

A STUDY OF THE EFFECT OF CHROMIUM AND COPPER
ON THE PERFORMANCE OF THE
ACTIVATED SLUDGE PROCESS

By

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1978

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
July, 1981

Thesis
1981
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Dedicated to my parents,
ROSARIO AND FLORY FURTADO



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ACKNOWLEDGMENTS

I express my sincere gratitude and appreciation to my principal adviser, Dr. Don F. Kincannon, for his intelligent guidance, patience and understanding which give his students a chance to find more than the answer to research problems.

My sincere thanks are due to my Advisory Committee members, Dr. (Mrs.) Marcia H. Bates and Dr. E. L. Stover, for their willing assistance and advisement. Special thanks are also due to Dr. T. S. Manickam for his valuable advice.

Constant help and understanding of my cousin Dr. R. N. Vaz is highly appreciated. The companionship and understanding of my cousins, Loretta, Ramona and Xavier Furtado is also appreciated. Mr. Suresh Balakrishnan deserves special thanks for all his help.

Special thanks are due to my parents and sisters for their love, sacrifice and support. My deepest gratitude to my Uncle Avertano and Aunt Rina Furtado for their encouragement, love and understanding.

Finally, special thanks are deserved by the faculty, staff and colleagues in the bioenvironmental engineering department, by Marcia Hickman for carefully and accurately typing this thesis and by Mr. Parweiz Khan for drawing the figures within.

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CHAPTER I

INTRODUCTION

Increasing number of regulations are going into effect which control the amount of toxic materials in municipal wastewaters which in turn wind up in drinking waters (if not controlled) due to reclamation and reuse. Due to the increasing demand for better water quality standards, the need for pretreatment or effectively managing these toxic metals has become more desirable.

In the past almost exclusive attention has been focused in the removal of biochemical oxygen demand (BOD), suspended solids and other conventional pollutants, as control of toxic metals has not traditionally been an important objective in the mind of wastewater treatment plant design and operations.

The sources of heavy metals that have the most adverse effect on the environment originate from weathering and disintegration of rock and soil, precipitation and atmospheric fallout (1). Metals resulting from mans activities can be attributed to agricultural and urban runoff, domestic wastewater and most of all industrial discharges.

The presence of toxic materials in wastewaters is of concern for several reasons. They have been found to inhibit biological activity like nitrification, which results in reduced treatment efficiency. They could also possibly pass through treatment plants threatening

aquatic life and also increasing the cost of drinking water. Finally, they could also hinder the beneficial use of sludges to land, e.g. Copper is found to be toxic to plants and iron immobilizes phosphates (2).

Life in rivers particularly may be poisoned by the action of these toxic materials on the organism itself or indirectly by the removal of suitable food sources. As an example, phenol is found to be about ten times as toxic to fresh water shrimps as to trout which feed on the shrimps. Thus trout may die as a result of depletion of the food. Even inert material like high count of inorganic suspended solids may blanket the river beds thus reducing the numbers of invertebrate animals which are a source of food for the fish. Evidence also indicates that suspended solids may coat the gills of fish thus hindering oxygen intake (3).

We learn about the toxicity of heavy metals on human beings from the misery of people who come in contact with them. To cite a few examples, mercury has adverse effects on human beings. Methyl mercury compounds accumulate on fish tissue and are transferred to brain tissue of human beings when consumed which results in paralysis and even death (1). Inhalation of mists, fumes or dust of copper results in pharyngeal congestion and even ulceration with perforation of nasal septum. No significant industrial illness has been attributed to Cr^{+3} salts, however chromates when administered subcutaneously to rabbits and guinea pigs resulted in kidney damage (4).

The activated sludge treatment processes have shown a capability for long-term removal of heavy metallic ions, that is superior to anaerobic processes. Accordingly the general aim of this research is to study the effects of copper at concentrations of 5 and 20 mg/l and

chromium (5 and 10 mg/l). Emphasis are placed on biochemical oxygen demand (BOD), chemical oxygen demand (COD), mixed liquor suspended solids (MLSS) and total organic carbon (TOC).

CHAPTER II

LITERATURE REVIEW

During the past few years, heavy metal toxicity to waste treatment system has received considerable attention. Literature review on the toxicity of heavy metals indicates a general trend towards the loss of treatment efficiency. These studies also indicate¹ that the effect of heavy metals in aerobic systems are not linear with concentration as shown in Figure 1. It is also seen in Figure 1 that increasing metal concentration has a linear effect on anaerobic digestion. However Barth et al. (5) reports that combinations of four different metals (Cu, Cr, Ni, Zn) at varying different concentrations had no effect at all on anaerobic digestion. Barth et al. (6) also indicates from his individual studies that the presence of primary clarifier decreases the amount of metal entering the aeration tank and also the chemical and physical characteristic of the sewage alter the form of the soluble metal introduced.

Chromium

The chromous ion Cr^{+2} has a tendency to oxidize to the trivalent state of chromic ion Cr^{+3} . The hexavalent states are the chromate ion CrO_4^{-2} and the dichromate ion $\text{Cr}_2\text{O}_7^{-2}$, which may be reduced by heat or reducing agents to the trivalent CrO_3^{-3} state. Under aerobic

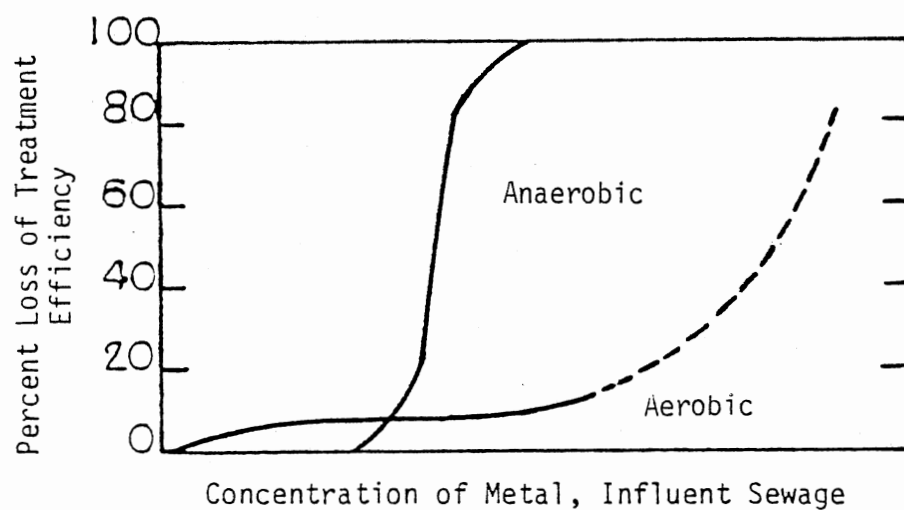


Figure 1. Effect of Increasing Metal Concentration on Loss of Treatment Efficiency for Aerobic and Anaerobic Biological Wastewater Treatment

conditions, Cr^{+6} in natural waters is stable and will persist for long periods. Under anaerobic conditions, Cr^{+6} will reduce to Cr^{+3} , whose salts hydrolyze in neutral or weakly alkaline solution. The chromic oxide thus formed, is insoluble, deposits at the bottom and is unlikely to cause toxicity problems (7).

Chromium (III) is not used as extensively as chromium (VI). Cooling waters recirculated through varied systems use high quantities of chromates to reduce corrosion. The following is a measure of typical untreated chromium concentrations (7):

TYPE	CONCENTRATION (mg/l)
Metal plants - Bright dip waste	10,000 - 50,000
- Pickle bath or plating	600
Leather industry wastes	40
Cooling tower blowdown waters	10 - 60

Trivalent chromium is much more toxic and when present in sufficient quantities will kill the organisms in filters or in activated sludge. It will also be carried over to sludge digestion tanks resulting in retardation or complete stoppage of digestion which may not be the case if secondary treatment is used (8). Coburn (8) set the concentration limit of chromium in sewage at 5 p.p.m. without affecting the sludge digestion process, which is the same value set by Laboon (9). Wise (10) reports that when 200 p.p.m. of precipitated chromium are present in the sludge, it decreases the rate of digestion and when the concentration of chromium exceeds 1 p.p.m., a decrease in sludge digestion efficiency is to be expected. Moore et al. (11) states that a slug dose of 50 mg/l of chromium directly introduced into the digester

effected the gas production and a slug dose of 500 mg/l deteriorates the digester. However they also suggest that hexavalent chromium will not reach the digester as it will be either reduced in the primary or aeration basin, or pass out in the effluent.

The effect of chromium depends on the form of chromium that is used (trivalent or hexavalent) or on the type of treatment (primary or secondary). It also depends on how it is introduced (continuous or shock load). Moore (11) studied this last effect. His findings conclude that concentrations ranging from 0.5 to 50 mg/l fed on a continuous basis to an activated sludge plant had no effect on BOD or COD removal. However, when 4 hour period slug doses of 100 mg/l and 500 mg/l were introduced, it showed an increase in the BOD and COD of the final effluent. The tolerance concentration seems to be a controversial matter. Ross (12) reported that at Richmond, Ind., the activated sludge plant handled without difficulty 1 p.p.m. (Cr) of chromate wastes. Tebbut (3) indicates that Cr (VI) at 0.45 and 4 mg/l concentration results in BOD reduction of 10 to 20 percent respectively. Barth et al. (13) concludes from his field survey of four municipal wastewater treatment plants that a range of 1-9 mg/l cause no serious reduction in the efficiency of aerobic or anaerobic treatment of sewage.

At Grand Prairies, Texas, Wells (14) obtained poor settling, high dissolved oxygen and interference with bacterial life resulting in low BOD results in an activated sludge plant due to sufficient amounts of chromium to color the aeration liquor yellow. Edwards & Nussberger (15) reports a similar instance at Tallman's island plant (New York) in which the plant received during a two day period 430 p.p.m. chromate (as Cr) with a pH of 4.2 the first day, and 1,440 p.p.m. chromate (as Cr) with

a pH of 4.0 the second day. As a result, suspended solids rose from 7 p.p.m. to 31 p.p.m. on the first day and then dropped to 28 p.p.m. on the second day and then gradually decreased to the normal value of 6 p.p.m. and also the D.O. increased and remained at a much higher level, even 14 days later, than for some time previous. It is believed that this may have been caused by reduction in activity of organisms, as the air ratio remained practically constant. Microscopic examination of the activated sludge showed almost complete disappearance of filamentous bacteria, such as *sphaerotilus*, which had been present in moderate amounts. The stalked ciliates also decreased in number after a few days. Before the discharge of chromate wastes, the free ammonia ordinarily decreased from 30 to 15 p.p.m. in passing through the aeration tanks, and the effluent contained about 1 p.p.m. nitrite and 2 p.p.m. nitrate. Immediately after the addition of chromate there was no reduction in free ammonia and practically no nitrites or nitrates were produced. In 10 days the nitrites approached normal value.

Another similar instance is reported by Stankey (16) at Fairfield, Conn. A 4MGD activated sludge plant was colored greenish yellow due to discharge from a chromium plating company which had recently moved to town and had connected its industrial waste discharge to the sewer system without notification. As a result of this discharge, the microbial floc, instead of having sharply defined edges, became very fine and pin-point in appearance. The final effluent became turbid and activated sludge began to flow over the weirs, and the pH dropped from a normal value of 6.9 to 6.0. The BOD removal dropped from 95 to 70 percent and suspended solid removal dropped from 96 to 78 percent. A drop in pH of digesting sludge and a slight decrease in gas production was

was also noticed. Total alkalinity also dropped from 2,200 to 1,400 mg/l.

Jenkins and Hewitt studied the effect of chromium compounds on the operation of trickling filters (17) and activated sludge process (18). They found that in the operation of trickling filters 1 p.p.m. of chromium in the form of potassium chromate had a slight effect, 10 p.p.m. appreciably reduced the quality of effluent, and 100 p.p.m. reduced nitrification by 66 to 78 percent and produced an effluent containing twice as much organic matter as the effluent from the control filter. In the activated sludge process they found that in the presence of 2 p.p.m. of chromium as chromate, the nitrification begins to deteriorate. The process is arrested by addition of 3 or 4 doses of sewage containing 5 p.p.m. of chromium as chromate. Higher concentrations accelerate the process of inhibition. The ability of activated sludge to oxidize organic matter and to flocculate dispersed solids is reduced in the presence of chromate. It was found that respiratory activity, as determined by the amount of carbon dioxide evolved on aeration, was greatly reduced by addition to sewage of 10 p.p.m. of chromium as chromate. The process of nitrification may be arrested, sometimes for a long period, without actually killing the organism. Prolonged aeration of chromate treated sewage seems to be the most effective way of restoring nitrifying activity.

In a batch study conducted at Tinker AFB on attached slimes on rotating biological contactor, Reid et al. (19) found small concentrations of Cr^{+6} was toxic, but with continuous food supply, concentrations up to 2 mg/l were found to be tolerable. He also found that concentration as high as 85 mg/l resulted in loss of digester efficiency

18 percent. Spencer (44) described a trickling filter in which biological action was stopped completely by chromates, the concentration ranging from 3.5 to 67.6 p.p.m. as chromium. No life could be detected by microscopic examination of the filter. Monk (20) added various concentrations of CrO_3 to suspensions of *B. aerogens* in order to estimate the chromate strength which might be allowed on sewage without harm to biological purification processes. He concluded that 26 p.p.m. of Cr (50 p.p.m. chromate as CrO_3) may be considered a safe figure for chromate concentration in sewage arriving at treatment works. This suggestion is based on his observation that 5.2 p.p.m. of Cr killed 16 percent of the organisms in two hours, while 26 p.p.m. Cr killed 46 percent. According to Southgate (21) wastes containing chromate caused excessive accumulation of film on rocks, and reduced the efficiency of biological treatment when in concentrations as low as 1 p.p.m.

Placak et al. (22) reports that hexavalent chromium at a concentration of 0.3 p.p.m. present in BOD bottle or dilution water will give lower results than the true BOD, whereas concentration between 0.3 and 0.1 p.p.m. will inhibit nitrification but will allow 100 percent of the carbonaceous BOD to be recovered. When 0.9 p.p.m. of chromium is present 80 percent of the BOD is recovered and greater amounts of chromium have no further effect. This is in direct agreement with the figure shown on page 5.

Barth et al. (6) conducted pilot-scale studies on the effect of heavy metals on biological treatment processes and reported a material balance of the metals through an activated sludge process. They found that the average efficiencies of the process for removing the metals were 44, 75, 28 and 89 percent for hexavalent chromium, copper, nickel

and zinc, respectively. A survey of four municipal wastewater treatment plants was conducted by Barth et al. (13) and the distribution of chromium, copper, nickel and zinc through these plants indicated a satisfactory correlation with pilot plant results.

Ingols and Kirkpatrick (23) indicate that hexavalent chromium is much more toxic under anaerobic conditions than under aerobic conditions and trivalent chromium is relatively more toxic under aerobic conditions than under anaerobic conditions. Ingols (24) points out that when one considers the effect of chromium upon the aerobic treatment devices, it must be realized that the chromates are relatively non-toxic in raw sewage because of its high organic matter concentration. Thus, at the first point of addition of the raw sewage, treatment will proceed at a normal rate. As the organic matter concentration decreases, the relative toxicity of chromium increases. Therefore, the effect of chromium upon sewage treatment device (trickling filter or activated sludge) will increase as the effectiveness of the treatment device upon the BOD progresses. Hence poorer sewage treatment should be more evident with the trivalent chromium than with the hexavalent chromium.

Ingols and Fetner (25) have reported that moderate concentrations of chromate produce chromosomal aberrations in developing cells. This is an important observation as these chromosome aberrations are a radiometric effect and could be related to the possibility of long term genetic effects. Ingols and Hilly (26) have shown that the respiration of activated sludge under aerobic condition with a high food-to-sludge ratio was depressed by 70 percent for small concentrations of chromate. Under anaerobic conditions, Meredith and Ingols (27) have shown that a

small amount of chromate persisting in the digesting mixture can cause the organisms to remain dormant for a prolonged period. They also indicated that fungi might be more resistant to a given chromate concentration than bacteria as mold mycelic appeared on the surface of those digesting mixtures which were unable to reduce all of the added chromate rapidly. Ingols and Fetner (28) found that chromate at concentration of 500 mg/l prevented the growth of bacteria to an extent that they did not compete for the food and space in the agar plate but molds were resistant to this concentration. This particular observation should enable bacteriologists or mycologists to make the separation of a mixed culture of mold and bacteria. They also studied the effect of chromates on mixed cultures (a culture simulating activated sludge) under aerobic conditions. It was found that sludges having a predominance of sphaerotilus or zoogloeal masses gave different responses to the same concentration of chromate. The sludge became very bulky with filamentous growth when the sludge was dosed with chromate to evaluate the degree of acclimatization. Hence *E. coli* were used in pure culture as they produce carbon dioxide under aerobic conditions and to count the number of organisms surviving the respiration. It was found that 10 mg/l of chromate had no effect on the respiration of *E. coli*, and only one percent of the organisms as a colony could be counted. Yeast cells yielded the same results, with 99 percent of the yeast recovered as colony-producing viable organisms. This indicates that bacteria are much less able to produce visible colonies on the nutrient agar than is the yeast. Protozoa gave results similar to those of yeast. However an excellent correlation was obtained between respiration and surviving organisms

with all three of the organisms when similar studies were run with trivalent chromic ion instead of hexavalent chromate ion.

Copper

It is an essential trace metal for animals and man because it is required for the formation of erythrocytes and hemoglobin as well as oxidative enzymes such as catalase, cytochrome oxidase, peroxidase etc. It is widely distributed in nature as native copper, as well as in several oxide, carbonate and sulfide ores. Copper in the form of copper sulfate is used for the manufacture of copper articles by electrodeposition, for recovery of copper from ore (electrorefining) and, to a lesser extent, for electroplating. In some of the plating baths, copper could be found as a simple cation or a complex anion or a soluble molecular complex. Copper is also (9) used as a catalyst in synthetic chemical manufacturing operation and in mercaptan removal processes of the petroleum refining industry (4).

Copper could be present in domestic sewage and industrial waste mixtures in several forms, depending upon its source and subsequent reactions. McDermott et al. (29) studied the effect of copper sulfate fed on a continuous basis to experimental units each consisting of three separate components, a primary clarifier, an aerator and final clarifier. His observations at copper concentrations of 10, 15 and 25 mg/l yielded the following results:

1. A decrease in BOD and COD removal efficiency.
2. An increase in suspended solids.
3. Copper removal efficiency of 75, 79 and 79 percent respectively.

4. Increase in protozoa and rotifers.

5. Sludge exhibited good settling characteristic.

Slug doses also showed similar results. During this stage much of the copper was adsorbed on the biological floc in the aerator. The sorbed copper was gradually released to the final effluent resulting in an extended period during which copper at relatively low levels was in the final effluent. From his other studies at lower concentrations, he concludes that the maximum concentration of copper that has a detectable effect on treatment efficiency is 1 mg/l.

In a study conducted at different seasons at Lake Orta (Italy) polluted by copper and ammonia (30) from an industrial waste where the concentration of these two toxicants varied from 0.066 mg-Cu/l and 5.8-7.2 mg-N(NH₃+NH₄⁺)/L resulted in findings of mortality rate of Rainbow trout up to 70 percent (max.).

Walker (31) showed that equivalent molar concentrations of copper and cadmium inhibit the biodegradation of nitrolotriacetate (detergent builder), but the presence of iron reduces the inhibitory effect and that of copper by water hardness.

Nitrification is an important aspect of heavy metal toxicity, because failure to nitrify essentially means production of ammonia instead of nitrates which can create a high chlorine demand if break-point chlorination processes are employed, and cause a high oxygen usage due to stream nitrification after dilution. Tomilson et al. (32) confirmed earlier studies that pure culture of nitrosome europaea are more susceptible to small concentrations of heavy metals as compared to the mixed cultures which exist in an activated sludge process. From his studies, he found that a concentration of 0.1 mg/l of copper

appeared to be slightly stimulatory, but 4 mg/l reduced the rate of oxidation by 75 percent of *N. europaea*. However 50 times this concentration was required to have the same effect on mixed cultures. He also found that continuous addition of copper with increasing concentration from 1-10 mg/l produced no effect, but a further increase to 20 mg/l showed a decrease in nitrification. In another experiment in which a concentration of 20 mg/l was added for 20 days, ammonia appeared after 7 days, nitrification stopped for the last 7 days and did not recover for 14 days. He concludes that this was probably because of complexing of copper with the organic matter in the sludge. Kalabina (33) found that 0.5 p.p.m. of copper sulfate as copper was toxic to all microorganisms, and 0.1 p.p.m. was toxic only to bacteria. Nitrification is retarded at 0.5 p.p.m. copper concentration. Rate of ammonia formation is retarded if copper is above 0.5 p.p.m. He set the limiting concentration at 0.1 p.p.m. for biological treatment. Southgate (21) states that wastes from the pickling of copper slow down or stop biological action in trickling filters.

Placak et al. (22) found that 0.01 p.p.m. of copper present in a BOD bottle or dilution water appreciably reduces BOD and 0.05 p.p.m. reduces the BOD by about 23 percent and inhibits nitrification. 1.0 p.p.m. will permit only about 34 percent BOD recovery. Tebbut T. (3) indicates that copper at 0.2 and 0.4 results in BOD reduction of 25 and 42 percent respectively. Stones (34) found that BOD was only partially suppressed by most of the metallic compounds that he investigated and that above a certain relatively small limit of concentration which differs for different metals was little further effect.

Barth et al. (6) observed that copper present continuously at 0.4 mg/l showed no noticeable effect on COD, however 1.2 mg/l showed significant increase. From this he concludes that 1 mg/l present continuously is the threshold dose for the aeration phase. He also found that sludge acclimates to the continuous presence of copper showing no difference in effects on treatment efficiency.

Reid et al. (19) studied the effect of copper at 0.5, 1 and 2 mg/l concentrations and found that the reduction in gas production did not exceed 8 percent. Coburn (8) set the concentration of copper in sewage at 1.0 p.p.m. when sludge digestion is to be practiced. Siverp and Fransemeier (35) also set the concentration at 1.0 p.p.m. for activated sludge process.

Copper wire works and other copper wastes discharged into the sewer precluded the use of the activated sludge process for the treatment of sewage at New Haven, Conn. (36). Dodge (37) states that at Ann Arbor, Mich., sewage treatment plant received a heavy discharge of copper waste from an unknown source which resulted in an increase in suspended solids from 225 p.p.m. to 625 p.p.m. This waste arrived continuously for 4 days, resulting in serious retardation of the aeration process.

Different theories have been proposed to explain the removal efficiency of toxic material by activated sludge. These have been summarized by Rudolfs and Zuber (38). They also conducted an intensive study on the removal of toxic material by sewage sludges. The three sludges studied were activated sludge, life sludge and fresh solids, which showed that toxic metals, such as copper and zinc are readily removed by them. They indicate that the extent to which the metal is removed is a function of the concentration of the sludges, the contact time,

and the character of the sludge. They found that a decrease in sludge volume index results in a decrease in metal uptake. They also suggest that base exchange between the metal and the organic matter of the biological material, plus biological activity appears to be the cause for metal uptake and not adsorption by surface. Jackson and Brown (39) indicates that bacterial populations have remarkable capacities to acclimatize to the point of actually utilizing many toxic compounds as substrates. This may be achieved by the adaptation of enzyme balance in all the members of a bacterial population, but in other cases only a few individuals in the population may be genetically capable of adaptation in this way, and they will become preponderant by natural selection. In a study conducted at OSU, Dehkordi (40) reported high copper removal efficiencies by RBC. Stones (41) indicated that activated sludge treatment removes about 80 percent of the copper present in the settled sewage, the remaining 20 percent passing out with the effluent.

Moulton & Shumate (42) studied the effect of copper dosages at 1, 10, 15, 30, and 45 mg/l. Their findings conclude that all the units recovered from the initial effects of copper as measured by COD. He also found that copper was retained by the units in varying amounts. He attributes this to the tendency of copper to form complexes or chelates with the mixed liquor. If this was not the case, then the large concentrations of copper built up in the mixed liquor in the case of 10 mg/l unit, where there was no wasting would have certainly exerted a significant and progressively increasing toxic effect. There was also an increase in bacterial cells in the effluent, causing optical density proportional to effluent COD. This probably points to an interference in the metabolism of the cells rather than to a strictly chemical

interference of the copper in the forces binding the cells to the floc. His final findings is a linear decrease in respiratory activity with a steady addition of copper.

Heukelekian and Gelman (43) studied the effect of copper, nickel, zinc, cadmium, trivalent chromium, hexavalent chromium and cobalt on oxidation of sewage and activated sludge sewage mixtures by using a Warburg respirometer. A few of the conclusions which the author feels important with respect to this thesis are mentioned below:

1. As pH increases (5-8) toxicity for particular concentrations of copper and trivalent chromium decreases. This could be due to variations in solubility with variations in pH.
2. A characteristic critical pH range exists for each metal where there is a sharp change in toxicity.
3. As the sewage strength is decreased, an increase in retardation of oxygen utilization occurs for a given metal ion concentration.
4. By adapting the seed to repeated addition of trivalent chromium and copper, an increase in tolerance is developed as measured by oxygen consumption.
5. The order of decreasing toxicity for activated sludge sewage mixtures was Ni^{+2} , Cu^{+2} , Cr^{+3} , Cd^{+2} , Co^{+2} and Cr^{+6} .

CHAPTER III

MATERIALS AND METHODS

Experimental Apparatus

A plexiglass pilot plant activated sludge unit with total internal cell recycle as shown in Figure 2, was used for continuous flow experiments. The aeration and settling compartments were contained in the same reactor and separated by an adjustable plexiglass baffle. The baffle was placed just above the tank bottom, leaving a small gap so that the aeration tank mixed liquor could pass to the settling tank, and sludge could recycle to the aeration tank. The total volume of the system was 4.76 liters (approximately 2.80 liters of aeration capacity), and 1.96 liters in the settling tank. Air was provided to the aeration basin by two stone diffusers with air passing through a cotton filter flow meter to assure adequate supply of oxygen to biological solids and for mixing the aeration tank solids, and to provide "suction" to recycle the settled biological solids from the settling chamber into the aeration tank.

The temperature where the unit was installed, was maintained fairly constant throughout the study and the pH in the reactor was held between 6 and 8 by addition of potassium hydroxide if needed. Operations under continuous flow conditions was accomplished by pumping the feed solution to the aeration tank. A Sigma motor pump provided a continuous flow to the system, pumping at a rate of 5.6 ml/min. This provided a

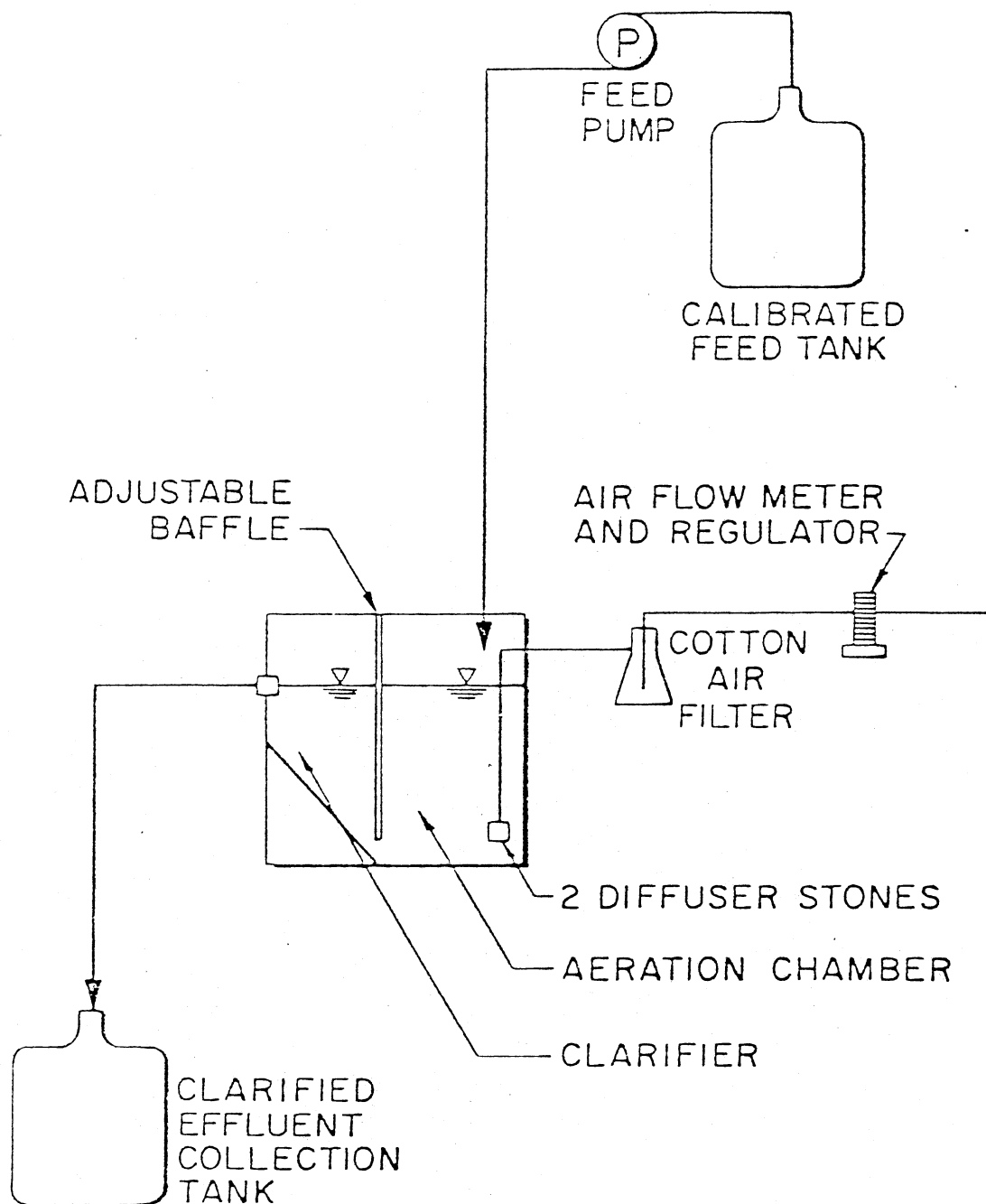


Figure 2. Activated Sludge Pilot Plant
With Internal Recycle

detention time of 8.3 hours in the aeration tank, and 5-8 hours in the settling tank or total hydraulic detention time of 14.1 hours.

A 20 liter glass bottle was used to mix and hold the feed for pumping. The effluent flowed by gravity from the settling compartment to a plastic bottle, where it was collected. The heterogeneous biological population employed in this study was obtained from anaerobic digester sludge taken from the Stillwater Municipal Wastewater Treatment Facility.

Feed Preparation

The synthetic waste used in this study with organic and inorganic constituents, is shown in Table I. The nutrients and minerals required for growth and synthesis by heterogenous microbial population employed were provided by the inorganic constituents as can be seen. 15 ml each of the organic and inorganic constituents were added to the feed bottle and diluted to a volume of 20 liters and then stirred manually with a glass rod for about 5 minutes till the feed constituents were soluble.

Operation and Sampling Procedures

The continuous flow internal recycle reactor described above was operated for about 30 days, at a constant mean cell resident time (θ_c) of approximately 9.33 days. This was done to ensure steady state conditions. The reactor was then fed hexavalent chromium (5 mg/l) in the form of potassium dichromate on a continuous basis for 15 days. The reactor was then maintained without any hexavalent chromium for 30 days until steady state conditions were achieved. The reactor was then again fed 10 mg/l of hexavalent chromium for 14 days. The hexavalent chromium

TABLE I
FEED CONSTITUENTS

Organic Feed Constituents	
Ethylene Glycol	113 ml
Ethyl Alcohol	113 ml
Acetic Acid	113 ml
Glutamic Acid	113 gms
Glucose	113 gms
Phenol	22.6 gms

Inorganic Feed Constituents	
$(\text{NH}_4)_2\text{SO}_4$	200 gms
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	80 gms
K_2HPO_4	48 gms
CaCl_2	8 gms
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.4 gms
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	8 gms

Fill to 1 liter with distilled water and dissolve.

was then stopped, and steady state conditions were achieved. The reactor was then fed 5 mg/l of copper sulfate for 22 days. The reactor was then maintained without copper sulfate for about 25 days. The final stage consisted of feeding the reactor with 20 mg/l of copper sulfate for 30 days. Copper sulfate was then stopped and the whole process was brought to a halt after about 10 days.

Sampling consisted in measuring BOD, COD and TOC of the influent and effluent from the start to the end of the experiment. Mixed liquor suspended solids of the reactor and effluent solids was also monitored. Metal determination was carried out when the metals were being fed.

Analytical Techniques

The methods employed for the analysis of the experimental data are given below.

Biochemical Oxygen Demand (BOD₅)

Standard methods for the examination of water and wastewater (45) was used for this purpose. The probe method was used for determining dissolved oxygen.

Chemical Oxygen Demand (COD)

COD of the influent and effluent was measured. The procedure is outlined in Standard Methods (45).

Total Organic Carbon (TOC)

The Beckman 915 TOC analyzer was used to carry out this test.

MLSS and Effluent Solids

The membrane filter technique as given in Reference (45) was used. The filter employed was a 0.45 micron Millipore filter.

Metal Determination

The methods for determination of hexavalent chromium and copper sulfate are described in the Handbook of Water Analysis by Hach Chemical Company (46).

CHAPTER IV

RESULTS AND DISCUSSION

Chromium

The activated sludge bench unit was first operated as a control (i.e. without introducing any metal in the feed). The influent and effluent characteristics as measured by BOD, COD and TOC are shown in Figure 3. Mixed liquor suspended solids (MLSS) and effluent solids (X_e) are also shown on this figure. The statistical analysis of the data is provided in Table II. The average of mean cell residence time (θ_c) at which the unit was operated is also shown on this table.

When no chromium is introduced, the MLSS averaged about 2488 mg/l. This value is rather high, as can be seen from the figure. At the initiation of the experiment the MLSS were rather high but during the later stages decreased to a lower value. When 5 mg/l of chromium is introduced there is a noticeable increase in MLSS. It averaged 2534 mg/l during this period. The COD decreased to an average of 23.6 mg/l from an average of 39.5 mg/l. The BOD and TOC also showed a decrease from 3.5 to 1.8 mg/l and 17.3 to 15.5 mg/l respectively. The effluent SS averaged 14.3 mg/l before the introduction of 5.0 mg/l of chromium and 2.6 mg/l during the time 5.0 mg/l of chromium was part of the wastewater.

The concentration of chromium in the reactor as well as the effluent was monitored every two hours. It was found that no chromium was

TABLE II
STATISTICAL ANALYSIS OF DATA TO
SHOW THE EFFECT OF CHROMIUM

Para- meter	S_i			S_e			\bar{x}	\bar{x}_e	θ_c	Chromium concen- tration mg/l
	BOD mg/l	COD mg/l	TOC mg/l	BOD mg/l	COD mg/l	TOC mg/l	MLSS mg/l	SS mg/l	days	
N	6	5	5	6	6	17	33	34	33	None
\bar{x}	315.8	540.2	186	3.5	39.5	17.3	2488	14.3	8.6	
σ	21.6	68.6	25.1	1.7	9.4	10.1	308.3	14.8	1.0	
cv%	6.9	12.7	13.5	47.6	23.8	58.3	12.4	103.2	11.8	
N	5	5	3	5	5	5	16	16	16	5.0
\bar{x}	276	524.8	193.3	1.84	23.6	15.5	2534.8	2.6	9.1	
σ	19.8	18.6	10.3	1.24	5.9	6.3	133.1	6.1	0.5	
cv%	7.2	3.5	5.3	67.4	25.3	40.5	5.3	240	5.5	
N	7	8	4	7	8	11	25	20	22	None
\bar{x}	351.1	541.6	150.6	3.7	42.6	17.2	2311.7	6.4	8.7	
σ	64.6	18.1	41.3	2.9	23.0	3.8	349.4	9.3	0.78	
cv%	18.4	3.4	27.4	78.0	54.0	22.2	15.1	145.3	8.9	
N	4	4	5	4	4	10	13	13	13	10.0
\bar{x}	294.8	512.4	155.5	3.3	46.3	15.8	2221.7	12.3	8.2	
σ	40.5	20.5	22.1	0.21	21.7	2.9	47.1	6.4	0.49	
cv%	13.8	4.0	14.2	6.5	46.9	18.2	21.3	52.0	6.0	

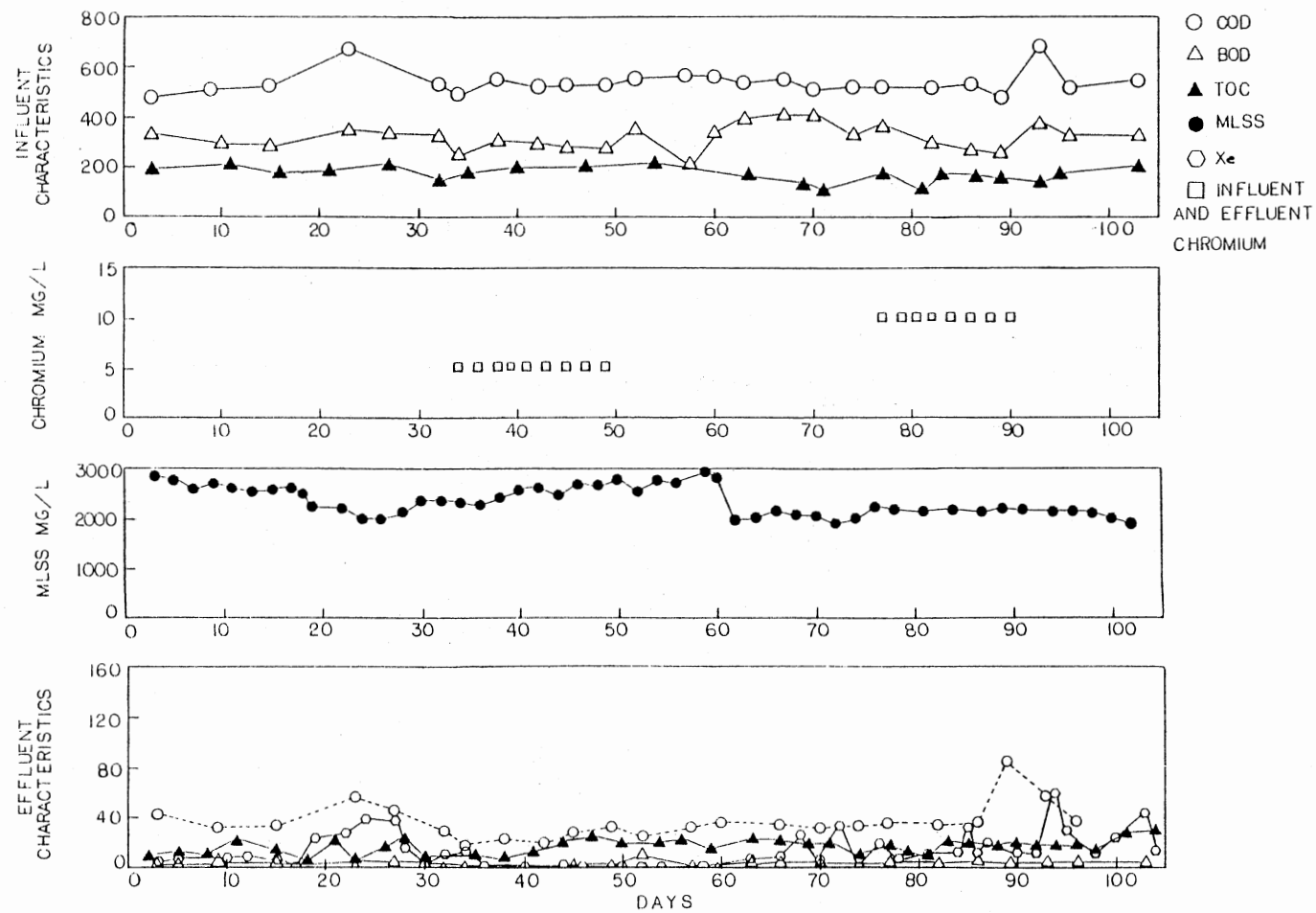


Figure 3. Operational Characteristics of Activated Sludge Process in the Presence and Absence of Chromium

adsorbed and all the chromium introduced through the influent came out through the effluent. This is shown in Figure 3.

The student 't' value seen on Table IV at no metal and 5 mg/l chromium falls within the range of L_1 and L_2 , and end points for 95% confidence interval and show no significant difference. However, the overall effect due to the introduction of 5 mg/l of chromium appears to be a production of better quality effluent and a stimulation of growth.

The unit was then operated without any metal as seen from days 50-76. A sharp decrease in MLSS (Figure 3) can be observed on day 61. This is due to unintentional addition of chromic acid to the unit when cleaning the feed lines. This caused a foaming in the aeration tank and a loss of solids through the effluent. Data during this period was not collected and is not shown in the figures. It required about 10 days for the unit to recover from the shock and the biological solids then remained constant at about 2000 mg/l as seen in the figure.

It can be observed on Table IV that student 't' values are in the range of L_1 and L_2 , at "no metal and no metal -(1)" indicating that no significant difference was observed between the data collected at the beginning of the experiment and that collected after 5 mg/l of chromium was stopped.

The performance of the unit when 10 mg/l of chromium is introduced is seen from days 77 to 90. The MLSS decreased from an average of 2312 mg/l to 2222 mg/l. Although this does not appear to be a significant difference, a more realistic difference can be observed in effluent SS wherein they increased by 50% (increase in average of 6.4 to 12.3 mg/l). The average COD values also showed an increase from 42.6 to 46.3 mg/l.

TABLE IV
STUDENT 't' ANALYSIS OF DATA

BOD ₅ , S _e			
L ₁	L ₂	Student 't'	Conditions
4.24	- 0.24	2.01	no metal and 5 mg/l chromium
3.71	- 3.37	0.17	no metal and 10 mg/l chromium
51.49	13.77	-3.81	no metal and 5 mg/l copper
131.09	29.19	-3.40	no metal and 20 mg/l copper
3.17	- 3.13	-0.01	no metal and no metal -(1)
23.15	- 4.17	-1.51	no metal and no metal -(2)
COD, S _e			
28.58	1.50	2.56	no metal and 5 mg/l chromium
38.65	-34.17	-0.14	no metal and 10 mg/l chromium
69.73	0.89	-2.31	no metal and 5 mg/l copper
158.95	20.33	-2.79	no metal and 20 mg/l copper
33.37	-22.47	-0.44	no metal and no metal -(1)
23.10	-10.64	-0.81	no metal and no metal -(2)
TOC, S _e			
17.05	-13.49	0.27	no metal and 5 mg/l chromium
8.07	0.27	2.53	no metal and 10 mg/l chromium
26.62	1.34	-2.41	no metal and 5 mg/l copper
44.86	7.18	-3.12	no metal and 20 mg/l copper
19.35	1.77	2.59	no metal and no metal -(1)
12.35	-9.73	-0.27	no metal and no metal -(2)

However a decrease in average BOD can be observed from 3.7 to 3.3 mg/l. The chromium present in the effluent BOD bottles could have produced an inhibitory effect. No explanation can be given for a decrease in the average TOC values from 17.2 to 15.8 mg/l.

Figures 4 and 5 show the comparative effect of 5 and 10 mg/l of chromium on effluent COD, BOD, TOC, and SS. It can be observed here that a better quality effluent was produced at 5 mg/l than at 10 mg/l.

The effect of chromium on the saturation constant (K_S) and Eckenfelders substrate removal rate coefficient (K_e') is represented in Figures 6 and 7. The saturation constant (K_S) decreased under the influence of 5 mg/l indicating better biodegradability of the base mix. It then increases due to 10 mg/l of chromium which indicates that this concentration appeared to inhibit biodegradability. However the BOD values show a further decrease, no reliable conclusions can be drawn from this observation. Similar conclusions can be drawn when one observes K_e' values on Figure 7. An increase in K_e' indicates better performance and a decrease indicates the toxic nature of the metal.

The reactor was then operated without any metal for 34 days. Part of the data collected during this period is shown on Figure 3 (day 91 to 105) and the next part is continued on Figure 8. The statistical analysis is presented on Table III.

Copper

Divalent copper in the form of copper sulfate was fed at 5 and 20 mg/l to study the effect of copper on removal efficiency.

When 5 mg/l of copper was introduced (Figure 8) the effluent SS increased from an average of 28.3 mg/l to 32.7 mg/l (Table IV). A

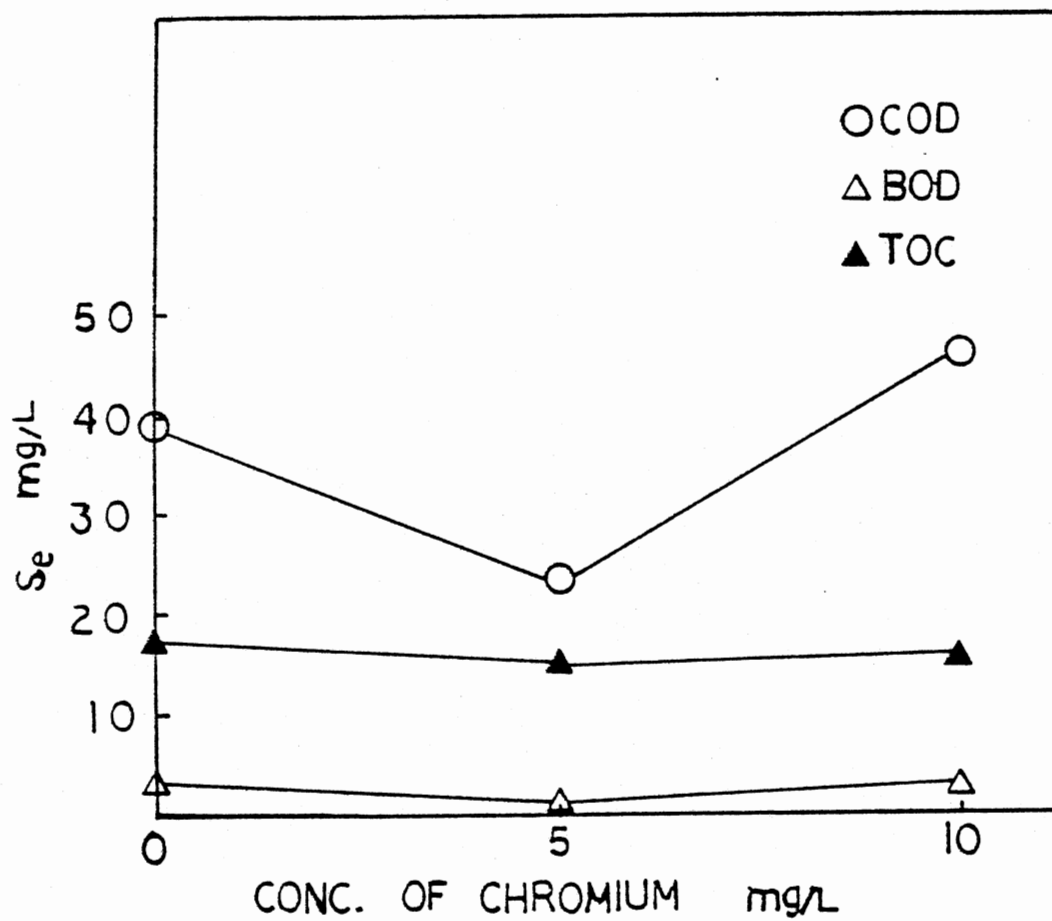


Figure 4. Effect on Effluent COD, BOD and TOC Due to Chromium

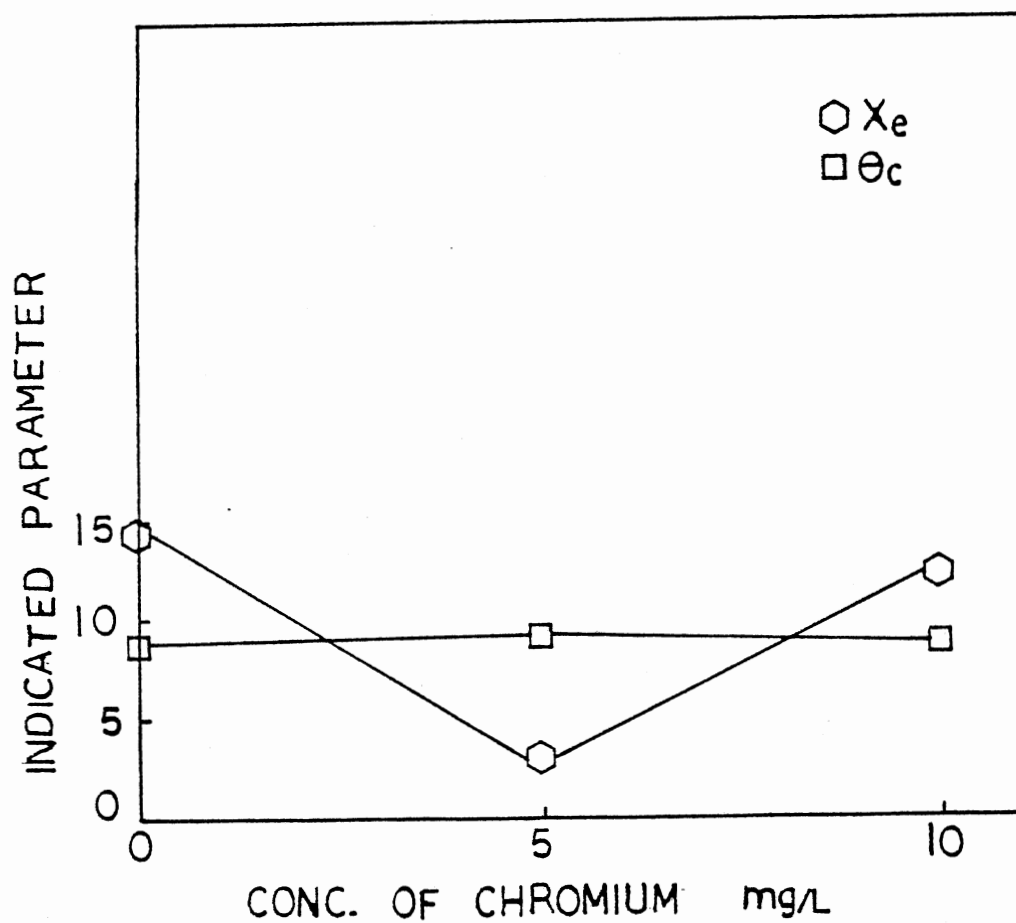


Figure 5. Effect on Effluent SS(X_e) and θ_c Due to Chromium

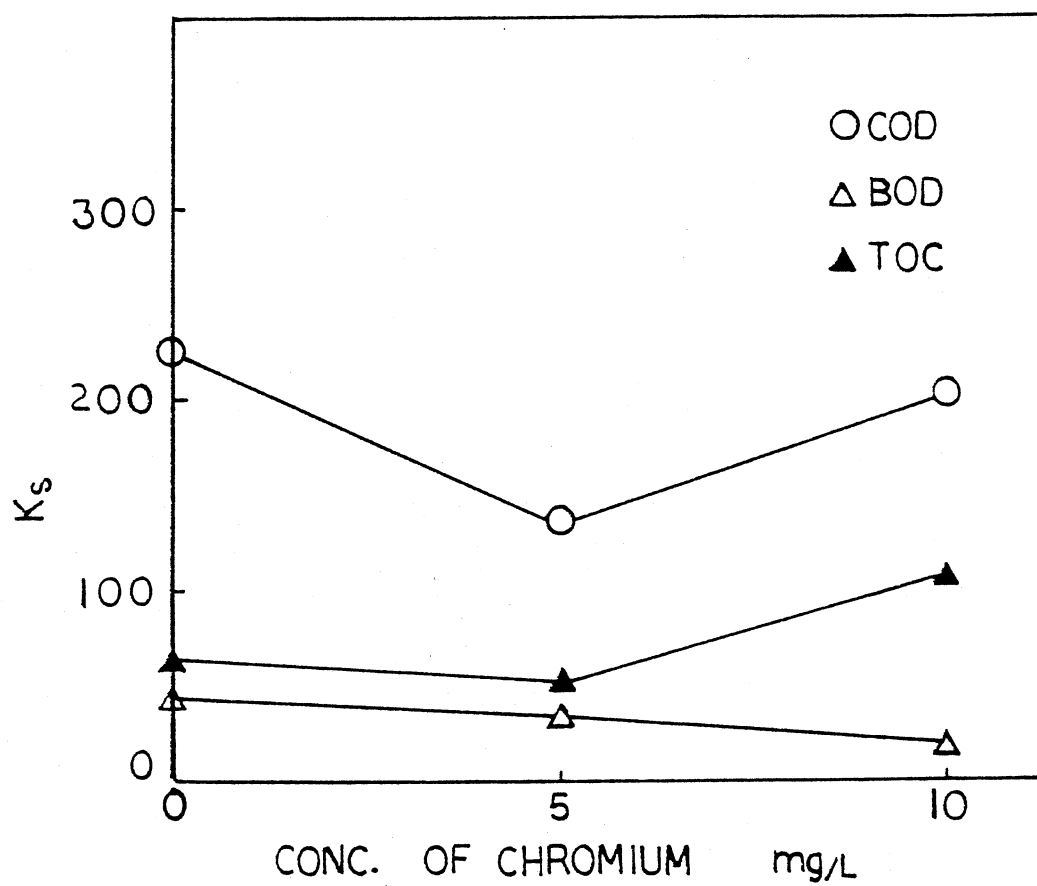


Figure 6. Effect on K_s Due to Chromium

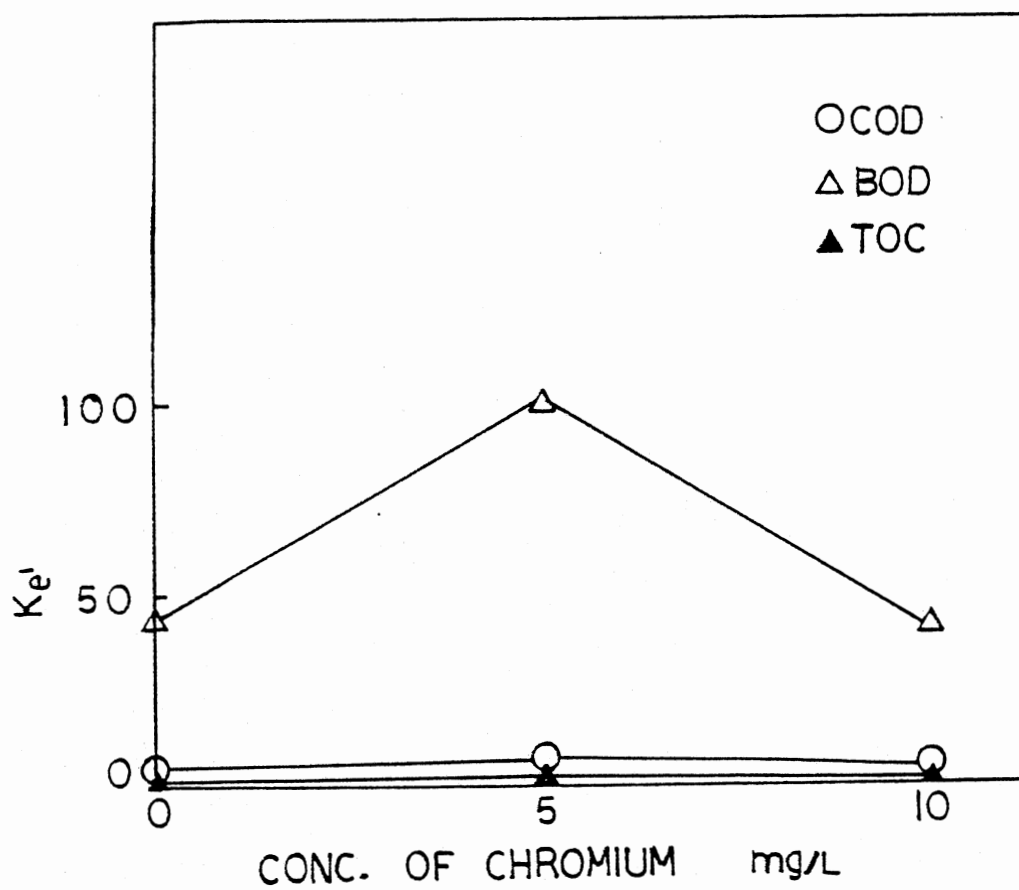


Figure 7. Effect on K_e' Due to Chromium

TABLE III
STATISTICAL ANALYSIS OF DATA TO
SHOW THE EFFECT OF COPPER

Parameter	S _i			S _e			X	X _e	θ _c	Copper concentration mg/l
	BOD mg/l	COD mg/l	TOC mg/l	BOD mg/l	COD mg/l	TOC mg/l	MLSS mg/l	SS mg/l	days	
N	8	9	9	8	9	22	25	24	25	None
x	344.9	565.0	167.9	2.8	41.3	20.5	1887.3	28.3	7.1	
σ	16.5	65.3	14.5	0.99	15.0	8.4	224.4	15.6	1.14	
cv%	4.8	11.6	8.6	35.2	36.4	41.2	11.9	55.1	16.0	
N	5	4	6	5	4	17	17	17	17	5.0
x	364.2	535	179.6	35.3	78.8	32.6	1778.8	32.7	6.5	
σ	25.9	13.4	11.9	22.2	34.3	14.1	130.1	17.6	1.1	
cv%	7.1	2.5	6.6	62.8	43.5	43.3	7.3	53.7	16.2	
N	6	6	6	6	6	14	19	17	19	None
x	360.4	568.1	176.6	12.1	49.7	26.2	1800	16.9	7.5	
σ	27.1	65.2	26.0	16.3	11.2	7.7	127.4	4.9	0.44	
cv%	7.5	11.5	14.7	135.0	22.5	29.5	7.1	29.1	5.8	
N	9	9	6	9	9	23	25	25	25	20.0
x	282.9	380.9	126.2	92.3	139.3	51.2	1088	43.1	4.8	
σ	24.1	53.6	3.4	52.0	72.4	16.5	341.8	10.8	1.05	
cv%	8.5	14.1	2.7	56.3	52.0	32.1	31.4	25.1	21.9	
N	2	2	1	2	2	7	6	6	6	None
x	316.6	394.2	120.2	136.4	195.3	69.9	374.0	38.3	2.9	
σ	36.7	4.22	0	5.3	3.9	5.1	122.1	5.9	0.81	
cv%	11.6	1.1	0	3.9	2.0	7.3	32.7	15.5	27.8	

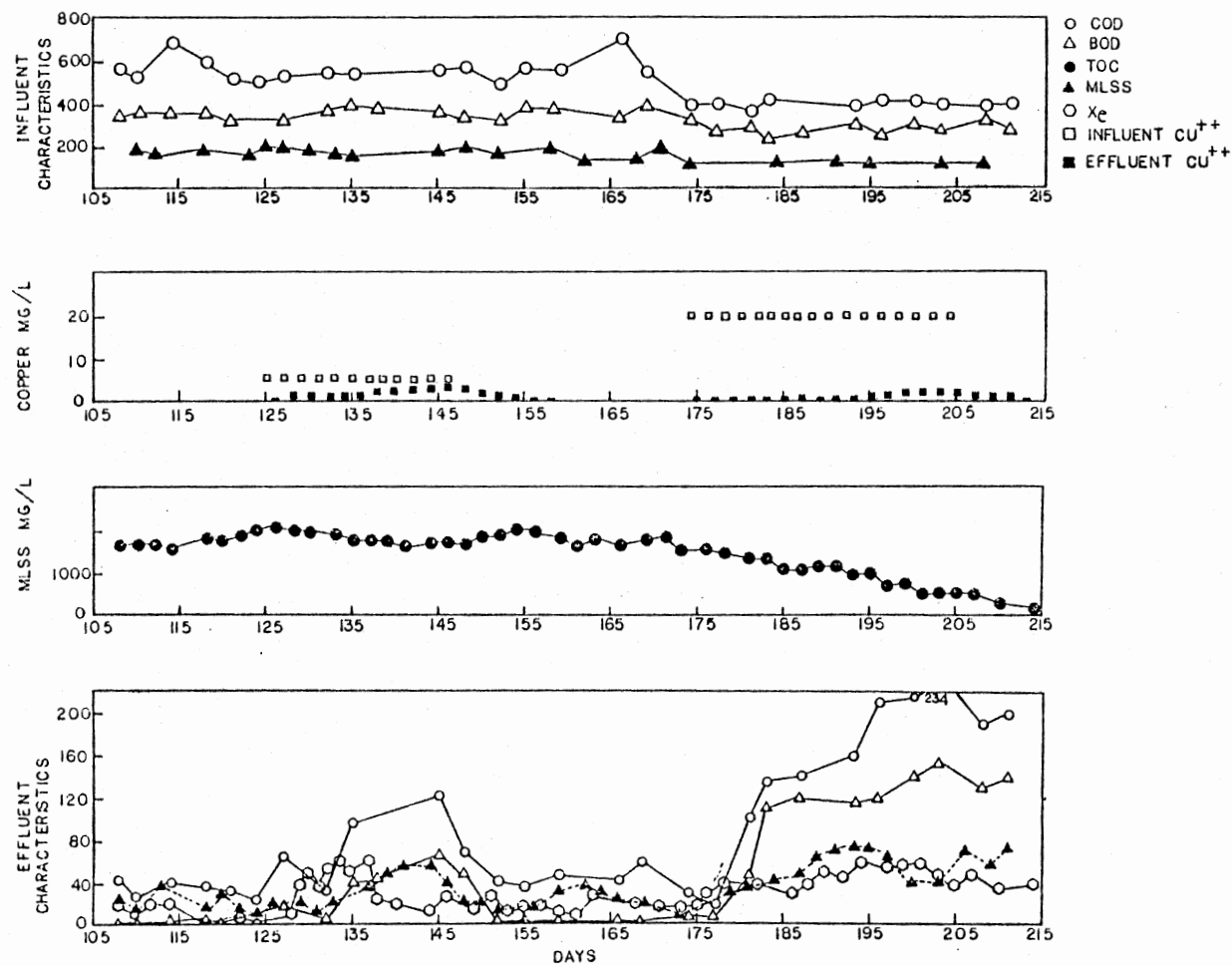


Figure 8. Operational Characteristics of Activated Sludge Process in the Presence and Absence of Copper

decrease in MLSS can be observed in Figure 8 at this metal concentration. This is also evident from Table III which shows a decrease in average value of 1887 to 1779 mg/l. An increase in effluent COD can also be observed during this period. The average value increased from 41 to 78.8 mg/l. BOD and TOC values also show an increase in the figure as well as the average values. BOD increased from 2.8 to 35.3 mg/l and TOC from 20.5 to 32.6 mg/l. The overall effect appears to be a significant reduction in effluent quality. This can be confirmed on Table IV wherein the student 't' values at no metal and 5 mg/l copper are not in the range of L_1 and L_2 , showing that there is a significant reduction in effluent quality.

To study the removal of copper by activated sludge the amount of copper in the influent as well as the effluent was measured during each day that the tests were run. In contrast to chromium, copper was adsorbed by the solids and the study indicated that the amount of copper in the effluent increased with time as seen as Figure 8. At the beginning, removal efficiency was about 95.4% and 20 days later, just before copper was stopped from being fed, the removal efficiency had decreased to about 45.8%. It was also observed that even when the influent copper was stopped, there was considerable amount of copper in the effluent. It finally disappeared after 10 days. The sludge also appeared to be dark brown in color and then regained its original light brown color when the copper disappeared. This indicates that the sorbed copper was gradually released by the biological solids.

The reactor was then operated without any metal for a period of 26 days. Table IV shows no significant difference at "no metal and no metal -(2)", i.e., the data collected before 5 mg/l of copper was

introduced and that collected before 20 mg/l of copper was introduced. 20 mg/l of copper was then introduced through the influent. The presence of 20 mg/l of copper drastically reduced the effluent quality. Average COD jumped from 49.7 to 139 mg/l. Average BOD and TOC values increased from 12.1 to 92.3 mg/l and 26.2 to 51.2 mg/l respectively. The MLSS (Figure 8) decreased to 500 mg/l on day 201. The student 't' values on Table IV at no metal and 20 mg/l of copper do not fall in the range of L_1 and L_2 indicating a significant reduction in effluent quality.

The comparative effect of 5 and 20 mg/l is seen on Figures 9 and 10. A much greater decrease in effluent quality can be observed at 20 mg/l than at 5 mg/l. It appears that 20 mg/l deteriorated the activated sludge unit.

K_S and K_e' values obtained during this period are shown in Figures 11 and 12 respectively. The only reliable values in Figure 12 appear to be that of COD wherein K_S increases indicating less biodegradability due to the presence of copper. Figure 12 shows more reliable results wherein K_e' decreases indicating the toxic nature of copper. However, not much significance can be attached to the K_S and K_e' values obtained in this study as the θ_c was kept constant.

Similar observations to 5 mg/l were obtained when the removal efficiency was measured at 20 mg/l of copper. (i.e. a decrease in removal efficiency of the metal with time and also small amounts of copper were in the effluent even when the copper was from begin fed). This can be seen on Figure 8. However the decrease in removal efficiency was much less as compared to that obtained from 5 mg/l. The removal efficiency at the beginning was about 98.7% and 30 days later just before copper

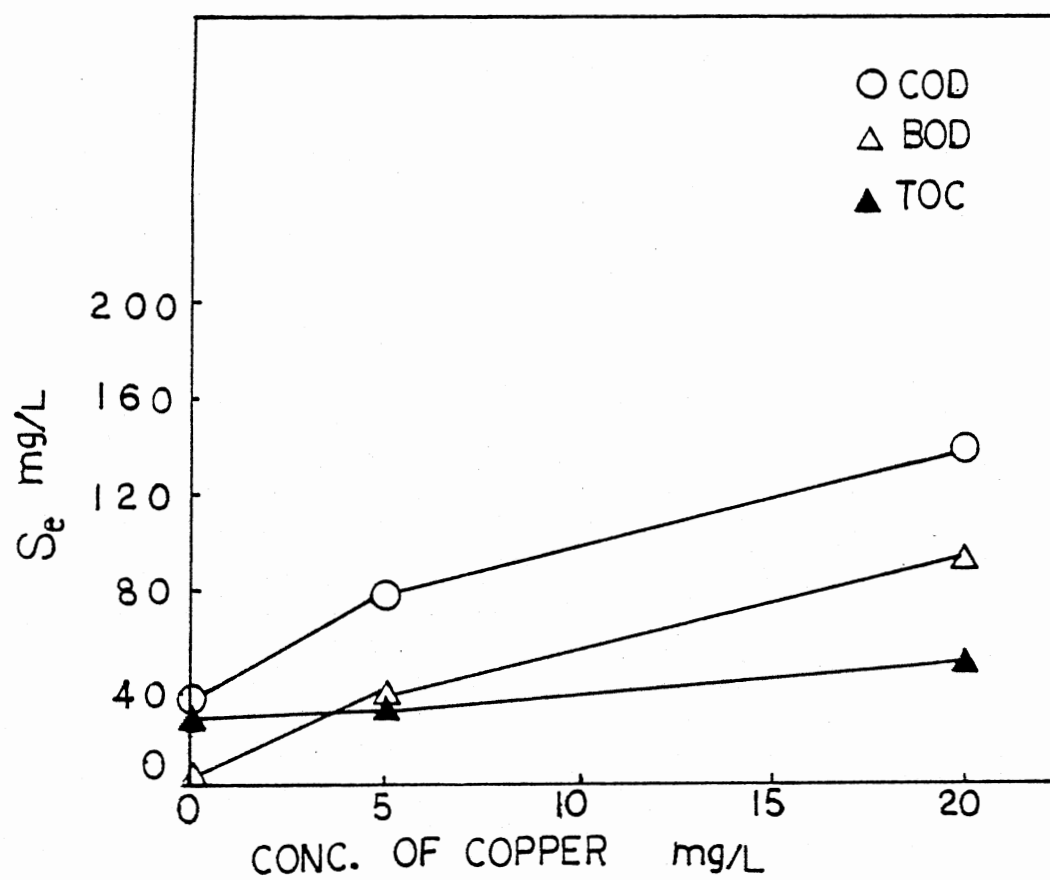


Figure 9. Effect on Effluent COD, BOD and TOC Due to Copper

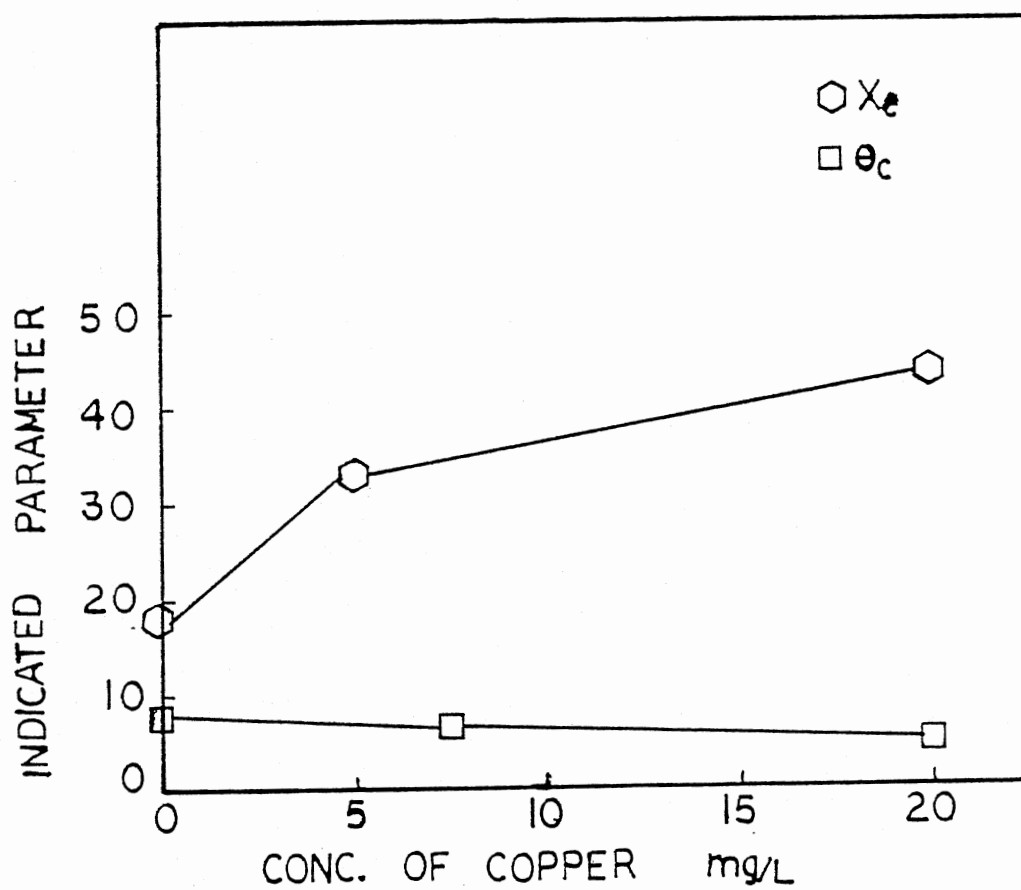


Figure 10. Effect on Effluent SS (X_e) and θ_c Due to Copper

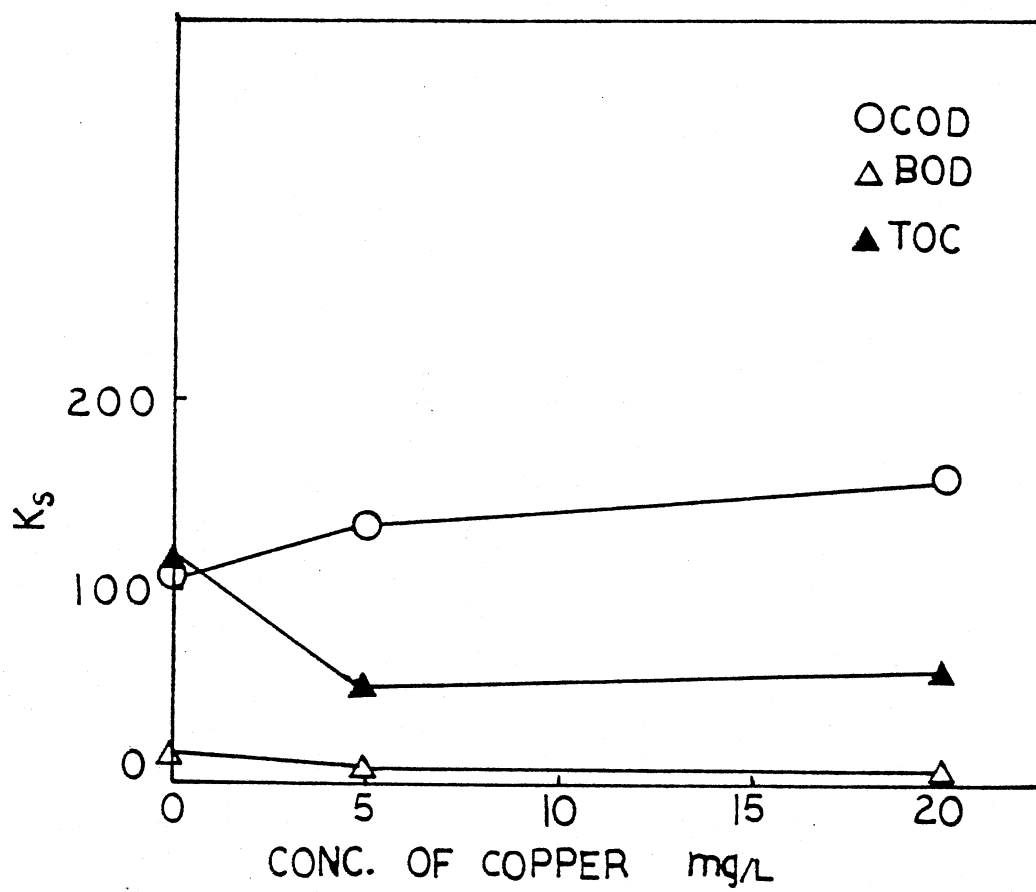


Figure 11. Effect on K_s Due to Copper

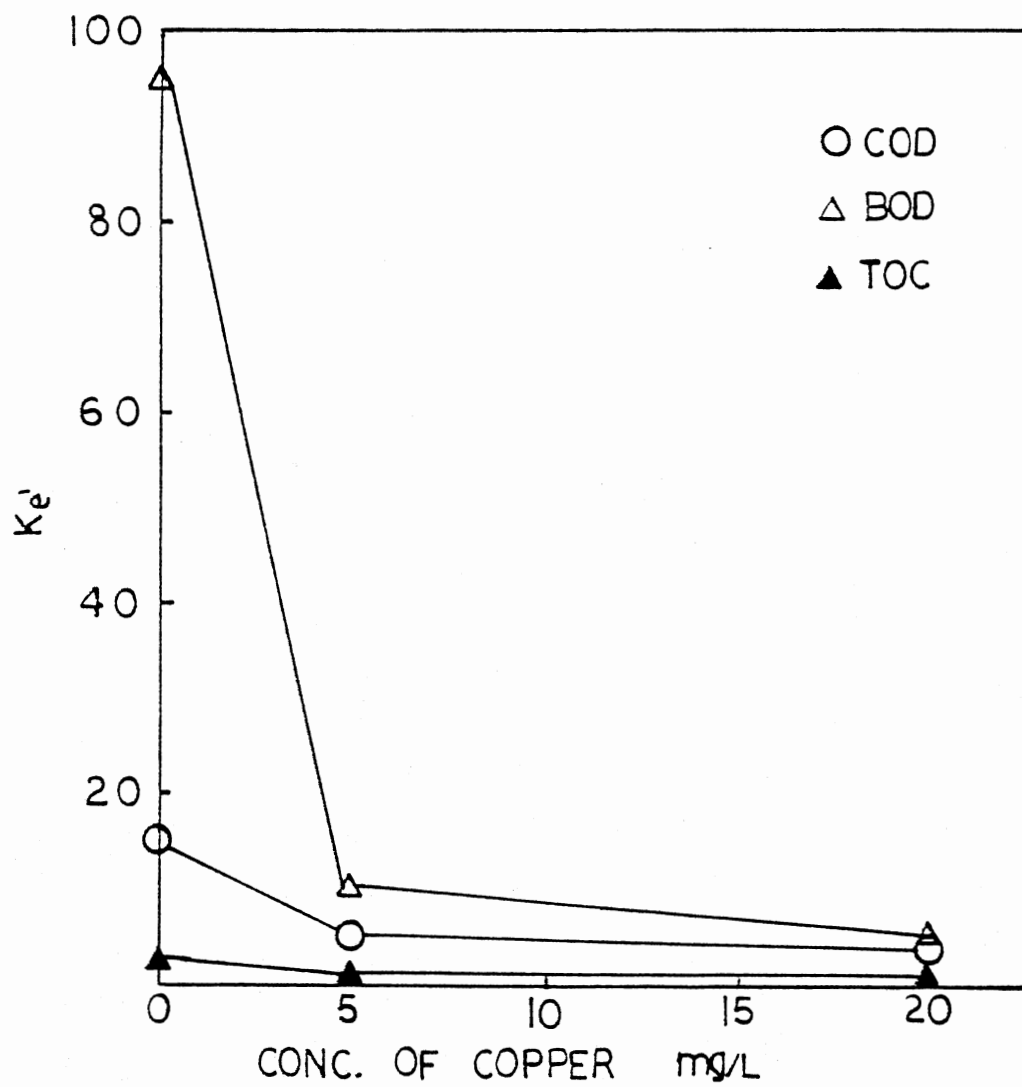


Figure 12. Effect on K_e' Due to Copper

was stopped the removal efficiency was 89%. This indicates that better removal efficiency of copper was obtained at 20 mg/l than at 5 mg/l.

The final statistical analysis shown on Table III indicates the effect when 20 mg/l of copper was stopped from being fed. It can be observed here that the biological solids and effluent quality decreased to such an extent that it refused to recover from the shock of 20 mg/l of copper.

CHAPTER V

CONCLUSIONS

1. Hexavalent chromium at 5 mg/l stimulated growth and produced a better quality effluent whereas 10 mg/l appeared to be toxic.

2. Copper in the form of copper sulfate at 5 mg/l was found to be inhibitory whereas 20 mg/l deteriorated the system to such an extent that it did not recover even when copper was withdrawn.

3. No removal of chromium either at 5 or 10 mg/l was obtained. However, good removal of copper both at 5 mg/l and 20 mg/l was obtained. Also the removal efficiency decreased with time more at 5 mg/l than at 20 mg/l, of copper.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

1. The effect of metal toxicity at various mean cell residence time.
2. The effect of chromium and copper on nitrification.
3. The effect of metal toxicity due to variations in pH and temperatures.
4. Determination of biokinetic constants under the influence of the metals and comparing these with those obtained without feeding any metal.
5. The degree of metal toxicity could also be determined from oxygen uptake.
6. The toxic effect of 10 mg/l of hexavalent chromium could be compared with trivalent chromium.

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