

A STUDY OF THE EFFECT OF SILVER AND ARSENIC ON THE
PERFORMANCE OF THE ACTIVATED SLUDGE UNITS

By

RAJU BERNARD

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Bachelor of Science

University of Mysore

Karnataka, India

1960

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Thesis Approved:

John W. Hearst

Thesis Adviser

Marion Bates

Don F. Kencannon

Newman D. Rucker

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Of late, heavy metal toxicity is gaining more and more importance. One of the reasons is that some of the heavy metals such as mercury, silver, and arsenic are found on the Environmental Protection Agency's (EPA) list of priority pollutants (1). Many other metals such as cadmium, chromium, lead, selenium, and zinc are listed as health hazards by the United States EPA (2).

Also, the presence of heavy metals in large concentrations in water is known to be toxic to aquatic organisms. The elimination of these metals from water through physical chemical processes has been found to be very expensive.

Toxic heavy metals enter wastewater from a variety of sources. Many industries using heavy metals discharge their effluents to the sewer system. The combustion of carbonaceous fuels may end up in the sewer system through urban runoff. As more and more developments are taking place in the industries, new uses of these metals are continually being discovered.

There are, of course, the standards for metals in the industrial discharges, but these standards reduce the quantities of metal discharged to municipal sewers by industries but they do not eliminate them, and they have no effect on the contributions from the domestic sources, runoff, or atmospheric deposition. Thus, it is inevitable

that as long as heavy metals are produced, there will be a certain irreducible quantity present in wastewaters.

During the past few years, the removal of heavy metals by biological treatment has received considerable attention. One can find in the literature, a large amount of work done on heavy metals such as copper, chromium, nickel, zinc, lead, and cadmium using biological systems.

The reasons for selecting silver and arsenic for this study were these two metals are listed on EPA's priority pollutant list, and very little work has been done on these two metals using biological systems as compared to other heavy metals found in wastewaters.

CHAPTER II

LITERATURE REVIEW

The activated sludge treatment process has been proven to remove heavy metals from wastewaters. Heavy metals have been defined by Murphy, Jr. (3). He based the definition on the specific quantity of the metals, location within periodic table and a specific zoological/botanical exchange. For the purpose of the review, the author says the heavy metals will be considered as those having atomic numbers 22-34 and 40-52 as well as the lanthanides and actinides. The most common heavy metals include Ti, V, Cr, Fe, Ni, Cu, Zn, As, Ni, Ag, Cd, Sn, Hg, and Pb. Heavy metals have also been defined similarly by Murphy and Spiegel (4).

The exact mechanism of the removal of heavy metals by microorganisms is not clear, but several possible theories have been proposed. Lester (5) states that the possible mechanisms are

1. Physical trapping of the precipitated metals in the sludge floc matrix.
2. Binding of soluble metals to bacterial extracellular polymers.
3. Accumulation of soluble metal by the cells.
4. Volatilization of metals to atmosphere.

Suzarittanonta and Sherrard (6) stated that the extent of removal of metals depends on various factors such as the mean cell resident time (θ_c), the type of metals in wastewater, the pH of wastewater, and the concentration of the metal in wastewater. Sterrit and Lester (7)

worked on ten different heavy metals at six different sludge ages. They found that the removal efficiency increased with the increase in sludge age. They also observed relative affinity of different heavy metals for the biomass at different sludge ages. They found the following series, in decreasing order of affinity of the metals for the biomass.

Cr > Cd > Ag > Pb > Zn > Cu > Ni, Co, Mn, No

Nelson et al. (8) have also confirmed that the biological solids retention time (θ_c) has an effect on the metal adsorption and that the metal affinity for the bacterial solids increases as θ_c increases.

Oliver and Cosgrove (9) state that the metals are removed by the activated sludge system in two stages. The first stage is primary settling of insoluble metals or metals adsorbed to particulates. The second stage is by adsorption of dissolved metals or fine particulate metals to the biological floc and final settling in the secondary clarifier.

Geesey (10) has gone into detail about the mechanism of adsorption of the metals to the microorganisms. He has stated that

A primary mechanism that has evolved to establish and maintain associations between one microbe and another or between one microbe and its environment involves the action of extracellular polymeric substances (EPS). These substances are of biological origin and participate in the formation of microbial aggregates. These aggregations may range in size from microcolonies which contain only a few cells to thick masses of slime that engulf an entire lake or stream. (p. 9)

The author further states that there are two types of extracellular polymers, one, the capsules which adhere to cell walls, and two, the slime which is released from the cell and exists free in the medium.

Extensive work on the effect of heavy metals on activated sludge was carried out in 1965 and the results were published by the United States Public Health Service (11). The metals used were chromium, copper, nickel, and zinc; and the parameters examined were the BOD, COD, and suspended solids. These experiments did not provide a basis for the rational prediction of the toxic behavior. However, the experiments revealed useful information for others to pursue further. The report stated that the metal concentration applied to the influent was less than or equal to 10 mg/l. At this dose they found a 5% reduction in treatment efficiency. Nitrification was almost totally inhibited, and there was a decrease in the oxygen uptake.

At the same time, Barth et al. (12) reported that completely mixed activated sludge units removed 50 to 60% of the heavy metals applied. Jackson and Brown (13) further reported that activated sludge units were able to remove 54 to 93% copper, 10-100% chromium, and 60-100% zinc. The total metal concentrations of these metals in the influent were less than 10 mg/l.

Yemada et al. (14) reported an order of magnitude estimation of the mercury in the activated sludge unit. They claim that, with a liquid phase concentration of 100 mg/l of HgCl_2 , the equilibrium solid phase concentration is 96 mg/g of HgCl_2 in dry sludge solids or 7.1 weight % mercury. The latter metal concentration also permitted 90% COD removal of a synthetic glucose-peptone feed in the semi-continuous activated sludge systems.

Dehkordi (15), working on activated sludge unit and using cadmium, lead, and zinc, found 96.5% metal removed and 90% COD removal using 17.20 mg/l of cadmium and 20 days SRT, 95.5% metal removal and 92% COD

removal using 19-26 mg/l lead and SRT of 12 days. Also, 99.5% metal removal and 96.5% COD removal using 37.63 mg/l zinc and SRT of 12 days.

Brown and Lester (16), using a pure, continuous culture of a capsular strain of K aerogenes (NCTC 8172) which was grown at a range of dilution rates in an Ultraferm fermentation system and a laboratory activated sludge unit with a synthetic sewage medium, analyzed the extracellular polymers for various θ_c from 3 to 18 days. They extracted the extracellular polymers from the activated sludge at different sludge ages and came up with the following facts. The residual protein and hexose sugar concentrations showed a very slight increase from 3 to 18 days θ_c . Hexose sugar and DNA concentrations in extracted samples increased considerably from 3 to 9 days θ_c and showed little further increase up to 18 days θ_c . The protein concentrations increased up to 12 day θ_c and showed little further increase from 12 to 18 day θ_c . The ratio of hexose : protein : DNA remained almost constant at 5:2:1 at different sludge ages. This showed that increasing the sludge age from 3 to 9 days increased the concentrations of bacterial extracellular polymers present in activated sludge mixed liquors and further increases in θ_c had only a marginal effect on the extracellular polymers.

Nelson et al. (17) worked with a completely mixed internal cell recycle laboratory model activated sludge unit under steady state. They used copper, cadmium, and zinc as the toxic metals and sludge ages of 1 to 5. They came up with the fact that the adsorption of metals increased as the θ_c increased from 1 to 5 days. They also found that for the same θ_c , the adsorption increased as the pH increased from 6.5 to 7.9. Further, they found that the affinity of the bacterial solids for the metals was in the order of $Zn > Cu > Cd$.

Brown and Lester (16) working on the metal removal in activated sludge state that it is the combination of flocculation and settling that is the mechanism by which the metal removal is achieved. They say that many activated sludge bacteria produce extracellular polymers, and these polymers appear to play an important role in flocculation. They further state that metal removal efficiency in activated sludge varies enormously depending on the conditions prevailing. The plant-operating factors such as SVI, sludge age, suspended solids removal, and dissolved oxygen, and the physical and chemical factors affecting removal are temperature, pH, metal concentration, metal solubility, metal valences, concentration of complexing agents and particle size. The main biological factor is the concentration of extracellular polymer present.

They also state that the metal toxicity varied from metal to metal and in a study lasting 5 days with a concentration of 20 mg/l metal, the following series of decreasing toxicity was noticed.

Hg > Ag > Cr (III) > Al > Fe > Cu > Ni > Cd > Co > Cr (VI) > Sn > Zn.

Examining the literature it is found that very few investigators have carried out the work on silver and arsenic using activated sludge.

Silver

Poon and Bhayani (18) using silver, chromium, copper, nickel, and zinc up to concentrations of 25 mg/l, worked on the activated sludge culture and Geotrichum candidum culture and showed that silver is the most toxic of the metals studied to Geotrichum candidum and to the activated sludge bacteria. The authors also found that the toxicity

of various heavy metals varied with biological species and sludge age. They found that the aged cultures were affected less by toxic metals.

Sterritt and Lester (7), working on silver along with nine other metals using activated sludge found that the silver removal efficiency increased with the increase of sludge age. They found the variation very marked with silver; they found a minimum efficiency of 1% at sludge age of 9 days and 70% removal at a sludge age of 15 days. They further generalized that the optimum metal removal occurred at sludge ages of 15 days and 18 days. They have also found silver stood third in a series of decreasing order of affinity of metals for the biomass. Chromium and cadmium were the other two metals which had better affinity than silver.

Heitmuller et al. (19) evaluated the acute toxicity of 54 industrial chemicals to Sheepshead minnows and found antimony was most toxic followed by thallium and silver.

Murphy and Spiegel (4), discussing the toxicity of heavy metals on biomass, state that silver is a strong inhibitor of enzyme activity.

Arsenic

Murphy (3), working on bioaccumulation and toxicity of heavy metals, states that of all the arsenic compounds (arsenic III, arsenic V, sodium dimethyl arsenate, and disodium methyl arsenate), arsenic III was found to be the most toxic form and subjected to the greatest organism accumulation.

In the article "Trace Metal Removal by Waste Water Treatment" by United States EPA (20), it is reported that 28 to 73% of arsenic can be removed by secondary treatment.

Kincannon and Esfandi (21) working with activated sludge, PAC activated sludge, granular activated carbon, and a resin column for the removal of priority pollutants from a pharmaceutical wastewater found that arsenic was the metal of most concern. They had a removal efficiency of 20.6% using an activated sludge unit with an influent concentration of 5.2 mg/l.

CHAPTER III

MATERIALS AND METHODS

Experimental Apparatus

Two bench-scale activated sludge units were used in the experiments. The activated sludge units, operated as continuous flow systems with (total) internal cell recycle and were constructed entirely of 1/4 inch thick plexiglass. The unit consisted of an aeration compartment and a settling compartment that were separated by an adjustable baffle (also of plexiglass). The dimensions of the aeration tank were 7" long x 4" wide x 6" deep and the volume was 2.75 liters; the volume of the clarifier was 1.40 liters. The feed lines from the feed bottle to the reactors were polyethylene tubes with stainless steel connections at the pump head. The apparatus is shown in Figure 1.

Air was provided to the aeration basin by two stone diffusers, 5/8" diameter and 1" long, with air passing into a cotton filter to trap any water or grease, to assure an adequate supply of oxygen to the biological solids. The D.O. remained at 5 to 7 mg/l. The same air also served the purpose of mixing the solids in the aeration tank. The air stones were so adjusted as to provide a suction to recycle the settled biological solids from the settling chamber into the aeration tank.

The ambient air temperature in the room where the units were

located was maintained fairly constant throughout the study at about 25°C, and the pH in the reactors held between 7 and 8 throughout the study.

The continuous flow condition was accomplished by continuously pumping the feed solution to the aeration tank. A "milroyal" controlled volume pump provided continuous flow to the system pumping at the rate of 4.6 ml/min. This provided a hydraulic detention time of 10 hours.

A 25 liter glass carboy was used to hold the feed solution for pumping. The effluent flowed by gravity from the settling compartment from each unit and was collected in two 25 liter glass carboys.

The heterogeneous biological population used to originally start-up the units in this study was obtained from the activated sludge units at the Southside Wastewater Treatment Plant in Tulsa, Oklahoma.

Feed Supply to the Organisms

The synthetic waste used in this study consisted of a dilute solution of "SEGO", a diet drink manufactured by PET, Incorporated, and supplemental nutrients (N,P). The feed concentration was adjusted to a BOD of about 250 mg/l, a COD of 600 mg/l, and TOC of 175 mg/l. The other nutrients added, as shown in Table I, were required for growth and synthesis of the heterogeneous microbial population. Seventy ml of SEGO and twenty ml of the salt-solution (N & P) were added to the feed bottle and diluted with tap water to a volume of 25 liters. The dilution water was added in such a way as to promote mixing to obtain a uniform feed solution.

TABLE I
SALT CONSTITUENTS

Ammonium Sulfate - $(\text{NH}_4)_2\text{SO}_4$	200 grams
Magnesium sulfate - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	80 grams
Ferric Chloride - $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.4 grams
Phosphoric Acid - H_3PO_4	32 ml
Calcium Chloride - CaCl_2	8 grams
Make up to 1 liter in tap water and dissolve.	

A separate solution of silver, using silver nitrate (AgNO_3) and arsenic V, using sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) were prepared in required dilutions and used along with the feed for the approximate concentrations of the metals.

Operation and Sampling Procedures

The two continuous flow internal recycle reactors described above were initially operated for three months at constant mean cell resident times (θ_c) of six days and eighteen days. This was done to ensure steady state conditions.

The reactors were then fed 0.05 mg/l of silver in the form of AgNO_3 for about 60 days. This concentration was selected because the MCL of silver in drinking water is 0.05 mg/l. Then a shock load twelve times the initial silver concentration (0.6 mg/l) was administered and

continuously fed while the units were operated for another 60 days. Another shock load ten times the previous dosage (6.0 mg/l) was used and, after operating at this condition for about 23 days, a final shock load of 18 mg/l was used and the units were run under this condition for seven days, at which time the units were terminated.

After the completion of the experiments with silver, the sludge was discarded. New sludge was again obtained from the Southside Water Treatment Plant in Tulsa, Oklahoma. The new sludge was allowed to reach steady state at the same θ_c of 6 days and 18 days. This time, arsenic doses of 1 mg/l for 25 days, 6 mg/l for 22 days, 20 mg/l for 21 days, and 80 mg/l for 7 days were fed to the activated sludge units. Samples of influent, effluent, and MLSS were collected for analysis. The parameters analyzed for consisted of COD, TOC, and BOD of the influent and effluent; metal concentrations in feed, effluent, and the sludge; D.O. uptake and sludge settling characteristics, along with suspended solids of the reactor and the effluent.

Analytical Technique

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

Biochemical Oxygen Demand (BOD₅)

The method set forth in the 14th edition of Standard Methods for the Examination of Water and Wastewater (22) was used for this purpose. The probe method was used for determining dissolved oxygen. The BOD of influent and effluent were measured once a week.

Chemical Oxygen Demand

The chemical oxygen demand of the influent and effluent were measured three times a week using the procedure as outlined in the Standard Methods (22).

Total Organic Carbon

The TOC of the influent and effluent were measured three times a week. The Beckman 915 TOC Analyzer was used to carry out this analysis.

MLSS and Suspended Solids

Whatman 934-AH glass microfiber filters were used to filter the MLSS and the effluent samples. The procedure for solids determination is given in Standard Methods (22).

Dissolved Oxygen Uptake

Dissolved oxygen uptake by the mixed liquor in the reactor was determined using the procedure given in Standard Methods (22).

Sludge Settling Characteristics

Sludge settling characteristics were determined using the procedure given in the Standard Methods (22).

Metal Determination

A Perkin-Elmer 5000 atomic absorption spectrophotometer with a CA-400 graphite furnace was used for metal determination. The methods used for analysis of both silver and arsenic are given in Analytical

Methods for Atomic Adsorption Spectrophotometry (23) by Perkin-Elmer. The metal concentrations in feed, effluent, and sludge were determined on samples drawn three times a week.

The flame was used for samples containing higher concentrations of silver and arsenic. The furnace was used for samples containing low concentrations. The procedure given in Analytical Methods for Atomic Adsorption Spectrophotometry (23) by Perkin-Elmer was used for silver low and high concentrations and arsenic high concentration samples. For analyzing low concentrations of arsenic, method number 206.2 given in the Methods for Chemical Analysis of Water and Waste by the United States EPA (24) was used.

Sludge Digestion and Sample Preparation

Concentrated HNO_3 was used to digest the silver sludge. The procedure followed was by Krishnamurthy (25).

For digesting arsenic sludge, nitric acid with 30% H_2O_2 was used. For the sample preparation for use with the furnace, a 5% nickel nitrate solution was used. The procedure was given in the Methods for Chemical Analysis of Water and Wastes published by the United States EPA (24).

CHAPTER IV

RESULTS AND DISCUSSIONS

The investigation consisted of two parts. The first part was to determine the effect of AgNO_3 on the performance of the activated sludge treatment process. The four different concentrations of silver introduced into the influent were 0.05 mg/l, 0.6 mg/l, 6 mg/l, and 18 mg/l at a constant flow rate of 6.624 l/day. The effects were studied using 6 days and 18 days SRT.

The second part of the investigation was investigation of the effect of sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) on the activated sludge treatment process, keeping the same SRT's of 6 days and 18 days. Four different concentrations of sodium arsenate, 1 mg/l, 6 mg/l, 20 mg/l, and 80 mg/l, were used. The flow rate in this case was also maintained at 6.624 l/day.

The above concentrations of silver and arsenic were selected based on a literature survey. It is mentioned in the book Waste Water Treatment Plant Design, by a joint committee of the W.P.C.F. and A.S.C.E. (26), that the threshold concentrations of silver and arsenic inhibitory to carbonaceous removal in the activated sludge process are 5 mg/l and 0.1 mg/l, respectively. To verify the inhibitory levels reported in the literature for silver and arsenic, an inhibition screening test as described by Stover and Kincannon (27) was conducted. The results of these tests are shown in Figures 2 and 3.

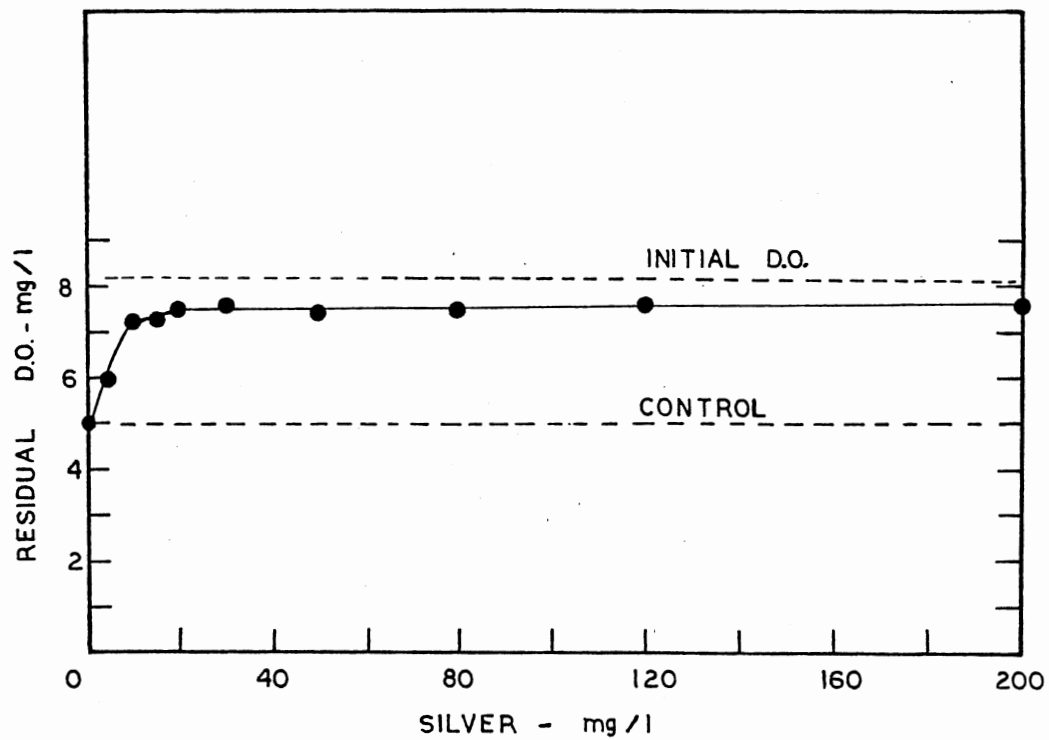


Figure 2. Inhibition Screening Testing for Silver Using an Unacclimated Seed

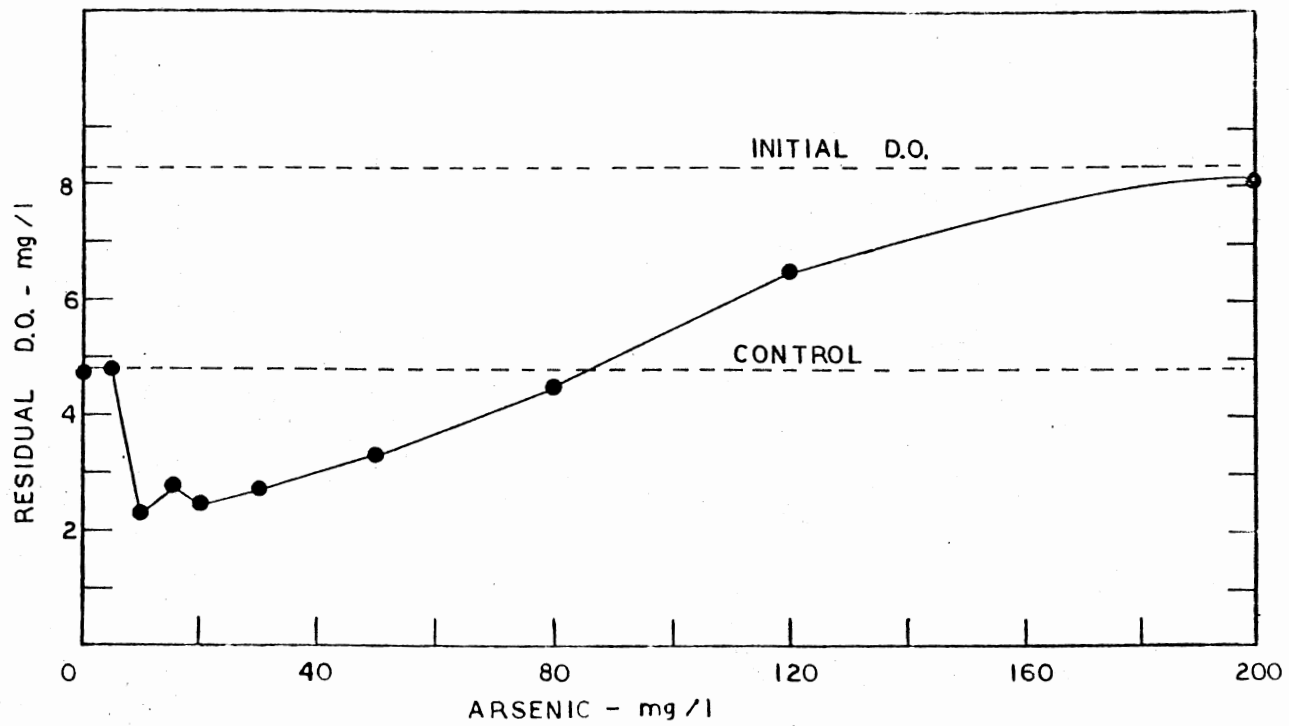


Figure 3. Inhibition Screening Test for Arsenic Using an Acclimated Seed

Silver Results

Tables II and III summarize the results of the average BOD, TOC, COD, and metal concentrations under the different metal loadings. Table II is for the units with an SRT of 6 days while Table III is for units with an SRT of 18 days.

It can be seen that, in both the 6-day and 18-day units, the organic removal efficiency decreased steadily as the concentration of silver increased from 0.05 to 6 mg/l. When 18 mg/l of silver was added to the influent, the organic removal efficiency went down considerably, from an effluent BOD of 19 mg/l to 105 mg/l for the 6-day unit, and from 18 mg/l to 84 mg/l for the 18-day unit.

The MLSS in the reactor steadily decreased as the concentration of silver increased from 0.05 to 6 mg/l. The maximum decrease normally occurred on the day of the shock load and gradually increased thereafter. When 18 mg/l was added to the influent, the solids in the effluent increased and the units showed no signs of recovery. This can be seen in Figure 4 and Figure 5.

The metal removal efficiency was very good up to 6 mg/l of silver, and when 18 mg/l silver was added, the efficiency went down from 99% to 86%. The concentration of metal in the sludge increased steadily as the metal concentration in the influent was increased to 18 mg/l. This can be seen in Figure 6. Also, when the 18 mg/l silver shock load was added, the concentration was very toxic and the microorganisms started dying, and within seven days, the solids concentration in the reactors were reduced considerably from 1510 mg/l to 810 mg/l in the 18-day unit, and from 920 mg/l to 597 mg/l in the 6-day unit.

TABLE II

SUMMARY OF ACTIVATED SLUDGE SYSTEM TREATMENT PERFORMANCE
USING SILVER AND ARSENIC AND SRT 6 DAYS

Compound	BOD			TOC			COD			Metal Analysis			
	Inf. mg/l	Eff. mg/l	Trt. Eff.	Inf. mg/l	Eff. mg/l	Trt. Eff.	Inf. mg/l	Eff. mg/l	Trt. Eff.	Inf. mg/l	Eff. mg/l	Sludge mg/gm	Trt. Efficiency
Control	257	2	99.1	135	5	96.1	605	16	97.4	--	--	--	--
0.05 mg/l silver	245	9	96.1	131	9	93.1	607	31	94.9	0.053	0.002	0.04	98.0
0.6 mg/l silver	240	14	94.2	150	10	93.2	599	42	93.0	0.64	0.014	1.03	97.5
6 mg/l silver	254	19	92.6	149	20	86.6	600	50	91.7	6.2	0.05	16.08	99.0
18 mg/l silver	252	105	58.2	149	34	76.9	616	190	69.2	18.3	2.5	59.01	86.4
Control	251	6	97.61	152	4	97.5	544	12	97.7	--	--	--	--
1.0 mg/l arsenic	258	9	96.4	156	6	96.3	588	21	96.4	1.06	0.51	1.05	52.76
6 mg/l arsenic	252	14	94.5	153	8	94.6	552	30	94.3	6.12	3.09	7.16	50.09
20 mg/l arsenic	262	23	91.2	152	13	91.6	550	42	92.3	20.97	13.3	17.60	36.65
80 mg/l arsenic	260	42	83.7	151	32	78.8	539	92	82.9	81.53	68.22	33.87	16.32

TABLE III

SUMMARY OF ACTIVATED SLUDGE SYSTEM TREATMENT PERFORMANCE
USING SILVER AND ARSENIC AND SRT 18 DAY

Compound	BOD			TOC			COD			Metal Analysis			
	Inf. mg/l	Eff. mg/l	Trt. Eff.	Inf. mg/l	Eff. mg/l	Trt. Eff.	Inf. mg/l	Eff. mg/l	Trt. Eff.	Inf. mg/l	Eff. mg/l	Sludge mg/gm	Trt. Efficiency
Control	257	3	98.7	135	6	95.6	605	18	97.1	--	--	--	--
0.05 mg/l silver	246	7	97.2	131	8	94.1	607	29	95.2	0.053	0.002	.06	96.2
0.6 mg/l silver	240	10	95.9	150	9	93.9	599	30	94.9	0.64	0.006	1.11	99.1
6.0 mg/l silver	254	18	92.9	149	18	81.1	600	47	92.1	6.2	0.035	12.47	99.4
18.0 mg/l silver	252	84	66.7	149	52	65.0	616	216	69.3	18.3	2.08	82.99	88.6
Control	251	3	98.3	152	3	97.9	544	13	97.5	--	--	--	--
1.0 mg/l arsenic	258	8	97.0	156	7	95.5	587	16	97.3	1.06	0.46	1.05	56.6
6.0 mg/l arsenic	252	11	95.5	153	7	95.2	552	27	95.0	6.12	3.0	4.74	50.98
20 mg/l arsenic	262	19	92.7	152	10	93.2	550	37	93.3	20.97	15.22	14.97	27.41
80 mg/l arsenic	260	38	85.4	151	20	86.8	539	71	86.8	81.53	64.50	22.82	20.89

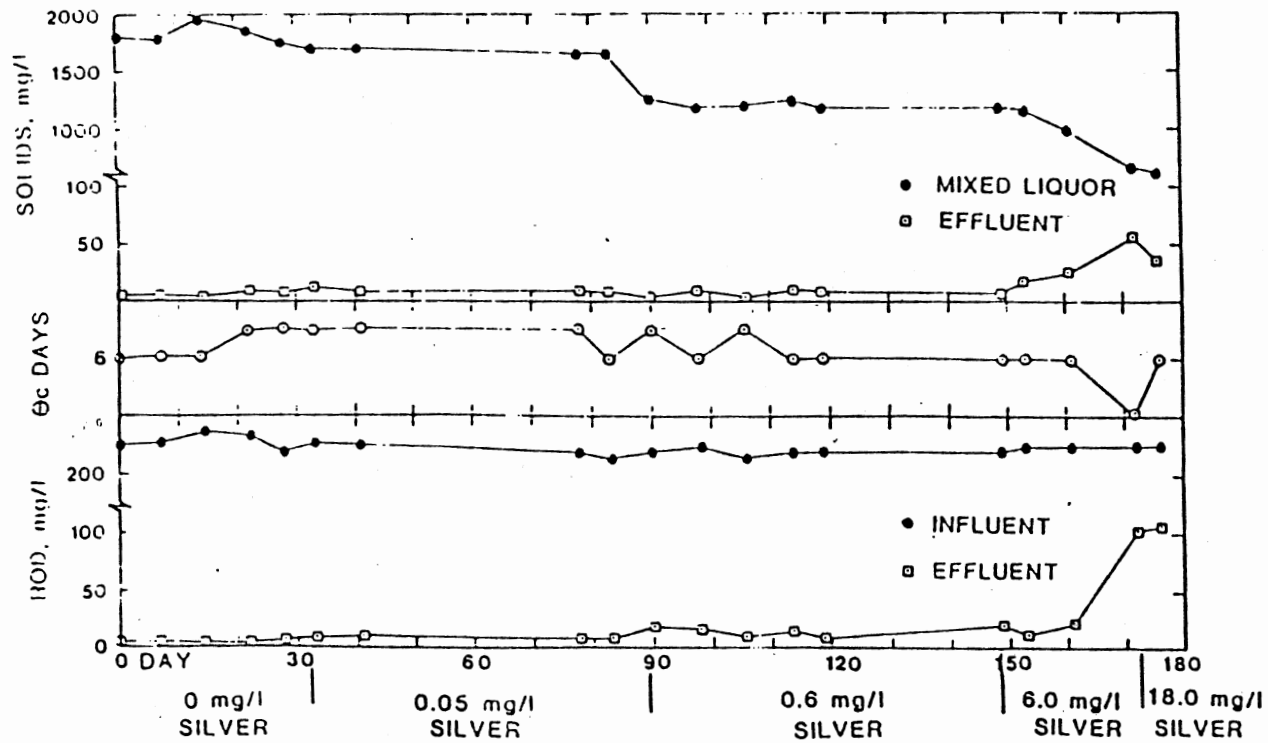


Figure 4. Operational Data for 6 Day θ_c Activated Sludge with Silver

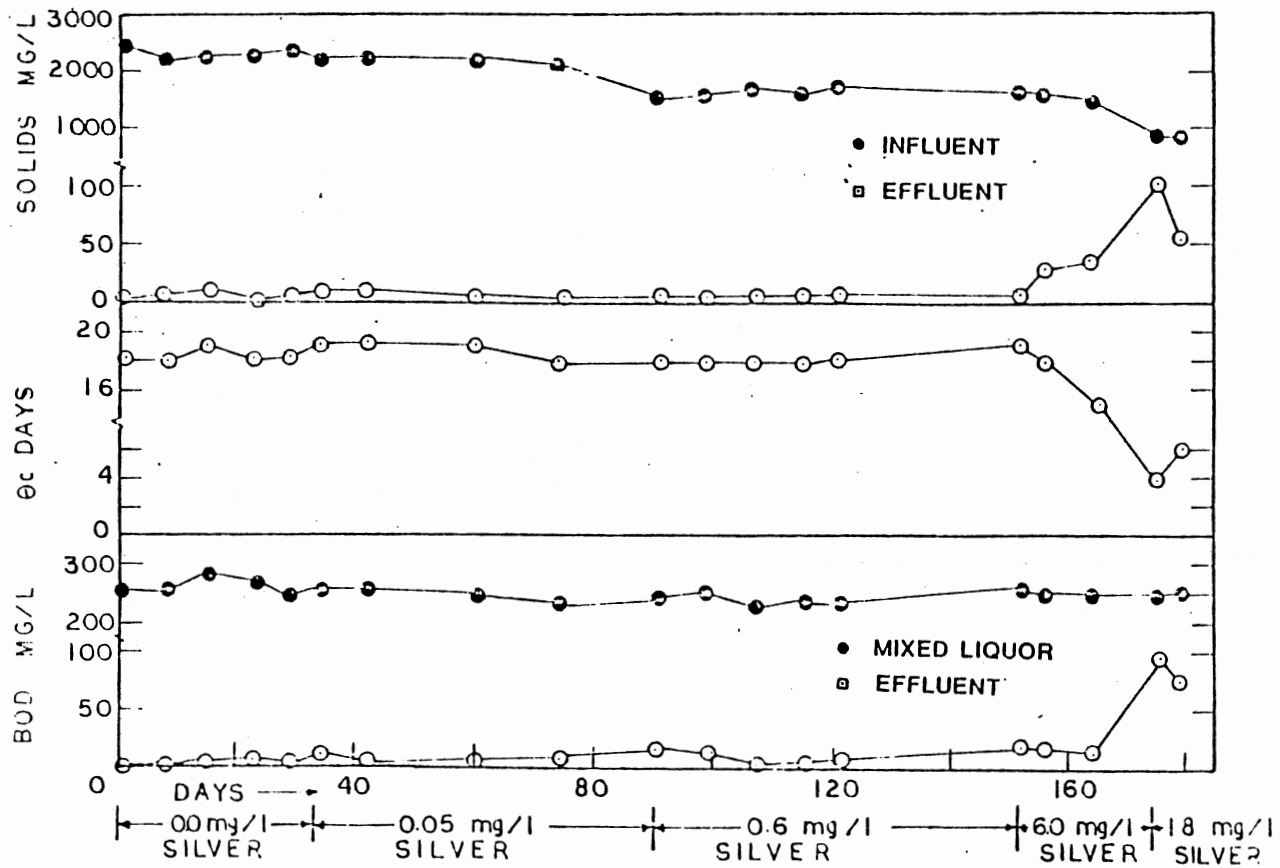


Figure 5. Operational Data for 18 Day θ_c Activated Sludge Unit with Silver

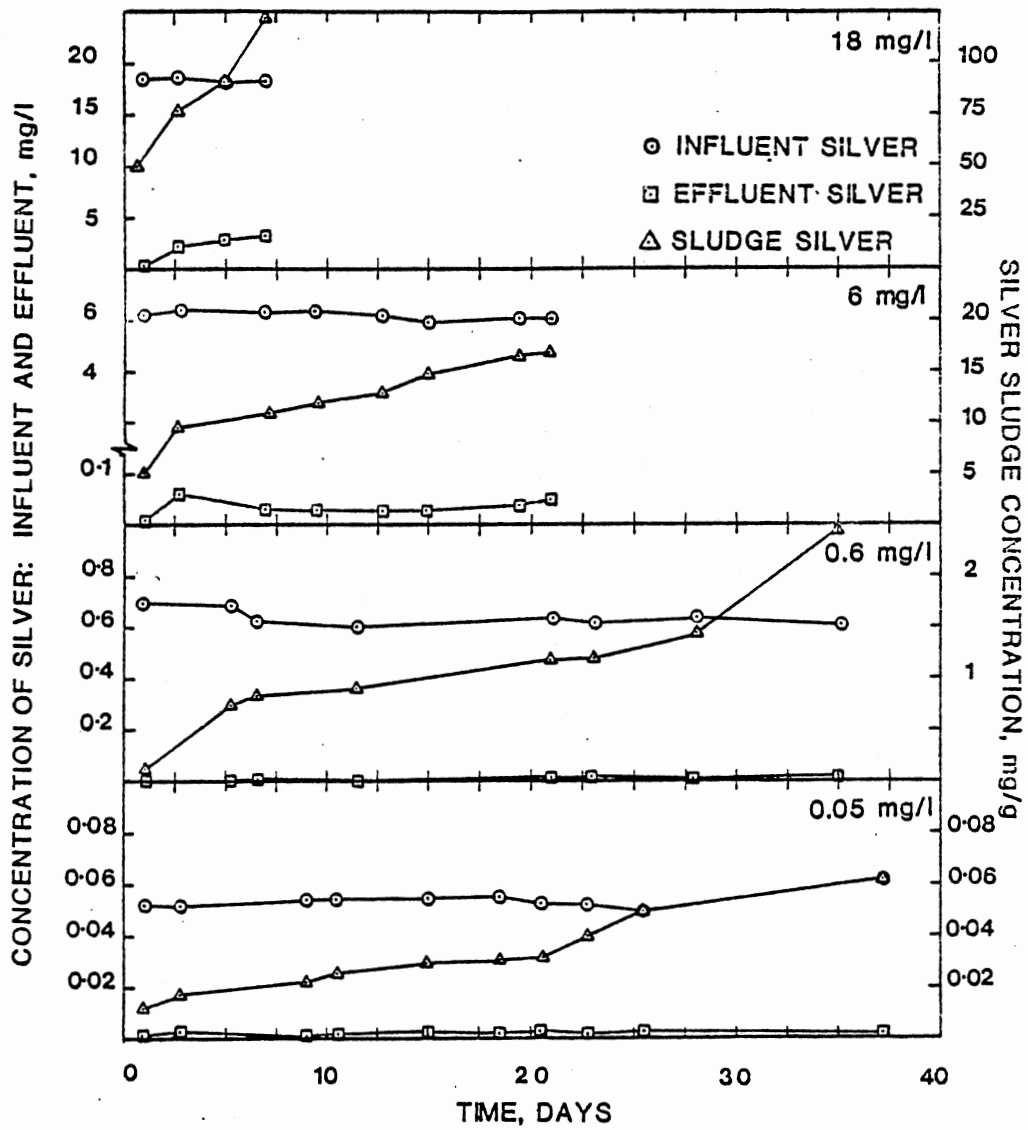


Figure 6. Fate of Metal in Silver Unit at 18 Day θ_c

The settling characteristics of the sludge improved with increases in the metal concentration. The SVI decreased from 251 to 156 in the 6-day unit, and from 354 to 160 in the 18-day unit. This can be seen in Figures 7 and 8. Also, the microorganisms were put under the microscope and no trace of filamentous growth at higher concentrations of silver was found.

Although in the literature many types of models exist for the activated sludge process, only one model's biokinetic constants were calculated from the data obtained in this study. The biokinetic constants calculated were those using the Kincannon and Stover model (28) (29).

The inverse of substrate utilization versus the inverse of the food-microorganism ratio ($1/U$, $1/F/M$) was plotted for each concentration as can be seen from Figures 9, 10, 11, 12, and 13, and the calculated values for U_{\max} and K_B are tabulated in Table IV. It is seen that the U_{\max} and K_B steadily decreased as the silver concentration increased. This proves that, as the concentration of the pollutant increases, the substrate utilization, U_{\max} decreases. This indicates that the silver concentration of 18 mg/l was highly toxic to the microorganisms. This is in agreement with the work done by Brown and Lester (16), who stated that silver is only second to mercury in toxicity to microorganisms.

Another interesting point came from the results of the DO uptake experiments. On the day the shock load was administered to the units, the DO uptake increased by about 4.0 mg/gm/hr. The day after the shock, however, the DO uptake had returned to approximately the same value as before the addition of the higher metal concentration. This

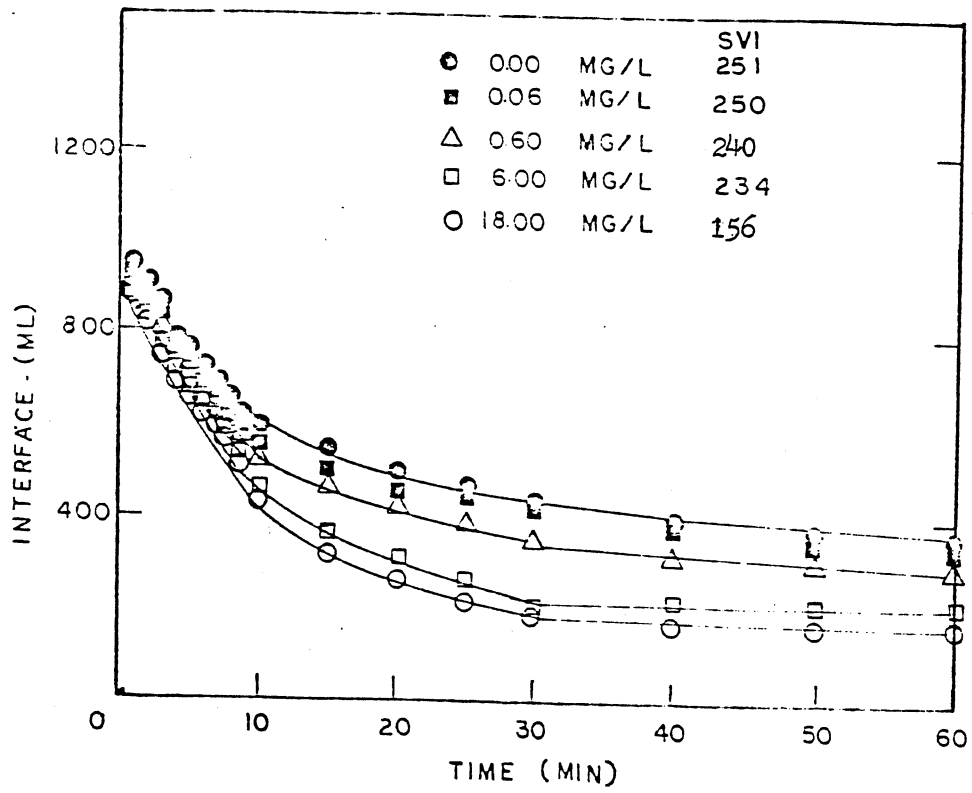


Figure 7. Sludge Settling Characteristics for Activated Sludge Unit with SRT of 6 Days and Using Silver

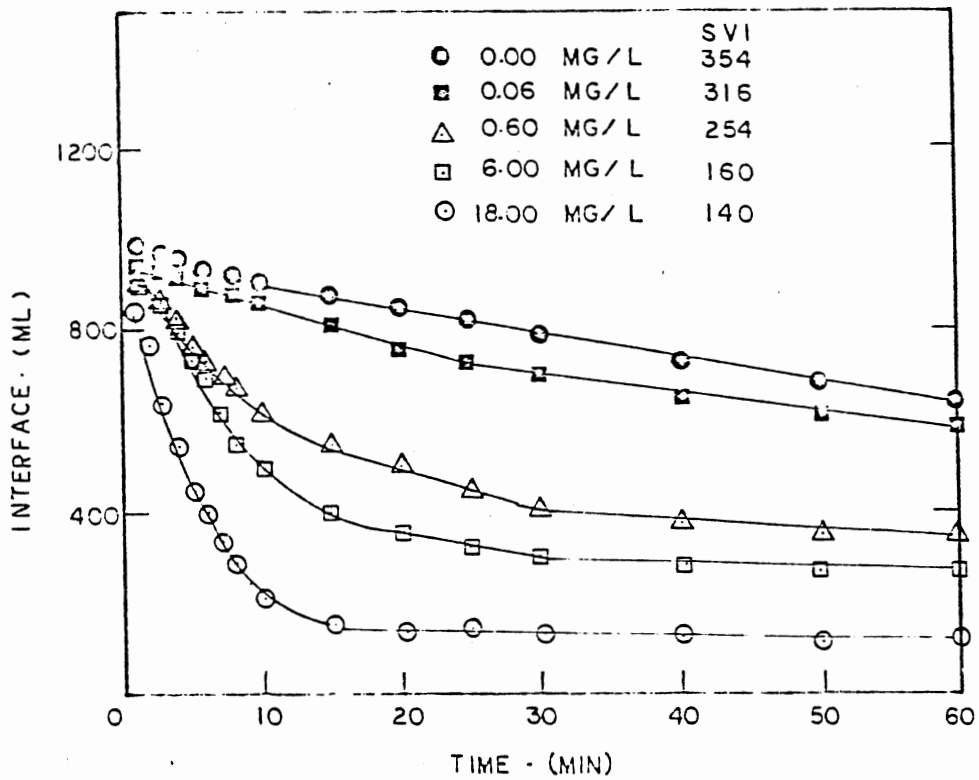


Figure 8. Sludge Settling Characteristics for Activated Sludge Unit with SRT of 18 Days and Using Silver.

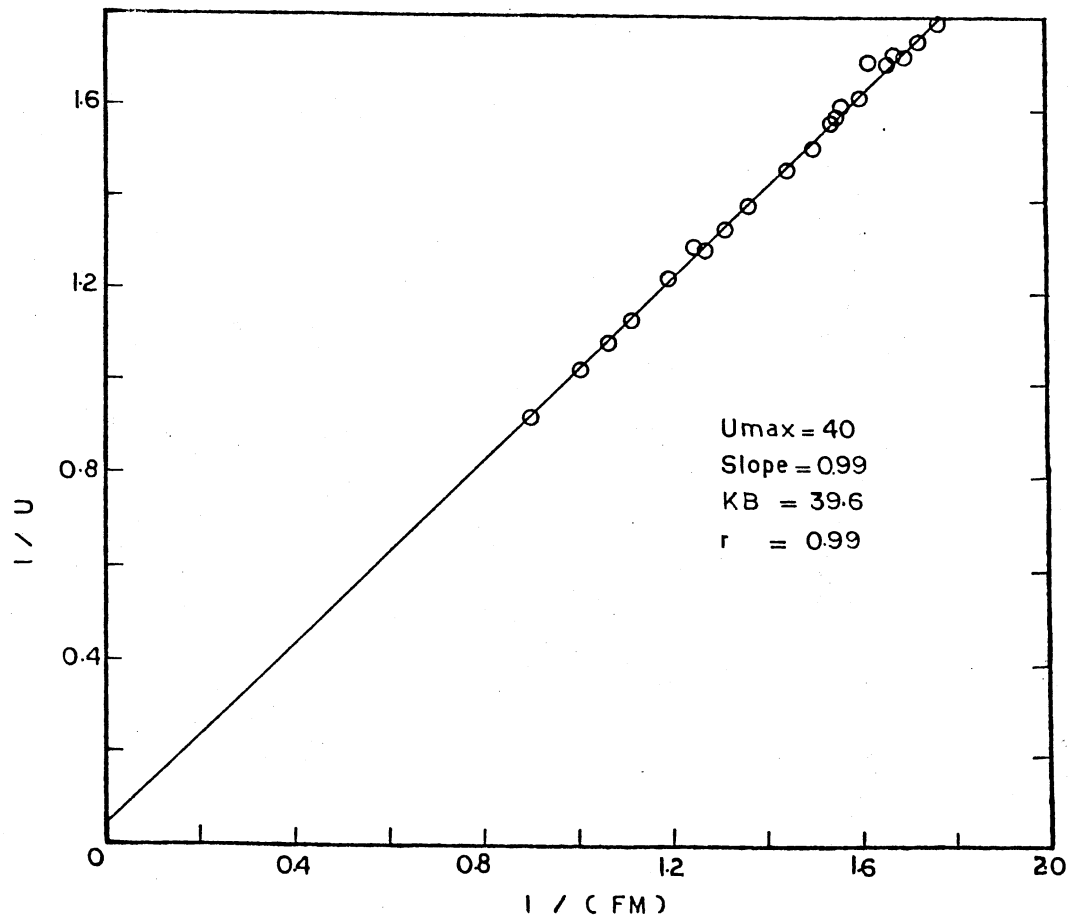


Figure 9. Substrate Utilization vs. Food-Microorganism Ratio for Control (0 mg/l Silver Based on COD Values)

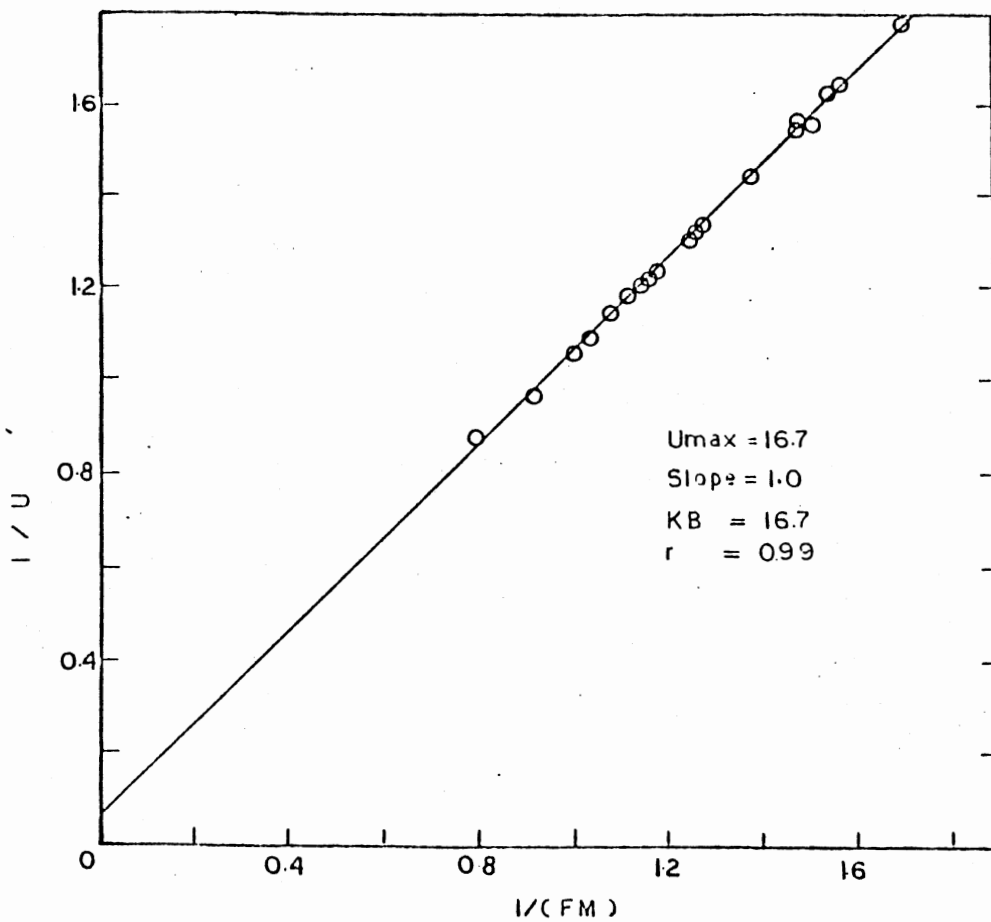


Figure 10. Substrate Utilization vs. Food-Microorganism Ratio for 0.05 mg/l Silver Based on Cod Values.

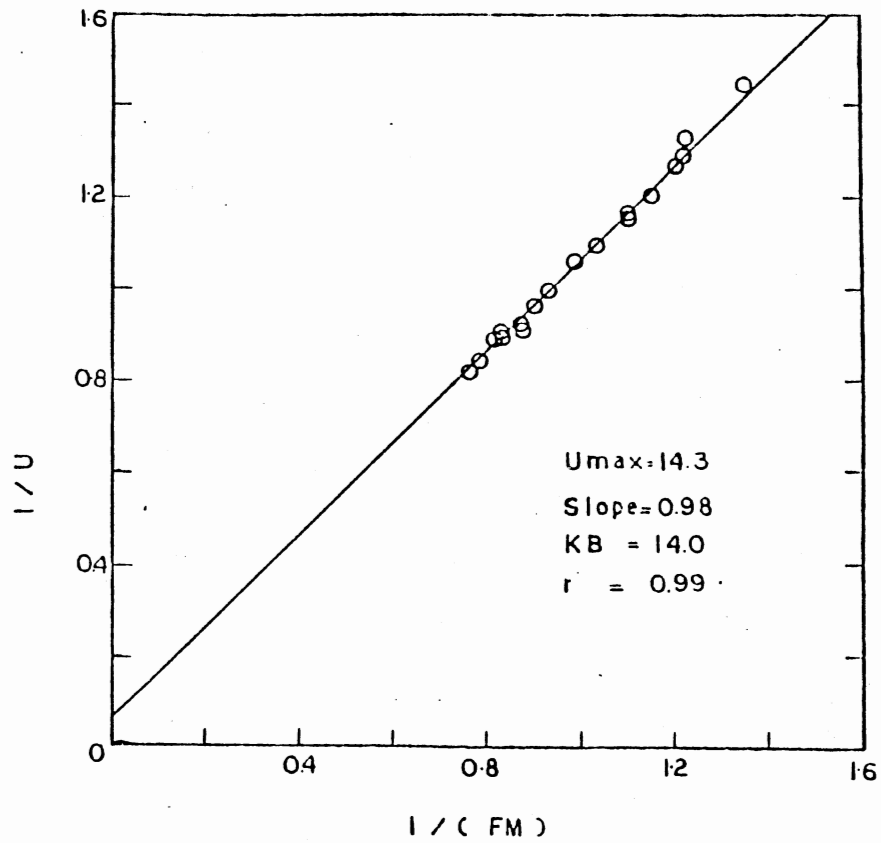


Figure 11. Substrate Utilization vs. Food-Microorganism Ratio for 0.6 mg/l Silver Based on COD Values

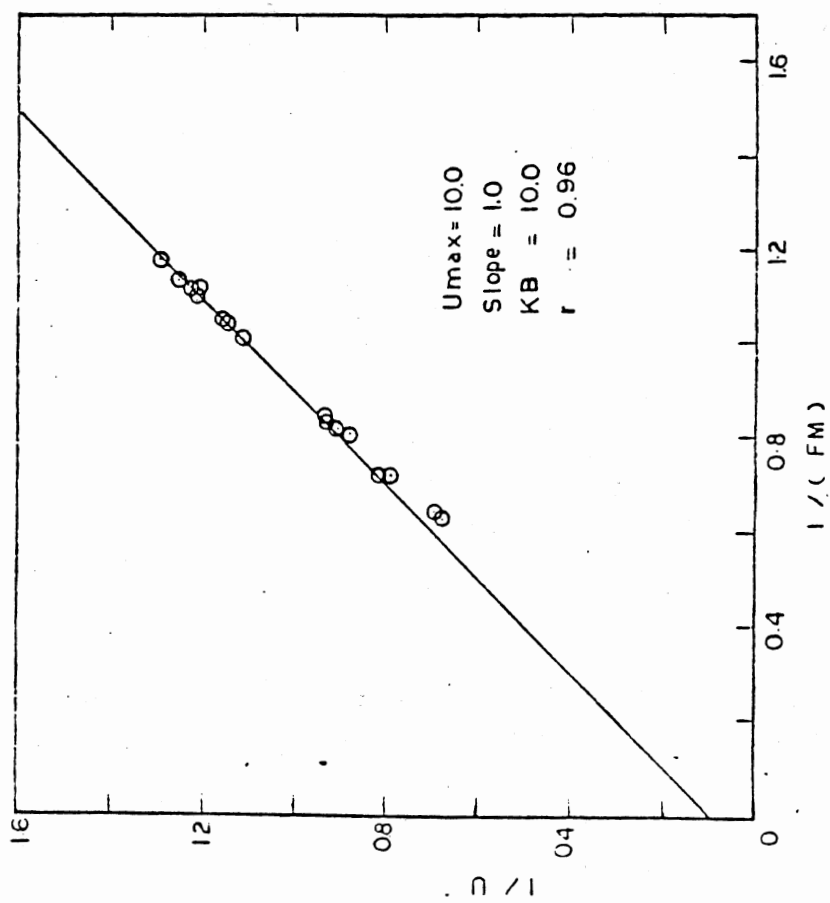


Figure 12. Substrate Utilization vs. Food-Microorganism Ratio for 6 mg/l₂ Silver Based on COD Values

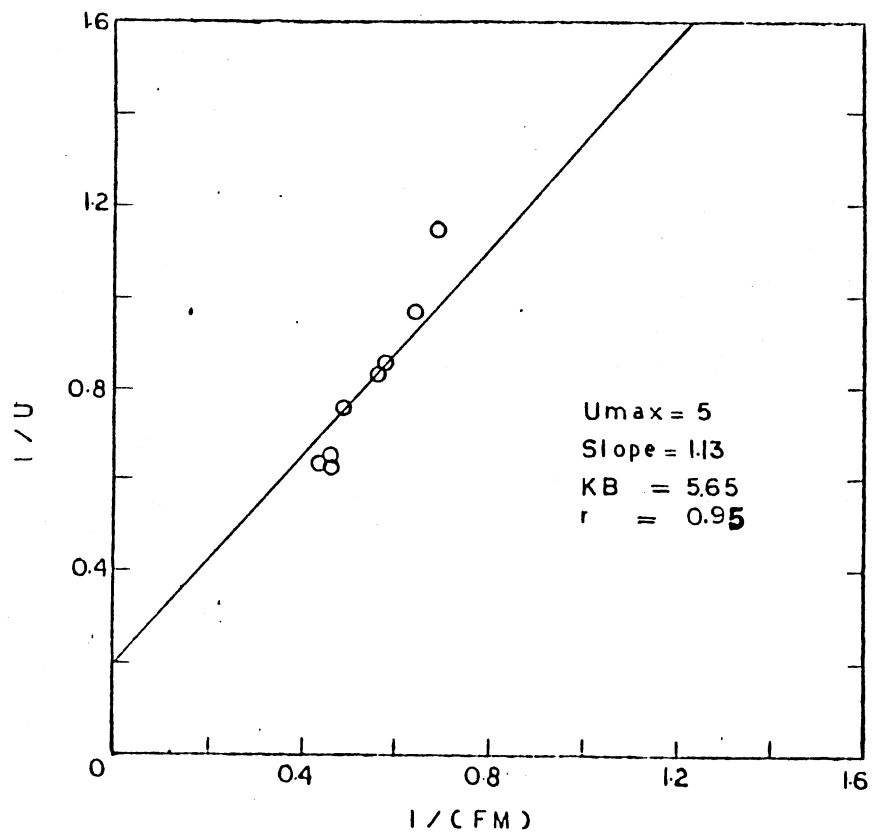


Figure 13. Substrate Utilization vs. Food-Microorganism Ratio for 18 mg/l Silver Based on COD Values

TABLE VI

U_{\max} , K_B AND r VALUES FOR DIFFERENT CONCENTRATIONS
OF SILVER BASED ON COD VALUES

Concentrations of Silver in Feed	U_{\max} day ⁻¹	K_B day ⁻¹	r
0 mg/l (control)	40.0	39.6	0.99
0.05 mg/l	16.7	16.7	0.99
0.6 mg/l	14.3	14.0	0.99
6 mg/l	10.0	10.0	0.96
18 mg/l	5.0	5.65	0.95

Unlike silver units, the MLSS in the arsenic units increased steadily with every shock load of arsenic, as can be seen from Figures 14 and 15. This may be due to the fact that arsenic was not as toxic to the microorganisms, and also may be due to the type of extracellular polymer the microorganisms produce. In the case of arsenic, the MLSS was visually very slimy.

Geesey (9) stated that there are two types of extracellular polymers, one is the capsule and the other is slime and can be released from the cell and exist free in the medium. The microorganisms might have produced the slimy polymers which may be the cause for the increasing MLSS in the reactors.

As in the case of silver, the settling characteristics improved with the increase in the metal concentration. The SVI decreased from 384 to 48 in the 6-day unit and from 258 to 51 in the 18-day unit. This can be seen in Figures 16 and 17.

The adsorption of metals to microorganisms also increased as the concentration of metal in the influent increased. However, the increase in the adsorption was very poor compared to silver. This can be seen in Figure 18. This also shows that the affinity for arsenic is very poor.

The inverse of the substrate utilization versus the inverse of the food-microorganism ratio ($1/U$, $1/F/M$) was plotted for each concentration. This can be seen from Figures 19, 20, 21, 22, and 23. The calculated values for U_{\max} and K_B values are tabulated in Table V and it can be seen that, as in the case of silver, the substrate utilization, U_{\max} , is considerably reduced as the arsenic doses are increased,

On the whole, the performance of the 18-day units were slightly

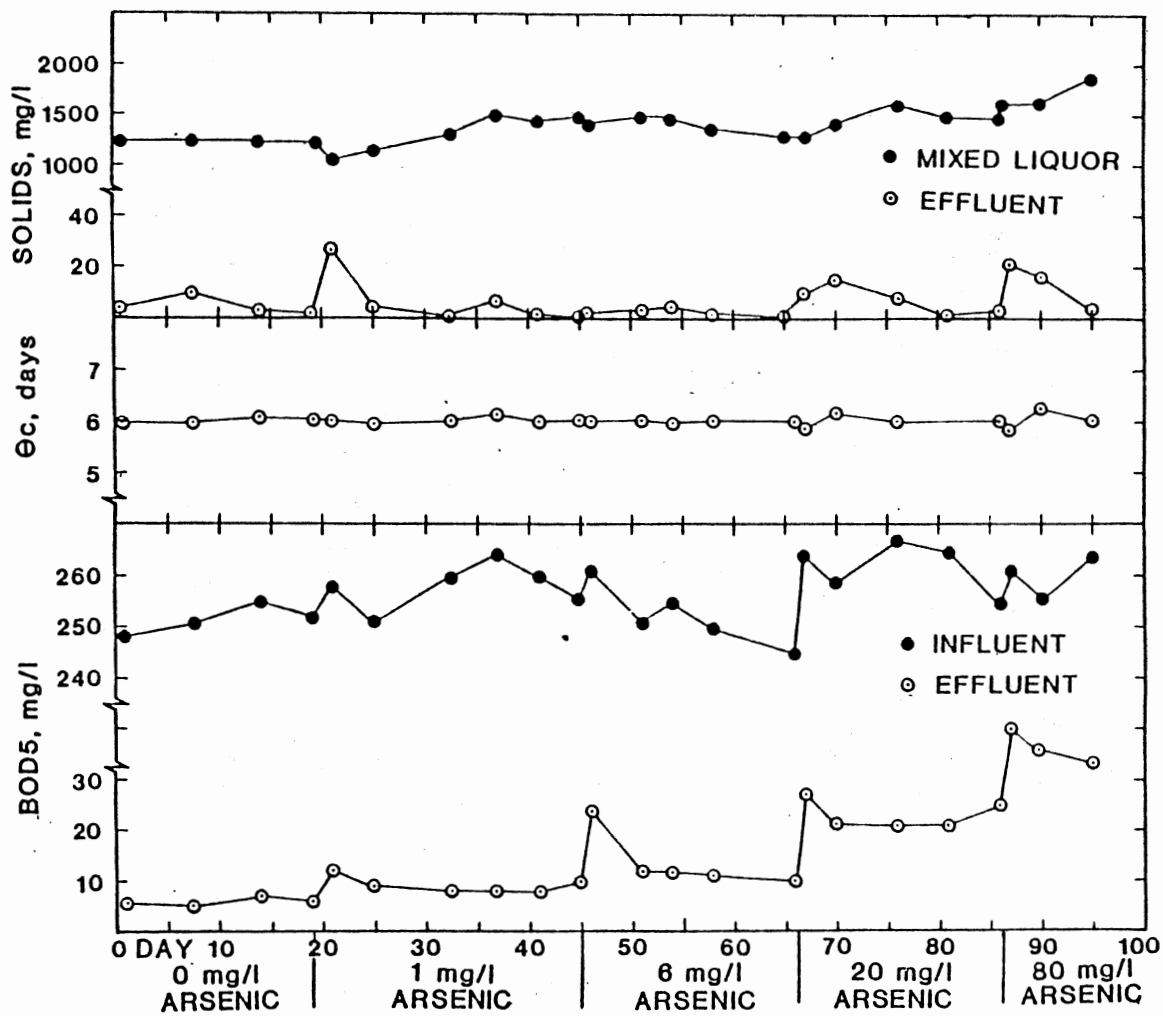


Figure 14. Operational Data for 6 Day θ_c Activated Sludge Unit with Arsenic

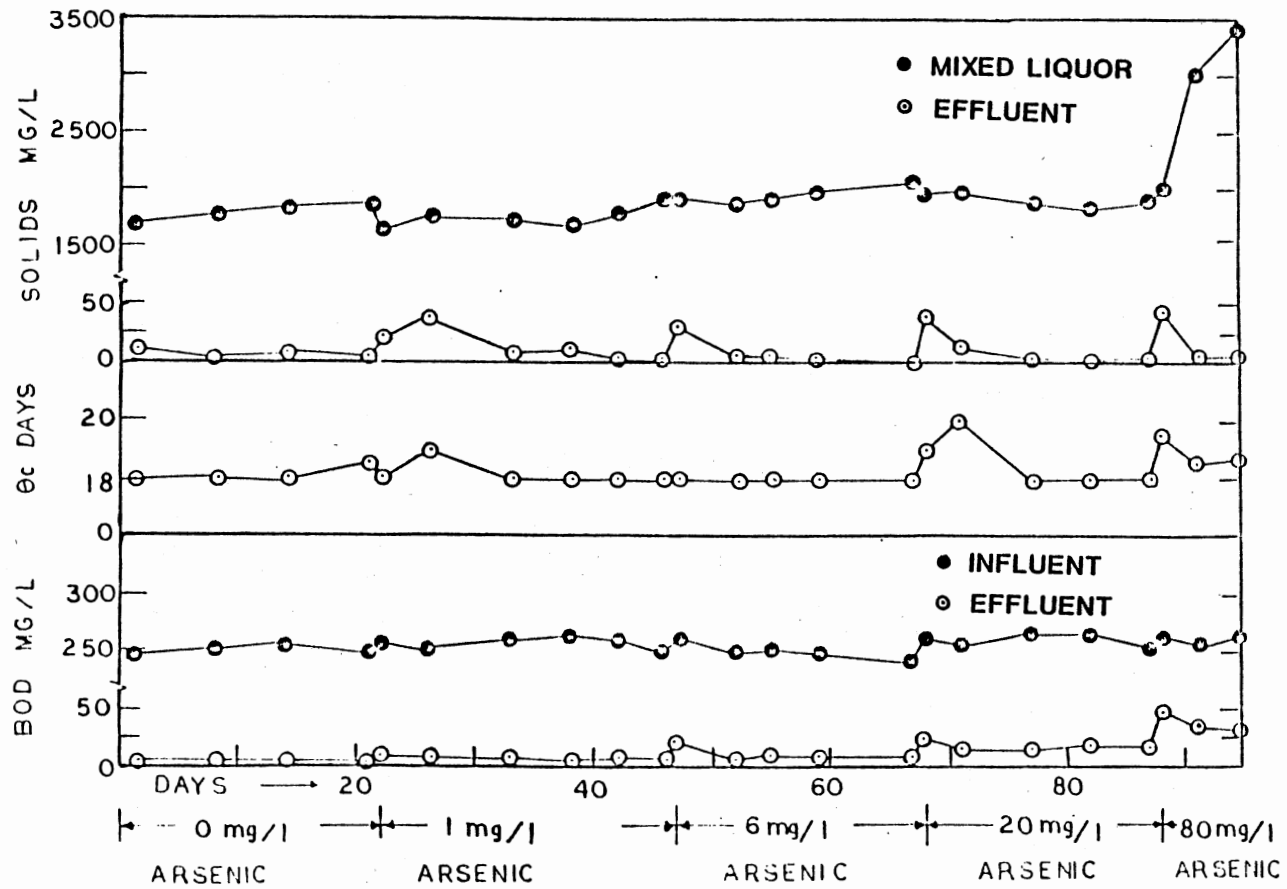


Figure 15. Operational Data for 18 Day θ_c Activated Sludge Unit with Arsenic

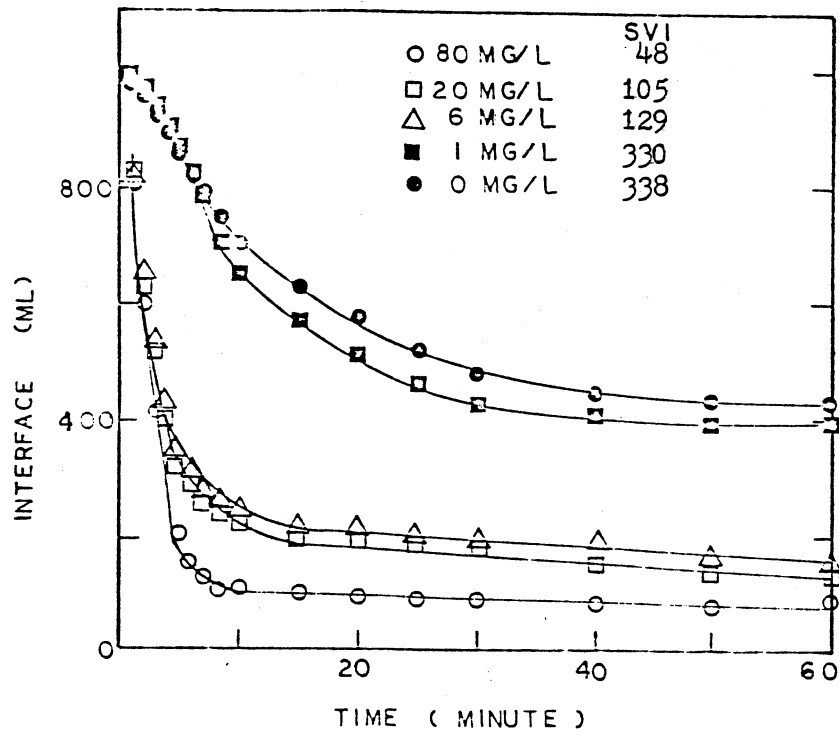


Figure 16. Sludge Settling Characteristics for Activated Sludge Unit with SRT of 6 Days and Using Arsenic

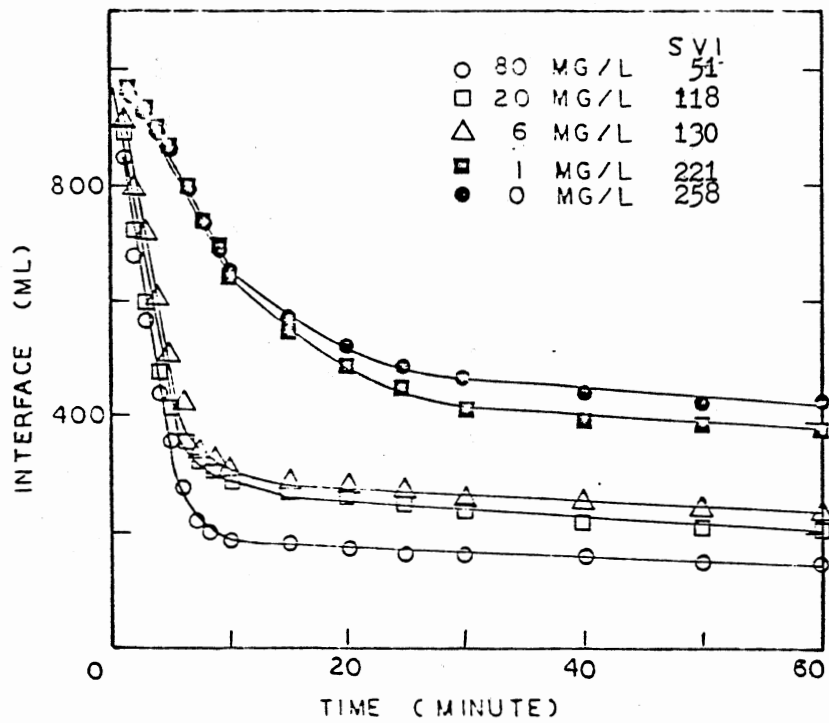


Figure 17. Sludge Settling Characteristics for Activated Sludge Unit with SRT of 18 Days and Using Arsenic

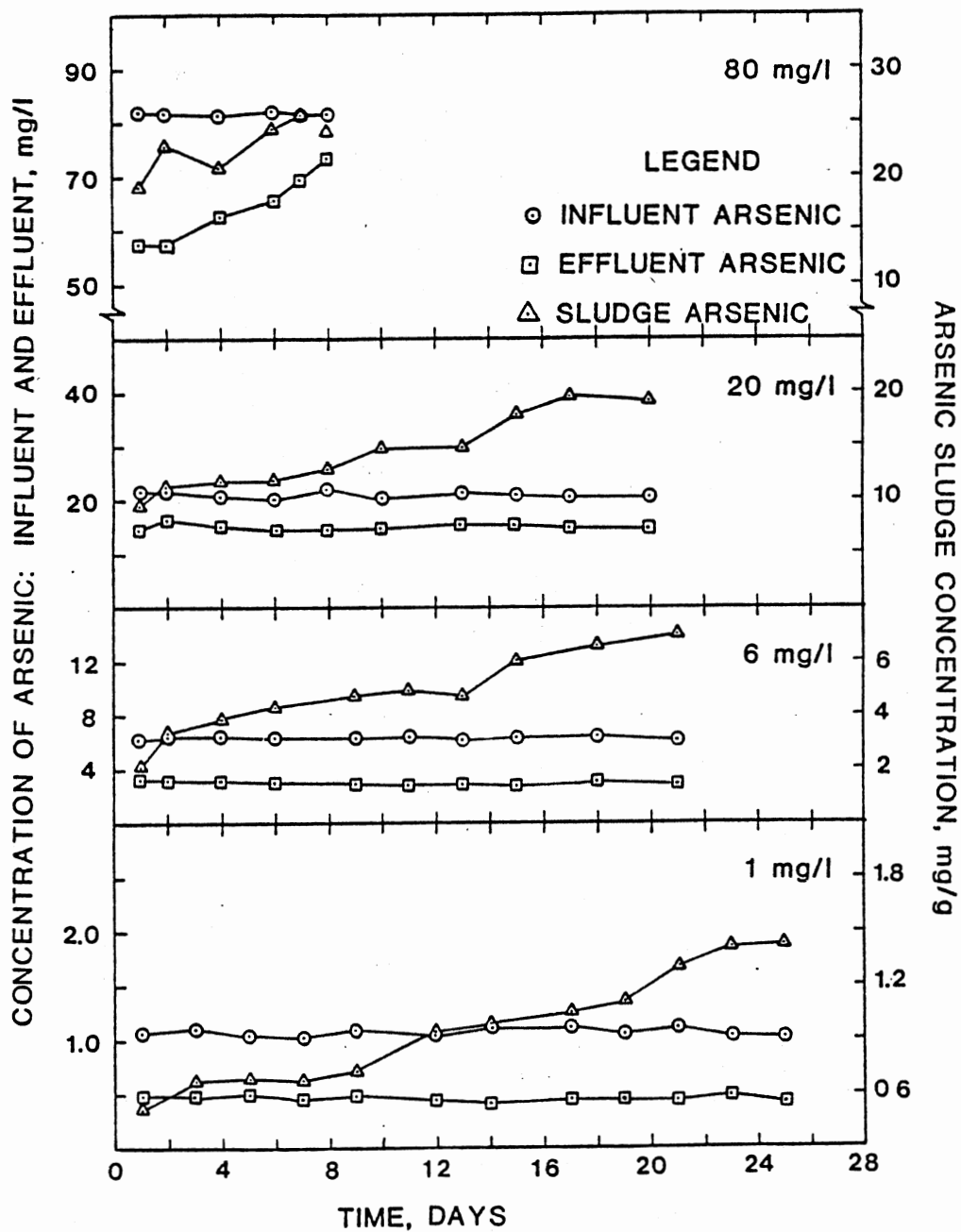


Figure 18. Fate of Metal in Arsenic Unit at 6 Day θ_c

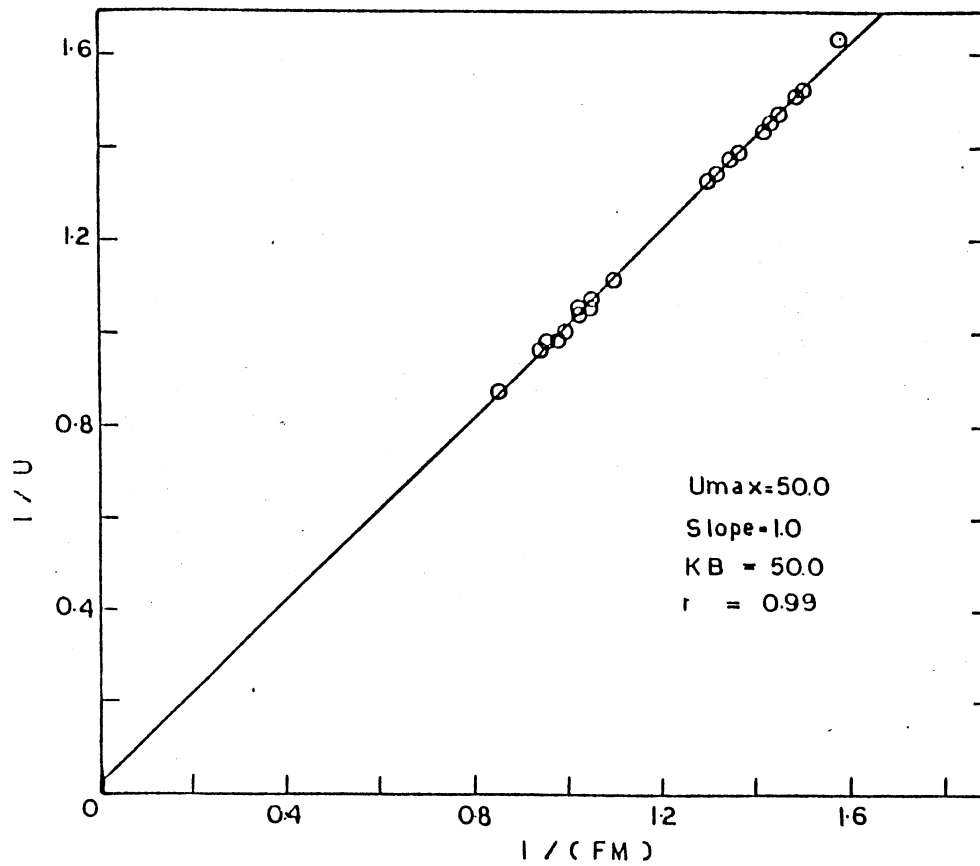


Figure 19. Substrate Utilization vs. Food-Microorganisms Ratio for Control (0 mg/l Arsenic) Based on COD Values

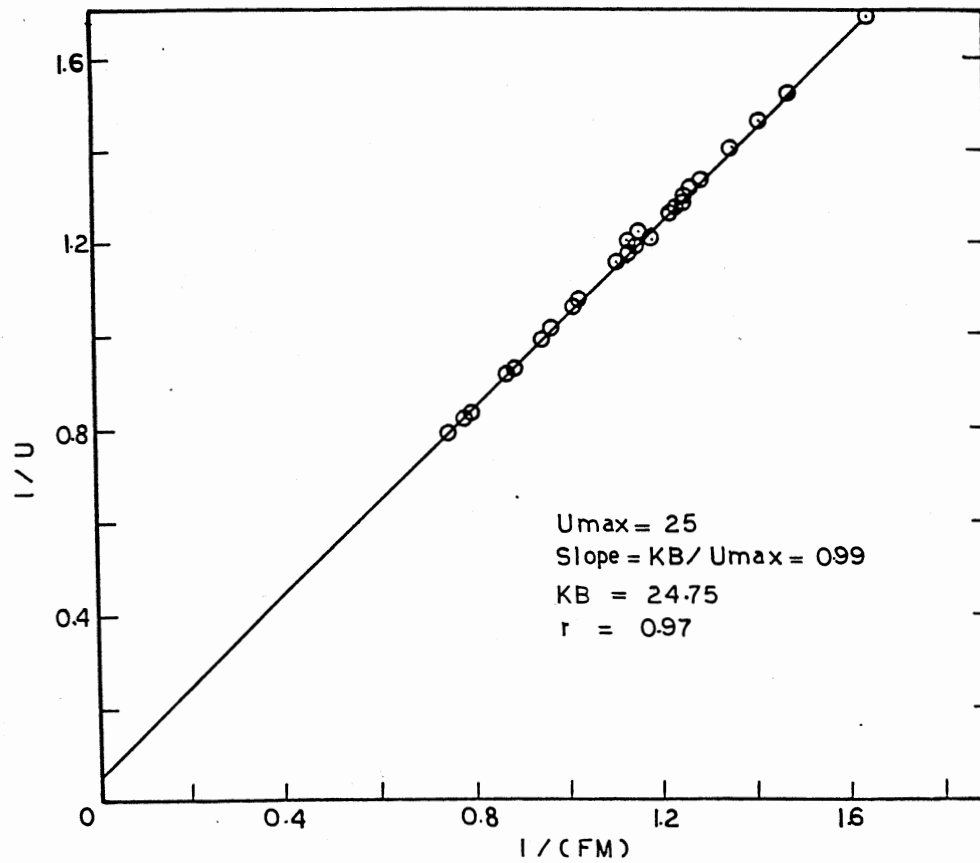


Figure 20. Substrate Utilization vs. Food-Microorganisms Ratio for 1 mg/l Arsenic Based on COD Values

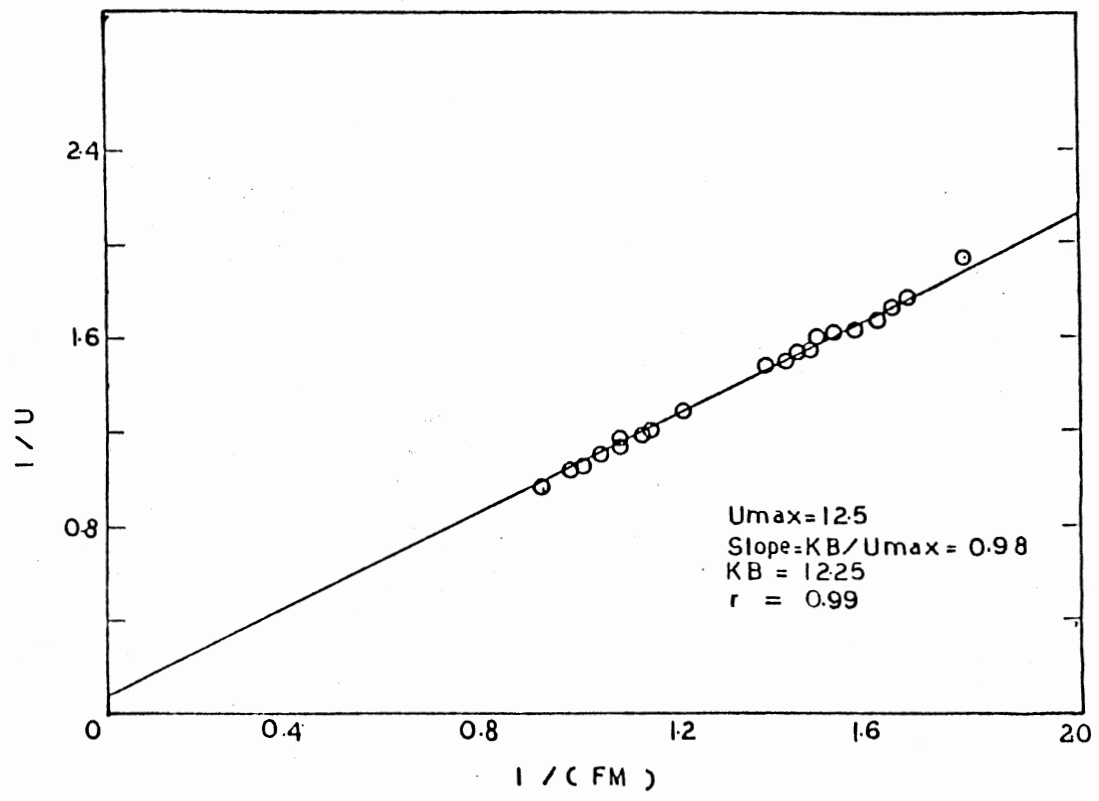


Figure 21. Substrate Utilization vs. Food-Microorganisms Ratio for 6 mg/l Arsenic Based on COD Values

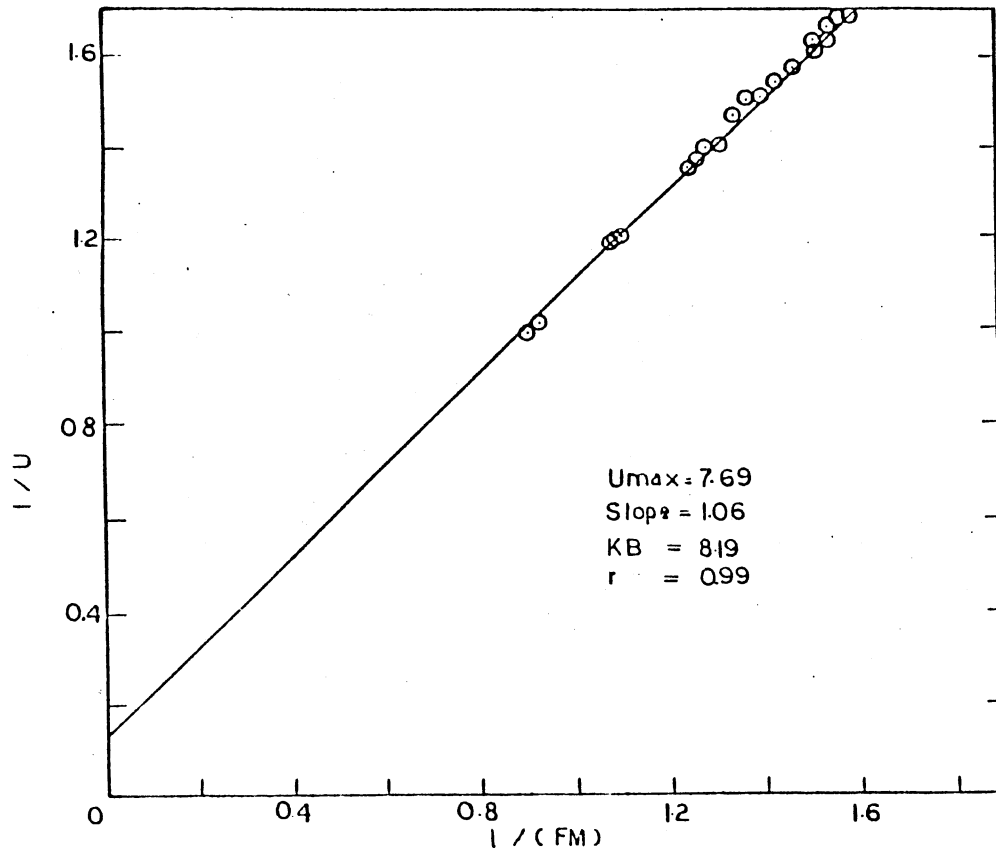


Figure 22. Substrate Utilization vs. Food-Microorganisms Ratio for 20 mg/l Arsenic Based on COD Values

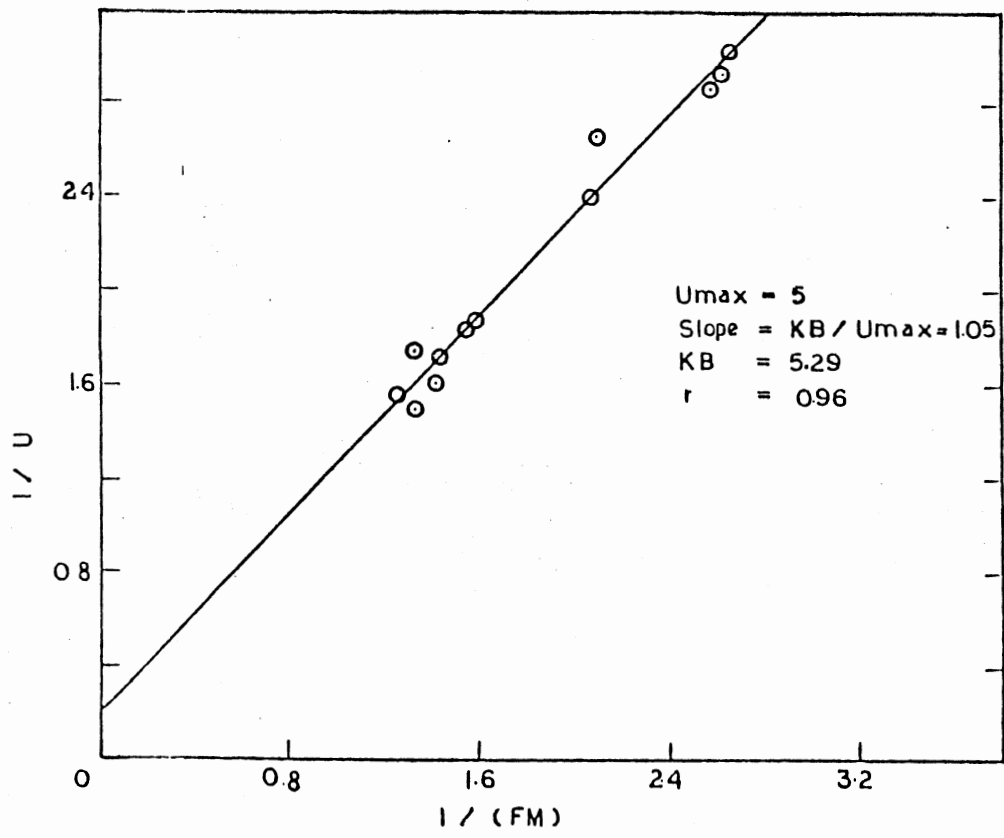


Figure 23. Substrate Utilization vs. Food-Microorganisms Ratio for 80 mg/l Arsenic Based on COD Values

TABLE V
 U_{\max} , K_B , AND r VALUES FOR DIFFERENT CONCENTRATIONS
OF ARSENIC BASED ON COD VALUES

Concentrations of Arsenic in Feed	U_{\max} day ⁻¹	K_B day ⁻¹	r
0 mg/l (control)	50.0	50.0	0.99
1 mg/l	25.0	24.75	0.97
6 mg/l	12.5	12.25	0.99
20 mg/l	7.69	8.19	0.99
80 mg/l	5.0	5.29	0.96

better than the performance of the 6-day units in terms of organics removal for both silver and arsenic. Up to 6 mg/l silver and 20 mg/l of arsenic additions, the effluents were very clean and contained almost no solids. The results clearly proved that silver was much more toxic to the microorganisms than was arsenic, and also, that microorganisms have more affinity to silver than arsenic.

CHAPTER V

CONCLUSION

The investigation showed that wastewater containing the heavy metals silver and arsenic can still be treated using biological activated sludge units provided the concentrations of the metals are within the toxic limits to the microorganisms.

Each metal has its own toxic limit to the microorganisms. In this case, silver at 18 mg/l was very toxic to the microorganisms whereas arsenic at 20 mg/l did not affect them. Also, the affinity of the metals to the microorganisms varied with the metals. It was found that silver removal was much higher than arsenic removal. It also proved that it was possible that a wastewater containing silver can easily be treated for both organics removal and metal removal using biological treatments if the concentrations are within the toxic limits. Wastewaters containing arsenic at high concentrations can be treated using biological treatment for removal of organics since it was found that even at high dosages of 80 mg/l, arsenic was not toxic to microorganisms. However, the process cannot be used for the removal of arsenic as it was found that the affinity of the metal to the microorganisms was very poor. Also, as proven by Kincannon and Esfandi (22), the biological treatment process can be used in conjunction with granular activated carbon for better removal of arsenic.

As for the two SRTs of 6 days and 18 days used, it was found that both worked well in removing the organics and the metals. However, the performance of the 18-day unit was slightly better in the organics removal and the metals removal. It was also found in this study that the 18-day units were better able to withstand the metal shock loads than the 6-day units.

The settling characteristics of the microorganisms improved tremendously as the concentrations of both silver and arsenic were increased, and there was almost no filamentous growth when the metal concentrations were introduced.

It was also noticed that the DO uptake increased on the day of the shock load but returned back to normal after the second day.

In conclusion, it can be said that the removal efficiency of both organics and metals depends on the concentration of the metals in the influent, and as the metal concentration increased, the substrate utilization rate decreased. When the toxic limit of the metal concentration was added, the microorganisms failed to function and the units began to die.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

This study was done by keeping the organic loading constant and increasing the metal concentrations. As in the actual treatment process, the organic loading may vary. It is recommended that the effect of metals removal may be studied varying organics loadings.

In this study, the effect of a shock load was studied for a period of three weeks at each concentration. It is suggested that the concentrations of the metals may be increased by 1 mg/l at a time and one could see at what concentration the metals become toxic to microorganisms.

In the present study, only two SRTs, namely 6 days and 18 days were used. It is suggested that the study could be conducted at other SRTs such as 3, 9, 12, and 15, in order to find the difference, if any, in the organics removal or metal removal efficiencies.

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VITA I

Raju Bernard

Candidate for the Degree of

Master of Science

Thesis: A STUDY OF THE EFFECT OF SILVER AND ARSENIC ON THE PERFORMANCE OF ACTIVATED SLUDGE UNITS

Major Field: Civil Engineering

Biographical:

Personal Data: Born March 6, 1939 in Mysore, India, the son of Rangaswamy and Elizabeth Raju.

Education: Graduated from Saradavilas High School, Mysore, India; received Bachelor of Science degree in Chemistry from Mysore University, India, in 1974; received Diploma in Business Administration in 1976 and received Diploma in Materials Management in 1977 from St. Joseph's College of Business Management, Bangalore, India; completed requirements for the Master of Science degree at Oklahoma State University in December 1983.

Professional Experience: Materials Management Departments from 1960 - 1980. Graduate Research Assistant from January, 1981 to July, 1983.

Professional Societies: Member of Indian Materials Management Association, India; member of National Society of Professional Engineers; member of Water Pollution Control Federation.