REMOVAL OF HEAVY METALS FROM WASTEWATER USING GRANULAR COAL

by

THIRUGNANA SARAVANABAWAN
B.Sc., University of Wales, 1973

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
(Department of Civil Engineering)

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
January 1980

Department of CIVIL ENGINEERING

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date MARCH 14, 1980

ABSTRACT

Batch tests were performed to evaluate the relative performance of four B.C. coals (Hat Creek Oxidised, Kaiser-stock pile refuse, Kaiser-special plant feed and Cominco Ash) in removing heavy metals copper, lead, zinc and mercury from filtered primary sewage treatment plant effluent. Emphasis was placed on metal concentrations of 10 mg/l and less. Hat Creek coal was found to be much superior to the other three and its efficiency is comparable to that of Darco activated carbon 12 x 20.

Hat Creek and Kaiser-stock pile refuse coals were further used in column tests to evaluate the relative performance of these coals in removing copper, lead and zinc under dynamic conditions. Again emphasis was placed on influent metal concentrations of 10 mg/l and less and once more the performance of Hat Creek coal was much superior to that of Kaiser coal. Tests with activated carbon indicate Hat Creek coal to be a close competitor for use in advanced waste treatment for heavy metal removal.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Page

FIGURE

Page

FIGURE

ACKNOWLEDGEMENT

I am grateful to my research supervisor, Dr. W.K. Oldham, for his patience and encouragement throughout this study. His support and guidance were of the utmost importance and are sincerely appreciated. My thanks are also due to Dr. K. Hall for making a critical survey of my typescript and weeding out some analytical errors.

This study was supported by Grants from the Ministry of Environment of the Province of British Columbia.

Chapter 1

INTRODUCTION AND RESEARCH RATIONALE

Increasing population and industrial growth has produced adverse effects on the environment and human life such as the mercury contamination of fish and the subsequent human health hazards. Similar incidents have focused attention on the pollution potentials of heavy metals in wastewater effluents and receiving waters. The public's concern for the preservation of the environment has forced the Federal and Provincial Governments of Canada to enact strict pollution control standards for municipal and industrial effluent discharges.

A review of literature[1,2] indicates that copper, zinc and lead contribute the bulk of the heavy metal loading to receiving waters, and mercury with its inherent cumulative nature and multiplying effect in the food chain poses the utmost concern in the aquatic environment.

Crushed anthracite coal has been used for many years as a filtering medium for water supplies. However its use as a sorption medium for purifying wastewater has been examined only recently with special emphasis towards the removal of organics from domestic sewage[3]. A significant advantage is that coal exhausted of its sorption capacity is still potentially useful as an energy source. A U.S. Department of Interior report[3] recommends the use of coal for post, or "tertiary" treatment of secondary sewage treatment plant effluent.

The ability of certain British Columbia coals to remove dissolved constituents from water has been investigated by Coulthard[4] and Hendren[5] and their findings are encouraging. However, most of the work was carried out with relatively high metal concentrations and with only two coals found in British Columbia. Recent studies by Riaz[6] and Tin Tun[7] were carried out with relatively lower copper, zinc, lead and mercury concentrations and the results obtained from both batch and laboratory scale column tests are promising.

Riaz[6] carried out batch tests with six coal samples:

Kaiser coal - Special waste lagoon sample

Kaiser coal - Stock pile refuse sample

Kaiser coal - Special plant feed sample

Kaiser coal - Oxidised stock pile sample

Northern coal mines - Unoxidised sample and

Northern coal mines - Oxidised sample.

On the basis of batch test data obtained, the best two coals (Kaiser coal - stock pile refuse and Kaiser coal - special plant feed) were tested in a continuous flow laboratory - scale column. The emphasis was placed on metal concentrations of 2 mg/l and less for copper, lead and zinc and 5 μg/l for mercury. The effect of influent concentration, flow rate through the column (contact time), pH of influent, and mixture of metals on the adsorptive capacity of coal were investigated. On the basis of adsorptive capacity, Kaiser coal - Stockpile refuse sample was found to be the best of six coals tested. Its metal removing efficiency was compared with activated carbon and nitrohumic acid and results indicate that coal may be a feasible alternate to remove heavy metals from waste effluents.

Tin Tun[7] carried out batch tests with five coal samples:

Hat Creek oxidised

Hat Creek unoxidised

Cominco oxidised

Cominco ashwaste and

Cominco production.

Based on batch test results, the best performing coal from each of the Hat Creek and Cominco groups, namely Hat Creek oxidised and Cominco ashwaste were tested on a continuous flow laboratory - scale column. The influent concentration was 2 mg/l and less in the case of copper, zinc and lead and was 5 μg/l and less for mercury. The effect of pH, influent metal concentration, flow rate and the synergistic effects of multiple metals were investigated. Hat Creek oxidised was found to be superior to others with regard to adsorptive capacity and also compared favourably with Darco activated carbon.

The study reported in this thesis is an extension of the work carried out by Riaz[6] and Tin Tun[7]. Readers are strongly recommended to refer to these references for further background information on heavy metal pollution problems, their magnitudes, and methods presently available and used to control them.

Synthetic waste waters produced by mixing metal solutions with distilled water to desired concentrations were used by the above workers in adsorption studies. In the study reported herein, the performance of coal in removing heavy metals from sewage treatment plant effluent was investigated. The specific objectives of this investigation were:

1. To evaluate the relative efficiencies and capacities of four different B.C. coals in removing heavy metals from wastewater in batch tests;
2. To evaluate heavy metal removal capacity of the best two coals in continuous flow column tests;
3. To compare the metal removing capacity of coal from wastewater with that of Darco activated carbon grade 12 x 20.

During the investigation, information was obtained on the influences of the following characteristics on removal efficiency and adsorption capacity of coal;

1. Concentration of adsorbate;
2. Flow rate or contact time;
3. pH.

Chapter 2

MATERIAL AND PROCEDURE

2.1 Types of Coal

Four different coal samples were used of which two were chosen from Riaz's[6] study and the other two from Tin Tun's[7] work.

Kaiser coal - Stock pile refuse (K.C. SPR)*

Kaiser coal - Special plant feed (K.C. SPF)

Hat Creek oxidised (H.C. OX)

Cominco Ashwaste (CO. ASH)

Activated carbon (ACT. CARB.)

*Abbreviations used throughout the text.

The performances of the above four coals were compared with Darco activated carbon grade 12 x 20 by parallel testing.

2.2 Coal Preparation

Coal was first washed with water to remove all foreign particles and subsequently dried at room temperature. The dried coal was then crushed to the desired grain size (28/48 mesh) by passing it first through a Taylor Gyrator and then through a Massco cone crusher. Crushed coal was dry sieved using 28/48 mesh screens and mechanical shaker.

The 28/48 mesh fraction was then wet sieved and back washed in a plexiglass column to remove fines. Finally, the granular coal was dried at 103°C for about 40 hours and stored in sealed bottles flushed with nitrogen gas.

2.3 Wastewater

Wastewater was prepared from unchlorinated effluent from the Lions Gate Primary Sewage Treatment plant of the Greater Vancouver Regional District. The primary effluent, which has total volatiles of about 200 ppm and suspended volatiles of about 70 ppm, was filtered by vacuum into glass carboys using Whatman No. 541 filter paper and stored under refrigerated conditions. Removal of suspended solids was necessary to prevent settling and entrapment of these solids during column testing within the pore spaces of the 28/48 mesh coal column. As a result, it was possible to achieve throughput volumes of up to 10 liters instead of less than one.

The filtered effluent with non-detectable initial metal concentrations was "spiked" with standard metal solutions to desired concentrations, and heated to room temperature (23°C) before use as wastewater for testing. Standard solutions used to spike the filtered effluent were copper, lead, zinc and mercury atomic absorption standard (stock) solutions with 1000 mg/l (ppm) metal concentration.

Since the above standard metal solutions are acidic, the spiked wastewater turned acidic, the final pH depending on the quantity of metal solution added. Whenever the prepared wastewater was found to have pH less than 4.0, and pH was adjusted to 4.0 by addition of sodium hydroxide which was shown by preliminary tests not to interfere with the adsorption process. If the pH of spiked wastewater was greater than 4.0, pH adjustment was not carried out.

2.4 Measurement of Concentration

A Jarrell Ash MV - 500 atomic absorption spectrophotometer was used for the measurement of metal concentration. For copper, zinc and lead and mercury at concentrations of 2 mg/l and higher the flame atomic absorption technique was used. For lower mercury concentration the cold vapour or flameless method[8] was utilised. Samples having mercury concentrations of 2 mg/l and higher were acidified to pH below 2.0 using NHO_3 and then analysed by the same method as copper, zinc or lead.

2.5 Batch Testing Procedure

Known quantities of granulated coal were mixed with one hundred milliliters of wastewater containing known concentrations of copper, zinc, lead or mercury in a flask for a predetermined contact time using a mechanical shaker. The mixture was then filtered and the filtrate analysed to find the residual metal concentration. These tests were utilised to study the relative efficiencies of the different coals in removing heavy metals from wastewater.

2.5.1 Determination of Optimum Contact Time

Batch tests were performed with different coals to determine equilibrium copper concentration at different contact times and the results are shown in Figure 2.1. From these results the following conclusions were drawn.

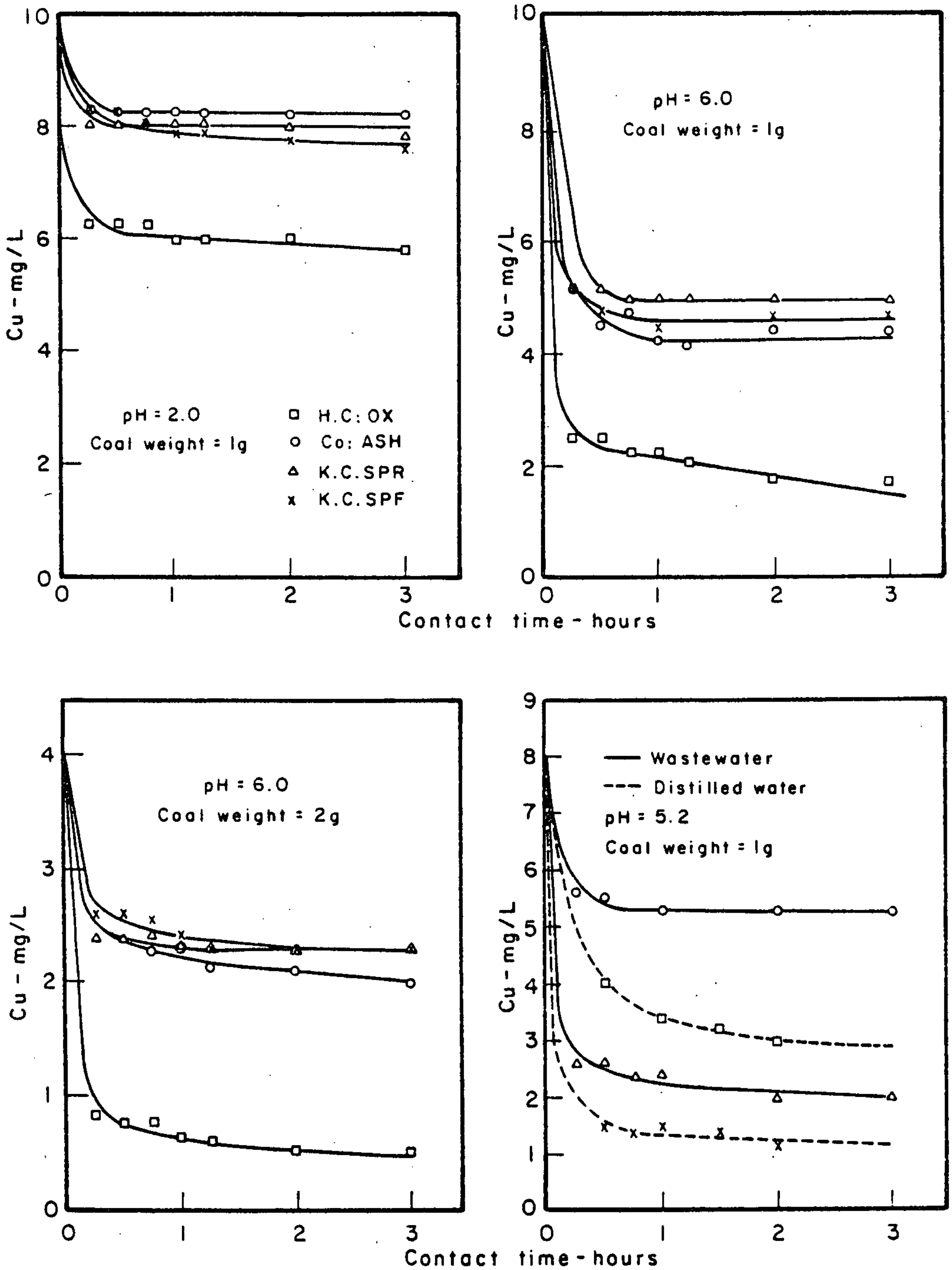

Figure 2.1 Effect of Contact Time on Adsorption of Copper

(a) Contact time of 90 minutes will achieve about 95% of the ultimate removal, and it was thus chosen as the optimum contact time for the rest of the study.

(b) Initial metal concentration and the pH of wastewater do not appreciably influence the optimum contact time.

2.5.2. Determination of Required Coal Quantity

Batch tests were carried out with wastewaters containing constant initial concentrations of the various metals, but with varying quantities of coal. The volume of wastewater used for each test was 100 ml. Results obtained are shown in Figure 2.2. From these results the minimum quantity of coal necessary for effective removal of heavy metals from 100 milliliters of wastewater was determined to be one gram.

2.5.3. Adsorption Isotherms

An adsorption isotherm which is derived from a series of batch tests can be defined as a constant temperature plot of the adsorbent capacity to remove a particular adsorbate from solution against the concentration of adsorbate in equilibrium with the adsorbent.

Conditions used in the batch tests for the preparation of isotherms were as follows:

Quantity of coal	=	1 gram
Coal size	=	28/48
Volume of wastewater	=	100 ml
Contact time	=	90 min
Temperature	=	$23^{o}C$ (room temperature)
pH of wastewater	=	4.0

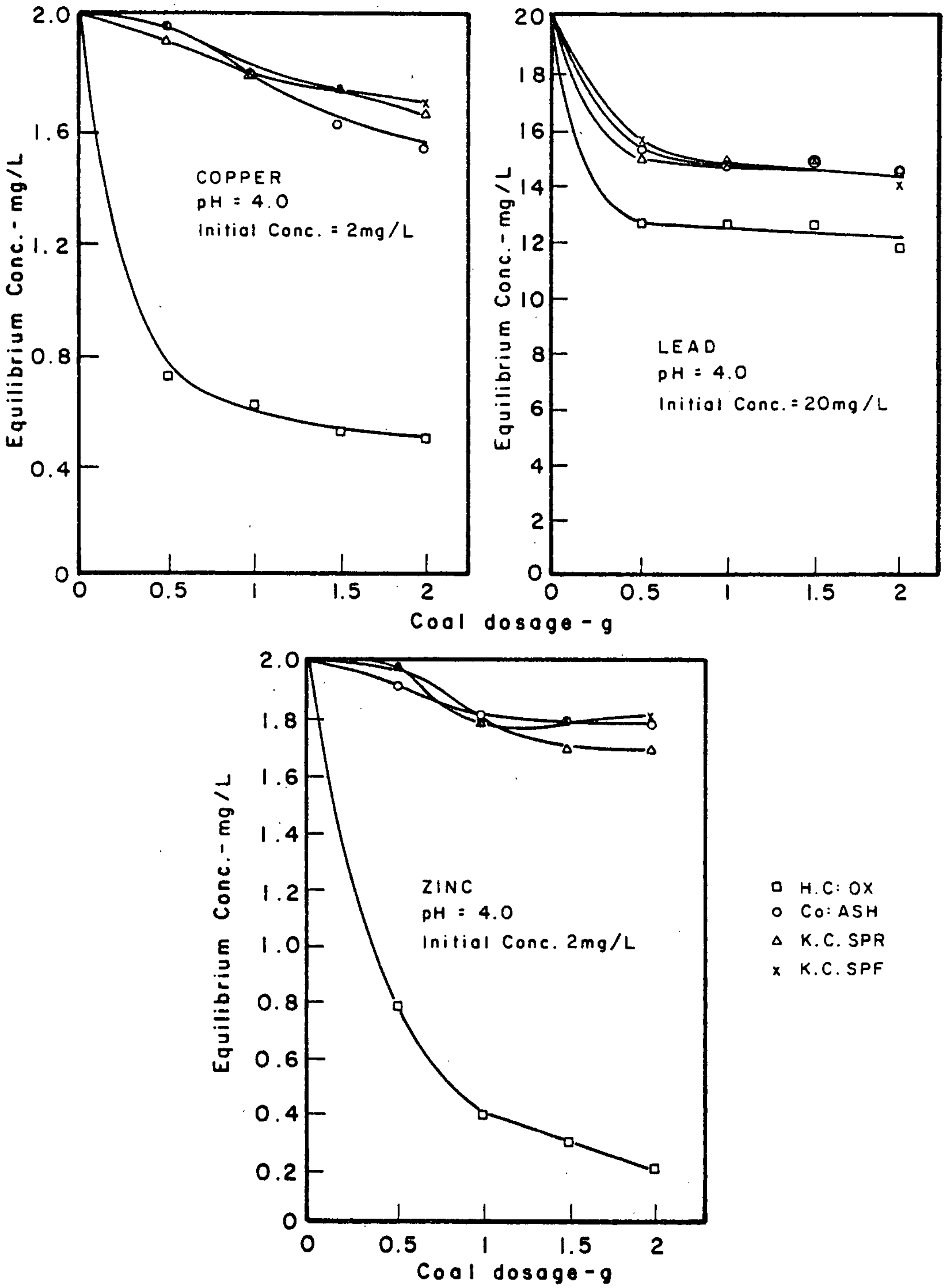

Figure 2.2. Effect of Coal Dosage on Metal Adsorption

Initial metal concentrations: Emphasis was placed on low metal concentrations (less than 10 mg/l) so that concentrations are of a similar order of magnitude to those found in municipal wastewaters that contain some industrial wastes. The sensitivity and minimum concentration detectable by the atomic absorption technique were taken into consideration when choosing the minimum metal concentrations.

Isotherms so developed reveal useful information in that they provide an easy comparison on the abilities of different absorbents to remove a common adsorbate from solution, and give some insight into design requirements for flow-through columns.

2.6 Columns Testing Procedure

2.6.1. Column Set Up

The ability of coal to remove metals from wastewater under continuous flow conditions was studied using column tests. This type of testing simulates the use of packed, or sorption towers which are designed to achieve mass transfer between the liquid and solid phases of the system.

The set up used is similar to that employed by Riaz[6] and Tin Tun[7] but with slight modifications. Fifty milliliter burettes of 0.9385 cm^2 (0.001 ft^2) cross sectional area were used as columns. It has been shown[7] that for column containing 28/48 mesh size particles, 0.001 ft^2 bed cross sectional area is greater than the critical area below which the column wall influences the fluid flow characteristics and thereby significantly reduces adsorption capacity. Glass beads and glass wool were packed under the coal column to avoid plugging the outlet flow control valve with coal. The burette inlet opening was connected to an acid washed 5 gallon glass carboy which functioned as a wastewater reservoir in the system. Care was taken to keep the rate of flow constant by frequent adjustments to the outlet valve.

2.6.2 Experimental Procedure

The entire study was intended to be carried out in a manner similar to those of Riaz[6] and Tin Tun[7] so that comparisons could be drawn with respect to the ability of coal to remove heavy metals from different types of wastewater. Most of the time this condition was satisfied, but at other times some deviations were necessary to accommodate the different properties of the wastewater used, as discussed later in this chapter.

Preliminary column runs revealed that a column depth of 10 inches as chosen by Riaz[6] and Tin Tun[7] was not suitable for work with primary sewage treatment plant effluent, since the column tends to plug due to microbial growth on the surface before metal breakthrough occurs. Tin Tun[7] reported that microbial growth on the coal surface was evident after about 65 hours of contact with his simulated wastewater. With the wastewater used in this study, the column became completely plugged and no flow occurred after some 40 hours of use. Sterilization of the wastewater to overcome this problem was considered but not carried out since microbial activity and its interference is one of the more important characteristics of this type of wastewater.

Since complete plugging occurred at about 40 hours, the coal column had obviously been microbially active for some time before that. Hence 20 hours was considered to be the maximum time the column should be operated to keep this interference to a minimum. This restricted the throughput volume to 5.5. liters at 4.88 ml/cm^2 min. (1 gpm/ft^2) flow rate and 27.5 liters at 24.41 ml/cm^2. min. (5 gpm/ft^2).

To select a suitable column depth tests were carried out with coal columns with depths of 19.1, 12.7 and 6.4 c.m. (7.5, 5.0 and 2.5 inch respectively). Emphasis was placed on breakthrough characteristics of Hat Creek oxidised coal which performed best in batch tests. A flow rate of 4.88 ml/cm^2. min. (1gpm/ft^2) was chosen for these tests.

Figure 2.3 indicates that for a flow rate of 4.88 ml/cm^2. min. using Hat Creek coal:

(1) A column height of 19.1 cm (7.5 inches) is too great as no significant breakthrough had occurred after 5 liters had been passed through the column.

(2) A column height of 6.4 cm (2.5 inches) is not adequate since metal penetration occurred at an early stage.

(3) A column height of 12.7 cm (5.0 inches) is more suitable since metal concentration in the effluent was constant and less than one-tenth of the influent concentration upto a throughput volume of 1 liter, and increased with increasing throughput volume thereafter. However complete breakthrough was not achieved with a throughput volume of 5 liters, indicating that optimum column depth for Hat Creek coal is smaller than 12.7 cm. and greater than 6.4. cm.

Test results with Kaiser coal and activated carbon plotted in Figure 2.4 indicate that a column height of 12.7 cm is not adequate for these adsorbates under stated operating conditions, since metal penetration occurred at early stages of such runs. From results of these tests it is obvious that one column height will not satisfy adsorption characteristics of the three adsorbates to be studied. Also,

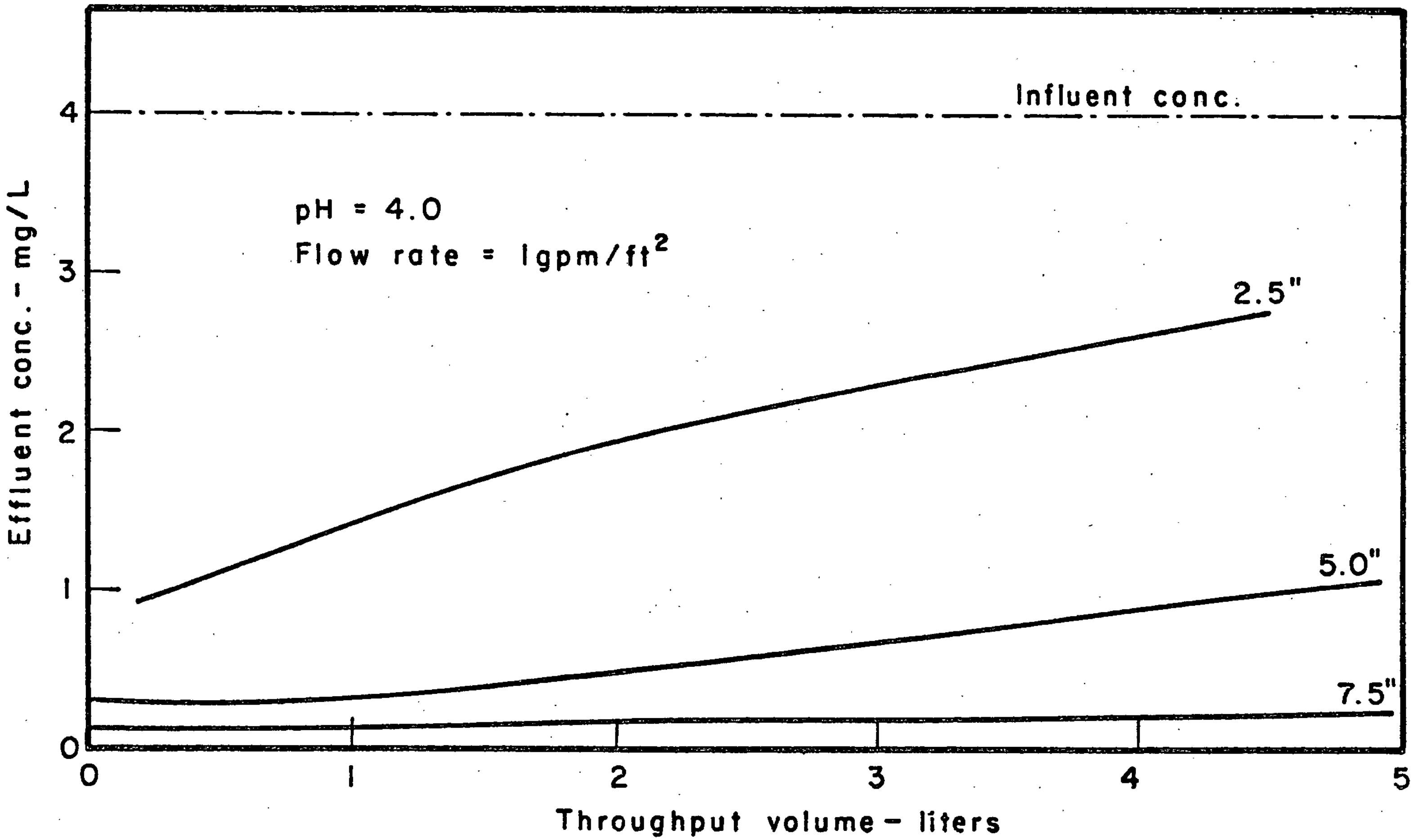

Figure 2.3. Breakthrough Curves for Copper Using Depths of Hat Creek Coal

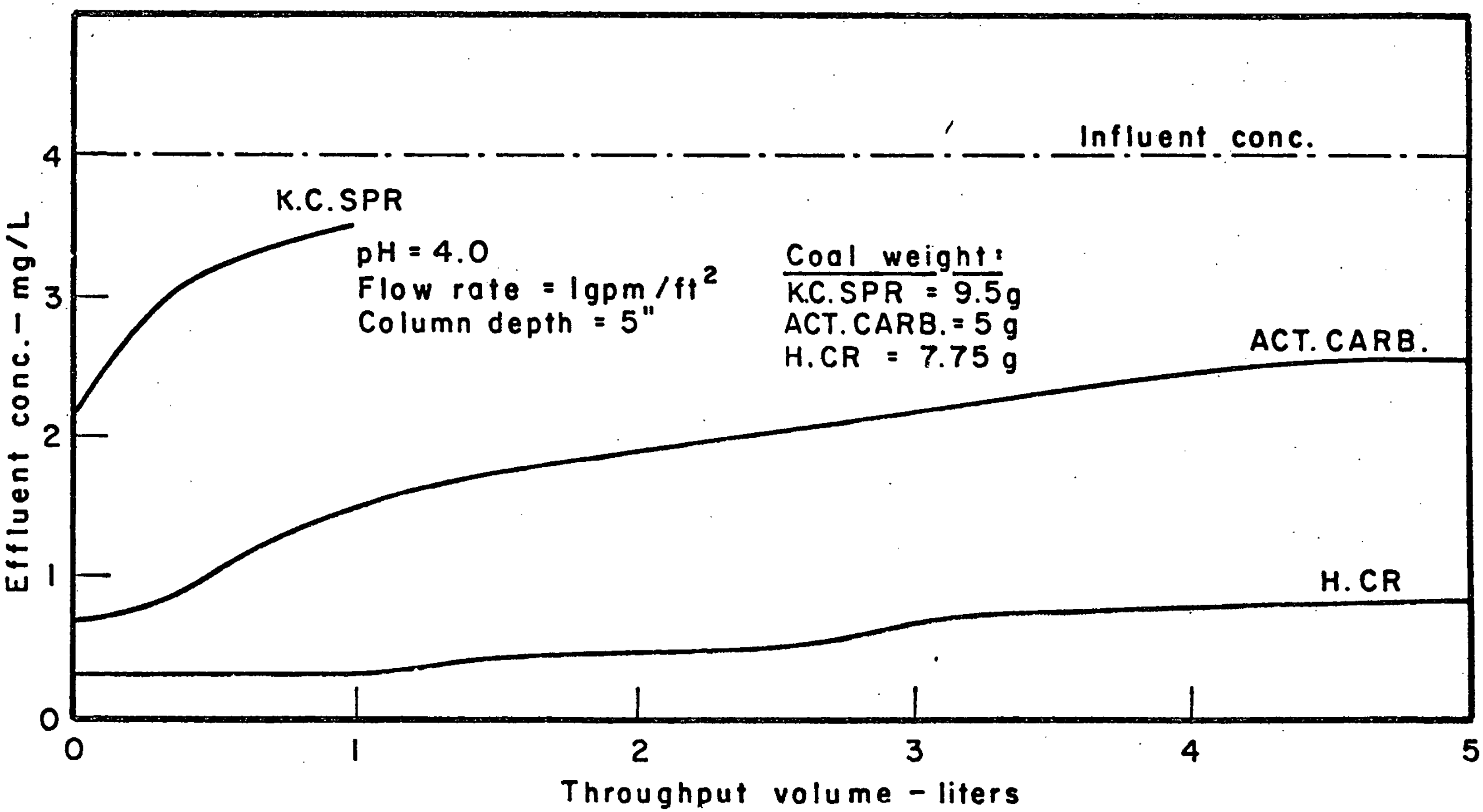

Figure 2.4. Breakthrough Curve for Copper With Different Sorbates

different metals would require different heights of adsorbate columns to exhibit adsorption and breakthrough characteristics.

It is extremely important to note that these column tests were devised and carried out only for the comparison of the performances of different coals and not to obtain absolute values for the adsorption capacity, minimum effluent metal concentration, etc. By altering the flow rate or column depth the effluent metal concentration can be significantly changed. For comparative purposes, the different coals must be tested under exactly similar conditions. That is, the same column height should be used for all coals in all tests if the effect of the other parameters (influent concentration, flow rate, etc.) were to be examined. Hence different column heights should not be used for different coals, to suit their individual characteristics.

If for a particular column height and flow rate, breakthrough was not obtained with say, coal A and metal penetration was obtained with coal B, it goes to prove that in order to remove that metal from waste-water coal A is much more suitable than coal B. Further column tests with coal A would be required in order to obtain more information, such as the minimum effluent concentration attainable, breakthrough concentration, optimum flow rate and column depth etc. Since this study is to obtain information such as the former and not the latter, a column depth of 12.7 cm (5.0 inches), which is between the requirements of Hat Creek and Kaiser coals, was considered suitable and was used in column testing.

Chapter 3

RESULTS AND DISCUSSION

3.1 Batch Tests

3.1.1 Effect of pH on Efficiency

Batch tests were carried out to examine the effect of pH on the efficiency of heavy metal removal. The results are shown in Figure 3.1 and 3.2. Hat Creek coal was chosen for these tests since it had continuously displayed greater adsorptive efficiency than the others. Tests were performed at pH values of 3.0, 4.0,5.5 and 7.0. With increasing pH, an increase in metal removal efficiency is evident. The influence of pH is greater in the adsorption of zinc than in the case of copper or lead, possibly due to precipitation of zinc at higher pH. Compared to work carried out by Riaz[6] and Tin Tun[7], the overall metal removal efficiency has dropped significantly in treated sewage effluent, as shown in Figure 3.1. This might be due to competition with organics for adsorption sites, resulting in fewer sites being available for heavy metals. This very important difference between pure solution and wastewater is discussed in detail later in this chapter.

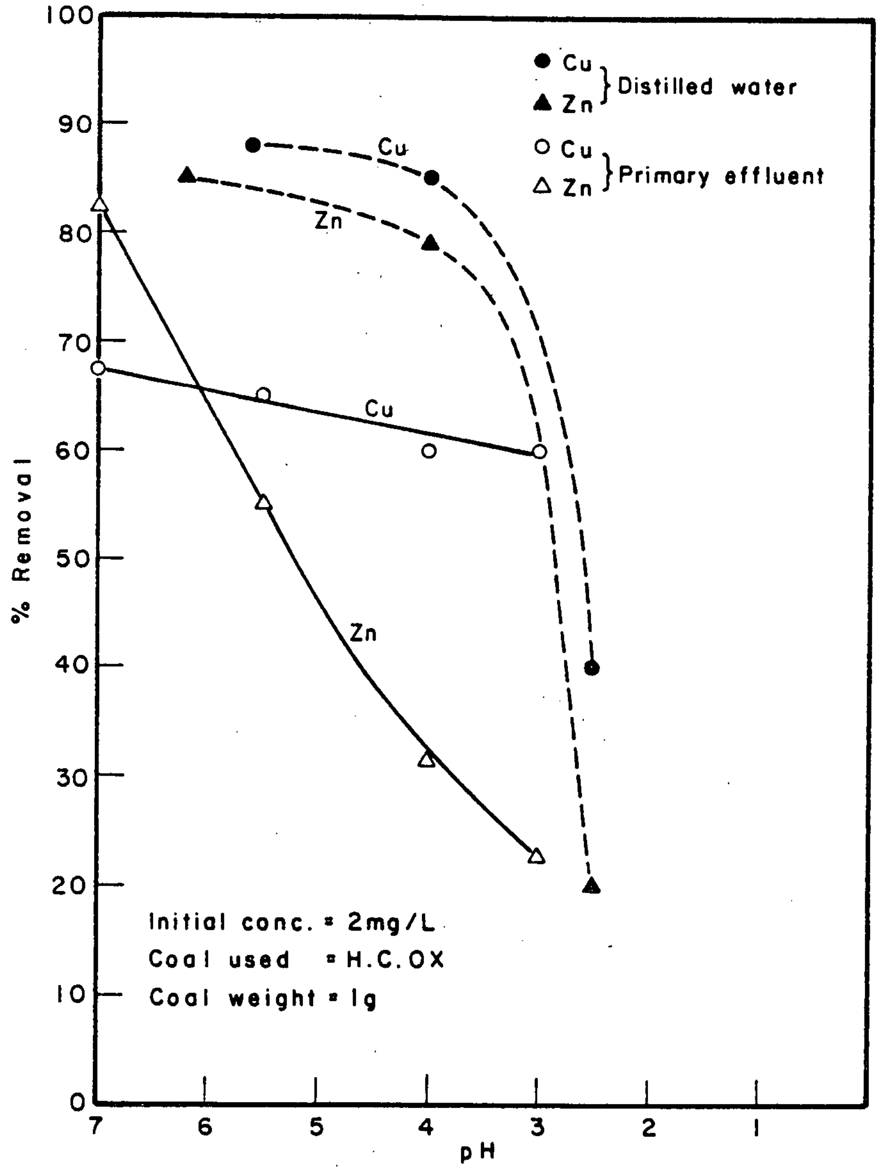

Figure 3.1 Effect of pH on Metal Removal at Lower Concentration

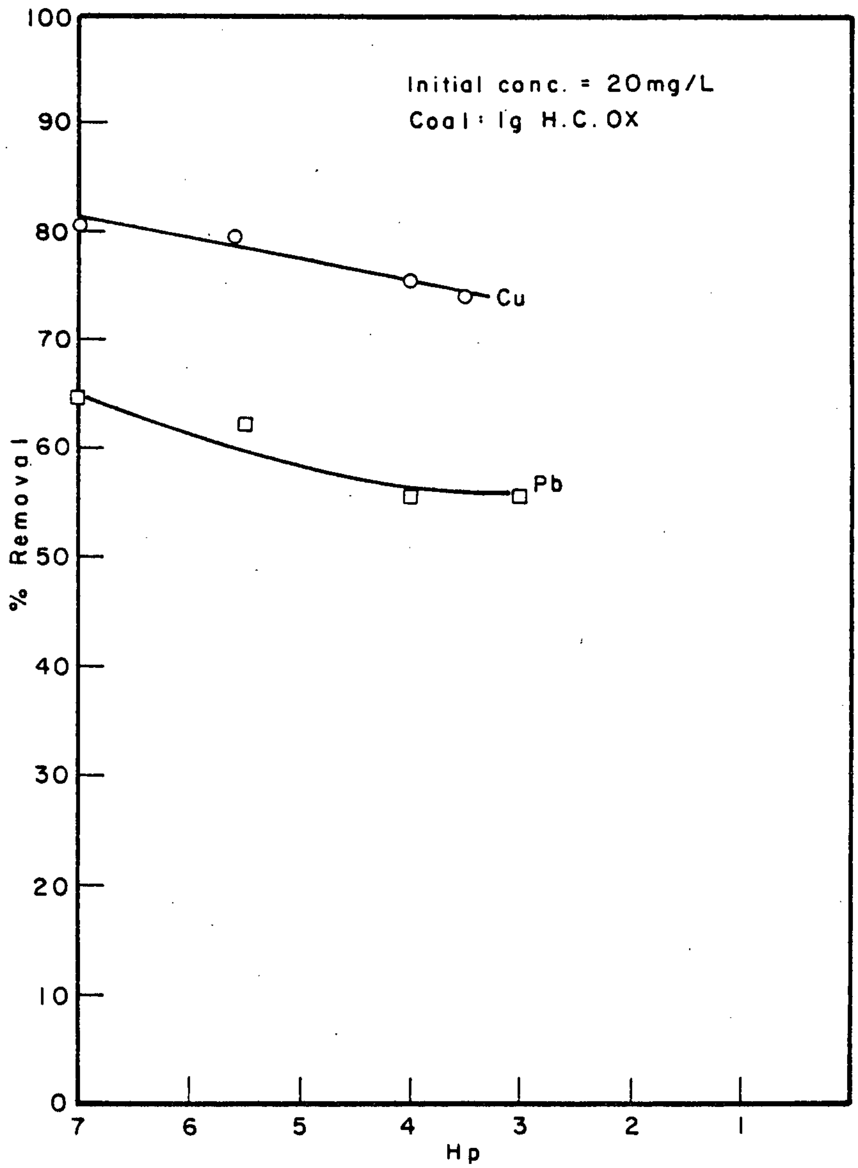

Figure 3.2 Effect of pH on Metal Removal at Higher Concentration

3.1.2 Capacity of Coals

(a) Copper

Copper adsorption isotherms obtained from batch tests are shown in Figures 3.3 to 3.5. Under batch test conditions already defined, the following coal properties were noted. (Refer to Table 3.1).

(1) The copper adsorption capacity of coal increased with increasing equilibrium concentration of the metal.

(2) By comparison to Riaz's[6] work in the 10 to 30 mg/l equilibrium concentration range, coals have shown greater trace metal removal capacities from sewage effluent than from water solution.

(3) Under much lower equilibrium concentrations (0.1 to 1.0 mg/l), the adsorptive capacities of the various coals have decreased significantly from those obtained with water solutions of copper.

(4) Hat Creek coal had the ability to produce a residual supernatant concentration of less than the detectable limit of 0.03 mg/l from an initial solution containing 0.1 mg/l of copper. (see Figure 3.5).

(5) In decreasing order of removal efficiency the four coals could be ranked (see Figure 3.6) as follows:

Hat Creek oxidised coal sample

Kaiser	-	Stock pile refuse	No significant difference between these three coals.
Kaiser	-	Special plant feed	
Cominco	-	Ash	

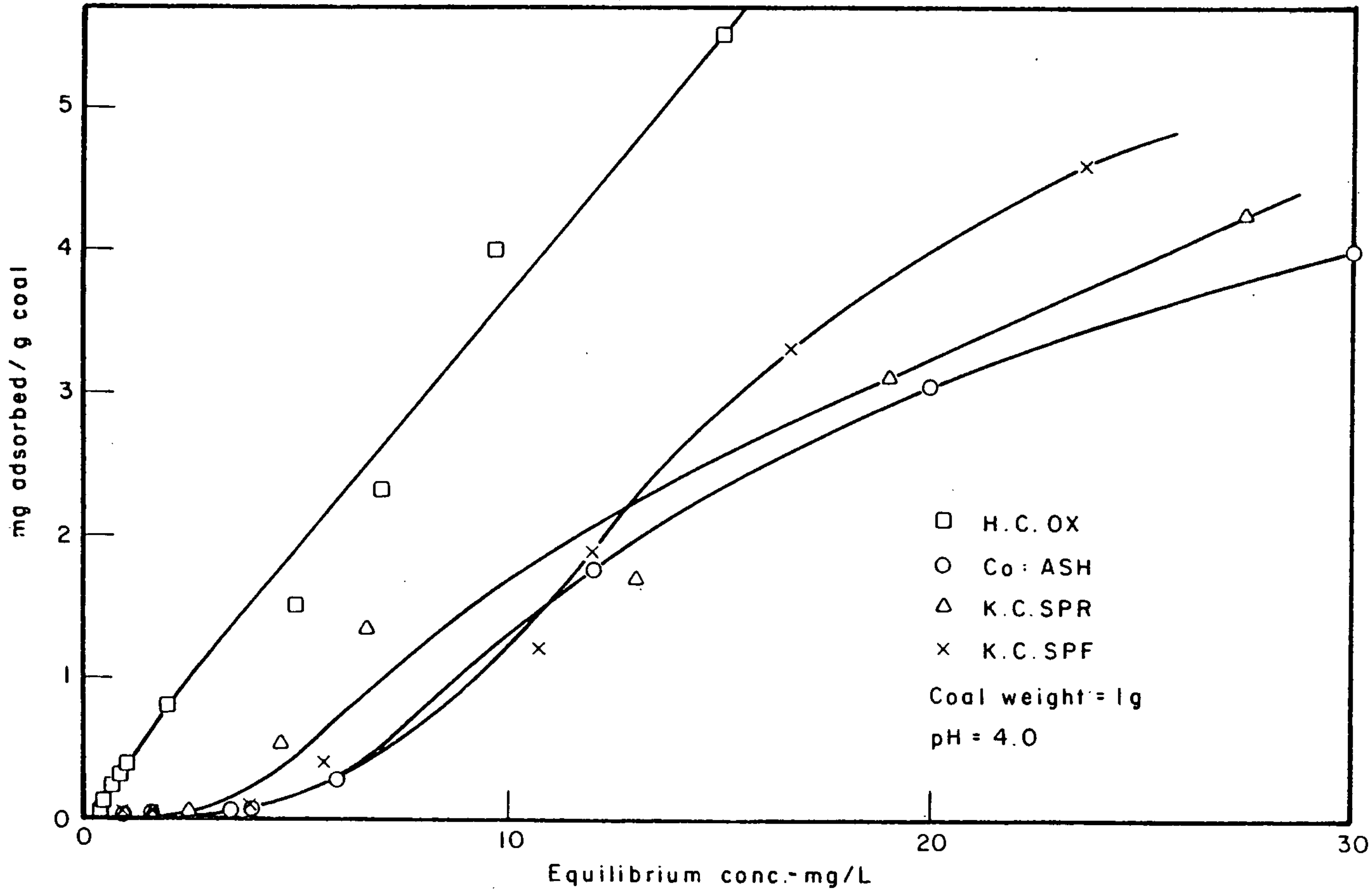

Figure 3.3 Copper Adsorption Isotherms

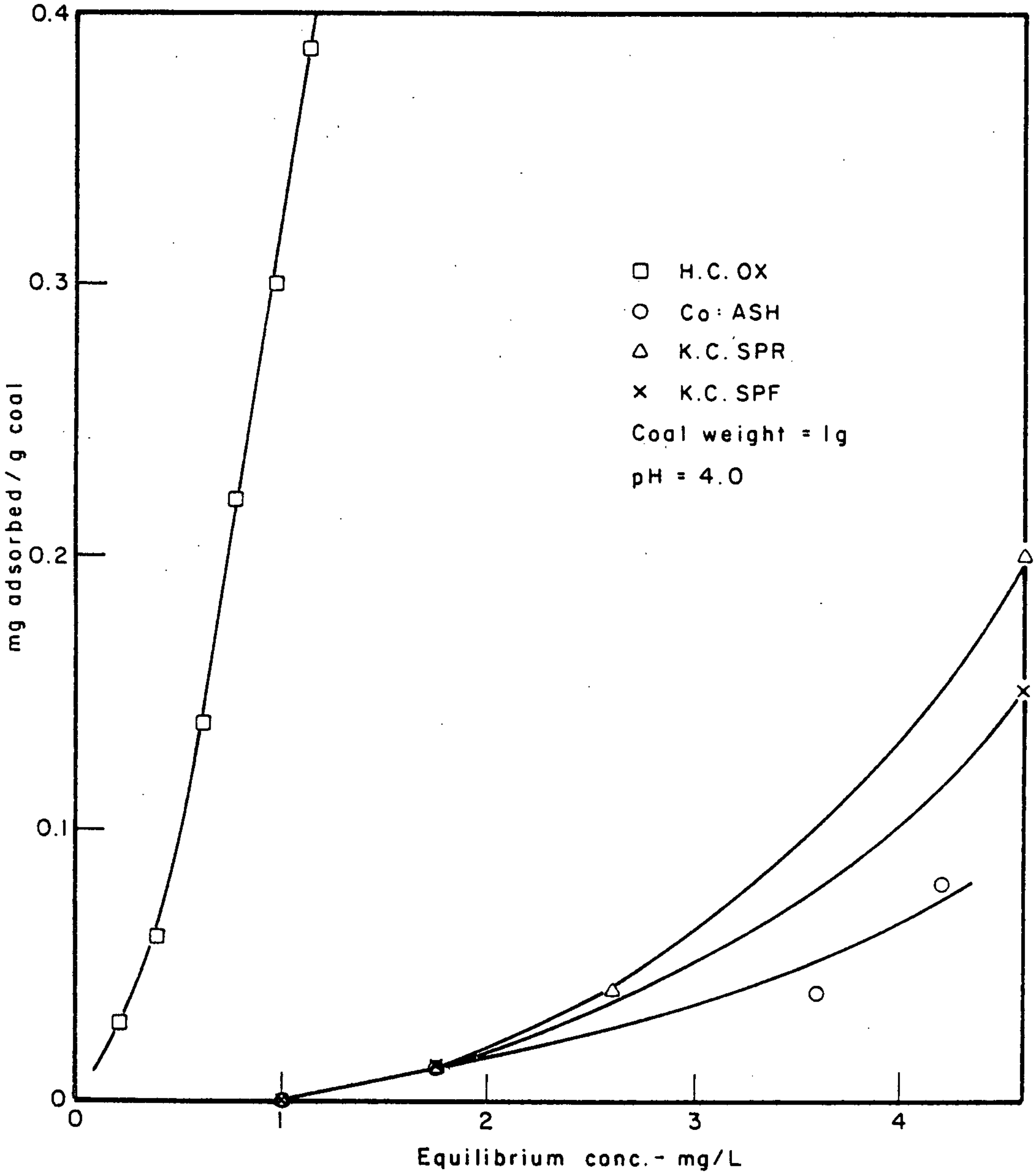

Figure 3.4 Copper Adsorption Isotherms

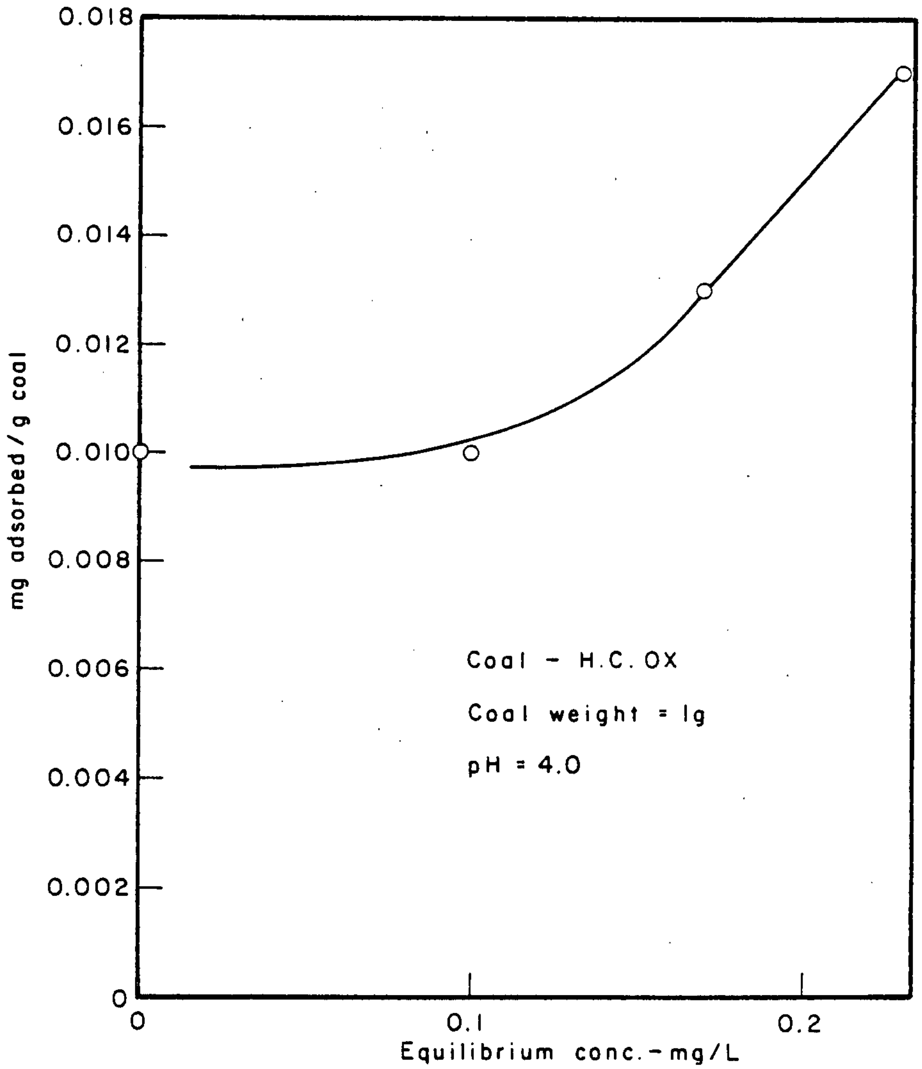

Figure 3.5. Copper Adsorption Isotherms

TABLE 3-1

SUMMARY OF COPPER ADSORPTION CAPACITIES

Coal Type	Equilibrium Concentration mg/1	mg Adsorbed/g Coal		
		Water Solution		Treated (primary) Sewage Effluent
		Riaz[6]	TinTun[7]	
H.C.OX	15		3.7	5.5
Co.Ash			1.4	2.3
K.C. SPR		0.85		2.5
K.C. SPF		0.7		2.9
H.C.OX	10		3.0	3.7
Co.Ash			1.25	1.3
K.C. SPR		0.71		1.7
K.C. SPF		0.6		1.2
H.C.OX	5		2.5	1.9
Co.Ash			0.9	0.2
K.C. SPR			0.6	0.4
K.C. SPF			0.5	0.2
H.C.OX	1.0		1.0	0.32
Co.Ash			0.5	0
K.C. SPR	0.10		0.2	0
K.C. SPF			0.15	0

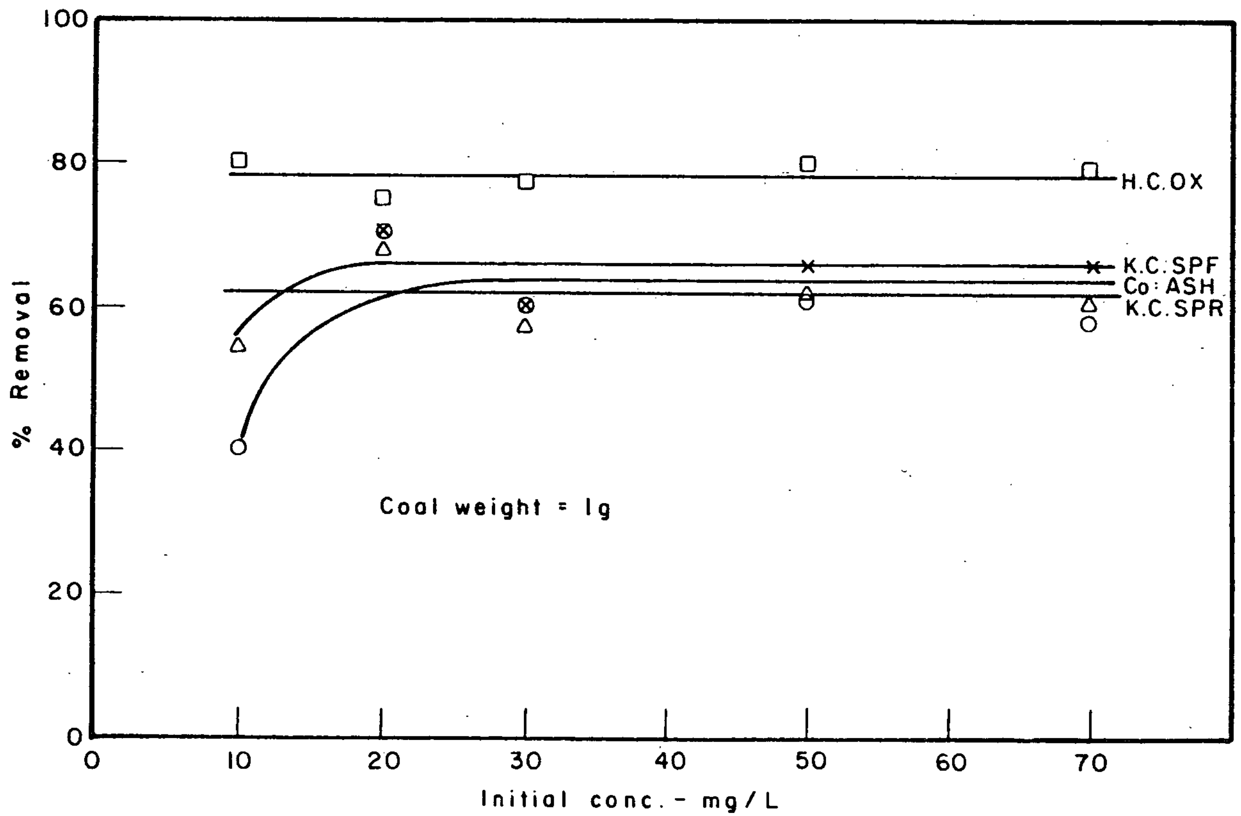

Figure 3.6 Copper Removal Efficiency

The above results could be explained using the principles of complex formation[9]. Assuming that complex forming reaction between metal ions (M) and organic reactant (L) occur rapidly and reversibly, they may be treated as a system in equilibrium.

$$M + L \rightleftharpoons ML$$

$$\text{Hence } K = \frac{ML}{M \cdot L}$$

Where K is the complex-formation or stability constant.

Applying Le Chatelier's principle[10] to the above system, when metal ions are present in high concentrations (as in item 2 above) the equilibrium will shift to the right resulting in significant metal-organic complex concentration. Thus the higher adsorption capacity obtained with primary effluent compared to pure solution is probably due to metal adsorption both directly and complexed with organics.

However when metals are present in lower concentrations (as in item 3 above) the equilibrium will shift to the left resulting in much reduced metal-organic complex concentrtion. Hence the metal ions and complexed organics will have to compete with high concentrations of organic species that have no metal ions attached, for adsorption sites and the latter is favoured since they are vastly more numerous. (This phenomenon is comparable to "competitive inhibition" in enzymatic reactions).

(b) Lead

Lead adsorption isotherms obtained from batch tests are shown in Figure 3.7. The following coal properties were noted: (Refer to table 3.2).

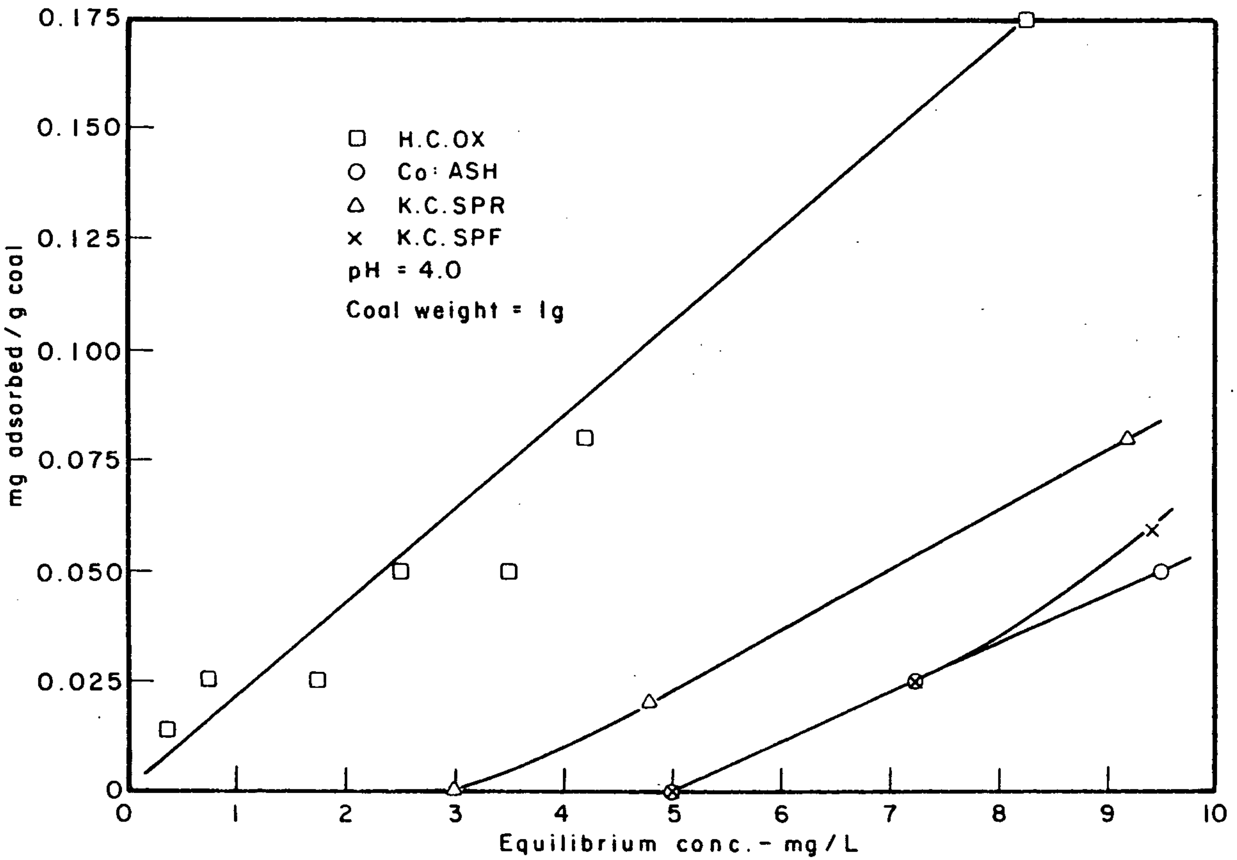

Figure 3.7   Lead Adsorption Isotherms

TABLE 3-2

SUMMARY OF LEAD ADSORPTION CAPACITIES

Coal Type	Equilibrium Concentration mg/1	mg adsorbed/g coal: water solution, Riaz[6]	mg adsorbed/g coal: water solution, TinTun[7]	mg adsorbed/g coal: treated (primary) sewage effluent
H.C.OX	8		5	0.17
CO. Ash			2.1	0.35
H.C.OX	6		5	0.125
CO. Ash			2.0	0.01
H.C.OX	4		5	0.085
CO. Ash			1.9	0
K.C. SPR		1.45		0.01
K.C. SPF		1.55		0
H.C.OX	1		4.65	0.02
CO. Ash			1.7	0
K.C. SPR		1.9		0
K.C. SPF		1.07		0

(I) The metal adsorption capacity of coal increased with increasing equilibrium concentration of lead;

(II) By comparison to Riaz's[6] work in the less than 10 mg/l equilibrium concentration range the adsorptive capacities of Kaiser coals are much lower with Sewage than with water, as in item 3 above.

(III) Lead removal with Hat Creek coal is much greater than with the other coals.

(IV) In decreasing order of removal efficiency the four coals could be ranked as follows:
(Refer to Figure 3.8)

Hat Creek oxidised

Kaiser - stock pile refuse
Kaiser - special plant feed
Cominco ash

} No significant difference between these three coals.

(c) Zinc

Zinc adsorption isotherms obtained from batch tests are shown in Figure 3.9. Under test conditions already defined the following coal properties were noted: (Refer to Table 3. 3).

(I) Metal adsorption capacity of coals increased with increasing equilibrium concentration.

(II) Hat Creek coal had the ability to produce a residual zinc concentration of 0.14 mg/l from an initial concentration of 0.5 mg/l

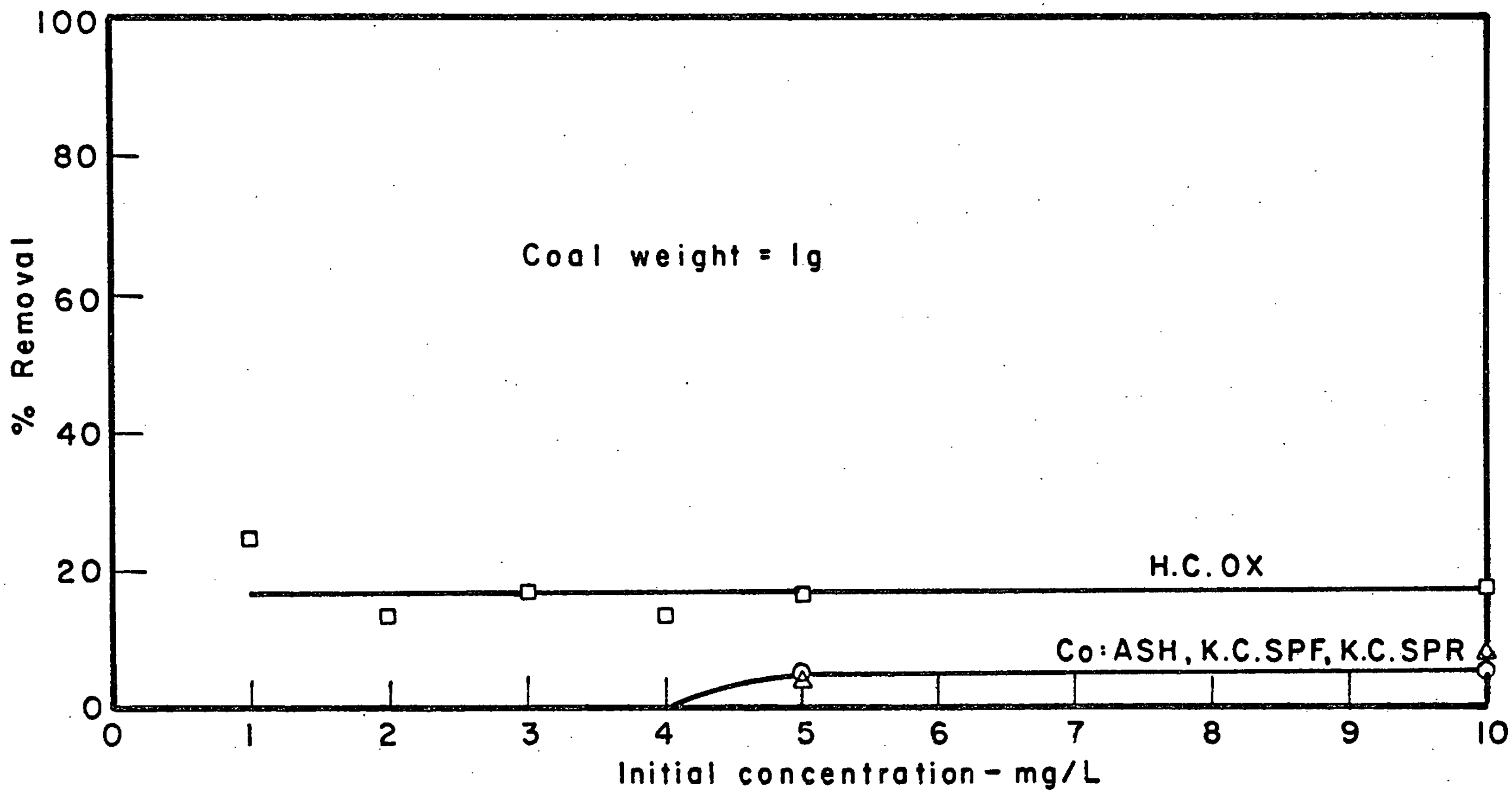

Figure 3.8 Lead Removal Efficiency

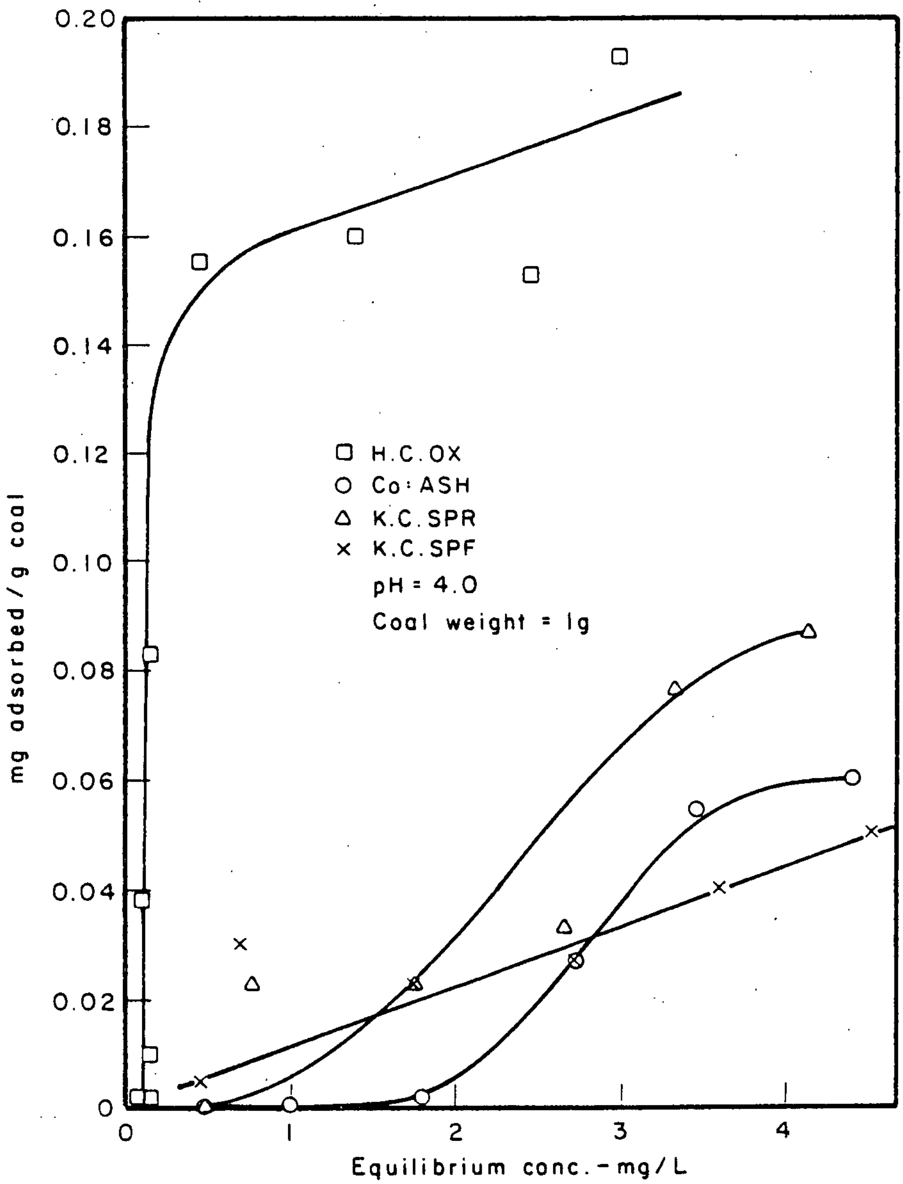

Figure 3.9 Zinc Adsorption Isotherms

TABLE 3-3

SUMMARY OF ZINC ADSORPTION CAPACITIES

Coal Type	Equilibrium Concentration mg/1	mg Adsorbed/g Coal: Water Solution, Riaz[6]	mg Adsorbed/g Coal: Water Solution, TinTun[7]	mg Adsorbed/g Coal: Treated (primary) Sewage Effluent
H. C. OX	4		0.9	0.19
Co.Ash			0.4	0.06
H.C.OX	2		0.6	0.17
Co.Ash			0.3	0.01
H.C.OX	0.4		0.28	0.15
Co.Ash			0.07	0
H.C.OX	.3		.19	0.14
H.C.OX	0.2		0.11	0.13
Co.Ash			.03	0
K.C. SPR		0.18		0
K.C. SPF		0.10		0
H.C.OX	.1		.03	0.002

(111) By comparison with Riaz's work at 0.2 mg/l equilibrium concentration, Kaiser coals have shown significantly reduced metal adsorption capacities:

(IV) In decreasing order of removal efficiency the four coals could be ranked (Refer to Figure 3.10) as follows:

Hat Creek oxidised

Kaiser - Stock pile refuse
Kaiser - Special plant feed
Cominco Ash

No significant difference between these coals.

(d) Mercury

Mercury adsorption isotherms obtained from batch tests are shown in Figure 3.1.3. Under test conditions already defined the following coal properties were noted; (Refer to Table 3.4).

(1) Capacities of Cominco ash and KC. SPR to remove mercury increase up to an initial concentration of about 40 mg/l and attained capacities of 0.3 and 0.6 mg/g respectively. The relative increase at higher concentrations were very small. KC. SPF was able to adsorb mercury only at initial concentrations higher than 20 mg/l.

(11) The lowest residual concentration was produced by H.C. OX and was 2.5 mg/l from an initial concentration of 5 mg/l. No measurable reduction in concentration was obtained with initial concentrations of less than 5 mg/l. Tin Tun[7] was able to obtain residual concentrations as low as 0.005 mg/l from pure solution of 0.03 mg/l initial mercury concentration, while it was possible down to only 2.5 mg/l with treated

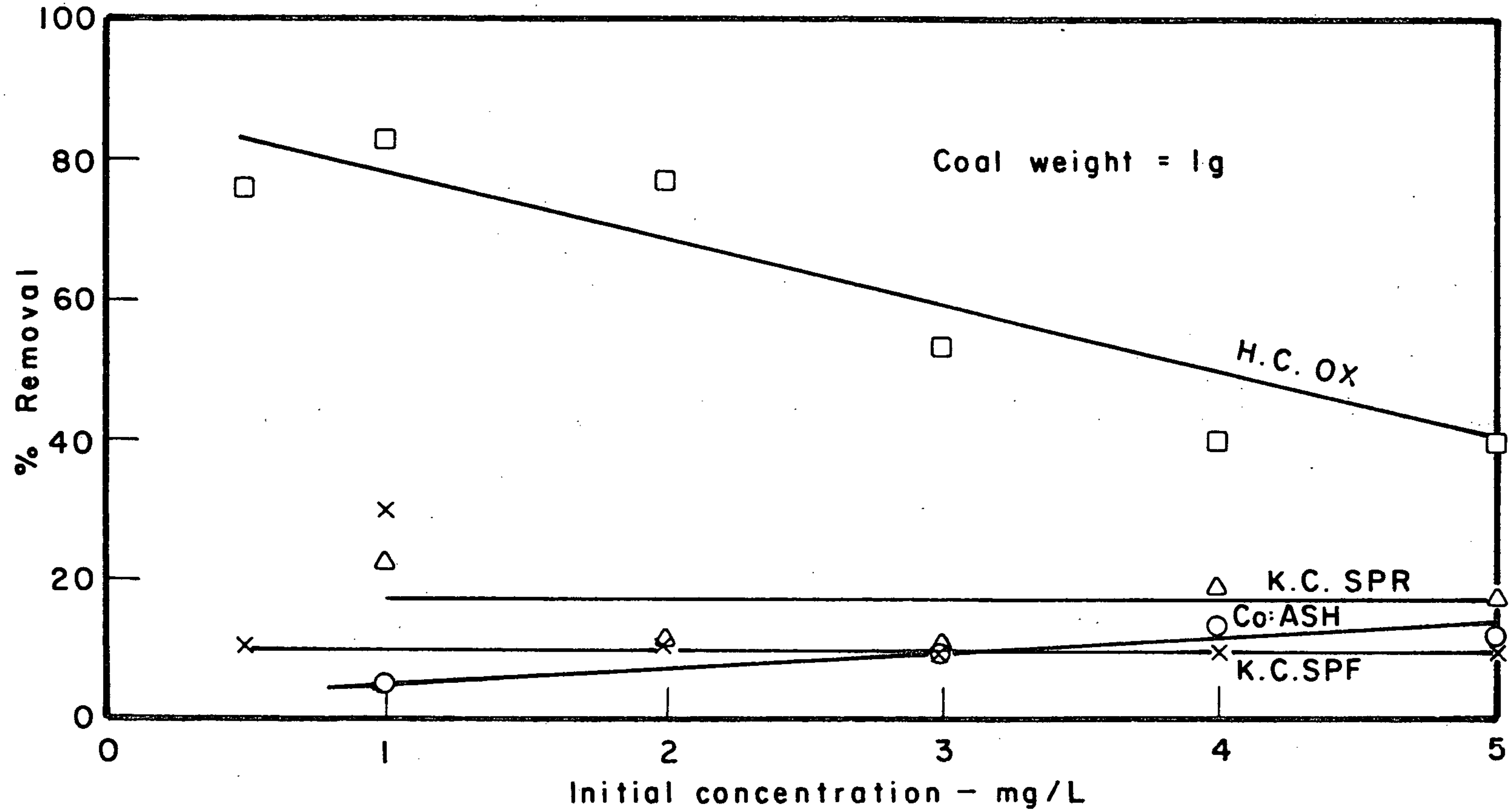

Figure 3.10 Zinc Removal Efficiency

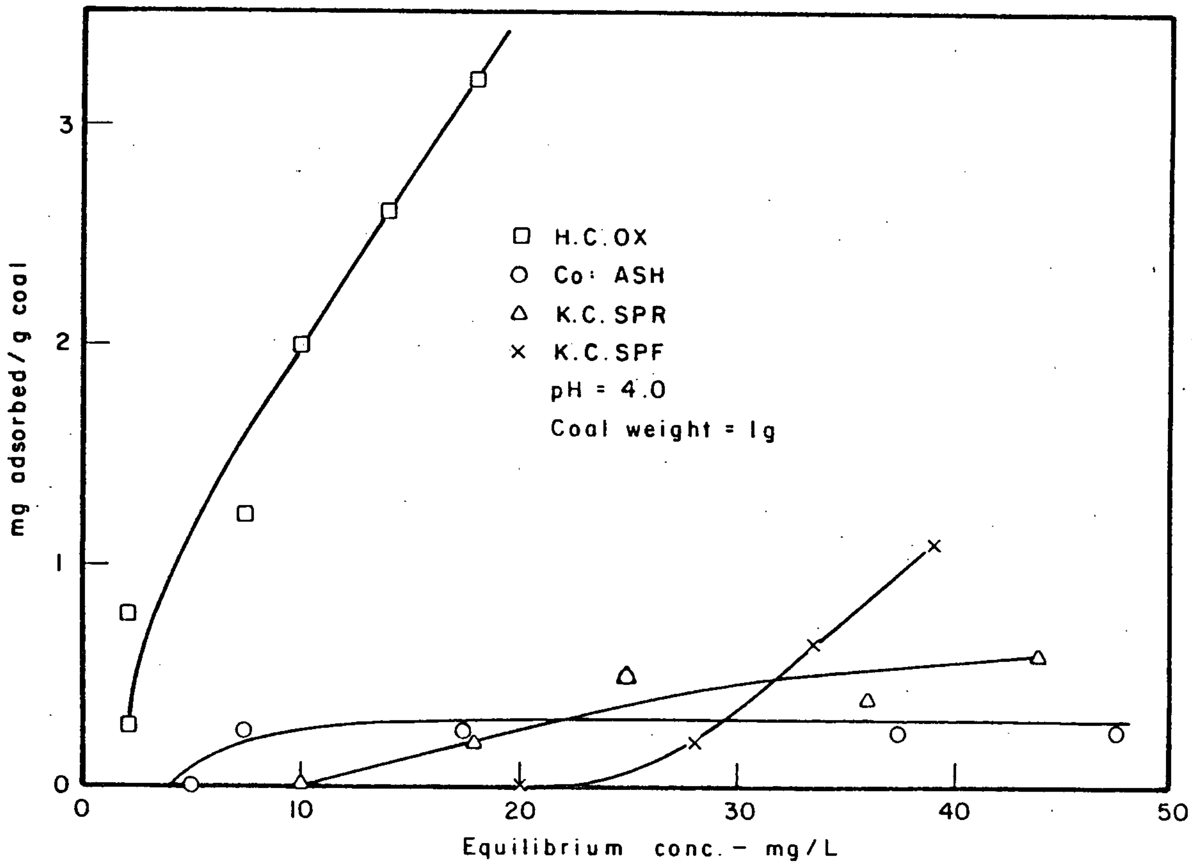

Figure 3.11 Mercury Adsorption Isotherms

TABLE 3-4

SUMMARY OF MERCURY ADSORPTION CAPACITIES

Coal Type	Equilibrium Concentration mg/l	mg adsorbed/g coal Water Solution Riaz[6]	TinTun[7]	Treated (Primary) sewage effluent
K.C. SPR	40	0.6		0.55
K.C. SPF		1.2		1.2
K.C. SPR	30	0.55		0.5
K.C. SPF		1.1		0.35
K.C. SPR	10	0.4		0
K.C. SPF		0.7		0
H.C. OX	.2		0.145	0
CO. Ash			0.015	0
H.C. OX	.01		0.0035	
CO. Ash			0.0026	
H.C. OX	.005		0.0008	

sewage effluent;

(III) By comparison to Riaz's[6] work, within a range of 30 to 40 mg/l mercury equilibrium concentration, Kaiser coals produced comparable adsorption capacities between treated sewage effluent and water solution. Under lower equilibrium concentrations (less than 10 mg/l) greater adsorption capacities were obtained with water solution than from treated sewage effluent. Again, these results can be explained using the same theory as in section (a).

(IV) In decreasing order of removal efficiency the four coals could be ranked (Refer to Figure 3.12 as follows;

Hat Creek oxidised sample
Kaiser - Stock pile refuse
Kaiser - Special plant feed

3.1.3 Overall Ranking of the Coals

The results of the batch tests show that of the four different coals tested, H.C. Oxidised was far superior compared to the other three in the removal of copper, lead, zinc and mercury from wastewater. K.C.SPF, K.C.SPR, and CO. Ash exhibited metal removing efficiencies very much similar to each other and no significant difference was present between these three. H.C. OX seem to belong to a class of its own. Its adsorption capacity was often observed to be more than double that of any other used. This observation suggests that H.C.OX has much greater surface area per unit weight and/or has greater concentration of active sorption sites per unit surface area than any of the other three coals tested.

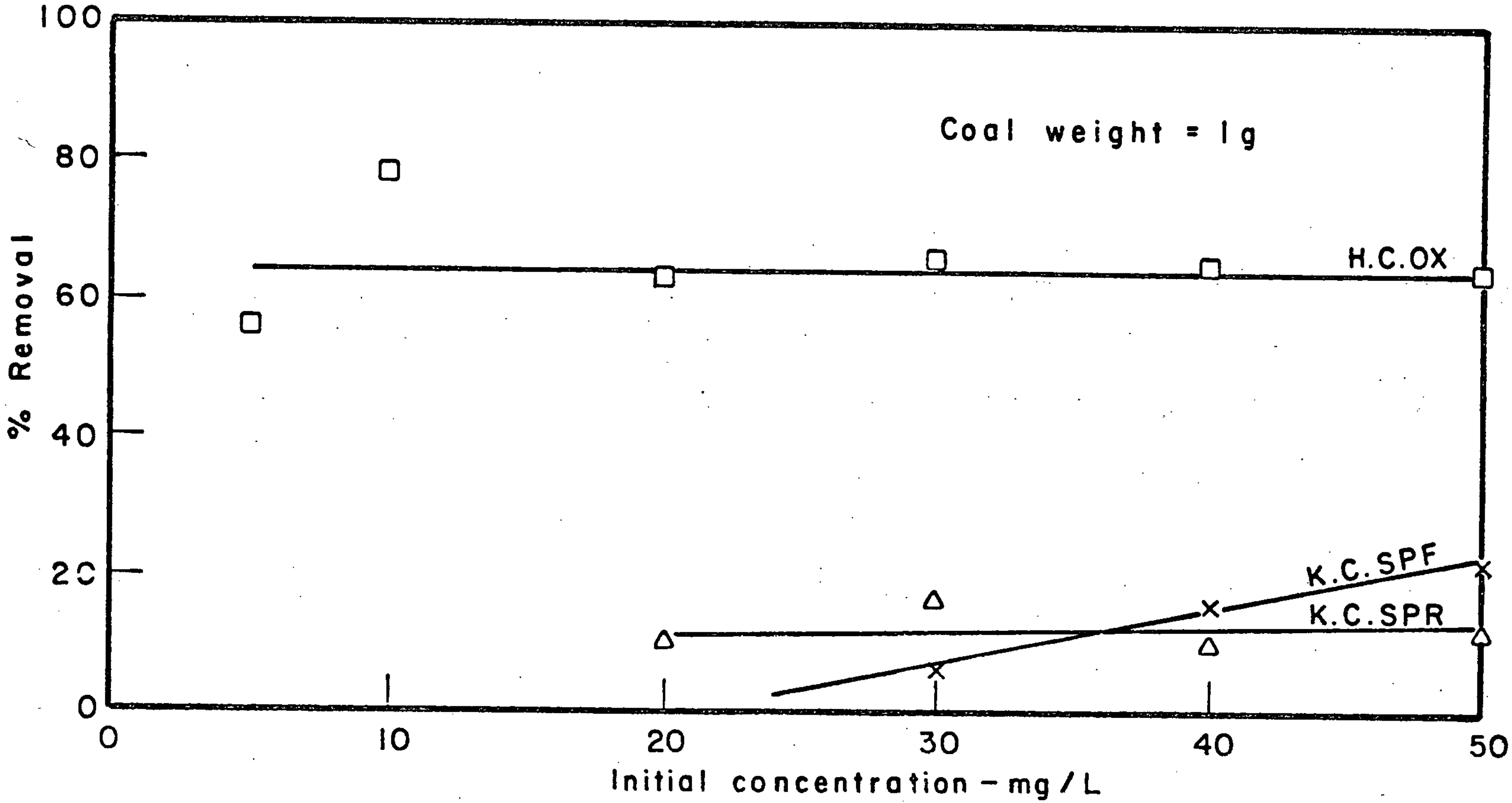

Figure 3.12 Mercury Removal Efficiency

Hence in decreasing order of efficiency the four could be ranked as follows;

Hat Creek Oxidised

Kaiser - Stock pile refuse

Kaiser - Special plant feed — No significant difference between these three coals

Cominco Ash

3.1.4. General Comments

Changes in adsorptive capacity or metal removing efficiency of coals will be described as "slight", "significant", "marked" etc, and the use of actual quantity, percentage, etc, will be avoided in most cases. Since this study is for comparative purposes only, the actual values have no significant meaning since they are dependent on so many variables. Riaz[6] chose to develop isotherms by changing the initial concentrations of the metal ions while keeping the coal weight constant. Tin Tun[7] in most cases changed the coal weight and kept the initial concentration constant. The isotherms developed by these methods will be identical within a small concentration range but will be different outside it. To be able to make accurate comparisons, it is necessary that the data taking procedures are consistent. As long as all coals were tested in the same manner, the comparisons are valid. Since isotherms in this study were developed by changing initial concentrations, K.C. SPR and K.C. SPF can be compared with Riaz's[6] results while H.C. OX and CO. Ash cannot be compared with Tin Tun's[7] results except when initial concentrations are similar.

3.1.5. Comparison of Hat Creek with Activated Carbon

Metal adsorbing capacity of H.C. OX was compared with Darco activated carbon grade 12 x 20, which is a commercially available adsorbent. Batch tests were performed with H.C. OX and activated carbon, using metal dissolved in both water and primary effluent.

Copper:

Adsorption isotherms for copper removal using activated carbon and H.C. OX are shown in Figure 3.13. Activated carbon exhibited better metal adsorption capacity than H.C. OX under test conditions. The difference between the two is comparatively uniform and the performance of H.C. OX is consistently lower over the concentration range tested. The increase in adsorption capacity for copper in water solution as compared to that in primary effluent is as much as 100%, particularly for higher equilibrium concentrations.

Lead:

The ability of both H.C. OX and activated carbon to adsorb lead from both primary effluent and water solution was tested and the isotherms are shown in Figure 3.14. Within the concentration range tested, both removed lead from water solution completely. The capacity was slightly lower for activated carbon and tremendously reduced for H.C. OX when used to treat primary effluent. This marked reduction makes H.C. OX much inferior to activated carbon in removing lead from primary effluent.

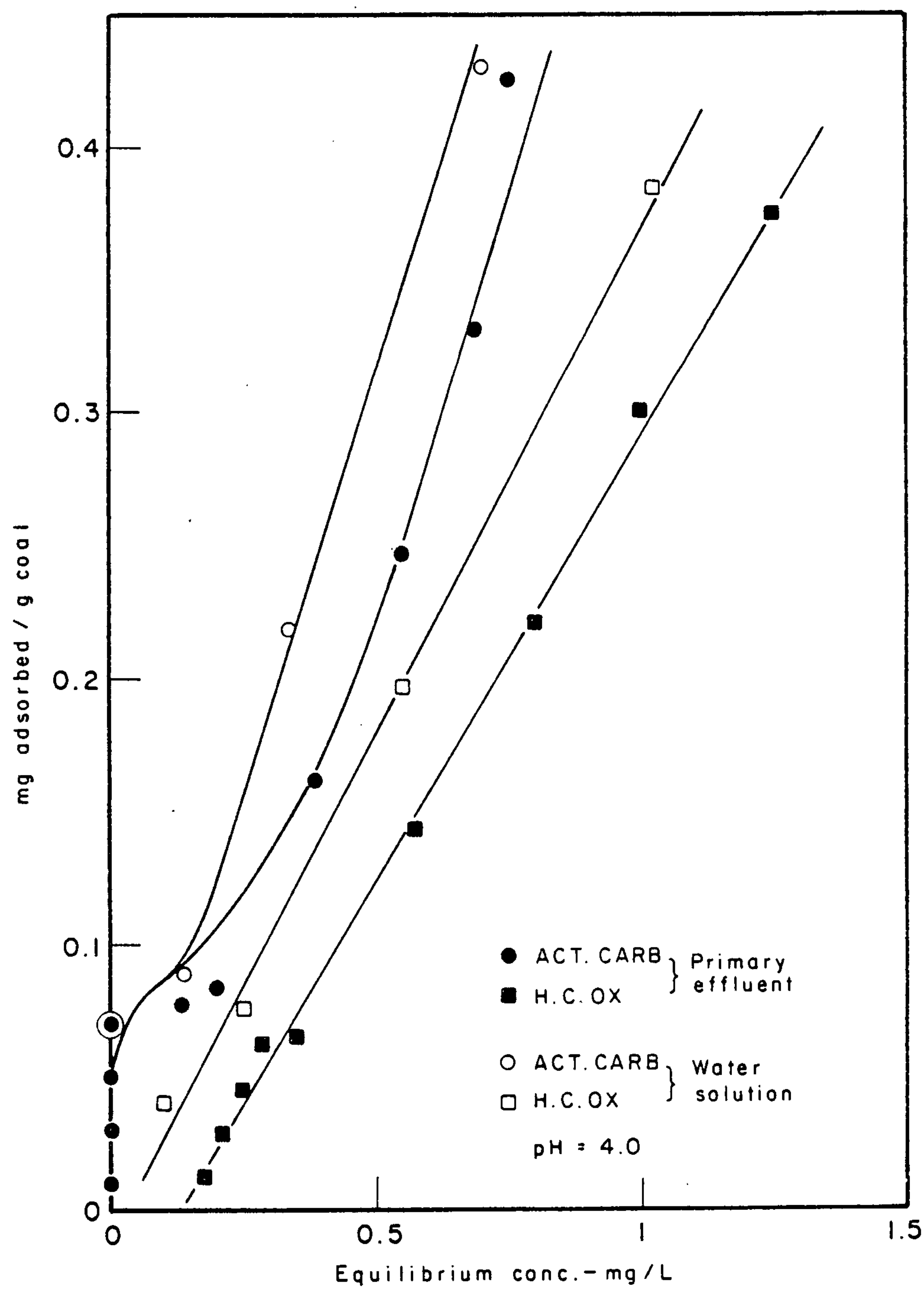

Figure 3.13 Copper Adsorption Isotherms

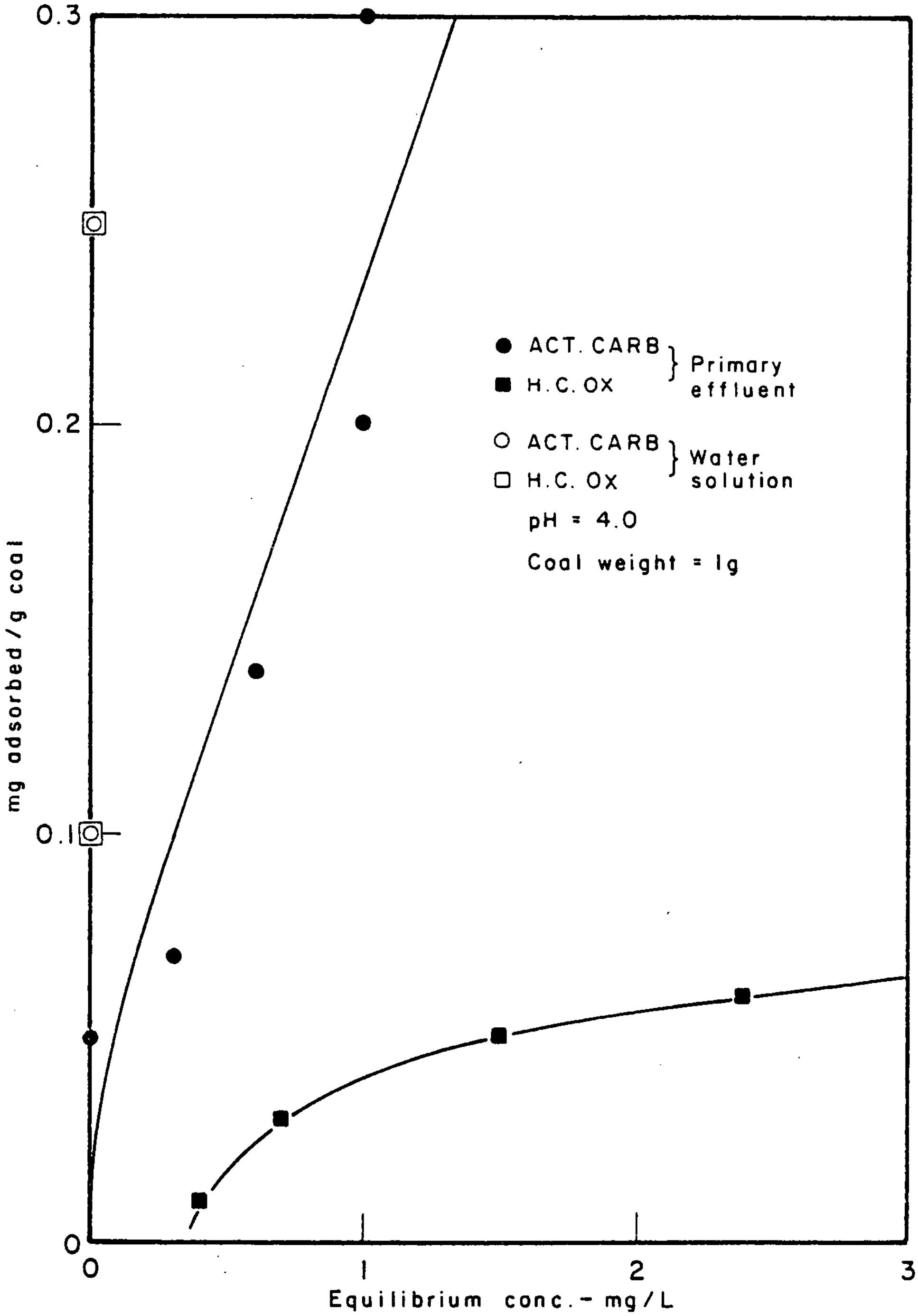

Figure 3.14   Lead Adsorption Isotherms

Zinc:

Adsorption isotherms are given in Figure 3.15. The ability of H.C. OX to remove zinc from water solution and from primary effluent was better than that of activated carbon. Furthermore, the metal adsorption capacities of both H.C. OX and activated carbon were higher when treating primary effluent than when treating a water solution of zinc. These observations are opposite to what were observed with copper and lead. Thus H.C. OX seems to be a better choice than activated carbon with regard to zinc removal from wastewater.

Mercury:

The performance of H.C. OX was compared with activated carbon (see Figure 3.16) in the removal of mercury from primary effluent. Activated carbon produced significantly better results than H.C. OX. The difference between the two was 100% or greater over the concentration range tested.

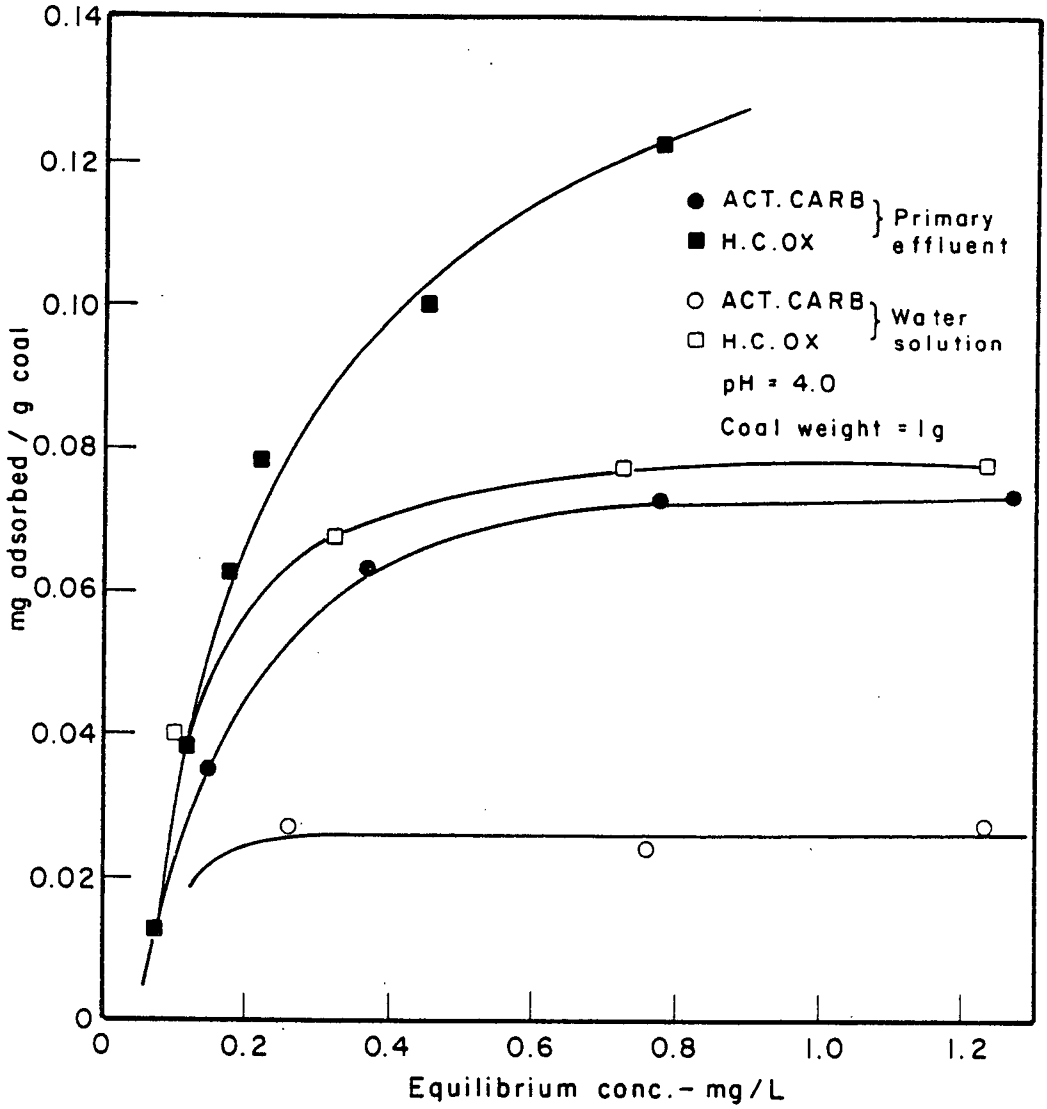

Figure 3.15 Zinc Adsorption Isotherms

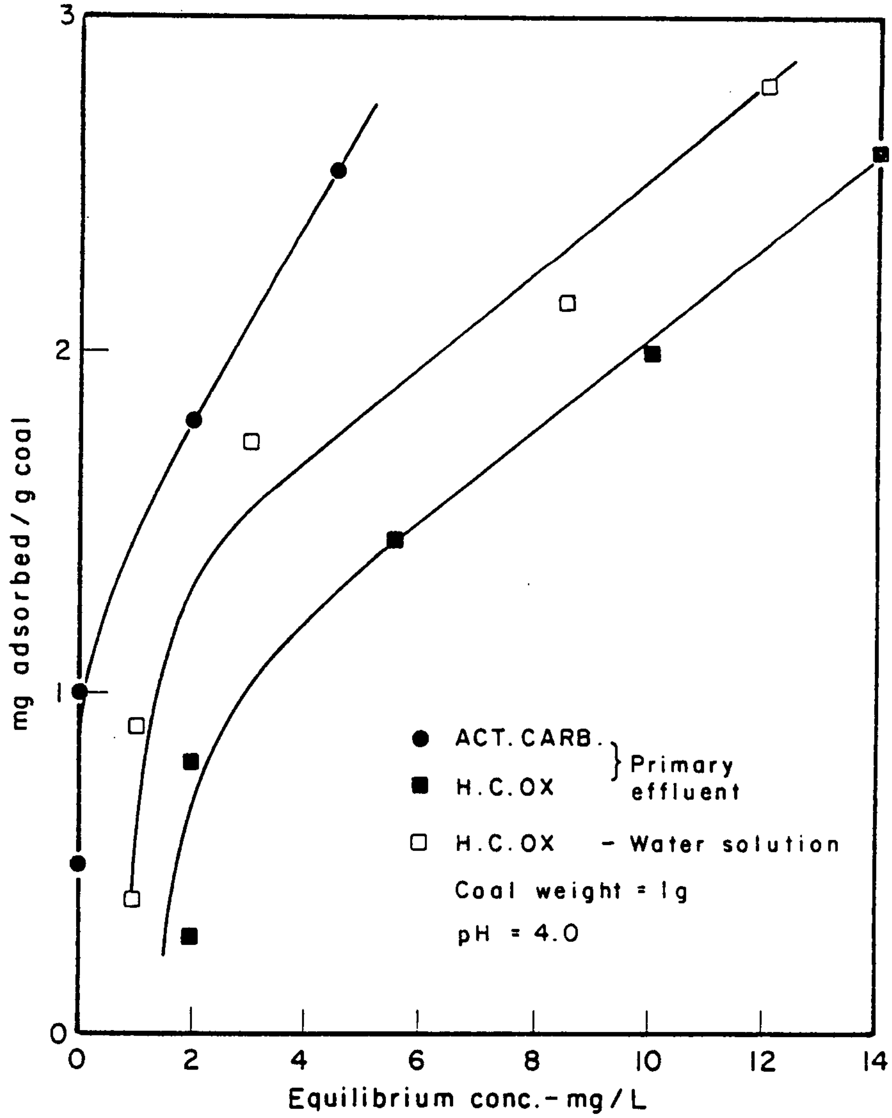

Figure 3.16 Mercury Adsorption Isotherms

Summary:

Table 3.5*

Summary of Comparisons Between Activated Carbon and Hat Creek Oxidised Coal

Metal	Activated Carbon		Hat Creek Oxidised Coal	
	Water Solution	Primary Sewage Effluent	Water Solution	Primary Sewage Effluent
Copper	1	2	3	4
Lead	1	2	3	4
Zinc	4	3	2	1
Mercury	1	2	3	4

*Numbers 1 to 4 denote batch systems in decreasing metal removal efficiency.
(See Figures 3.13 to 3.16).

Activated carbon has much greater surface area per unit weight than Hat Creek oxidised coal. Also a much greater percentage of surface area in activated carbon is available for sorption processes while only smaller percentage is available in the case of coal due to the presence of various surface deposits. Hence the former can be expected to show greater metal adsorption capacity than the latter.

Out of four metals tested, activated carbon was superior to H.C. OX with regard to adsorption of copper, lead and mercury, and inferior to H.C. OX with regard to adsorption of zinc. This is possibly due to the removal of zinc from solution by chemical reactions with surface deposits on coal, than by sorption means.

For reasons discussed earlier in this chapter, greater metal adsorption can be expected to occur in water solution than in primary sewage effluent. Out of four metals tested, greater adsorption capacities were obtained with water solution of copper, lead and mercury, and primary sewage effluent gave higher zinc adsorption.

Thus in both cases zinc behaved in a manner opposite to other three metals. (Refer Table 3-5). Literature research did not reveal this type of anomaly, nor did it suggest any reason why zinc might act differently. This behaviour is possibly due to greater stability of the zinc-organic complex that is formed, compared to the other three metal-organic complexes.

3.2 Column Tests:

Compared to batch testing, column tests represent continuous systems. As in batch tests, the capacity of coal to adsorb heavy metals can be calculated. A plot of metal concentration in column effluent against volume passed through gives the "breakthrough curve" from which metal adsorption capacities can be calculated. Thus this method of testing can also be used to compare the performance of different metals, but this time in a dynamic system. Sample calculations showing the procedure for calculating adsorption capacity is shown in Appendix II.[6]

Adsorbing materials for these tests were H.C. OX, K.C. SPR and Act. Carb. (Darco activated Carbon grade 12 x 20).

3.2.1 (a) Copper

The first run was carried out with an influent copper concentration of 4 mg/l at a flow rate of 1 gpm/ft^2. The breakthrough curves obtained from this run are shown in Figure 3.17. Breakthrough was not attained

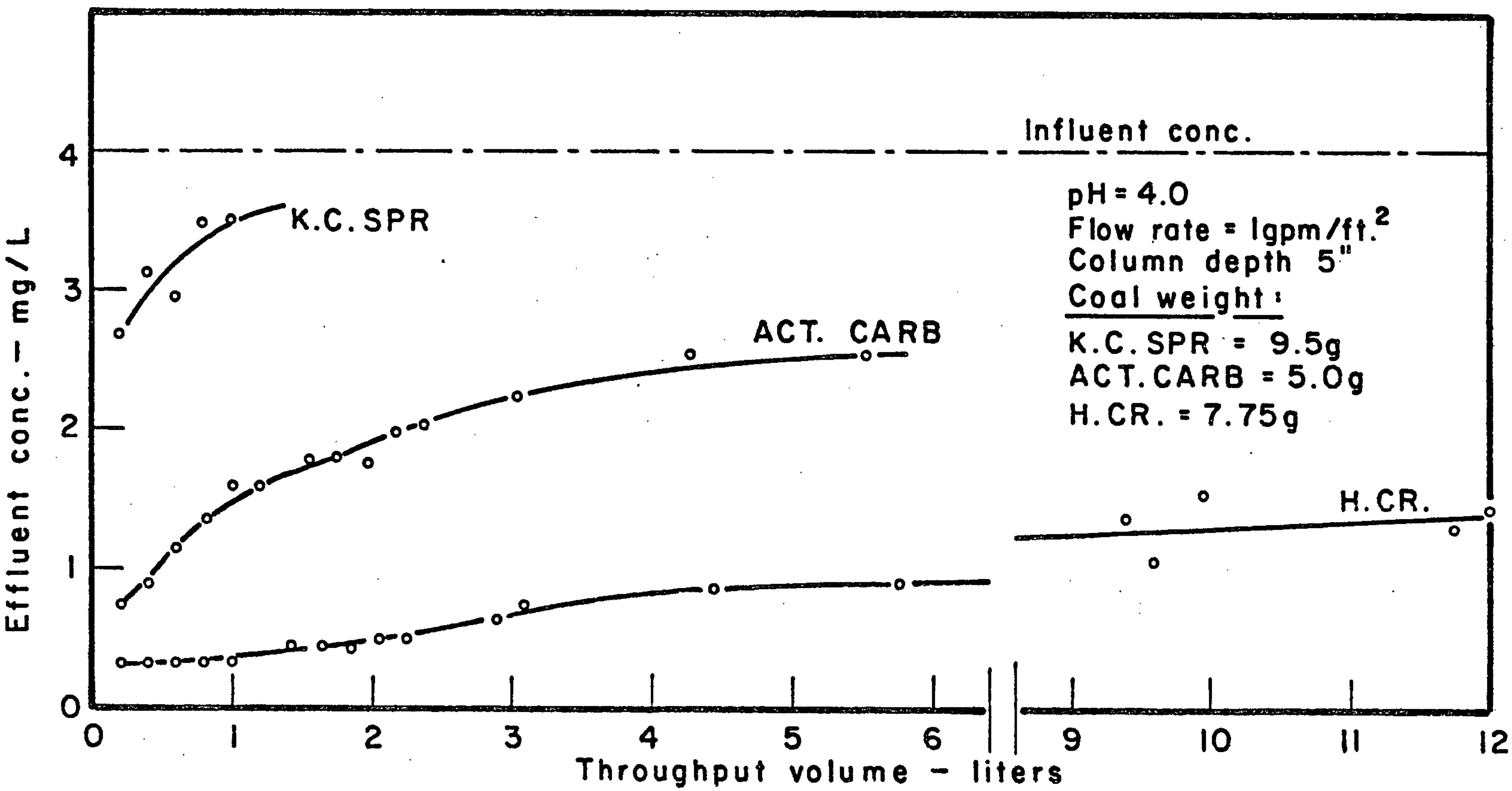

Figure 3.17 Breakthrough Curve for Copper

with H.C. OX coal, due to biological activity which plugged the column after a throughput of 12 liters.

From the breakthrough curves obtained it is evident that a column height of 5 inches is too great for H.C. OX, but not enough for K.C. SPR and Activated carbon to show metal breakthrough characteristics. The plots obtained with activated carbon and K.C. SPR also indicate comparatively low rates of adsorption and low metal adsorption capacities. The reasons for choosing a column height of 5 inch are explained in section 2.6.2.

In Figures 3.18 and 3.19 are shown breakthrough curves obtained with 5 gpm/ft^2 flow rate. From Figures 3.17, 3.18 and 3.19 adsorption capacities for the coals and activated carbon were calculated and plotted against the ratio of effluent to influent metal concentrations (C/Co) in Figure 3.20.

From Figure 3.20 it is evident that;

(I) Adsorption capacity of coals increase with increasing effluent concentration: (higher C/Co)

(II) For the same effluent concentration each coal has a higher adsorption capacity at the lower flow rate due to the higher contact time:

(III) Under column operating conditions, the three adsorbents can be ranked in the decreasing order of removal efficiency as:

Hat Creek Coal

Activated Carbon

Kaiser - Stock Pile Refuse.

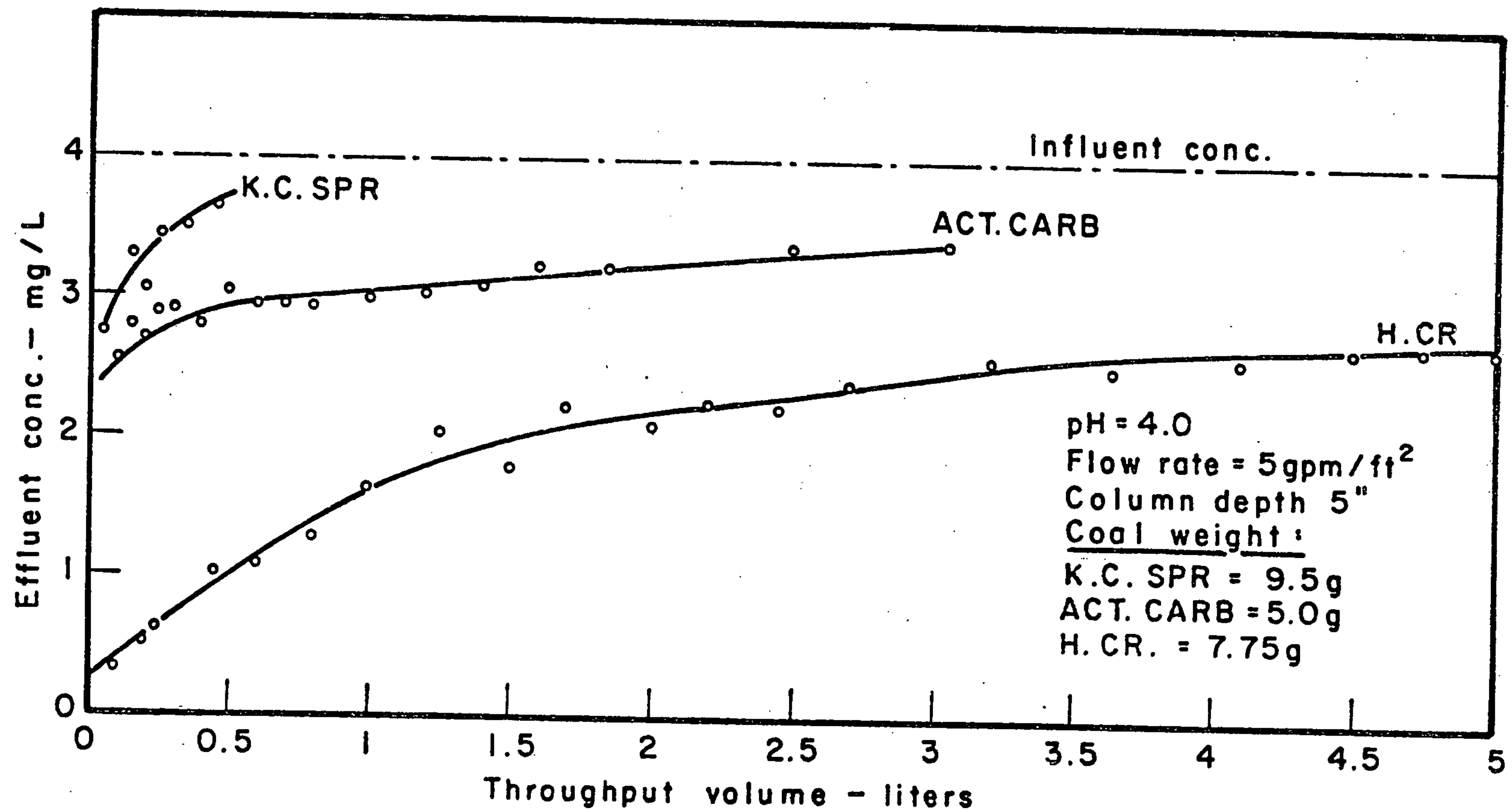

Figure 3.18 Breakthrough Curve for Copper

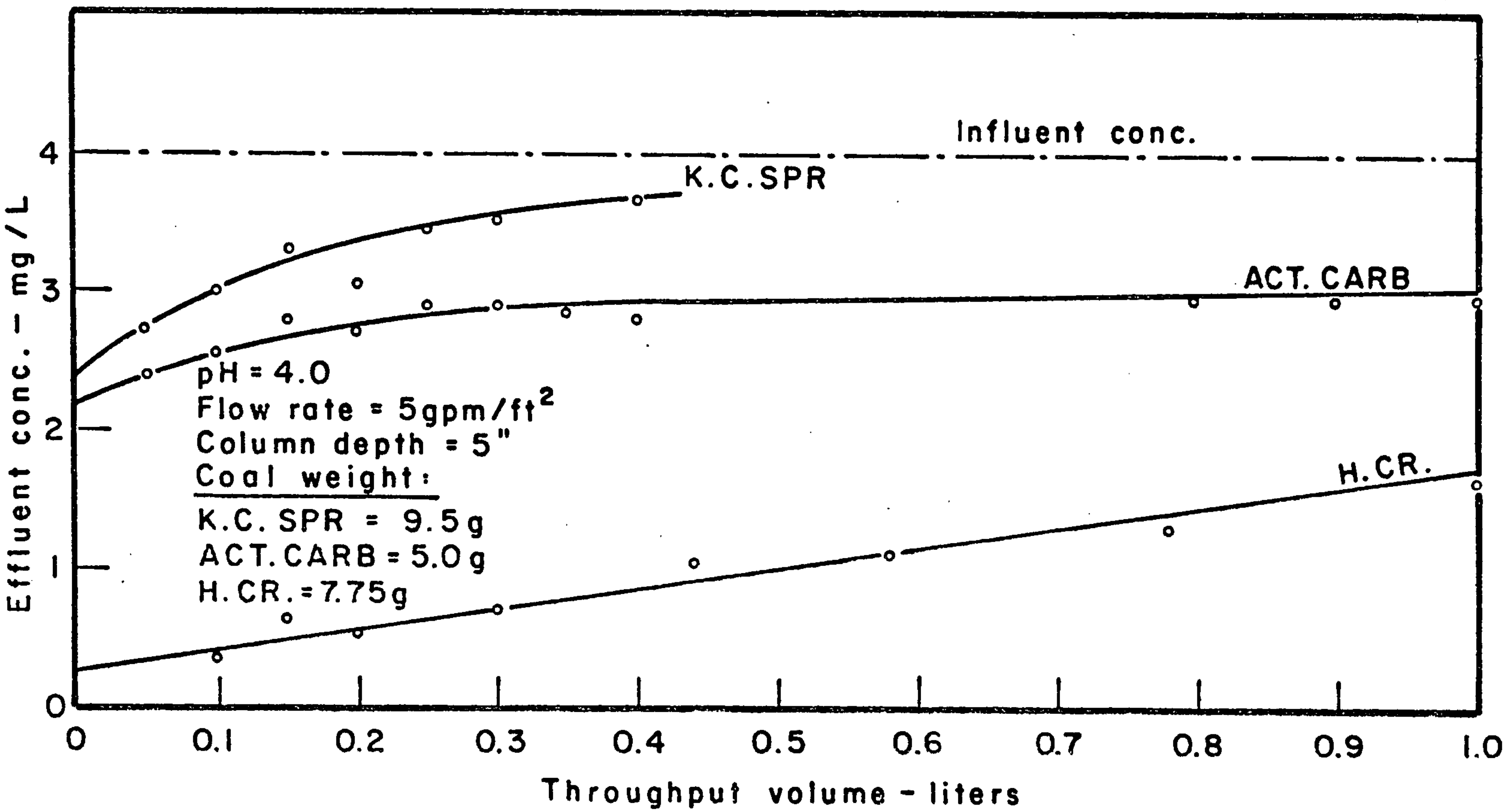

Figure 3.19 Breakthrough Curve for Copper

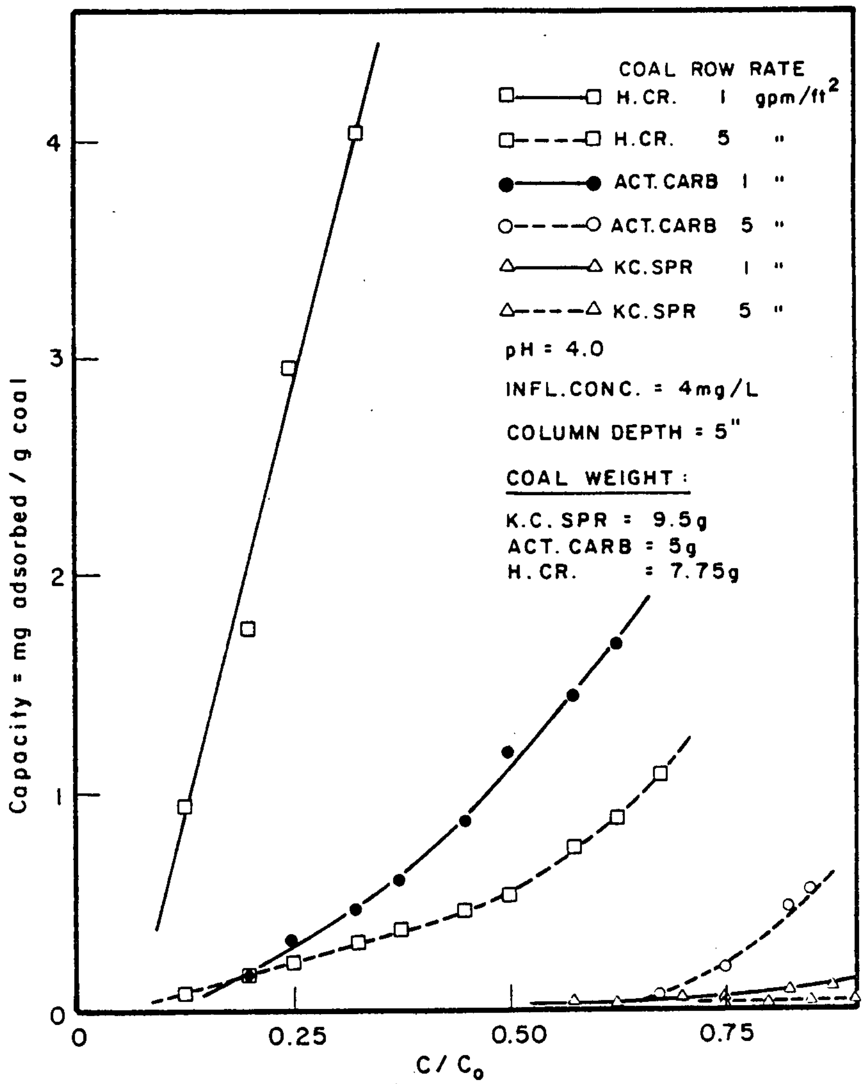

Figure 3.20 Comparison of Adsorption Capacity for Copper in Primary Effluent at Different Flow Rates

The effluent metal concentration before breakthrough is a function of the rate of adsorption, where the rate of adsorption is defined as the net quantity of metal ions which adsorb on the coal surface per unit time. This rate of adsorption is usually dependent on influent metal concentration, form of metal in solution, availability of adsorption sites, temperature and pH. Since all other parameters are kept constant throughout a column run, the effluent metal concentration in our tests is a function of available adsorption sites.

Usually "Total sites originally present" is a constant. "Sites already used" increases with increasing time. During the adsorption process sites already occupied are still active though they don't contribute to net adsorbtion. By a process of adsorption and desorption a state of equilibrium is approached on those sites while unused sites are still providing a net adsorptive trend. Since the wastewater used in this study is primary effluent from a sewage treatment plant, it is rich in microorganisms and biologically very active. When this wastewater is passed through a column of coal, microorganisms will attach themselves to coal and begin to multiply if environmental conditions are favourable. Continuous supply of dissolved oxygen and substrate provided by the flow of wastewater, and the availability of suitable growth surface, make environmental conditions inside the coal column ideal for growth and multiplication of microorganisms. Microbial growth is usually in the form of an expanding layer on the media surface, hence it tends to reduce the availability of the surface for adsorption continuously. Common fecal bacteria (*Esh. coli*) which predominate among the aerobic commensal organisms present in the healthy gut,[12] thus abundant in the wastewater used, are capable of multiplying once every 15 to 20 minutes under ideal conditions. With a column flow of 1 gpm/ft^2, the time required to pass 0.08 l of waste-water through the column is sufficient to double the number of Esh. coli present. This microbial growth on solid surfaces results in a microbial film, which due to its viscous nature, greatly reduces the rate of diffusion of the adsorbate through it.[13] Hence, by biological activity, an effective blanketing of coal surface occurs, and the rate of diffusion could be so reduced that a coal surface covered by microbial growth has a much reduced capability for adsorption. Hence the "total sites originally present" will continuously decrease and can be compared to a situation where the height of column is being continuously decreased by removing coal and thereby making it not available for adsorption. Hence the adsorption capacity of the coal can be expected to be lower when used to treat sewage effluent compared to pure metal solution.

Another very important difference between sewage effluent and metal solution is that the former contains dissolved organics in a relatively high concentration while the latter has none. As discussed in section 3.1.2 (a) the presence of organics can be expected to influence metal adsorption characteristics. Depending on the type of adsorbate (ionic charge, and size) type of adsorbent (pore sizes) and relative concentration of metal and organics, the rate of adsorption and adsorption capacity will be influenced. This could be as a result of direct competition between organic molecules and metal ions for adsorption sites or due to the formation of organo-metal complexes (as opposed to aquo complex) having a much slower or faster reaction rate for adsorption on to sites within the coal particles.

The combined effects of competition for adsorption sites between metal ions, organo-metal complexes and organic molecules and the blanketing effect of microbial growth within the adsorption column on the breakthrough curve are unknown. Perhaps the gradual and continuous rise in the effluent metal concentration as observed with H.Cr coal in Figure 3.18 was due to the influence of above combined effects. Tests carried out with water solution produced constant effluent metal concentration till breakthrough was achieved.

Column runs were also carried out with copper solution in water of 4 mg/l concentration at 1 gpm/ft^2, with the results shown in Figure 3.21. Adsorption capacities were calculated and given in Figure 3.22. Results indicate that Hat Creek and Kaiser coals have reduced adsorption capacities in primary effluent and it is somewhat unchanged for activated carbon. Hat Creek coal performed better than activated carbon under both conditions.

Column tests were carried out with sewage containing a copper concentration of 10 mg/l at 1 and 5 gpm/ft^2 flow rates, and the breakthrough curves are in Figure 3.23 and 3.24 respectively. Adsorption capacities at these two flow rates were calculated and shown in Figure 3.25. Again Hat Creek coal has shown a distinct superiority over activated carbon at both flow rares. Comparison of metal adsorption capacities for different copper influent concentrations are shown in Figure 3.26. Greater adsorption capacities were obtained with higher influent metal concentrations.

(b) Lead

Column runs were carried out with an influent lead concentration of 4 mg/l at 1.0 and 5.0 gpm/ft^2 flow rates, with breakthrough curves

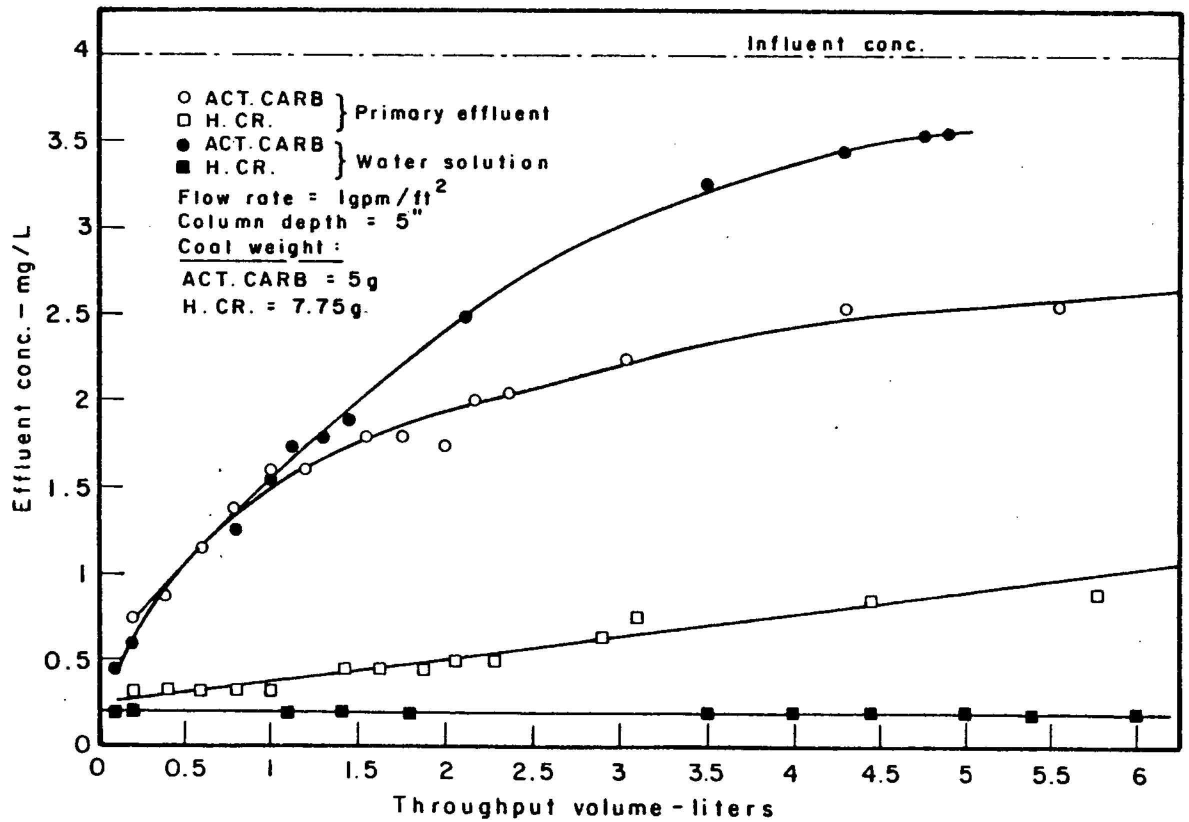

Figure 3.21 Comparison of Breakthrough Curve for Copper in Primary Effluent and Water Solution

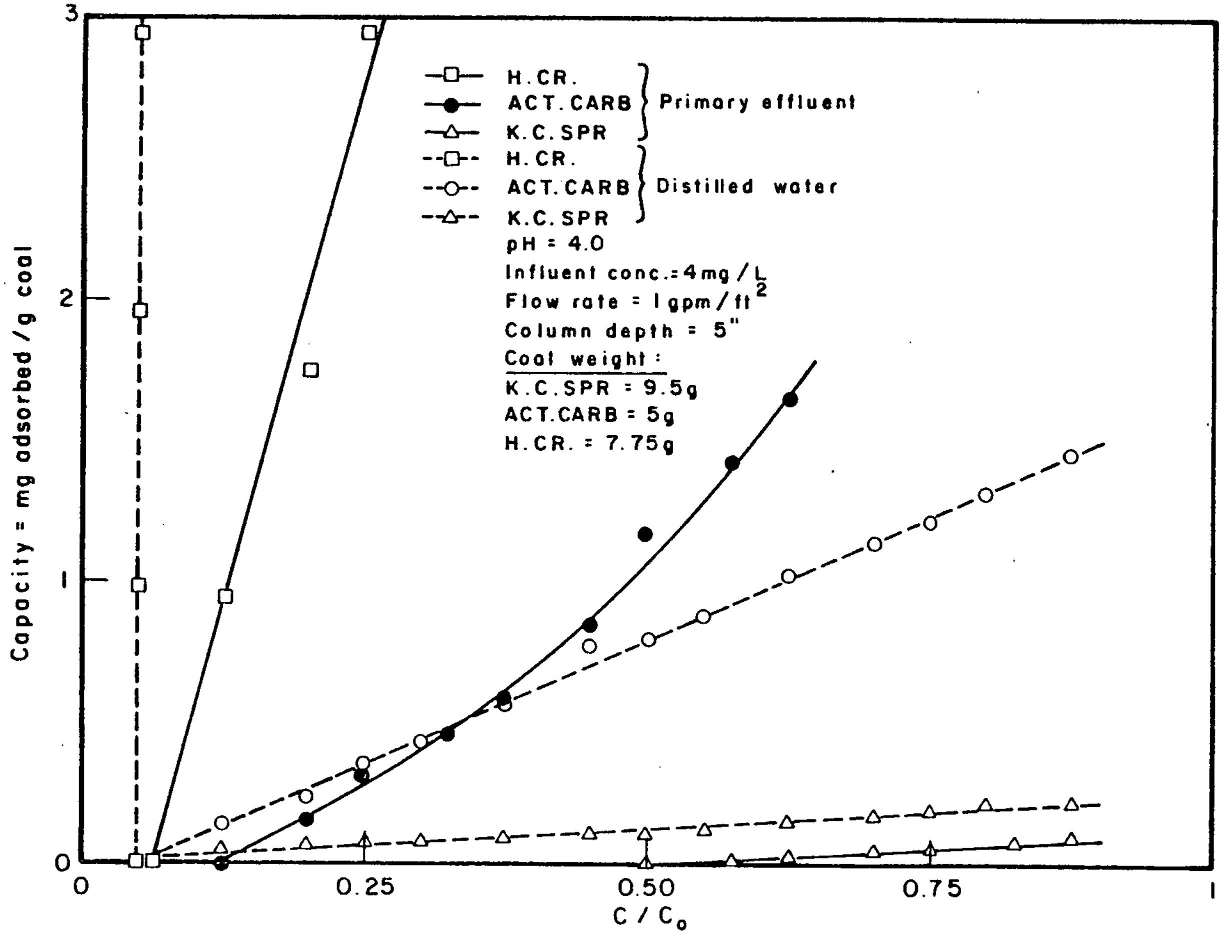

Figure 3.22 Comparison of Adsorption Capacity for Copper in Primary Effluent and Distilled Water

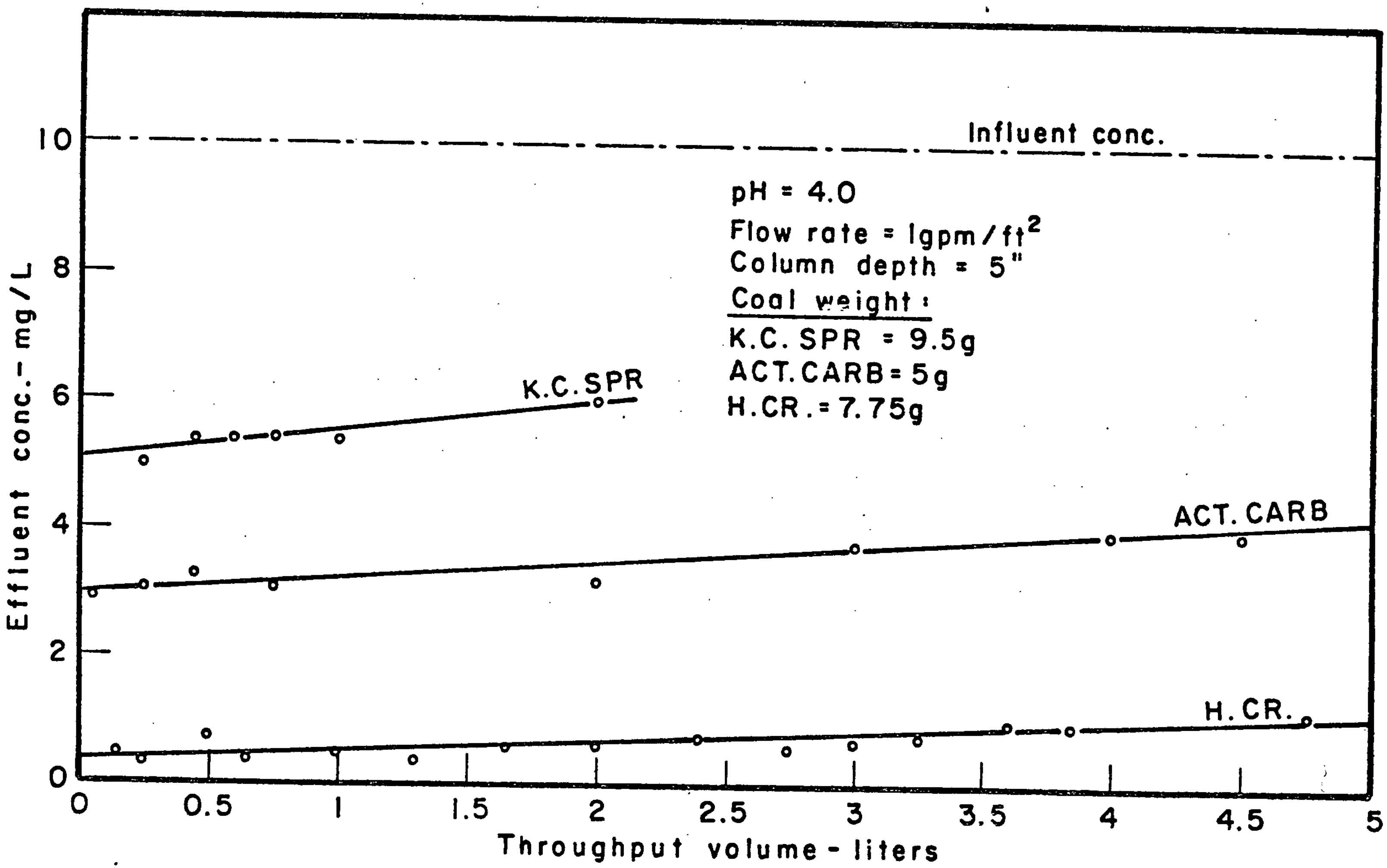

Figure 3.23 Breakthrough Curve for Copper

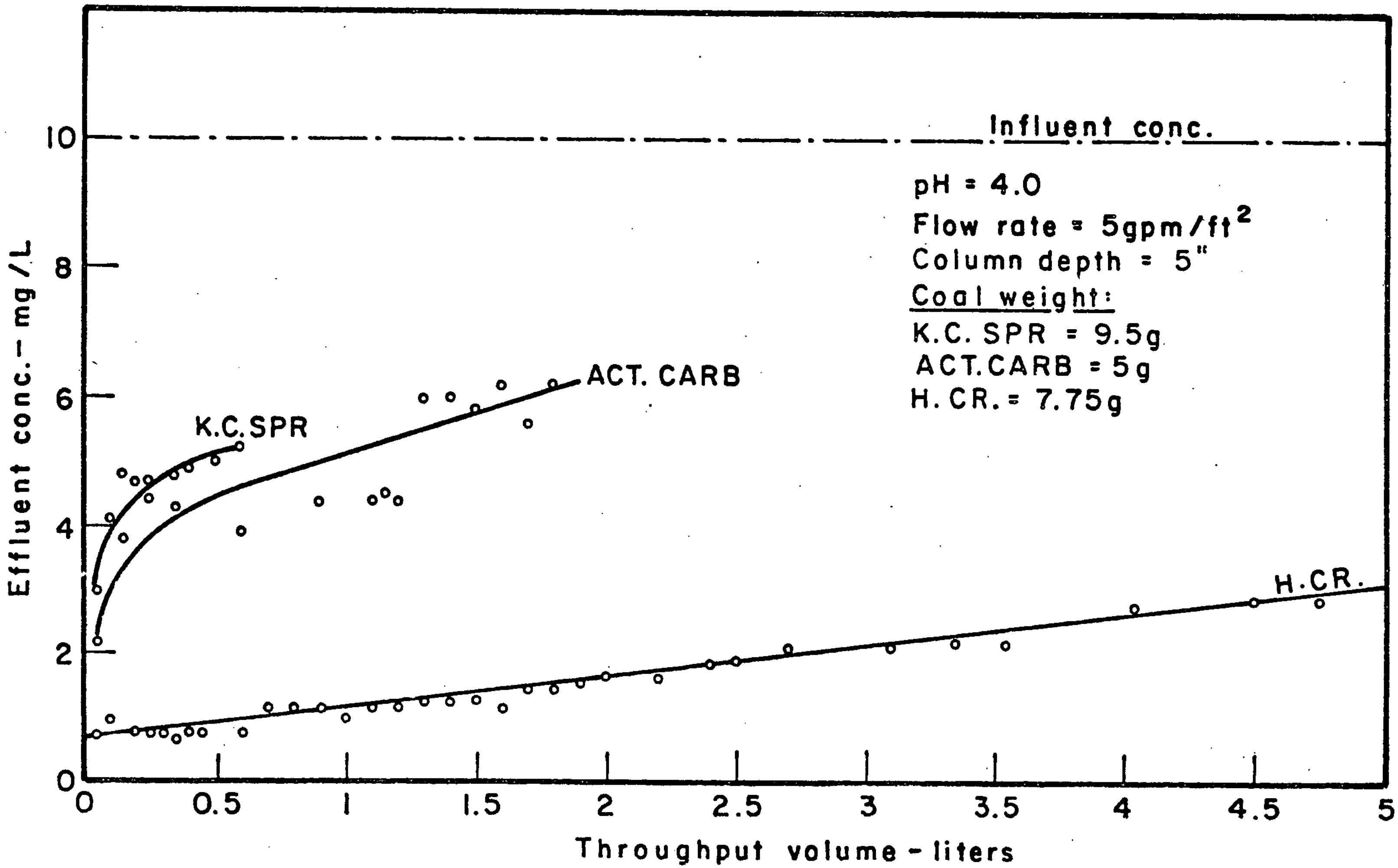

Figure 3.24   Breakthrough Curve for Copper

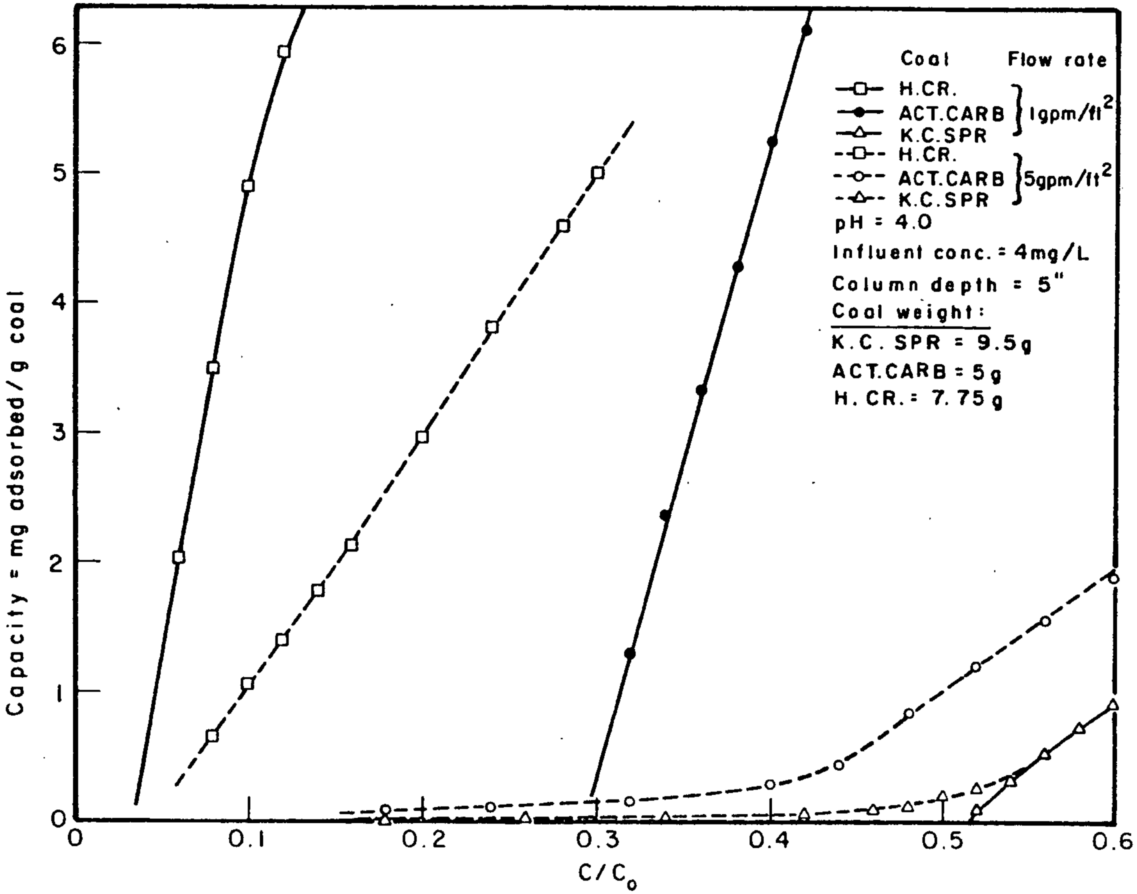

Figure 3.25 Comparison of Adsorption Capacity for Copper in Primary Effluent at Different Flow Rates

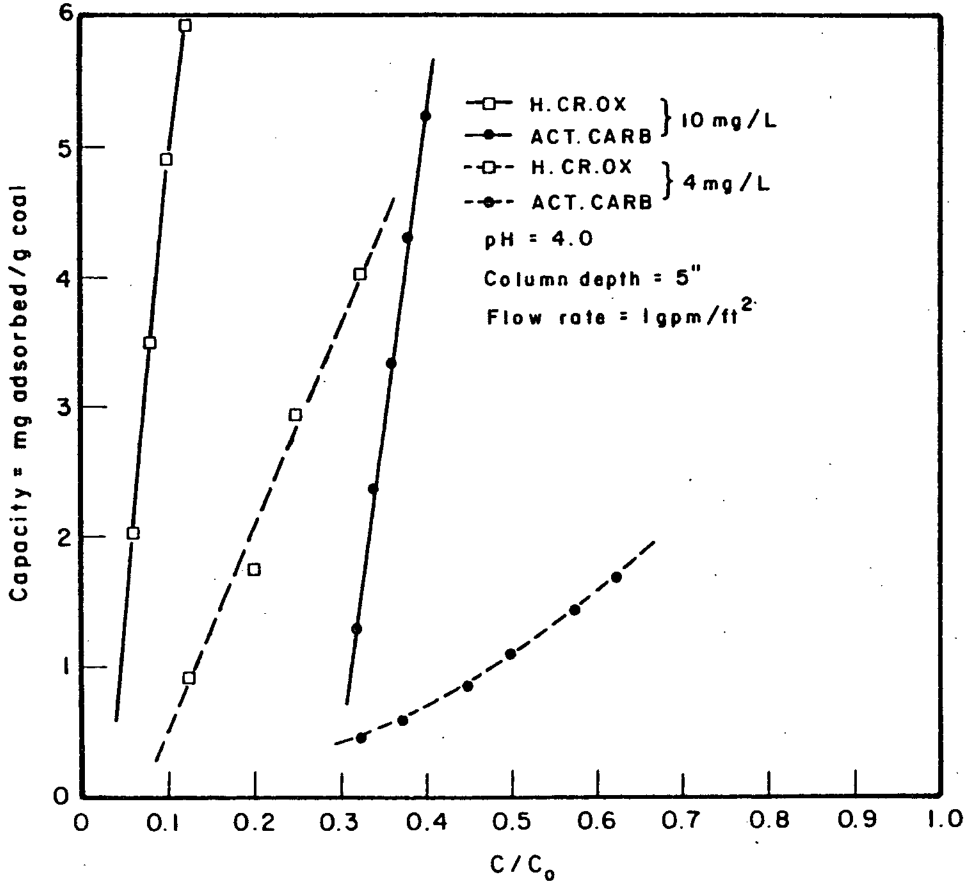

Figure 3.26 Comparison of Adsorption Capacity for Different Copper Influent Concentrations

being shown in Figure 3.27 and 3.28 respectively. Again, an inclined slope was obtained probably due to microbial growth as explained earlier. For both activated carbon and Hat Creek coal a high degree of scatter with regard to data points was obtained. The scatter seemed rather confined at early stages but developed over a larger range at later stages. The reason for this behaviour is unknown. It could be that lead ions were complexed to a particular type of organics which was used as a substrate by certain groups of microorganisms and thus got absorbed into microbial cells, after which due to cellular ionic regulation by osmotic processes were excreted outside the microbial cells.

Rate of substrate intake and cellular metabolism of microorganisms are dependent on the phase of microorganisms' life cycle (lag phase, growth phase, multiplying phase etc) and hence apart from the influence of adsorption characreristics of the coals, it is possible that effluent metal concentration has also been influenced by the phase of microorganisms' life cycle. Answers to such questions are not known at this time. Adsorption capacities were calculated from the lines of best fit from Figures 3.27 and 3.28 and plotted in Figure 3.29. Hat Creek coal and activated carbon performed in a much superior manner to Kaiser coal, with activated carbon performing somewhat better than Hat Creek coal.

Under column operating conditions, the three adsorbents can be ranked in the decreasing order of removal efficiency as:

Activated Carbon

Hat Creek Coal

Kaiser - Stock Pile Refuse

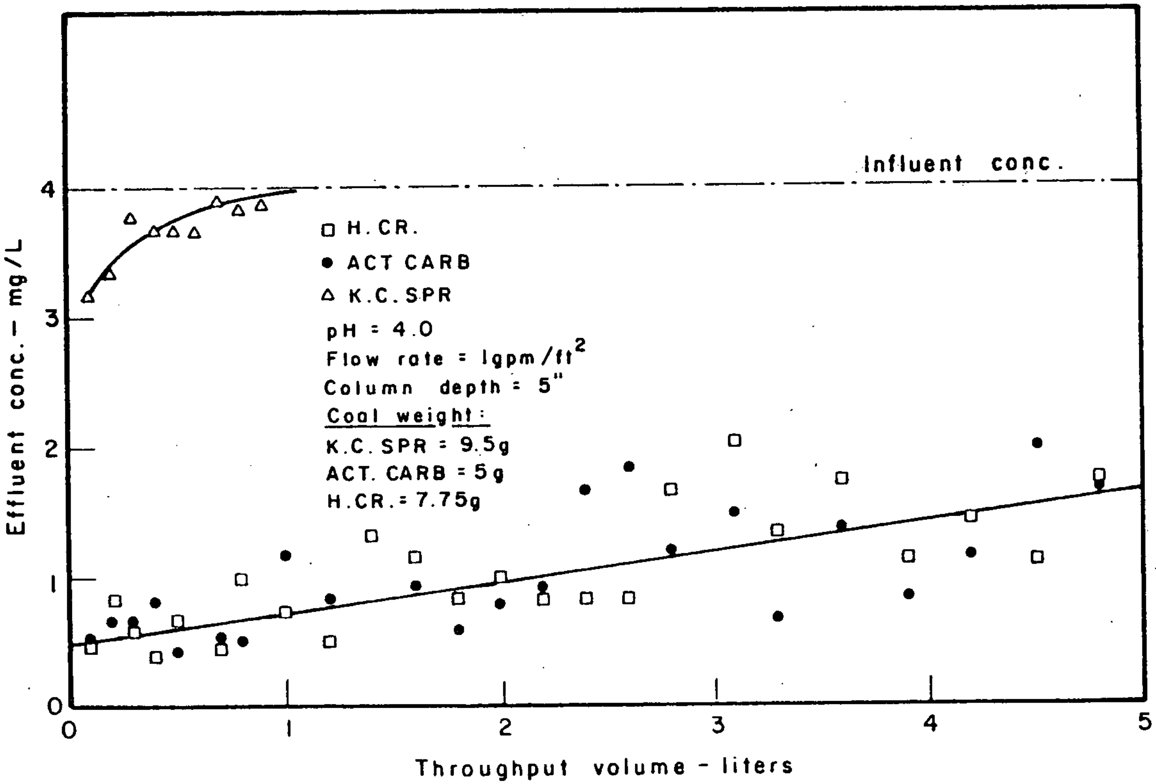

Figure 3.27 Breakthrough Curve for Lead

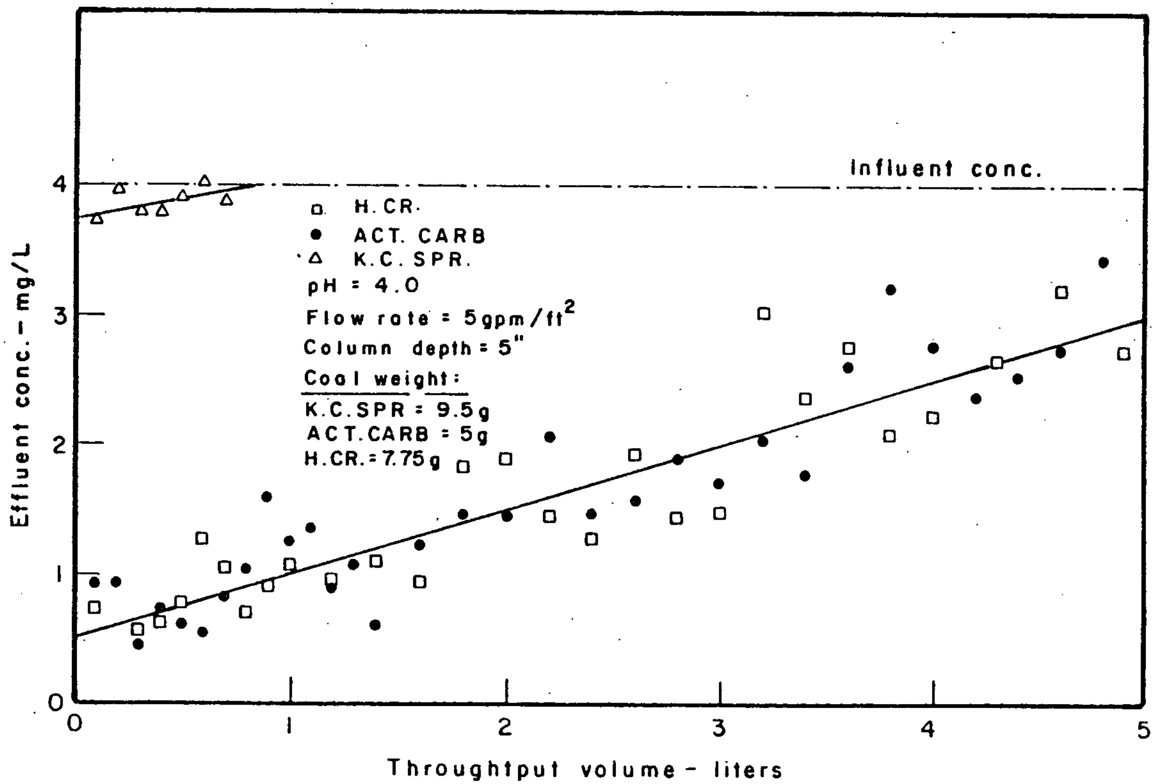

Figure 3.28 Breakthrough Curve for Lead

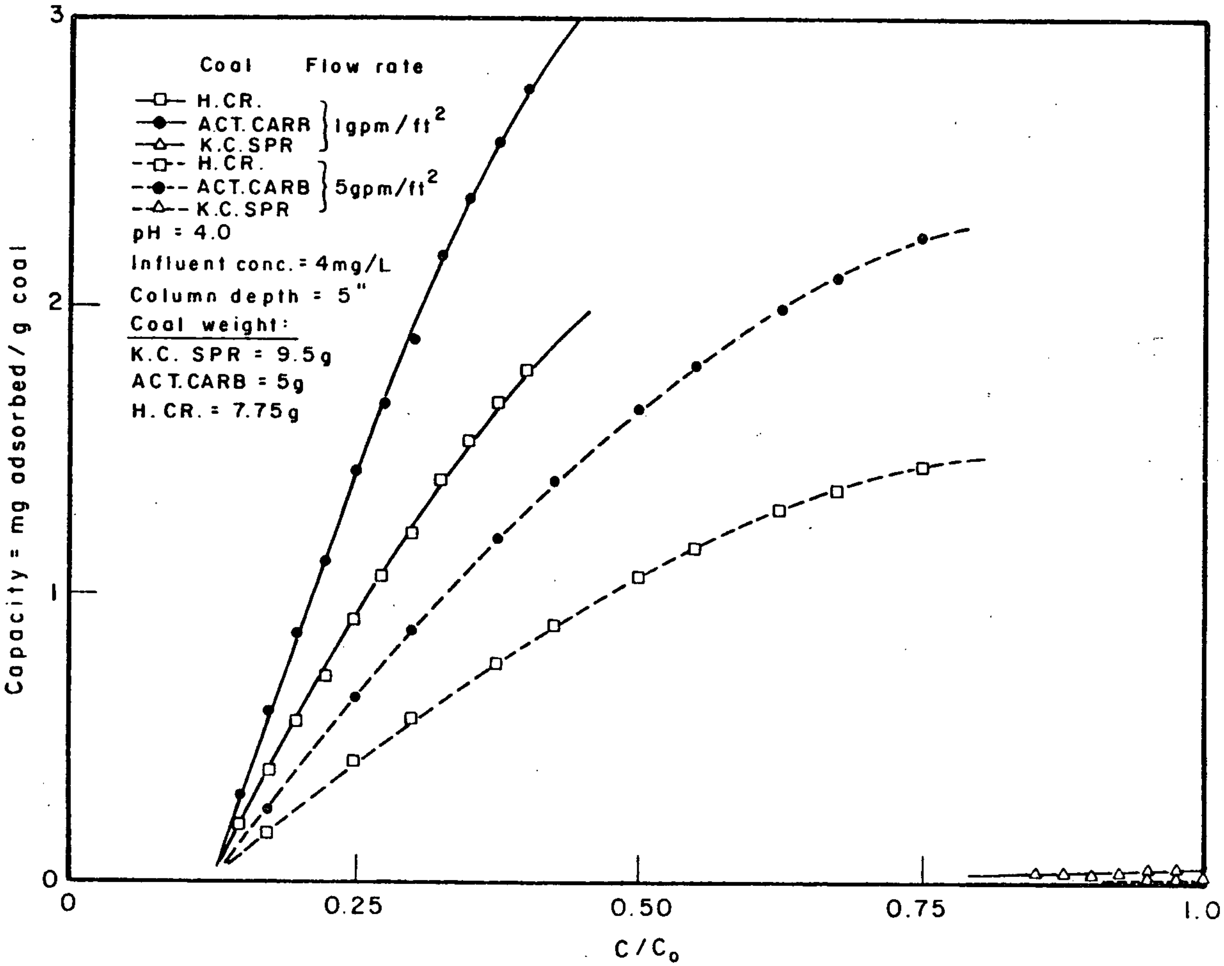

Figure 3.29 Comparison of Adsorption Capacity for Lead in Primary Effluent at Different Flow Rates

(c) Zinc

Column runs were carried out with an influent zinc concentration of 0.5 mg/l at 1.0 and 5.0 gpm/ft^2 flow rates, with breakthrough curves shown in Figures 3.30 and 3.31 respectively. Adsorption capacities were calculated from these and are shown in Figure 3.32. As expected Hat Creek and activated carbon performed much superior to Kaiser coal. As with Copper, once again Hat Creek performed better than activated carbon.

More column tests were performed with influent zinc concentration of 2.0 mg/l at 1.0 and 5.0 gpm/ft^2 flow rates and breakthrough curves are shown in Figure 3.33 and 3.34 respectively. Capacities calculated from these are shown in Figure 3.35. Again Hat Creek and activated carbon performed much superior to Kaiser coal and Hat Creek had much higher adsorption capacity than activated carbon under these column testing conditions. Greater adsorption capacities were obtained with higher influent metal concentrations.

Under column operating conditions the three adsorbents can be ranked in the decreasing order of removal efficiency as:

Hat Creek Coal

Activated Carbon

Kaiser - Stock Pile Refuse.

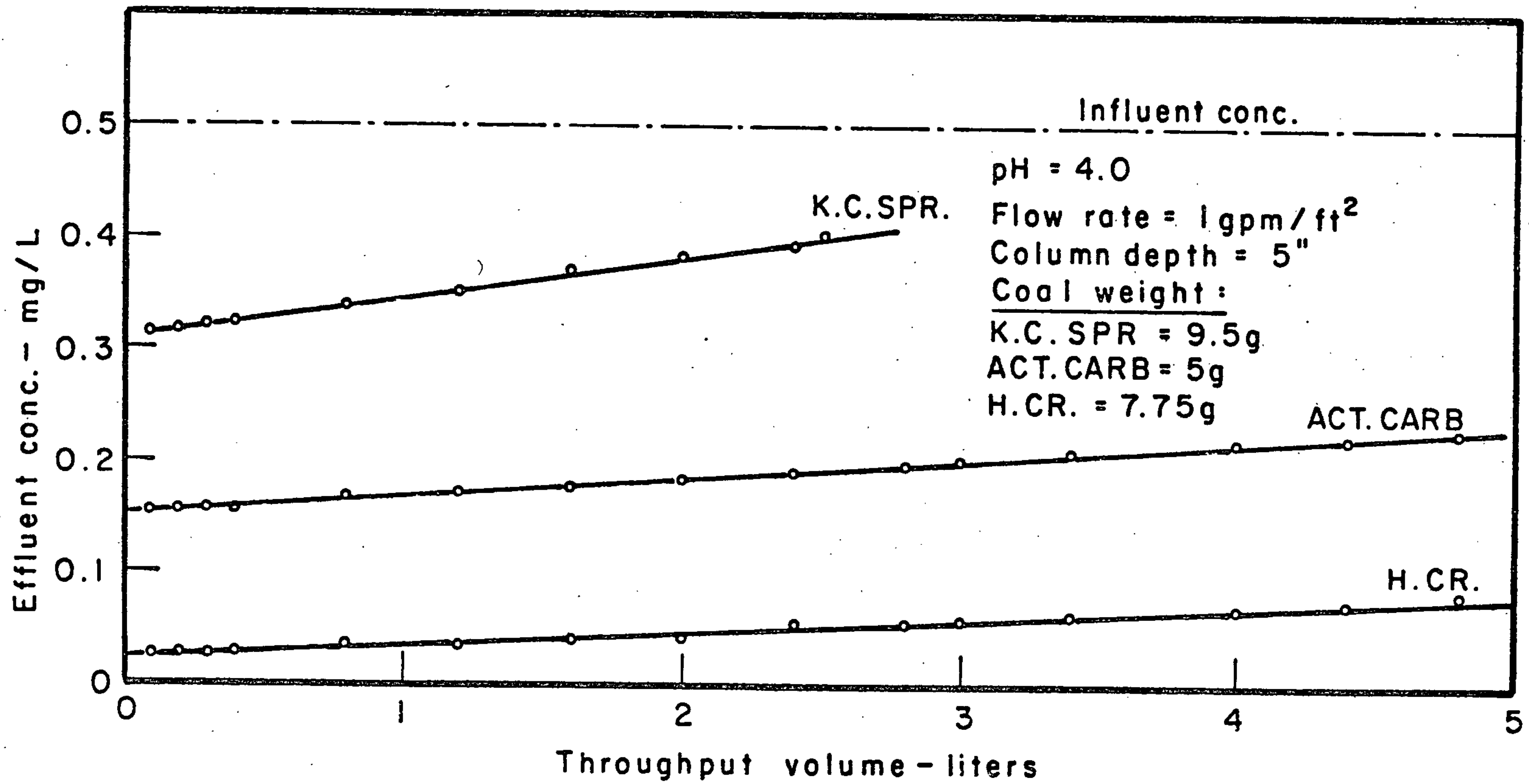

Figure 3.30 Breakthrough Curve for Zinc

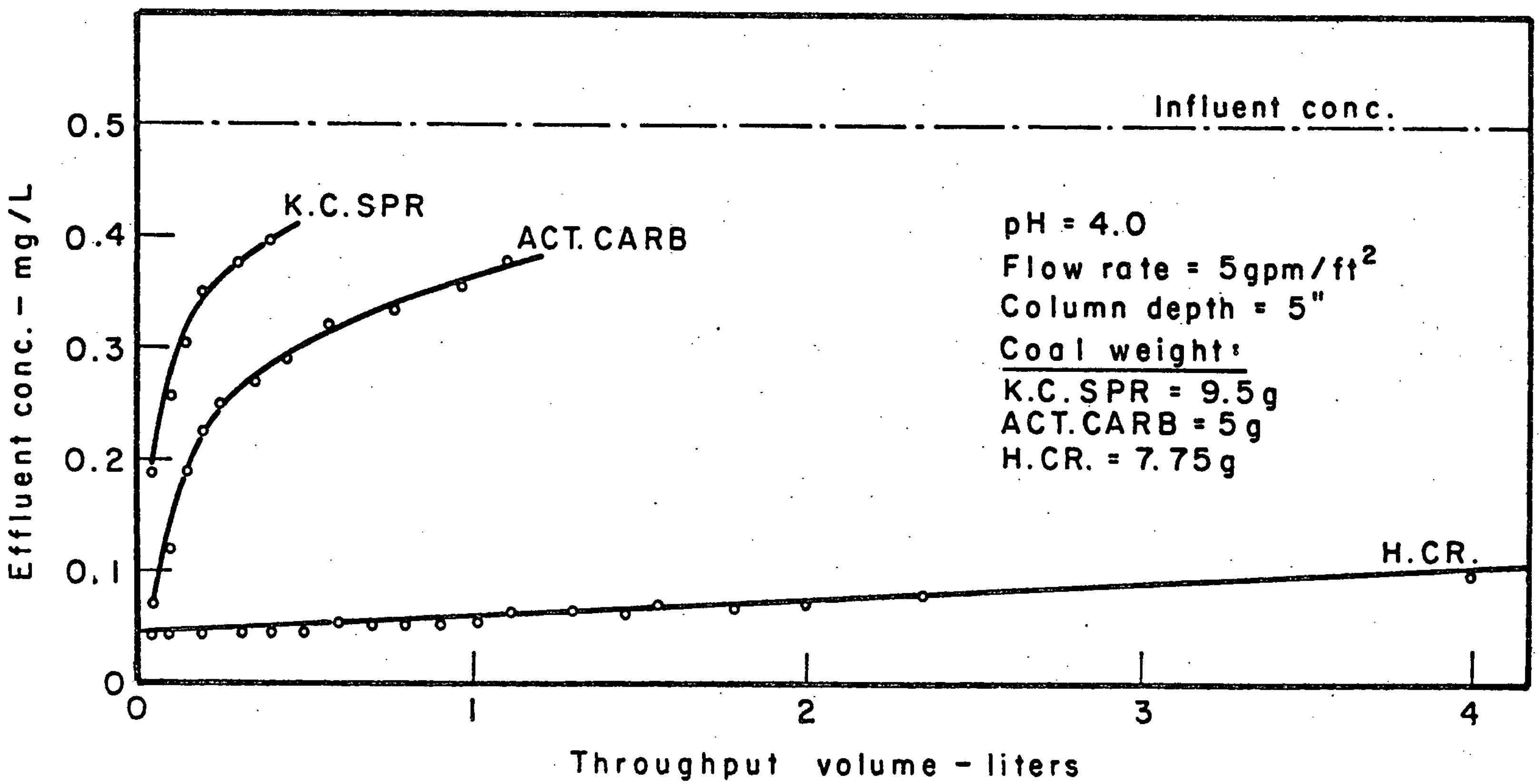

Figure 3.31 Breakthrough Curve for Zinc

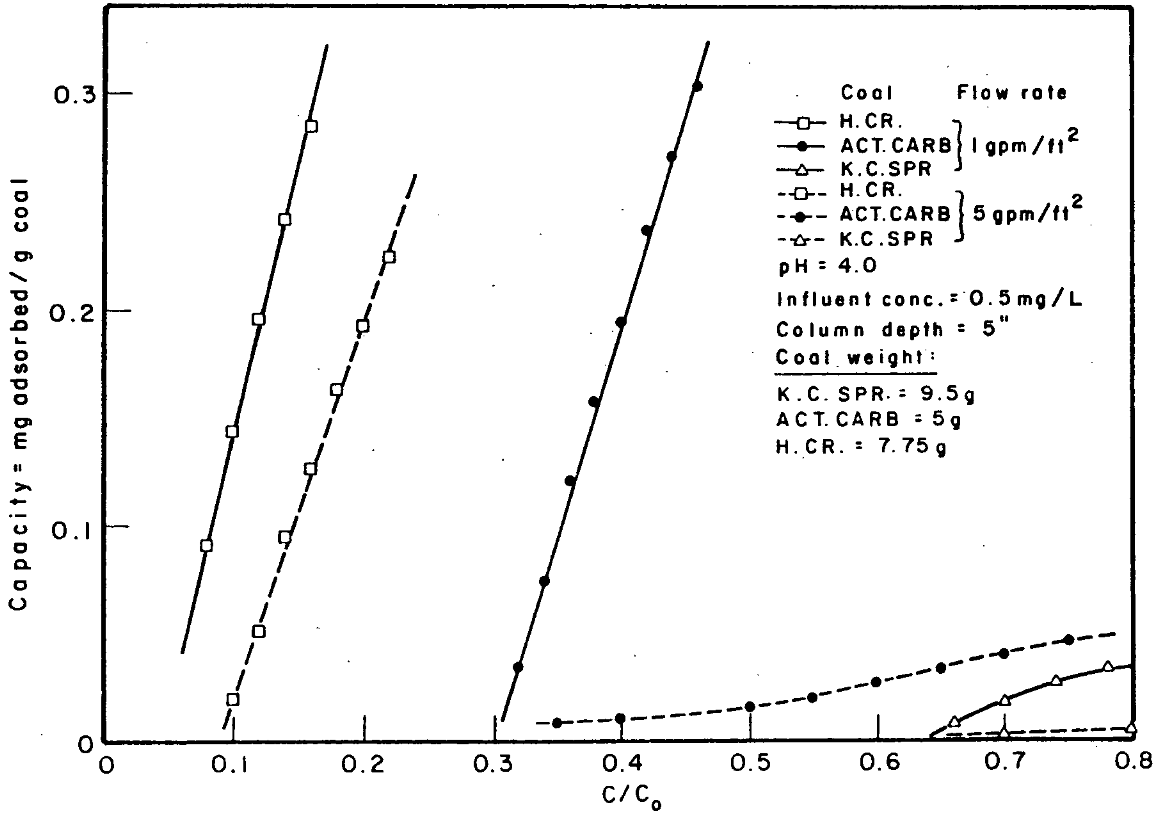

Figure 3.32 Comparison of Adsorption Capacity for Zinc in Primary Effluent at Different Flow Rates

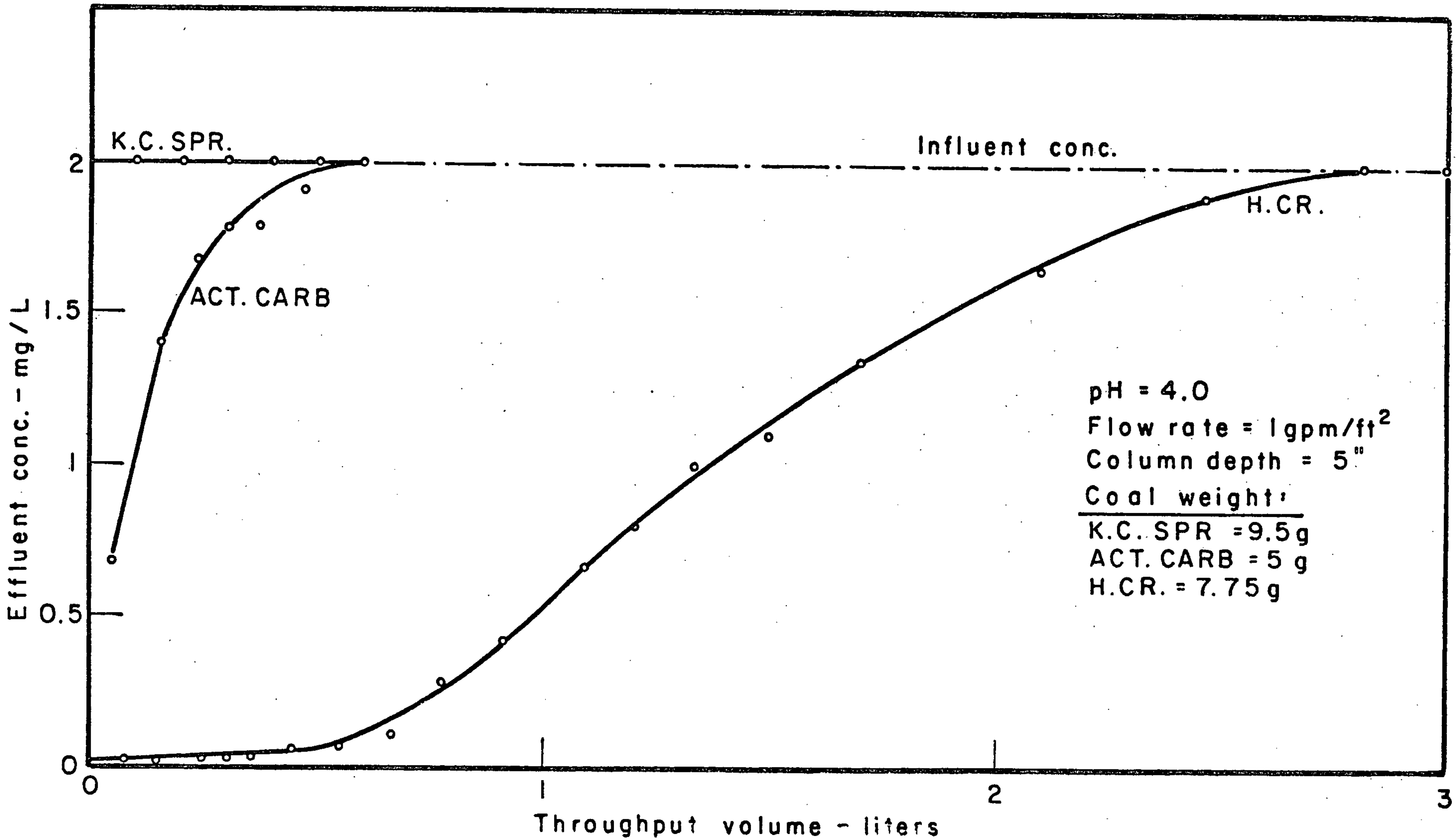

Figure 3.33 Breakthrough Curve for Zinc

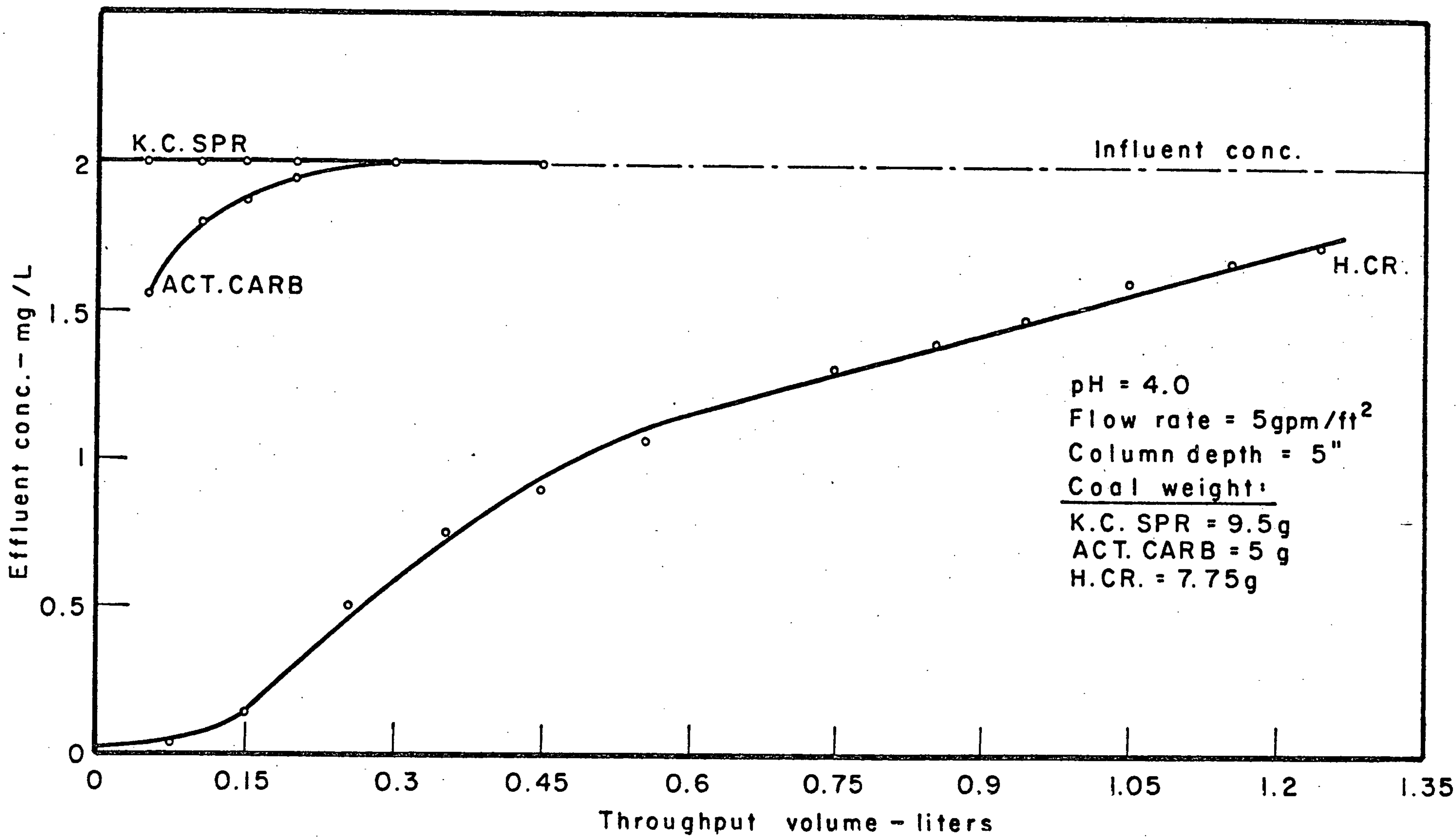

Figure 3.34 Breakthrough Curve for Zinc

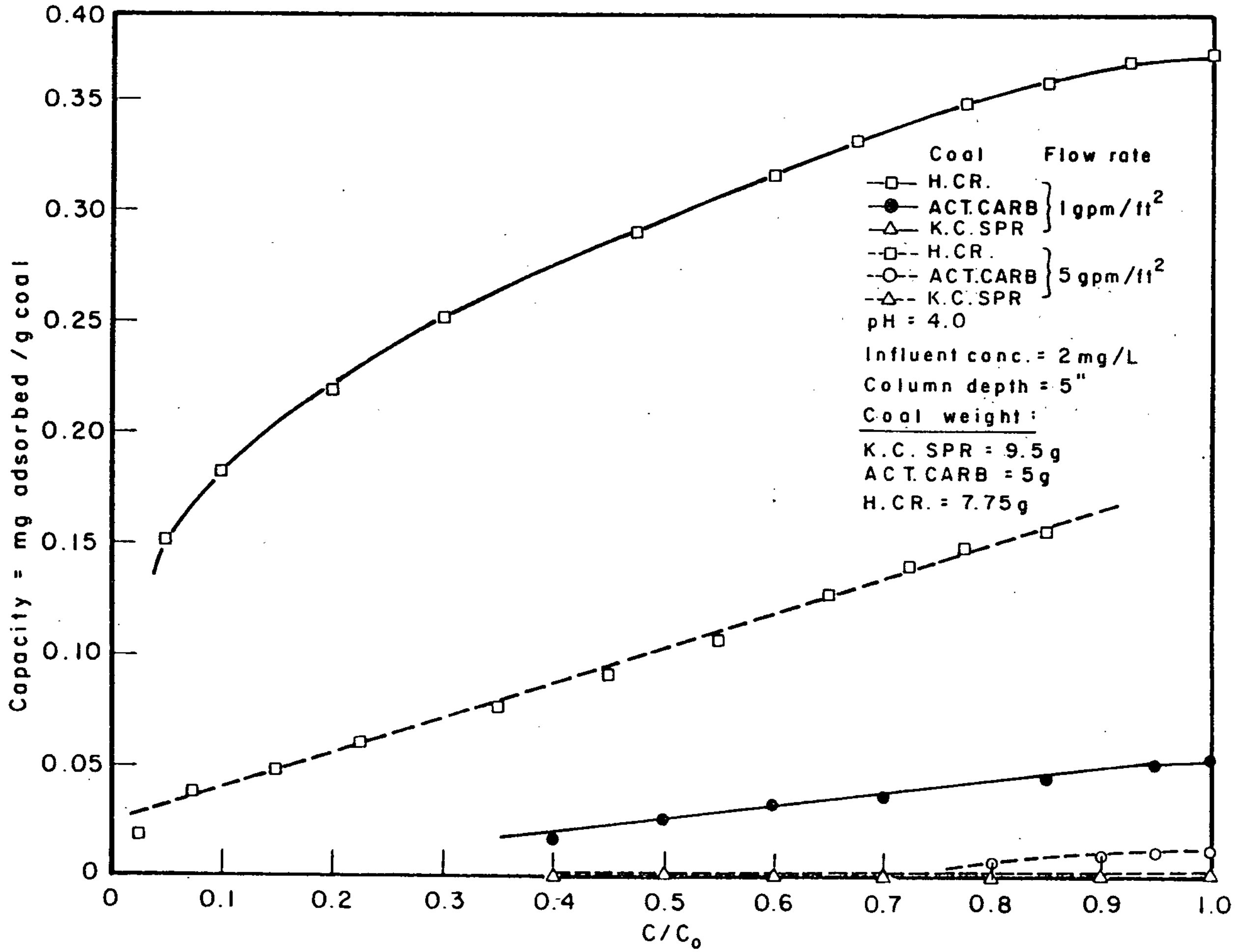

Figure 3.35 Comparison of Adsorption Capacity for Zinc in Primary Effluent at Different Flow Rates

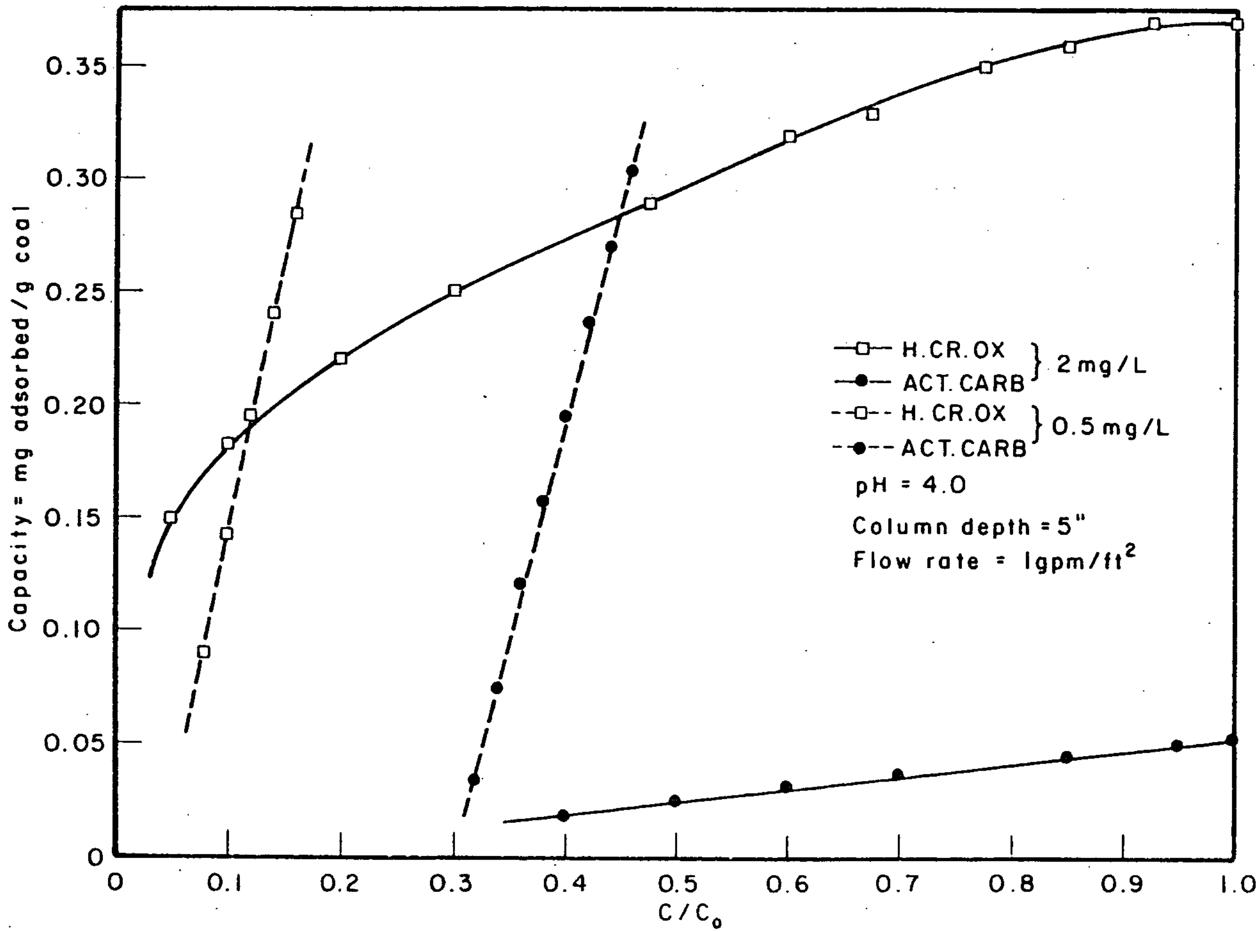

Figure 3.36 Comparison of Adsorption Capacity for Different Zinc Influent Concentrations

Chapter 4

CONCLUSIONS

Under batch test conditions with concentration ranges specified in the text;

1. Of four coals (Hat Creek Oxidised, Kaiser - stock pile refuse, Kaiser - special plant feed, Cominco-Ash) tested, Hat Creek coal had the ability to remove heavy metals from filtered primary sewage treatment plant effluent better than the other three;
2. With regard to removal of copper, Hat Creek coal was able to attain about 80% removal efficiency while the others managed about 60%;
3. With regard to lead, removal efficiencies obtained were very low. Hat Creek oxidised was about 17% efficient while the others were about 5%;
4. With regard to removal of zinc, Hat Creek coal was able to attain 80% removal efficiency while the others attained about 15%;
5. With regard to mercury Hat Creek coal had about 65% efficiency while the others had about 15%;

6. The adsorption affinities of the four metals tested towards Hat Creek coal ranked in a descending order were copper, zinc, lead and mercury;
7. When Hat Creek coal's performance was compared with that of activated carbon the latter was found to possess greater capacity to adsorb copper, lead and mercury while the former was superior with regard to removal of zinc;
8. All four coals had lower metal adsorption capacities from primary effluent than from water solution.
9. All coals indicated increasing adsorption capacity with increasing pH.

Under column test conditions with influent concentrations specified in the text, the following conclusions were drawn;

10. Of the two coals tested, Hat Creek coal had better ability to remove heavy metal from filtered priamary effluent better than the Kaiser coal sample;
11. Column tests were influenced by the growth of micro-organisms on coal surface and eventual plugging;
12. When the performance of Hat Creek coal is compared to that of activated carbon, the latter was found to possess greater capacity to adsorb lead while the former was superior with regard to adsorption of copper and zinc;
13. A five-fold increase in flow rate through the column reduced adsorption capacities of both coals and the activated carbon;
14. Greater adsorption capacities were obtained at higher influent metal concentrations;

15. Adsorption affinities towards Hat Creek coal ranked in the descending order are copper, zinc, and lead;
16. Of the four coals studied Hat Creek coal proved to be the most effective in heavy metal removal from wastewater and its adsorption capacities were comparable to that of the activated carbon tested.

Chapter 5

RECOMMENDATIONS

1. Hat Creek coal was proven to be much superior to other B.C. coals tested with regard to heavy metal removal from wastewater and hence any further detailed study should be restricted to this coal.

2. Further studies with Hat Creek coal should be carried out in parallel with different grades of activated carbon for comparative purposes.

3. Comparative studies between chlorinated and unchlorinated wastewaters must be carried out to evaluate the effect of chlorination on microbial activity.

4. Studies should be carried out to identify the type of microorganisms most predominant in the column and its influence on column properties.

5. If possible microorganisms should be made to assist in heavy metal removal since some forms have the ability to absorb heavy metals.

6. The ability of Hat Creek coal to remove dissolved organics from treated sewage effluent should be investigated, as should the influence of microbial growth on that removal process.

7. If microorganisms cannot be made to work to advantage, methods of stopping or controlling their growth on coal surface should be investigated.

8. Work should be directed to arrive at optimum flow rate, column depth, and particle size to yield high adsorption capacities.

9. Minimum equilibrium effluent metal concentrations and maximum adsorption capacities obtained at optimum operating conditions should be determined and compared with that for activated carbon.

10. Influence of pH on column performance should be studied, taking into consideration its effect on microorganisms. Microbial activity is sensitive tc pH condition. Also affect of pH on complexation and precipitation of different metals should be considered.

11. An economic feasibility study of using Hat Creek coal in advance waste treatment should be carried out taking into consideration its possible use as an energy source after waste treatment.

12. If coal is to be burned as a fuel, fate of metals adsorbed should be determined. If metals escape with stack gases, installation of air pollution control devices may be necessary. If metals remain in ash its disposal method should minimise escape of metal by leaching. These facts should be taken into account when conducting any feasibility study.

REFERENCES

1. Buhler, D.R., Environmental Contamination by Toxic Metals. Heavy metals in the Environment. Water Resources Research Institute, Oregon State University, SEMN WR016 73:1-36, January 1973.

2. Argo, D.G. and G.L. Culp, Heavy Metals Removal in Wastewater Treatment Processes : Part 1 Water and Sewage Works 119(8):62-65, August 1972.

3. Development of Coal Based Sewage Treatment Process. Research and Development Report No. 55. Office of Coal Research, U.S. Department of Interior, Washington, D.C. 1971.

4. Coulthard, T.L. and Mrs. Samia Fadl, The Adsorption of Water Pollutants by a Coal Sorption Process. Paper No. 73-506 presented at Can. Soc. Agr. Eng. Annual Meeting at Victoria, B.C. August 1973.

5. Henren, M.K., Heavy Metals Removal by Using Coal. Unpublished M.A.Sc. Thesis , University of British Columbia, Vancouver, B.C. 1974.

6. Riaz, M., Removal of Heavy Metals Using Granular Coal. Unpublished M.A.Sc. Thesis, University of British Columbia, Vancouver, B.C.,1974.

7. Tin Tun, U., Adsorption of Heavy Metals at Low Concentration Using Granular Coal. Unpublished M.A.Sc. Thesis, University of British Columbia, Vancouver, B.C., 1974.

8. Determination of Mercury by Flameless Atomic Adsorption Jarrell Ash - Atomic Absorption Analytical Method. No Hg-1, August 1970.

9. Fair, G.M., J.C. Geyer and D.A. Okun, Water and Wastewater Engineering, Volume 2, Chapter 28. John Wiley and Sons Inc. New York, 1968.

10. Sawyer, C.N. and P.L. McCarty, Chemistry for Sanitory Engineers, Chapter 2. McGraw-Hill Book Company, New York 1967.

11. Lehniger, A.L., Biochemistry. Chapter 8. Worth Publishers, Inc. New York, 1971.

12. Cruickshank, R., Medical Microbiology, Chapter 18, Churchill Livingstone, London, 1972.

13. Atkinson, B., Biochemical Reactors, Chapter 7, Pion Limited, London, 1974.