concentration, the capacity decrease was 40 percent when flow rate was changed from 1 to 3 $Igpm/ft^2$, and 58 percent when flow rate was changed to 5 $Igpm/ft^2$. At 25 percent breakthrough concentration, the capacity decrease was 29 percent at 3 $Igpm/ft^2$ and 43 percent at 5 $Igpm/ft^2$. At 50 percent breakthrough concentration, it was only 15 percent at 3 $Igpm/ft^2$ and 22 percent at 5 $Igpm/ft^2$.

Both coals displayed a significant drop in capacity when the flow rate was changed from 1 to 3 $Igpm/ft^2$. However, when the flow rate was further raised to 5 $Igpm/ft^2$, the additional percent decrease in capacity was much smaller. In the case of CO:ASH, at all three breakthrough concentrations, the additional percent decrease in capacity when flow rate was further raised to 5 $Igpm/ft^2$ was approximately half the percent decrease in capacity when flow rate was changed from 1 to 3 $Igpm/ft^2$ (i.e., at 25 percent breakthrough concentrations, the decrease was 29 percent at 3 $Igpm/ft^2$ and 43 percent at 5 $Igpm/ft^2$, an additional decrease of 14 percent, which is approximately half of 29 percent.) As for H.C. OX, this additional percent decrease in

capacity when flow rate was further raised to 5 Igpm/ft^2 was small compared to the percent decrease when flow rate was changed from 1 to 3 Igpm/ft^2.

Literature on activated carbon adsorption states that the throughput corresponding to a particular breakthrough concentration is decreased with increased flow rate. Figure 4.5 and Figure 4.6 agree with this general statement. An interesting point to note, however, is that the curves converge at higher breakthrough concentrations, indicating that the percent difference in capacity between different flow rates decreases as the permissible break-through concentration is increased. Thus, the choice between building thicker columns or stepping up the flow rate, as discussed earlier, would rest heavily on the pollution control regulations on allowed waste levels in the effluent. If the allowed level is very low, the breakthrough concentration will have to be correspondingly low and the use of high flow rates may be impractical. On the other hand, if a higher breakthrough concentration is permissible, then a higher flow rate may be contemplated. Of course, these decisions could be made only after a careful examination of the breakthrough curves and a thorough analysis of capital and operating costs.

d) Effect of Varying the Influent Concentration

Figure 4.7 shows the breakthrough curves for tests run with an influent concentration of 0.5 mg/ℓ. By changing the influent concentration from 2 mg/ℓ (as used in previous tests) to 0.5 mg/ℓ, an attempt was made to find out whether the capacity at a particular breakthrough concentration would increase or decrease, given all other parameters to be the same. The main objective here is to compare the capacities at a common breakthrough concentration, namely 0.2 mg/ℓ, for tests run at a pH of 5.7 but with different influent

FIG. 4.5
EFFECT OF VARYING FLOW RATE FOR CO:ASH

o———o 1 lgpm/ft.^{2}

●———● 3 lgpm/ft.^{2}

x———x 5 lgpm/ft.^{2}

Influent = 2 mg/l Zn.

pH = 5.7

Bed depth = 10 inches

Coal weight = 20 gm

EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)
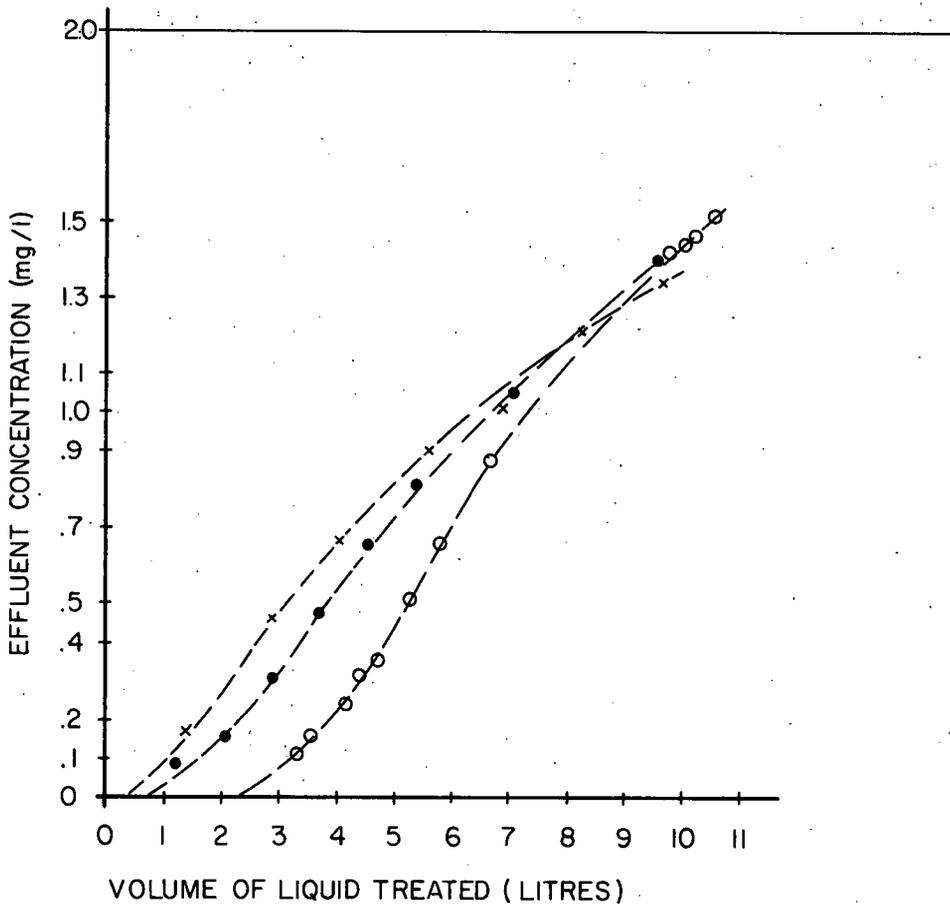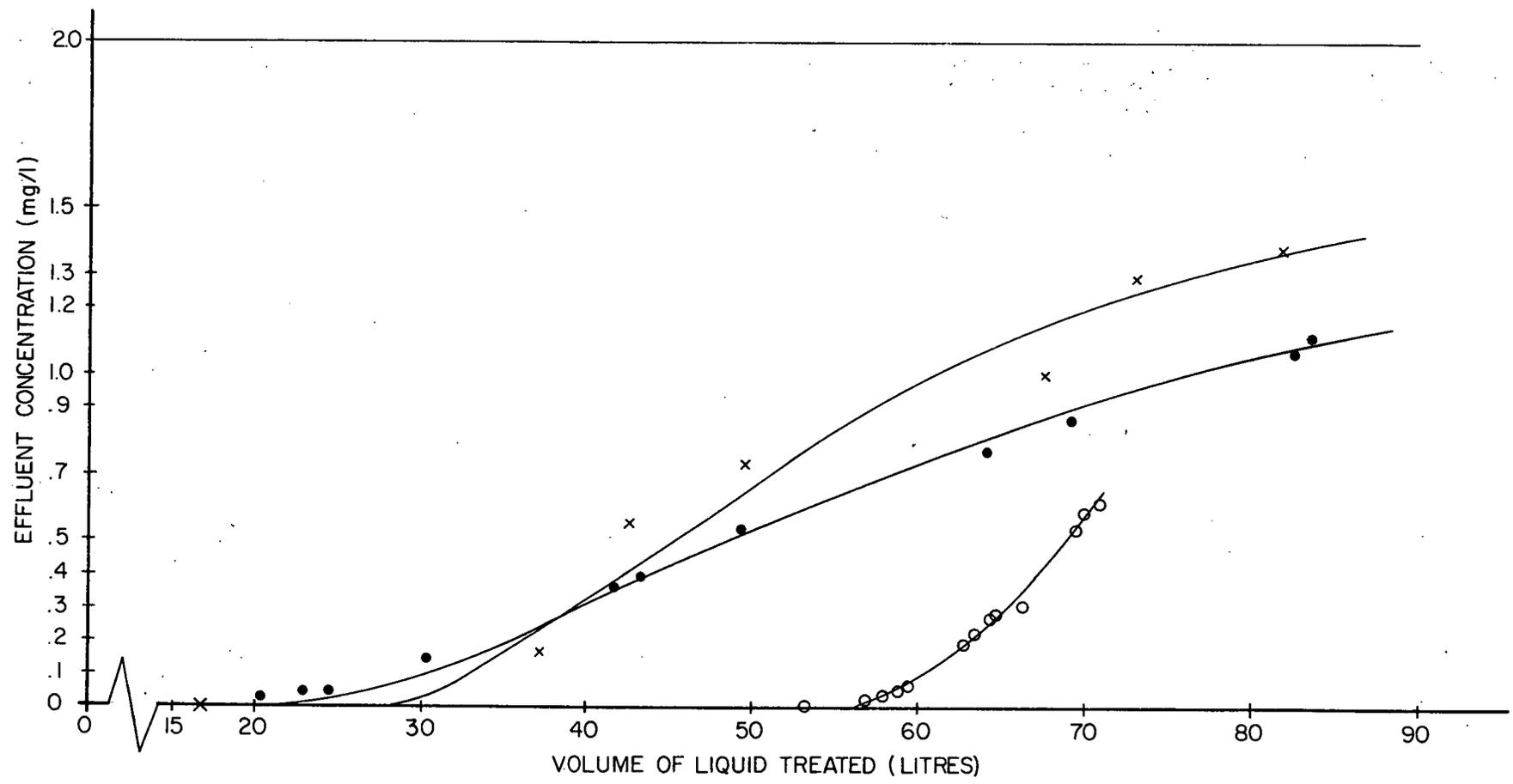
FIG. 4.6

EFFECT OF VARYING FLOW RATE FOR H.C. OX

Legend:
- o———o 1 lgpm/ft.^{2}
- •———• 3 lgpm/ft.^{2}
- x———x 5 lgpm/ft.^{2}

Influent = 2 mg/l Zn
pH = 5.7
Bed depth = 10 inches
Coal weight = 13 gm

EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)
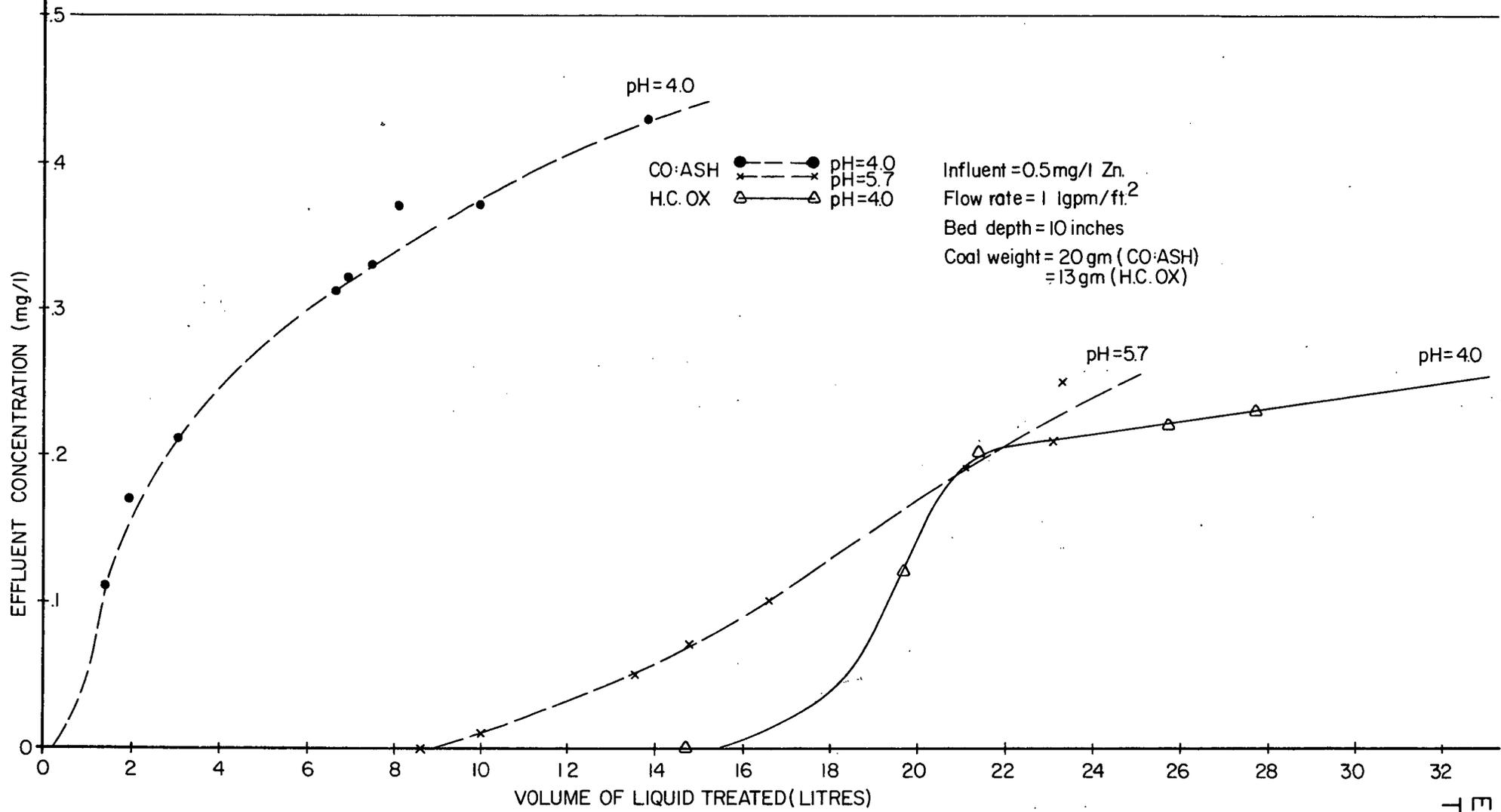
FIG. 4.7
EFFECT OF VARYING
THE INFLUENT pH

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concentrations.

The pertinent data on Figure 4.7 is shown in TABLE 4.5.

TABLE 4.5

EFFECT OF VARYING THE INFLUENT pH

Breakthrough Concentration as percent of influent conc.	Influent pH	Capacity (mg/gm)		Average Effluent Concentration (mg/ℓ)		Throughput (litres)	
		H.C.OX	CO:ASH	H.C.OX	CO:ASH	H.C.OX	CO:ASH
10% = .05 mg/ℓ	4	.708	.026	.003	.019	18.40	1.05
	5.7	**	.332	**	.009	**	13.43
25% = .125 mg/ℓ	4	.751	.037	.009	.050	19.75	1.60
	5.7	**	.426	**	.028	**	17.83
= .2 mg/ℓ	4	.786	.057	.021	.096	21.33	2.83
	5.7	**	.486	**	.051	**	21.66
50% = .25 mg/ℓ	4	1.025	.078	.090	.142	32.16	4.22
	5.7	**	.533	**	.074	**	24.71

Footnote:- A column was not run for H.C. OX at a pH of 5.7 due to time considerations. The capacity for H.C. OX at a pH of 5.7, flow rate of 1 Igpm/ft^2, influent concentration of 0.5 mg/ℓ Zn and at a breakthrough concentration of 0.2 mg/ℓ was arrived at by using a factor as described below.

Data from TABLE 4.3 and TABLE 4.5 were combined to form TABLE 4.6, which sho
which shows a comparison of capacities at a breakthrough concentration of

0.2 mg/ℓ for tests run with zinc influents of 0.5 mg/ℓ and 2.0 mg/ℓ, and at a

flow rate of 1 Igpm/ft^2. From TABLE 4.6, with influent concentration of 2 mg/ℓ,

CO:ASH displayed a capacity increase by a factor of $\frac{.370}{.074} = 5.0$ due to the pH

increase from 4 to 5.7. But at an influent concentration of 0.5 mg/ℓ and under

the same change in pH, it shows an increase by a factor of $\frac{.486}{.057} = 8.53$.

TABLE 4.6

COMPARISON OF ADSORPTIVE CAPACITIES OF COLUMNS

RUN WITH ZINC INFLUENTS OF 0.5 mg/ℓ AND 2.0 mg/ℓ

Breakthrough Concentration (mg/ℓ Zn)	Influent Conc. (mg/ℓ Zn)	Influent pH	Capacity (mg/gm)	
			H.C.OX	CO:ASH
0.2	0.5	4	.786	.057
		5.7	8.23*	.486
	2.0	4	1.582	.074
		5.7	9.716	.370

*by calculation, not test - see pg. 60

Therefore, the ratio:

$$\frac{\text{increase factor with 0.5 mg/}\ell\text{ influent}}{\text{increase factor with 2.0 mg/}\ell\text{ influent}} = \frac{8.53}{5} = 1.706.$$

For H.C. OX, with an influent concentration of 2 mg/ℓ and under the same change of pH, the capacity increase is by a factor of $\frac{9.716}{1.582} = 6.14$. Using the ratio described above, H.C. OX with an influent concentration of 0.5 mg/ℓ should experience an increase in capacity by a factor of 6.14 X 1.706 = 10.5 (i.e. assuming that the same ratio of factors is valid for H.C. OX also).

Therefore, the capacity of H.C. OX at 0.2 mg/ℓ effluent concentration, with an influent pH of 5.7 and an influent concentration of 0.5 mg/ℓ, should be about .786 X 10.5 = 8.23 mg/gm.

Looking at TABLE 4.6, at the common breakthrough concentration of 0.2 mg/ℓ, CO:ASH with an influent pH of 4.0 shows a decrease in capacity from .074 to 0057 (23 percent decrease) when influent concentration was changed from 2.0 mg/ℓ to 0.5 mg/ℓ. But at a pH of 5.7, CO:ASH, under the same changes, experiences an increase in capacity from .370 to .486 (31 percent increase).

Similarly, for H.C. OX, at 0.2 mg/ℓ breakthrough concentration and at a pH of 4.0, there is a decrease in capacity from 1.582 to 0.786 (50 percent decrease) and at a pH of 5.7 the decrease is from 9.716 to 8.230 (15 percent decrease) when influent concentration was changed from 2.0 mg/ℓ to 0.5 mg/ℓ.

This last figure of 8.230 for the capacity of H.C. OX at a pH of 5.7 is only an estimate arrived at by using derived factors as described previously. Only a long-term column test will provide a more exact evaluation of the coal capacity under the indicated operating conditions.

The pH of the influent seems to be an important factor in determining the change in capacity that occurs when the influent concentration is changed. For both coals, there is a decrease in capacity when influent concentration is lowered from 2.0 mg/ℓ to 0.5 mg/ℓ at a pH of 4.0. But at a pH of 5.7 and under the same influent concentration changes, CO:ASH experiences an increase while H.C. OX still shows a decrease in capacity.

Under a set of conditions where the capacity increases on lowering the influent concentration, an important practical application is obvious. For example, two volumetrically equal waste streams of, say, zinc and copper of 2 mg/ℓ each could be combined to result in 1 mg/ℓ each of Zn and Cu before being passed through a coal column. This would result in better adsorption capacities than if the waste streams were passed through separate columns individually.

From the data above, it is clear that close attention must be paid to the influent pH before any attempts are made in certain cases to better the adsorption capacity by lowering the influent concentration.

Investigating the capacity sensitivity to pH change at different influent concentrations, it is seen from TABLE 4.6 that at the common 0.2 mg/ℓ breakthrough, CO:ASH shows an 80 percent decrease with an influent concentration

of 2 mg/ℓ and an 88 percent decrease with an influent concentration of

0.5 mg/ℓ when the pH is changed from 5.7 to 4.0 in both cases. H.C. OX shows

a decrease of 84 percent with influent of 2 mg/ℓ, while at an influent of

0.5 mg/ℓ the decrease was 91 percent under the same change in pH. The percent

decrease in capacity due to lowering of pH is greater in the case of 0.5 mg/ℓ

influent concentration, indicating a greater sensitivity of capacity response

to pH change at lower influent concentrations.

4.6 Breakthrough Curves for Copper

The adsorption capacities for copper were investigated for both coals

using an influent of 2 mg/ℓ Cu and a flow rate of 1 Igpm/ft^2 at influent pH

values of 4.0 and 5.7.

There are only three breakthrough curves shown in Figure 4.8,

although four columns were tested. The curve for H.C. OX at a pH of 5.7 is

absent in Figure 4.8 since its effluent concentration was still undetectable

after 5 days of throughput (i.e. 33.4 litres). Therefore, rather than spend

more time waiting for the breakthrough, a decision was made to stop the column

and estimate the adsorption capacity of H.C. OX at a pH of 5.7 by the use of

a factor, as indicated in section 4.4(d).

A tabular summary of Figure 4.8 with respect to capacity and the

corresponding throughput and average effluent concentration is shown in Table 4.7.

The main objectives for running this series of columns were:

1) To determine the adsorption capacity for copper at a pH of 5.7

and under the test conditions described in Figure 4.8.

2) To determine the change in capacity for copper at different pH

values.

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FIG. 4.8
EFFECT OF VARYING THE
pH ON COAL CAPACITY FOR
COPPER

Influent = 2 mg/l Cu
Flow rate = 1 lgpm/ft.²
Bed depth = 10 inches
Coal weight – H.C. OX = 13 gm
              CO:ASH = 20 gm

CO:ASH ⊙———⊙
H.C. OX ×———×

pH = 4.0

pH = 5.7

pH = 4.0

VOLUME OF LIQUID TREATED (LITRES)

EFFLUENT CONCENTRATION (mg/l)
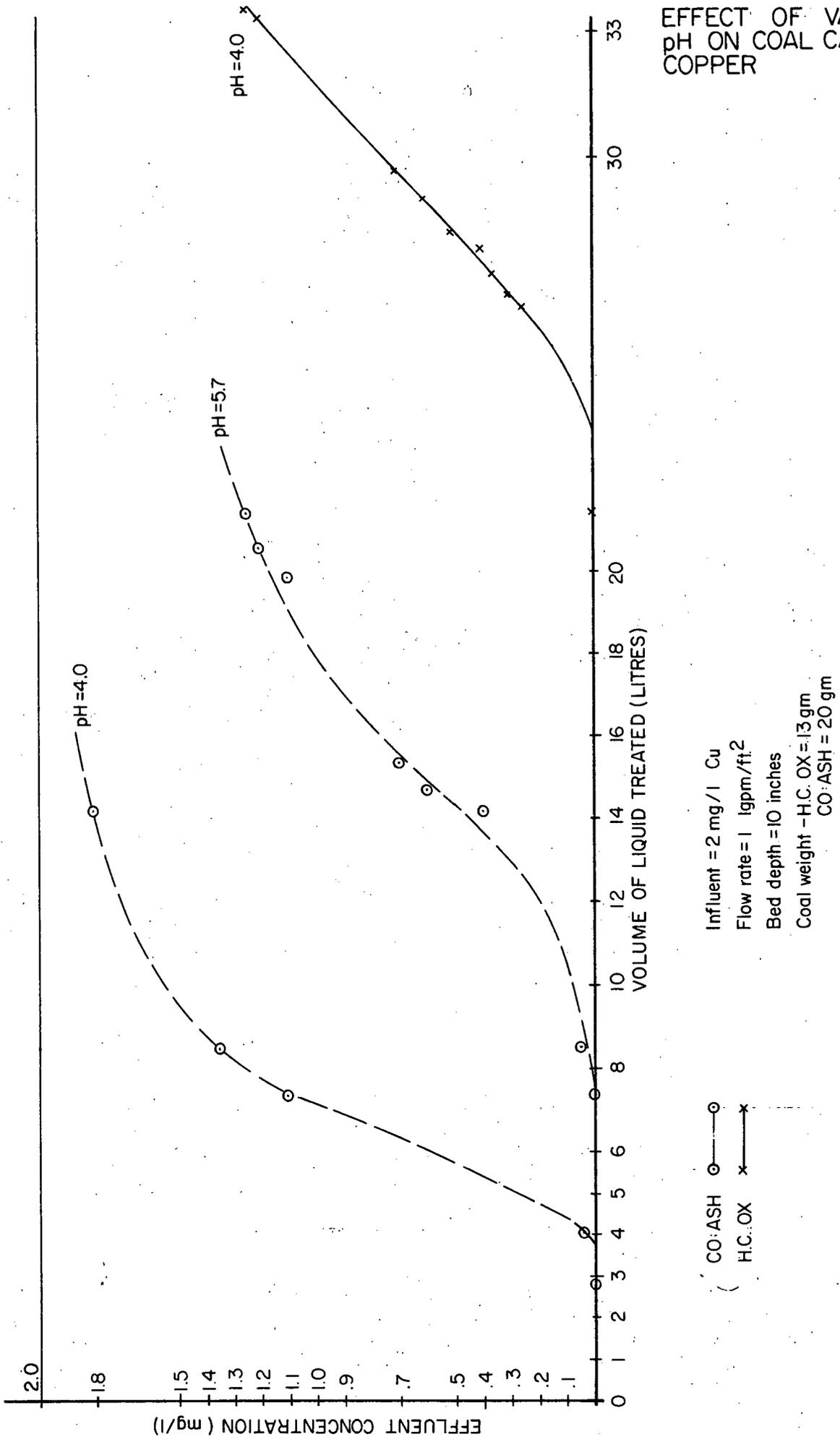
The adsorption capacities for H.C. OX at a pH of 5.7 are shown in italics in Table 4.7 since these figures were not arrived at experimentally,

TABLE 4.7

EFFECT OF VARYING pH WITH COPPER INFLUENTS

Breakthrough Concentration as Percent of Influent Conc.	Influent pH	Capacity (mg/gm)		Average Effluent Conc. (mg/ℓ)		Throughput (litres)	
		H.C.OX	CO:ASH	H.C.OX	CO:ASH	H.C.OX	CO:ASH
10% = 0.2 mg/ℓ	4	3.986	0.467	.008	.016	25.95	4.72
	5.7	*12.396*	1.182	—	.032	—	12.00
25% = 0.5 mg/ℓ	4	4.281	0.545	.038	.072	28.25	5.62
	5.7	*13.442*	1.370	—	.081	—	14.30
50% = 1.0 mg/ℓ	4	4.634	0.634	.116	.206	31.80	7.11
	5.7	*15.524*	1.601	—	.220	—	17.90

but estimated by the procedure described below. For CO:ASH with a zinc influent of 2 mg/ℓ (Table 4.3), at the 10 percent breakthrough concentration, the capacity increase factor due to the pH change from 4.0 to 5.7 is

$\frac{.370}{.074}$ = 5.00. Using a copper influent of 2 mg/ℓ under the same conditions, the increase factor is $\frac{1.182}{0.467}$ = 2.53 (Table 4.7). Therefore, the ratio of

$$\frac{\text{increase factor with Cu influent}}{\text{increase factor with Zn influent}} \cong \frac{2.53}{5.00} = .506$$

Now for H.C. OX with a zinc influent of 2 mg/ℓ, the capacity increase factor under the same conditions, is $\frac{9.716}{1.582}$ = 6.14. Therefore, for H.C. OX, with a copper influent of 2 mg/ℓ and under the same pH changes, the capacity increase factor should be 66.14 X .506 = 3.11. Multiplying the capacity of H.C. OX at

a pH of 4.0 (Table 4.7) by this factor provides a calculated capacity of H.C. OX at the higher pH of 12.396 mg/gm.

Similarly, at breakthrough concentrations of 25 percent and 50 percent, the increase factors with copper influents for H.C. OX are 3.14 and 3.35, respectively. Multiplying these factors by the corresponding capacities of H.C. OX at a pH of 4.0 results in the estimated capacities at a pH of 5.7 as shown in TABLE 4.7 in italics.

Data in TABLE 4.7 indicates a decrease in adsorption capacity with decreasing pH for both types of coal as in the case with zinc adsorbate. From TABLE 4.7 again, for CO:ASH at breakthrough concentrations of 10 percent, 25 percent and 50 percent, the percent decrease in capacity due to the pH change from 5.7 to 4.0 is 61 percent, 60 percent and 60 percent, respectively. Thus, over the range of breakthrough concentrations stated above, the average percent decrease in capacity for CO:ASH due to a change of pH from 5.7 to 4.0 is 60 percent. In the case of H.C. OX, due to the same change in pH, the percent decrease in capacity at 10 percent, 25 percent and 50 percent break-through concentrations is 68 percent, 68 percent and 70 percent, respectively. This gives an average percent decrease of 69 percent for H.C. OX under the same conditions. The average percent decrease due to the depression of pH is about the same for both coals, as was the case with zinc adsorbate.

Comparing the percent decrease in capacity of copper and zinc due to the lowering of pH from 5.7 to 4.0, it is seen from TABLE 4.3 and TABLE 4.7 that both coals display a lower percent decrease with copper influents.

From TABLE 4.3 and TABLE 4.7, the ratios of capacities for copper vs. capacities for zinc are shown in TABLE 4.8. It is clear from TABLE 4.8 that the difference in terms of percentage between adsorptive capacities for copper and zinc is greater at the lower pH of 4.0 for both types of coal.

TABLE 4.8

COMPARISON OF ADSORPTIVE CAPACITIES FOR COPPER AND ZINC

Range of Breakthrough Concentrations	Influent pH	$\dfrac{\text{Capacity for Copper}}{\text{Capacity for Zinc}}$	
		H.C. OX	CO:ASH
10% - 50%	4	22.4 ~ 25	4.3 ~ 6.3
	5.7	1.3 ~ 1.4	2.6 ~ 3.2

This difference is more pronounced in the case of CO:ASH.

4.7 Breakthrough Curves for Lead

Three columns were tested with lead as the adsorbate, two of them using CO:ASH with influent pH values of 5.7 and 4.0, and the third one with H.C. OX at a pH of 4.0. The other parameters were as stated in Fig. 4.9(a), H.C. OOX at a pH of 5.7 was not tested because there was good reason to believe that it would take an excessively long period of time for its breakthrough to occur. Thus, an estimate for the capacity of H.C. OX at a pH of 5.7 was the goal instead. This estimate would be based on the three columnstested and on previous data from zinc and copper tests.

The main objectives here were similar to those for copper tests; that is, to determine the capacity at a pH of 5.7 and under the test conditions stated in Figure 4.9(a) and also to investigate the percent decrease in capacity for lead on lowering the pH.

Figure 4.9(a) shows only one breakthrough curve, that of CO:ASH at a pH of 4.0. The other two columns were stopped without having reached their breakpoints due to excessive flow problems caused by the appearance of a fungus. As the fungus accumulated at the top of the coal column, the pressure drop

EFFLUENT CONCENTRATION
UNDETECTABLE AFTER

CO:ASH at pH=5.7 – 40 Litres

H.C. OX at pH = 4.0 – 60 Litres

Influent = 2 mg/l Pb

Flow rate = 1 lgpm/ft.^{2}

Bed depth = 10 inches

Coal weight – H.C. OX = 13 gm

CO: ASH = 20 gm

EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)

pH=4.0
(CO:ASH)
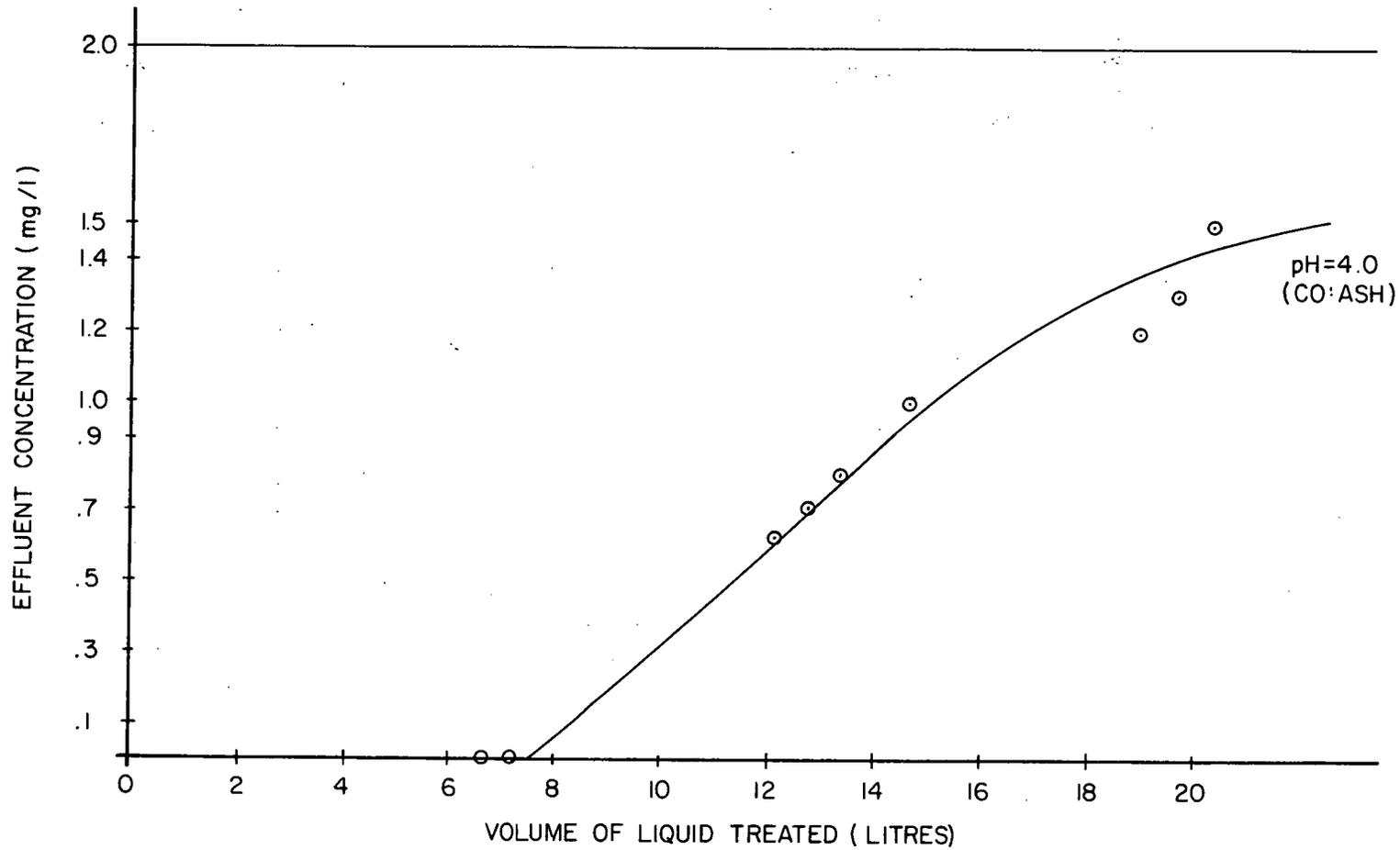
EFFECT OF VARYING THE pH WITH LEAD INFLUENTS

FIG. 4.9 (a)

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FIG. 4.9(b)

FUNGUS GROWING AT THE TOP OF COAL COLUMN

across the coal bed increased. When the flow rate could no longer be maintained at 1 Igpm/ft^2 even on fully opening the burette valve, a vacuum was applied at the effluent end of the burette. This enabled the maintenance of the flow rate a 1 Igpm/ft^2 for about another 8 litres of throughput. The flow rate then dropped again due to further accumulation of the fungus. At this point the runs were discontinued.

In the case of CO:ASH at a pH of 5.7, the throughput on discontinuation was 40 litres while for H.C. OX at a pH of 4.0, it was 60 litres. As shown on Fig. 4.9(b), the white fluffy fungus was about 1/8 inch thick on top of the coal column when the runs were stopped. It also permeated into the voids between the coal particles to about 1/4 inch from the top of the coal column. Figure 4.9(b) also shows pockets of gas created along the length of the coal column due to the vacuum applied at the exit end.

TABLE 4.9 is a tabular representation of Figure 4.9(a). No attempt is made to estimate the blanks shown in TABLE 4.9 because there are too many unknowns involved. However, a minimum estimate can be made for H.C. OX at a

TABLE 4.9

CAPACITIES FOR LEAD

Breakthrough Concentration As Percent of Influent Conc.	Influent pH	Capacity (mg/gm)		Average Effluent Conc.(mg/ℓ)		Throughput (litres)	
		H.C.OX	CO:ASH	H.C.OX	CO:ASH	H.C.OX	CO:ASH
10% = 0.2 mg/	4	—	0.903	—	.017	—	9.11
	5.7	—	—	—	—	—	—
25% = 0.5 mg/	4	—	1.101	—	.088	—	11.42
	5.7	—	—	—	—	—	—
50% = 1.0 mg/	4	—	1.329	—	.252	—	15.14
	5.7	—	—	—	—	—	—

pH of 4.0 from the data on MIXED INFLUENTS. (TABLE 4.10(a)). Since the capacity for a particular metal using an influent containing that metal only as adsorbate is greater than the capacity for the same metal when the influent contains that metal plus a mixture of other metals (See section 4.7), the capacity for lead of H.C. OX at a pH of 4.0 with mixed influents is a minimum estimate for the same capacity when the influent consists only of lead. At 10 percent breakthrough, this minimum estimate of the capacity for lead of H.C. OX at a pH of 4.0 is 2.536 mg/gm as shown in TABLE 4.10(a).

Data from TABLES 4.3, 4.7 and 4.9 show that for CO:ASH, at a pH of 4.0 and at 10% breakthrough concentration, the ratio of capacities for zinc : copper : lead is equal to 1 : 6 : 12.

4.8 Breakthrough Curves for Influents Containing a Mixture of Zinc, Copper and Lead

In waste streams such as municipal sewage, there usually is a mixture of dissolved heavy metals instead of just one single adsorbate. These various heavy metals in solution may mutually enhance adsorption, may act relatively independently or may mutually depress adsorption. Some researchers[9] have found with activated carbon and mixed solutions that each solute competes in some way with the adsorption of the other. It was found that the presence of the other solutes in the mixture adversely affects the adsorption of a particular solute, leading to a more rapid breakthrough of this solute when using a mixed solution than when using a pure solution containing only that particular solute.

A column each for H.C. OX, CO:ASH and DARCO Activated Carbon GRADE 12X20 was run at 1 Igpm/ft^2 and at a pH of 4.0. The influent used consisted of 2 mg/ℓ each of zinc, copper and lead. The pH was chosen as 4.0 instead of 5.7, because at 5.7 the breakthrough times would be excessively long, especially for H.C. OX. The basic objectives for running the above mentioned three columns

were the following:-

       1)   To compare the three types of adsorbents with regard to their

adsorptive capacities for zinc, copper and lead from water containing

a mixture of these metals at a pH of 4.0.

       2)   To determine the change in capacities for zinc, copper and lead

at a pH of 4.0 that occurs when a mixed influent is used rather than

a pure solution containing only one adsorbate.

     As in the lead tests, the white fungus appeared in all three columns.

For CO:ASH and DARCO Activated Carbon, the fungus appeared only after total

breakthroughs for all three metals had occurred. But in the case of H.C. OX,

the fungus appeared before the lead and copper breakthrough curves could begin

to rise sharply. It may be due to the fungus, that for H.C. OX, the effluent

concentration for lead began to drop and that for copper failed to rise sharply

after the appearance of the fungus at a throughput of about 18 litres. This

can be observed quite clearly in Figure 4.10(a). The appearance of the fungus

in the columns containing CO:ASH and DARCO Activated Carbon also took place at

a throughput of about 18 litres, but total breakthroughs for all three metals

in these two columns had occurred long before throughput reached 18 litres. The

curves for CO:ASH and DARCO Activated Carbon are shown in Figure 4.10(b) and

Figure 4.10(c), respectively.

     A summary of the important data from Figures 4.10(a), 4.10(b) and

4.10(c) is presented in TABLE 4.10(a). A performance comparison between

H.C. OX, CO:ASH and DARCO Activated Carbon with regard to their capacities for

the three metals from mixed influents, at a pH of 4.0, may be made from the

data in TABLE 4.10(a). For the sake of clarity and brevity, this comparison,

as shown in TABLE 4.10(b), is done only for the 10 percent breakthrough

concentration (i.e. 0.2 mg/ℓ). It is clear that H.C. OX is the best per-

former of the three. H.C. OX is about 12 times better than CO:ASH

CU

PB

ZN

Ph = 4.0

Influent = 2 mg/l each of Cu., Pb. and Zn

Flow rate = 1 lgpm/ft.^{2}

Bed depth = 10 inches

Coal weight = 13 gm

EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)

FIG. 4.10 (a)

BREAKTHROUGH CURVES FOR H.C. OX WITH MIXED INFLUENTS

CU

PB

ZN

Ph = 4.0

Influent = 2mg/l each of Zn,Cu and Pb

Flow rate = 1 lgpm/ft.²

Bed depth = 10 inches

Coal weight = 20 gm

EFFLUENT CONCENTRATION (mg/l)

2.0
1.9
1.7
1.5
1.4
1.2
1.0
.9
.7
.5
.3
.1
0

0 1 2 3 4 5 6 8 10 12 14 16 18 20 22 23

VOLUME OF LIQUID TREATED (LITRES)

CU.
PB.
ZN.

Ph = 4.0
Influent = 2mg/l each of Zn., Pb. and Cu.
Flow rate = 1 Igpm/ft.^{2}
Bed depth = 10 inches
Coal weight = 9.5 gm.

FIG. 4.10 (c)

BREAKTHROUGH CURVES FOR DARCO ACTIVATED CARBON WITH MIXED INFLUENTS

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EFFLUENT CONCENTRATION (mg/l)

VOLUME OF LIQUID TREATED (LITRES)

TABLE 4.10(a)

ADSORPTION CAPACITIES USING MIXED INFLUENTS

| Metal Tested = Zn,   Influent pH = 4.0 | | | | | | | | | |

Breakthrough Conc. as Percent of Influent Conc.	Capacity (mg/gm)			Average Effluent Conc. (mg/ℓ)			Throughput (litres)		
	H.C.OX	CO:ASH	Act.C	H.C.OX	CO:ASH	Act.C	H.C.OX	CO:ASH	Act.C
10%	0.871	0.072	0.088	.0188	.033	.062	5.70	0.77	0.41
25%	1.036	0.106	0.133	.086	.116	.168	7.00	1.09	0.60
50%	1.190	0.122	0.165	.196	.266	.326	8.50	1.42	0.85

Metal Tested = Cu, Influent pH = 4.0									
10%	2.393	0.201	0.337	.019	.037	.048	15.60	2.05	1.58
25%	2.773	0.280	0.443	.079	.137	.142	18.63	2.95	2.31
50%	—	0.347	0.603	—	.303	.330	—	4.08	3.44

Metal Tested = Pb, Influent pH = 4.0									
10%	2.536	0.675	0.489	.015	.041	.054	16.48	6.84	2.33
25%	—	0.931	0.659	—	.134	.136	—	9.95	3.33
50%	—	1.183	0.844	—	.313	.323	—	13.94	4.77

TABLE 4.10(b)

A COMPARISON BETWEEN H.C. OX, CO:ASH AND DARCO ACTIVATED CARBON WITH REGARD

TO THEIR CAPACITIES FOR THE THREE METALS FROM MIXED INFLUENTS AT A pH OF 4.0

M Metal Tested	Breakthrough Conc. as Percent of Influent Conc.	CO:ASH	DARCO Act. Carbon	H.C. OX	
Zn	10%	0.072	0.088	0.871	Capacity (mg/gm)
		1.0	1.2	12.1	Relative Capacity*
Cu	10%	0.201	0.337	2.393	Capacity (mg/gm)
		1.0	1.7	11.9	Relative Capacity*
Pb	10%	0.675	0.489	2.536	Capacity (mg/gm)
		1.0	0.7	3.8	Relative Capacity*

*"Relative Capacity" signifies the ratio of capacities with the capacity of CO:ASH as the base.

TABLE 4.10(c)

PERCENT DECREASE IN CAPACITY ON CHANGING THE INFLUENT TO ONE CONTAINING A

MIXTURE OF SOLUTES

Heavy Metal	H.C. OX Capacity (mg/gm)			CO:ASH Capacity (mg/gm)		
	Single Solute	Mixture of Solutes	% Decrease	Single Solute	Mixture of Solutes	% Decrease
Zn	1.582	0.871	45	0.074	0.072	3
Cu	3.986	2.393	40	0.467	0.201	57
Pb	——	2.536	——	0.903	0.675	25

Influent pH = 4.0
Breakthrough concentration = 10 percent of influent concentration

for zinc and copper and about 4 times better than CO:ASH for lead. DARCO

activated charcoal has the same range of adsorptive capacity as CO:ASH. It

is slightly better than CO:ASH in the case of zinc and copper, and slightly

worse than CO:ASH in the case of lead. It is somewhat surprising that an

activated carbon with a tremendous advantage in surface area showed a poor

performance in comparison with H.C. OX. But, on the other hand, the raw

material used to prepare the carbon, the method and temperature of activation

and the type of gas used for activation may all affect the selectivity of the

final product.

With the relevant data from TABLES 4.3, 4.7, 4.9 and 4.10(a), a

comparison was made between the capacities experienced with single solute

influents and with influents containing a mixture of solutes. The pH in both

cases was 4.0. The percent decrease in capacity, due to this change in the

nature of the influent, is calculated for zinc, copper and lead at a 10 percent

breakthrough concentration (i.e., 0.2 mg/ℓ), as shown in TABLE 4.10(c).

H.C. OX seems to experience about the same percent decrease in

capacity for both zinc and copper on changing the influent to one of mixed

solutes. Unfortunately, the figure for lead under single solute influent is

unavailable due to the fungus problem as described in section 4.6. Thus,

nothing can be concluded for lead in this respect.

The percent decrease in capacity displayed by CO:ASH under this

change of influent is greatest for copper (57%). In the case of lead, the

percent decrease is 25 percent, while for zinc the decrease was only 3 percent.

Therefore, it can be concluded that the capacity for a heavy metal

decreases when there are other heavy metals present in the influent. This is

probably due to the occupation of some active sites by these other heavy

metals. Under this environment of competition for active sites, the capacity

for a particular heavy metal is less than that obtained under a competition-

free environment of a single solute influent. .

It may also be noted that the total capacity for zinc, copper and

lead from a mixed influent displayed by the H.C. OX column is equal to

5.800 mg/gm which is much more than the capacity for any individual heavy metal

from a single solute influent. CO:ASH also exhibited this characteristic with

a total capacity for zinc, copper and lead of 0.948 mg/gm from a mixed influent.

With a single solute, a particular type of active site only is occupied. This

particular type may form just a small fraction of the total sites. But with a

mixture of solutes, more than one type of active site is used up. Thus, a

greater fraction of the total sites is utilised.

4.9 Correlation of Effluent pH with Effluent Concentration

In the early part of the column tests, the pH of the effluent was

measured at the beginning and just before the end of the run. (Just for the

sake of information, this was done with the first few columns.) It was noted

that the pH of the effluent was about 6.0 in the beginning and very close to

the pH of the influent just before the end of the test.

A notion was nurtured that the pH of the effluent could somehow serve

as an indicator of the effluent concentration of the metal. The hydrogen ion

is adsorbable. Therefore, when the effluent pH decreases from about 6.0 to

the pH of the influent near the end of the test, a conclusion may be drawn that

breakthrough with regard to the hydrogen ion has occurred. If this breakthrough

of the hydrogen ion coincides with that of the metal, then a clear-cut cor-

relation can be drawn between effluent pH and the effluent concentration of

the metal. If the two breakthroughs do not coincide, the pH of the effluent

corresponding to the breakthrough of the metal may be noted. Then this pH of the effluent noted can serve as an indicator of the metal breakthrough in future identical columns, provided:

1)   This value of the pH has been proven to remain constant whenever breakthrough of the metal occurs.

2)   The effluent pH steadily approaches that of the influent as the experiment proceeds, without suffering any random decreases and increases.

If some kind of correlation between effluent pH and effluent metal concentration can be brought to light, the author can think of two direct benefits such as:

1)   In the course of research work, an inexpensive and compact pH meter may be used to indicate the beginning of the metal breakthrough. Once the breakthrough is about to set in, then the effluent concentration may be tested on the more expensive and cumbersome Atomic Absorption Spectrophotometer to get the data for the breakthrough curve. This procedure would eliminate the time and trouble of using the Atomic Absorption Spectrophotometer before the beginning of the metal breakthrough.

2)   In the practical application of coal adsorption columns, the pH meter may be used routinely to indicate the saturation state of the column, once the correlation between the effluent pH and the effluent metal concentration has been worked out under actual plant conditions.

TABLE 4.11

COMPARISON OF EFFLUENT pH AND EFFLUENT CONCENTRATION

Test Parameters	TEST NUMBERS															
	(1)		(2)		(3)		(4)		(5)		(6)		(7)		(8)	
Coal Type	CO:ASH		H.C.OX		H.C.OX		CO:ASH		H.C.OX		CO:ASH		H.C.OX		CO:ASH	
Flow Rate (Igpm/ft^2)	1		1		1		1		1		1		1		1	
Influent pH	3.0		3.0		4.0		4.0		4.0		4.0		4.0		4.0	
Influent Conc.	2mg/ℓ Zn		2mg/ℓ Zn		2mg/ℓ Cu		4mg/ℓ Cu		2mg/ℓ Pb		2mg/ℓ Pb		0.5mg/ℓ Zn		0.5mg/ℓ Zn	
	A	B	A	B	A	B	A	B	A	B	A	BB	A	B	A	B
	0.00	5.8	0.00	5.2	0.00	7.0	0.00	6.4	0.00	6.2	0.00	6.2	0.00	6.0	0.00	6.1
	1.27	3.4	0.00	5.7	0.00	6.0	0.00	6.9	0.00	6.7	0.00	4.3	0.00	6.1	0.11	5.9
	1.27	3.3	0.00	5.4	0.00	5.9	0.00	6.3	0.00	6.6	0.40	4.2	0.00	5.8	0.17	5.4
	1.32	3.2	0.05	5.7	0.00	4.3	0.00	6.9	0.00	6.1	0.70	4.2	0.00	6.3	0.21	4.5
	1.35	3.3	0.18	5.4	0.00	4.2	0.00	5.6	0.00	4.0	0.80	4.2	0.00	6.1	0.31	4.2
	1.37	3.2	1.21	3.3	0.30	4.1	1.10	4.2	0.00	4.0	1.30	4.1	0.12	5.6	0.32	4.5
	1.51	3.2	1.22	3.2	0.40	4.1	1.35	4.2			1.50	4.1	0.20	4.8	0.33	4.2
	1.64	3.1			0.60	4.0	1.80	4.1					0.22	4.3	0.37	4.1
					1.23	4.0							0.23	4.2	0.43	4.0

NOTE:-   A   =   Effluent concentration in mg/ℓ

B   =   Effluent pH

TABLE 4.11   (Continued)

Test Parameters	TEST NUMBERS											
	(9)				(10)				(11)		(12)	
Coal Type	H.C. OX				CO:ASH				H.C. OX		CO:ASH	
Flow Rate (Igpm/ft^2)	1				1				1		1	
Influent pH	4.0				4.0				5.7		5.7	
Influent Conc.	2mg/ℓ each of Zn, Cu & Pb				2mg/ℓ each of Zn, Cu & Pb				2mg/ℓ Zn		2mg/ℓ Cu	
	A(Zn)	A(Cu)	A(Pb)	B	A(Zn)	A(Cu)	A(Pb)	B	A	B	A	B
	0.00	0.00	0.00	6.1	0.04	0.00	0.00	6.3	0.00	7.0	0.00	6.6
	0.00	0.00	0.00	5.8	1.70	0.20	0.00	5.6	0.00	6.0	0.00	6.0
	0.18	0.00	0.00	5.9	2.00	1.50	0.20	4.2	0.00	7.6	0.00	6.8
	0.42	0.00	0.00	5.6	2.00	1.70	0.30	4.1	0.00	5.9	0.05	6.2
	2.00	0.05	0.00	5.0	2.00	2.00	0.75	4.1	0.00	7.5	0.40	5.8
	2.00	0.10	0.00	4.6	2.00	2.00	1.45	4.0	0.00	7.0	0.70	6.9
	2.00	0.15	0.10	4.3	2.00	2.00	1.60	4.0	0.27	5.7	1.10	6.7
	2.00	0.65	0.15	4.1							1.20	7.0
											1.25	5.7

TABLE 4.11 (Continued)

Test Parameters	TEST NUMBERS									
	(13)		(14)		(15)		(16)		(17)	
Coal Type	H.C. OX		CO:ASH		H.C. OX		CO:ASH		CO:ASH	
Flow Rate (Igpm/ft^2)	3		3		5		5		1	
Influent pH	5.7		5.7		5.7		5.7		5.7	
Influent Conc.	2mg/ℓ Zn		2mg/ℓ Zn		2mg/ℓ Zn		2mg/ℓ Zn		0.5mg/ℓ Zn	
	A	B	A	B	A	B	A	B	A	B
	0.00	6.1	0.00	6.6	0.00	7.1	0.0000	6.33	0.0000	6.9
	0.04	7.0	0.15	6.8	0.00	7.2	0.17	6.1	0.00	7.0
	0.14	5.9	0.30	6.7	0.17	6.6	0.46	7.2	0.00	7.2
	0.53	7.0	0.47	6.6	0.55	5.8	0.67	7.1	0.00	6.3
	0.77	5.7	0.65	6.4	0.73	5.7	0.89	7.3	0.01	6.3
	0.85	5.7	0.81	6.5	1.00	6.1	1.21	6.5	0.05	6.7
	1.06	7.0	1.04	6.1	1.29	6.0	1.33	7.2	0.07	6.7
	1.11	7.2	1.39	6.3	1.37	5.7	1.44	6.0	0.10	6.2
							1.67	6.2	0.21	7.2

TABLE 4.11 is a comparison of the effluent pH with the metal con-

centration in the effluent. Tests #1 and #2 show that the effluent pH drops

steadily as the effluent concentration increases. Thus, a correlation is

possible under the test parameters described in Tests #1 and #2. The drop in

pH from about 5.0 to 3.4 occurred rapidly over a small change in effluent

concentration while the change in pH from 3.4 to 3.0 occurs more slowly. This

is due to the fact that for every unit change of pH, the molar concentration

of hydrogen ion undergoes a change by a factor of 10. Thus, when the pH drops

from 5.0 to 3.4, the change in molar concentration is $10^{-3.4} - 10^{-5} = 3.8 \times 10^{-4}$;

while it takes a change in molar concentration of $10^{-3} - 10^{-3.4} = 6.0 \times 10^{-4}$ to

bring about a drop in pH from 3.4 to 3.0. The pH of the effluent seems to

fluctuate in value when it is above 5.0 and only follows a definite downward

trend below a pH of 4.0 with increasing breakthrough of the metal. This is

easily understood when one understands that it only takes $10^{-5} - 10^{-5.7} =$

8.0×10^{-6} moles/ℓ of H^+ ion to cause a shift in pH of 5.7 to 5.0, while it

takes $10^{-3.9} - 10^{-4.0} = 26.0 \times 10^{-6}$ moles/ℓ for the needle to shift from 4.0

to 3.9. Thus, the fluctuation of the effluent pH between 5.0 and 5.7 may be

in part due to the dynamic nature of the equilibrium adsorption process where

the hydrogen ions are in a state of give and take with infinitesimal shifts

in the net gain or net loss during the unsaturated stage of the column. These

shifts in the net gain or net loss show up in the pH range of 5.0 to 5.7

because the changes in H^+ ion concentration necessary to produce a change in

pH in this range are extremely small.

Tests #3 to #10 have an influent pH of 4.0. Of these tests, pH cor-

relation is possible for Tests #3, 4, 6, 7 and 8. Test #5 shows no promist of

such a correlation. The influent consists of a zinc, copper and lead mixture in

Tests #9 & 10. For Test #9, correlation is possible for the copper breakthrough and

discouraging for zinc and lead breakthroughs. In the case of Test #10, the correlation is fair for copper and lead fractions and not possible for the zinc, since the breakthrough for zinc occurred at an effluent pH above 5.6, and as previously mentioned, the pH of the effluent randomly fluctuates in the range of 5.0 to 5.7.

The pH of the influent was 5.7 for Tests #11 to #17. Correlation is definitely not possible for all these tests since the effluent pH fluctuates randomly between 7.6 and 5.7 with increasing effluent metal concentration. The effluent pH is not likely to go below 5.7 since the influent pH happens to be 5.7. Therefore, tests with an influent pH of 5.7 have no hope of such a correlation.

A conclusion may be drawn that when the influent pH is as low as 3.0, a correlation between the effluent pH and the effluent metal concentration is most likely to occur. When the influent pH is above 5.0, the chances of such a correlation are practically nil. But, when the influent pH is about 4.0, the possibility of such a correlation will depend on the test parameters, i.e., the particular combination of coal type and type of heavy metal in the influent.

4.10 Breakthrough Curves for Mercury

Figure 4.11 shows plots of effluent concentration of mercury versus volume of liquid treated. The influent concentration of mercury is shown as a series of exponential curves joined by vertical lines. The influent concentration is at 5 µg/ℓ when a new batch of influent is made and put into the system. But the next day, about 6 hours before refilling the system with 5 µg/ℓ Hg, the influent in the system was tested and found to be 2.1 µg/ℓ Hg. This indicates that the mercury had volatilised overnight from 5 µg/ℓ to 2.1 µg/ℓ. For lack of more

AVERAGE INFLUENT = 3.10ug/1 Hg

pH = 7.5

FLOW RATE = 1 Igpm/ft.^{2}

BED DEPTH = 10 inches

INFLUENT ——△——△——

COAL WEIGHT

20 gm - CO·ASH ⊙——⊙——⊙

13 gm - H.C.OX ✕——✕——✕

Average Influent Concentration

EFFLUENT CONCENTRATION IN ug/l

VOLUME OF LIQUID TREATED (Litres)

FIG. 4.11
BREAKTHROUGH CURVES FOR MERCURY

84
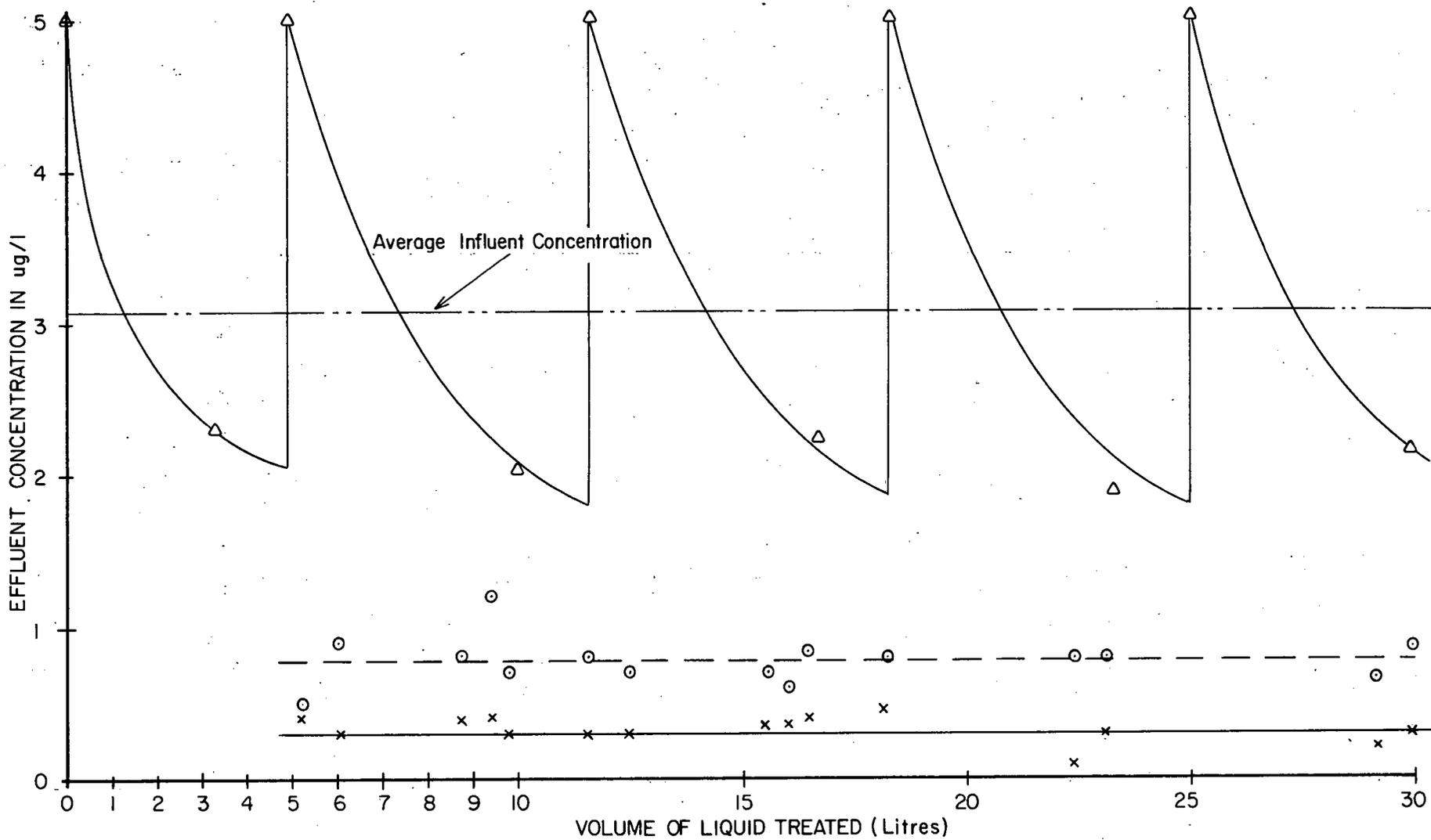
data, this deterioration of the influent concentration is assumed to be exponential and, therefore, represented by exponential decay curves. When a new batch of 5 µg/ℓ influent enters the system, the influent concentration shoots back up to 5 µg/ℓ and this moment is represented by the vertical lines joining the exponential curves. Sigworth and Smith[7] mentioned a similar fluctuation of the influent concentration in adsorption systems of activated carbon and methyl mercury chloride influents.

For purposes of capacity calculations if breakthroughs had been reached, 3.45 µg/ℓ would have been chosen as the average influent concentration for the time variation of influent mercury assumed in Figure 4.11.

A column each for H.C. OX and CO:ASH was run at a pH of 7.5. The main objective for running these two columns was to find out the capacities of the two coals for mercury in the influent range of 5 µg/ℓ and at near neutral pH of 7.5.

The breakthroughs for both columns failed to occur even after a throughput of 30 litres. It was decided to stop the runs rather than wait indefinitely for the breakthroughs that showed no signs of approaching. Sigworth and Smith[7] reported a column test involving granular activated carbon and methyl mercuric chloride influent of 25 µg/ℓ which failed to show a breakthrough even after a throughput time of 3 months. According to the two authors, mercury was categorised as a metal of good adsorption potential. Lead was also classed as good but a little below mercury. Copper was classed as a metal of slight adsorption potential and zinc was also in the slight category but below copper.

Since Figure 4.11 shows two horizontal lines for the effluent concentrations of the two columns without any hint of breakthroughs, the capacities at particular breakthrough concentrations cannot be calculated. It can be noted, however, that the percent removal of mercury is 75 percent in the case of CO:ASH

and 90 percent in the case of H.C. OX. The percent removals were based on

the average influent concentration of 3.1 µg/ℓ. The effluent from the H.C. OX

column has an average of 0.3 µg/ℓ and this concentration in the effluent stayed

almost constant with increasing throughput. The effluent from the CO:ASH

column exhibited the same sort of behavior with an average effluent concentration

of 0.8 µg/ℓ. It is suspected that the reason for the effluent concentration

never being at 0.0 µg/ℓ even at the beginning of the run may be due to the

extremely low driving force of 3.45 µg/ℓ influent concentration. This may make

it very hard for the adsorbent to totally adsorb the mercury even when the

adsorbent is highly unsaturated at the beginning of the test.

4.11 Column Tests – Summary and Conclusions

Conclusions drawn from the investigations carried out in the Column

Tests are as follows:

1)   No significant change in capacity occurs by varying the cross-

sectional area of the coal bed within the range of 0.001 ft^2–0.002 ft^2.

The 28/48 size fraction has an average diameter of 0.7 mm. The coal

bed cross-sectional area of 0.001 ft^2 has a diameter of 10.9 mm, which

is 16 times bigger than 0.7 mm. Similarly, cross-sectional area of

0.002 ft^2 corresponds to a diameter of 15.4 mm, which is 22 times

greater than the average particle diameter. For particles shaped as

those of 28/48 coal, the wall effect would most probably set in if

the column diameter were less than about 10 times the average particle

diameter. Therefore, the use of columns smaller than those selected

for this work would run the risk of providing unrealistic results.

2)   A definite decrease in adsorptive capacity is evident with

decreasing influent pH. The percent decrease in capacity for a

given decrease in pH is approximately the same for both H.C. OX and CO:ASH with zinc influents. Since the pH of the influent is a critical factor in determining the adsorptive capacity, special emphasis should be laid on the investigation of more detailed relationships between pH and capacity in future research of this type.

Of all the test parameters with the exception of coal type, the influent pH is the most crucial as far as adsorptive capacity is concerned. A decrease in pH means a decrease in capacity. Therefore, for acidic wastes, such as certain industrial wastes, some form of pre-treatment to raise the pH before passing the wastes through the coal column may be an important consideration.

3)   As the flow rate was increased from 1 Igpm/ft^2 to 5 Igpm/ft^2, a corresponding decrease in adsorptive capacity was noticed. This decrease was highly significant when the flow rate was increased from 1 to 3 Igpm/ft^2. On further increasing the rate by another 2 Igpm/ft^2 to 5 Igpm/ft^2, the corresponding decrease in capacity was much smaller than the previous one. This suggests the relative ease of changing the rate from 3-5 Igpm/ft^2, should occasion demand it, without suffering significant decreases in capacity.

The percent decreases in capacity, due to increasing flow rate, become lessmalleress at higher breakthrough concentrations. Thus, the choice of whether to use a higher flow rate or build a thicker column is also influenced by the permissible breakthrough concentration which would be set by the local regulatory agency.

4)   Whether the capacity would decrease or increase upon lowering

the influent concentration was found to depend on the influent pH and on the type of coal. At a pH of 4.0, the general trend is a decrease in capacity on lowering the influent concentration. At a pH of 5.7, the type of coal used determines the direction of change of capacity with decreasing influent concentration. This indicates the possibility of combining waste streams to lower the influent concentration of the waste components with the aim of raising the adsorptive capacities. Of course, this sort of dilution before treatment would pertain only to cases where the adsorbent – pH combination favours an increase in capacity on lowering the influent concentration.

The percent decrease in capacity due to a decrease in pH is more pronounced at lower influent concentrations. Consequently, more attention will have to be paid to pH conditions of waste streams of lower influent concentrations.

5) The capacity increases as the influent pH increases from 3.0 to 5.7. The highest capacities arrived at in this research were those corresponding to a pH of 5.7. TABLE 4.12 lists the capacities for zinc, copper and lead to 10 percent breakthrough concentration, where influent pH and concentration is 5.7 and 2 mg/ℓ, respectively, and the flow rate is 1 Igpm/ft^2.

Under the same conditions, but with an influent pH of 4.0, the ratio of capacities for zinc : copper : lead is equal to 1 : 6 : 12 for CO:ASH coal. The high capacity for lead may be partly due to the fact that lead has a high atomic weight. This order of magnitude of adsorptive capacities for the three metals is in agreement with the results of the Batch Tests.

TABLE 4.12

CAPACITIES AT A pH OF 5.7 AND AT A BREAKTHROUGH CONCENTRATION
OF 10 PERCENT OF INFLUENT CONCENTRATION

| | CAPACITIES mg/gm | | |
	Zn mg/gm	Cu mg/gm	Pb mg/gm
CO:ASH	0.370	1.182	—
H.C. OX	9.716	*12.396*	—

Note: 1) Capacity of H.C. OX for copper is shown in italics
since this figure is only an estimate and not
arrived at experimentally (Section 4.5)

2) The capacities for lead are undetermined since the
runs were stopped before the occurrence of break-
throughs (Section 4.7)

6)   From column tests at a pH of 4.0 with influents containing

2 mg/ℓ each of zinc, copper and lead, the adsorptive capacities of

DARCO Activated Carbon are in the same range as those of CO:ASH. The

capacities of H.C. OX are much higher than those of the activated

carbon or CO:ASH. With regard to zinc and copper, H.C.OX is 12 times

higher in capacity than CO:ASH. In the case of lead, H.C. OX dis-

played a capacity 4 times that of CO:ASH.

There is a mutual inhibition of adsorption when there is more

than one heavy metal in the influent. Although the adsorptive

capacity decreases for each individual metal when the influent is a

mixture rather than a single solute solution, the total capacity for

heavy metals achieved with mixed influents is higher than any of the

individual capacities encountered with single solute influents. This

suggests the possibility of combining waste streams, containing

different heavy metals, before passing them through the adsorption column. Such a procedure would result in a higher total capacity of the coal than would be achieved if the individual streams were passed through separate columns.

7)   An attempt was made to correlate the effluent pH with the metal concentration in the effluent. It was found that the effluent pH is generally around 6.0 at the beginning of each column test, and decreases with column age until the effluent pH reaches that of the influent when column exhaustion has occurred. The chances of a correlation between effluent pH and effluent metal concentration increase with decreasing pH of the influent. In other words, the correlation is more evident when the influent pH is farther away from 6.0. At an influent pH of 5.7, there was no correlation. At an influent pH of 4.0, the occurrence of a correlation depended on the combination of coal type and type of heavy metal in the influent. And at an influent pH of 3.0, the correlation was pronounced.

For columns where this correlation exists, a saving in time and expenses may be realised by using a pH meter instead of other sophisticated equipment that is more expensive and cumbersome.

8)   The tests with mercury proved to be somewhat difficult. The influent concentration of mercury deteriorated with time. Thus, for column capacity calculation purposes, the original influent concentration of 5 $\mu g/\ell$ could not be used as a base, but rather, an average influent concentration over the period of the test had to be determined.

Capacities could not be calculated since the runs were stopped before breakthroughs occurred. It might have taken intolerably long periods of time for breakthroughs to have occurred. The presence of

mercury in the effluent was detectable even at the very beginning

of each column test. The effluent concentration was 0.3 µg/ℓ and

0.8µg/ℓ for H.C. OX and CO:ASH, respectively, right from the beginning

to the end of the tests. This gives a percent removal, based on the

average influent concentration of 77 percent for CO:ASH and 91 percent

for H.C. OX.

For future research with mercury, a more stable form or complex

of mercury should be used instead of $HgCl_2$, which was used in this

research. Using a more stable complex of mercury, preferably a type

of complex found in sewage, would eliminate the problem of the

deteriorating concentration of mercury when running column tests with

influents of extremely low mercury concentrations.

Chapter 5

RECOMMENDATIONS

Based on this research and other works done on the adsorption of heavy metals by granular coals, further research is indicated:-

1) Since H.C. OX is far superior than the other types of coal tested, first priority should be given to this coal for use as an adsorbent in an advanced waste treatment process.

2) Attempts should be made to grow some cultures of the fungus, mentioned in this thesis, so that fungal spores could be obtained for an exact identification of the fungus. Research should also be done on the investigation of the heavy metal removal mechanism of the fungus. Is the heavy metal being converted into some form of a salt crystal and entrapped in the mycelium, or is it simply being adsorbed by the mycelium, are questions of high interest.

3) More detailed analysis on the correlation between effluent pH and metal concentration in the effluent should be done with columns where the influent pH is less than 4.0. There is no correlation when the influent pH is above 4.0. (Refer to Section 4.9)

4) For future research with mercury influents, a more stable complex of mercury should be used. This is to overcome the problem of deteriorating influent concentration experienced in this research, where $HgCl_2$ was used as an influent.

5) Removal of heavy metals in solution using granular coals should be further investigated with organics present in the waste solution. The goal of this investigation should be to determine the removal efficiencies at low heavy metal concentrations from a real municipal sewage.

6) The possible use of granular coal as a fuel source, after having used it as an adsorbent, should be investigated. Should this possibility prove to be feasible, then this advanced waste treatment system using granular coals may be economically superior to other treatment systems. Having a power plant close by the treatment facility would help the economic picture tremendously. Should H.C. OX be chosen as the adsorbent material, it should first be shown that H.C. OX possesses the required properties needed for use as a satisfactory fuel coal.

7) The final step taken should be to investigate where the adsorbed heavy metals would end up when the coal is burned as a fuel. If they stay down with the ash, then a landfill with the necessary precautions to prevent leaching would be their final destination. If they fly up the stack, then special air pollution control measures may have to be undertaken.

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