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THE UNIVERSITY OF OKLAHOMA

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SELECTION OF CHEMICALS FOR RECOVERIES OF GREASE, FATS AND PROTEINS IN FOOD PROCESSING WASTEWATER

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SELECTION OF CHEMICALS FOR RECOVERIES OF GREASE, FATS AND PROTEIN IN FOOD PROCESSING WASTEWATER

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CHAPTER I

INTRODUCTION

The discharge of industrial wastewater has become a significant area of concern and public regulating bodies have become increasingly involved with the establishment of water quality criteria. Many types of substances, when discharged into a receiving body of water, degrade the water quality to such an extent that the beneficial uses of the stream are no longer attainable. While no single industry will pollute a stream with all types of harmful substances, sufficient quantities or combinations of even a few pollutants can cause significant water quality degradation.

A recent EPA report (1) called the wastewater discharged from meat packing plants the number one potential polluter among the food and kindred products industries. Recent surveys of the pollutional load in meat packing wastewaters show the important significance of these types of wastes and the consequences they have on our wastewater treatment programs. A summary of the studies for packing plants is shown in Table 1.

A comparison of the various parameters between studies shows a remarkable similarity, indicating that all the surveyors sampled both poor and well

Table 1. Meat Packing Waste Load Characteristics (1).

Survey By	No. of Plants in Survey	Mean Values, lbs/1000 lbs Live Weight Killed			
		BOD	SS	Grease	Nitrogen
North Star	52	12.1	8.7	6.0	1.0
Mohlman	16	14.6	11.3	1.6	1.7
Hill	10	15.0	12.4	---	1.7
Kerrigan	10	11.8	9.0	8.2	0.9
Average	--	13.3	10.3	5.2	1.3

operated plants to about the same degree.

The amount of solids, BOD, grease, and nitrogen in the wastewater has a significant effect on costs of operating various units in a waste treatment system. The solids contribute a heavy load to primary clarifiers and add to the sludge disposal costs. In many cases, severe odor problems are experienced by the treatment plant because solids degrade rapidly and cause an anaerobic condition. A heavy load of grease interferes with the biological process. Grease coats the media of trickling filters, thus reducing treatment. Its presence also is reported to be detrimental to the performance of activated sludge systems (2).

Simple changes of in-plant methods can bring about large reductions in waste loads. It is not possible to process meat without concurrently producing a waste; however, it is possible to change the process to reduce the product loss which in turn significantly reduces the cost of waste treatment.

The Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) terminated the permit system established by the 1899 Refuse Act, and created a wastewater discharge permit system to be administered by EPA. The law requires pretreatment effluent standards on meat plants which discharge to municipal treatment works and national standards of performance on meat plants which have their own treatment works and discharge on a water course. The law also sets a deadline of July 1, 1983 for compliance with the discharge limitations.

By July 1, 1983, meat industry treatment works shall apply the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants. As stated in Sec. 306 of PL 92-500, elimination of the discharge of all poolutants by the meat industry will be required by this date if the Administrator of EPA finds that it is technically and economically feasible.

National pretreatment standards will limit discharges into municipal treatment works, necessitating in-plant controls and pretreatment facilities in the meat plant itself. Any industry failing to meet established limits must pay a higher charge.

The user charge, as it is known today, will change abruptly in the future. A significantly higher user charge is in the offing because PL 92-500 requires the municipality to recover, the operational costs and replacement value attributable to the industrial treatment portion of any municipal waste treatment system constructed with Federal grants. Pretreatment standards also prohibit the discharge of toxic materials and establish limits on pollutants not susceptible to the treatment or which interfere with operation of the municipal treatment works.

The law is quite inclusive and requires the Administrator of EPA to define the best practical control technology, the best available technology economically feasible and pretreatment standards. The Administrator must promulgate minimum requirements for data acquisition from owners and operators of point sources of discharge.

Presently, the lowest reported discharge achieved in treating waste in the meat industry has been, on an average, 3 mg/1 of BOD_5 and SS, 0.5 mg/1 phosphate as P, and 0.3 mg/1 Kjeldahl nitrogen and no detectable grease (3). These are more than satisfactory concentrations for meeting the present standards. However, it is reasonable to expect that discharge limitations will become more stringent as the deadlines suggested by PL 92-500 approach. If all of the meat industry can achieve these concentrations or zero discharge, it may be to their advantage to consider a closed-loop water system.

A new line of approach to the treatment of many wastewaters has been provided by the discovery and development of chemical processes, such as that for selectively precipitating certain organic compounds. In many instances, these processes represent an alternative to biological treatment systems. Methods have been developed for the recovery of protein contained in wastewater from the processing of beef, pork, poultry, fish and dairy products. By these methods 70-80 percent reduction in biochemical oxygen demand (BOD) can be achieved. The process involves precipitation of protein by the addition of precipitating agents (4, 5, 6). The precipitated protein, as well as grease and insoluble materials, is separated by dissovled air flotation or gravity separation. The effluent is greatly reduced in nitrogen, grase, suspended solids, BOD, and living organisms can then be discharged

into a stream. The sludge obtained after precipitation can be used as high grade food supplements for animals.

By the process described, it is possible to remove protein economically from industrial wastewater and recover it as a valuable by-product. The process has not been put into practice in industries in the United States. There is a need to identify the precipitating agents which could be used to treat the protein-containing wastewater economically.

CHAPTER II

LITERATURE SURVEY

Wasterwater Treatment Processes

Packinghouse wastes, being almost completely composed of biodegradable organic material, readily lend themselves to biological waste treatment methods. The exceptions to this are the large quantities of salt used in some processes such as the preservation of hides, and the detergents used in cleanup operations. Waste disposal methods have been found which encompass everything from no treatment to fairly complex treatment methods including primary, secondary, and, in a few cases, tertiary treatment.

In the past some meat processing industries discharged wastes, often containing waste materials such as paunch manure, whole blood and entrails, directly into the nearest stream. In general, this has been discontinued by all but the smallest and most remote slaughterhouses.

This section describes many of the techniques and technologies that are available or that are being developed to achieve the various levels of waste reduction in meat processing industries. Primary treatment in many cases is a materials recovery process, and is considered as part of the in-plant processing system. Many of these systems can be improved to reduce pollution levels.

Waste Segregation

Review of previously published meat packing literature suggests many areas of potential water and waste reduction. One of the major sources of in-plant pollution is the blood from the kill floor. Whole blood has a BOD_5 of 156,500 to 198,000 mg/l and an estimated ultimate biological oxygen demand (BOD_L) of 405,000 mg/l; this represents a potential BOD_5 load of 7 to 15 lbs per 1,000 lbs LWK (7, 8). Contents of the beef paunch, or rumen, also represent a primary pollution hazard. This partially digested material exerts a BOD_5 of 50,200 to 104,000 mg/l or 3 to 6 lbs per 1,000 lbs (7, 8).

Dehydrating cattle whole blood and rumen by gas-fired dryers is an economically feasible method of handling these materials in a beef-slaughtering operation. The dehydration of 92.4 percent of the blood and 75 percent of the rumen (the additional 25 percent of the rumen being either hauled away or rendered) represented a recovery of 82.4 percent of the total COD and 86.4 percent of the total BOD_5 generated by these materials (7).

Primary Treatment

Various combinations of facilities for in-plant primary treatment may be used, including screening, gravity grease and solids separation, dissolved air flotation, and biological treatment of various types (9). Since much of the pollutant matter in meat processing wastes is originally a solid (meat and fat particles), interception of the waste material by various types of screens is a natural first step. Static, vibrating and rotary screens are the primary types used for in-plant primary treatment. Up to 82 percent solids removal has been reported (9). Gravity clarifiers for grease and solids separation will remove 20-30 percent of the BOD, 40-50 percent of the

suspended solids, and 50-60 percent of the grease (12).

Dissolved air flotation systems without chemical treatment are capable of removing about 30-40 percent of the BOD, 55-60 percent of the suspended solids, and 80-90 percent of the grease (10, 11). Combinations of gravity catch basins (about 25-30 minutes detention) or grit chambers followed by dissolved air flotation produce somewhat better results (10).

Chemical coagulation and treatment of meat industry waste have also been investigated and used, although not extensively. Johnson indicated that the addition of alum improved BOD removal by 2.5 mg/1, and grease removal by 1.5 mg/1 for each mg/1 of alum added (11).

Several investigators reported that BOD, suspended solids, and grease removals of 75-85, 90-98, and 90-95 percent, respectively, had been attained by using dissolved air flotation systems with chemical treatment (12, 13, 14).

Larson, K.D. et al. (13) evaluated the BOD and suspended solids removal efficiency of chemical flocculation and settling using several chemicals listed in Tables 2 and 3. Of all the chemicals tested and treatment schemes demonstrated, a dual system of ferric chloride followed by a high molecular weight, anionic, organic polyelectrolyte proved to be the most effective. This system resulted in a 72 percent reduction in suspended solids and 54 percent reduction in BOD. This should be compared to a control flocculation plus settling without chemicals in which the removal efficiencies were 56 percent and 29 percent, respectively.

Garrison and Geppert (15) investigated several methods of waste treatment at the Rath Packing plant in Waterloo, Iowa. Liquid-solid cyclone separation was tried with interceptor wastes, and it was found that 59 percent of all solids and 69 percent of the grease were concentrated in 15 percent of

Table 2. Single Flocculant Evaluation (16).

Chemical	Optimum or maximum dosage (mg/l)	Results
Calgon ST-260	20	Medium, voluminous floc formed
Calgon 269	2	Poor flocculation
Nalco 607	20	Poor flocculation
Nalco 675	2	Poor flocculation
Nalco 610	20	Medium flow with some clarity
Nalco 603	40	No activity
Hercules 220	20	Large, dense floc formed
Dow A-21	4	Large, dense floc formed
Dow A-22	2	No activity
Dow A-23	2	No activity
Dow C-31	50	No activity
Dow C-32	50	No activity
Dow SA 118.1A	50	No activity
Dow SA 11881.F	50	No activity
Dow SA 1569	50	No activity
Dow SA 1767	40	No activity
Dow 1621.2	40	No activity
Dow N-11	2	No activity
Dow N-12	2	No activity
Dow N-17	2	No activity
$FeCl_3$ (anhydrous)	100	Medium voluminous floc, excellent clarity
General Mills* 162	35	No activity
General Mills* 263	35	No activity
Polyethylene imine	50	Fine voluminous floc formed

*General Mills Inc., Kankakee, Illinois.

Table 3. Dual Flocculant Evaluation (16)

Chemical #1	Chemical #2	Results
$FeCl_3$ (anhydrous)	Dow A-21	No synergism
$FeCl_3$ (anhydrous)	Nalco 610	No synergism
$FeCl_3$ (anhydrous)	Nalco 675	Synergism suspected
Calgon 260	Dow A-21	No synergism
Hercules 220	Dow A-21	No synergism
Calgon 260	Nalco 610	No synergism
Hercules 220	Nalco 610	No synergism
$FeCl_3$ (anhydrous)	Iron ore	No synergism
$FeCl_3$ (anhydrous)	Calgon 260	No synergism
$FeCl_3$ (anhydrous)	Reten 220	No synergism
$FeCl_3$ (anhydrous)	A-22	No synergism
$FeCl_3$ (anhydrous)	A-23	Synergism suspected
Dow A-21	Iron ore	No synergism

the total flow. It was decide that these separators would have been more effective if used in series. Vacuum filtration was tried on interceptor bottom sludge. This proved effective to the extent that 80 percent of the solids were removed. A filter aid was found helpful in improving solids recovery. Centrifugation was found to remove 70 to 83 percent of the solids but was too costly for this purpose.

Secondary Treatment

The secondary treatment methods commonly used for the treatment of meat processing and meat packing wastes include anaerobic lagoons, aerobic lagoons, variations of the activated sludge process, high-rate trickling filters, and rotating biological disks. These systems are capable of providing 70 to 97 percent BOD_5 reductions and 80 to 95 percent suspended solids reduction. Combinations of these systems can achieve reductions greater than 99 percent in BOD_5 and grease, and greater than 97 percent in suspended solids.

Anaerobic Lagoons

Organic concentrations, both particulate and dissolved, of industrial wastewaters are frequently an order of magnitude greater than those of municipal wastewaters. During recent years, the meat processing industry has recognized the inherent advantages of anaerobic lagoons for the stabilization of high strength organic wastewaters. The anaerobic lagoon is the treatment process widely used at meat packing and poultry processing plants. (16). The anaerobic process is especially suited for treatment of concentrated hot wastewaters from these plants (16).

A Summary of the operating data for representative anaerobic lagoons treating meat packing wastewaters is presented in Table 4. The effectiveness of anaerobic lagooning of meat processing wastes has been well

Table 4. Data for Anaerobic Lagoons BOD Meat Processing Wastewaters.

Investigator/s Reference	BOD (mg/1) Influent	BOD (mg/1) Effluent	BOD Removal %	BOD Loading $_3$ lbs/1000 ft^3	Temperature C
Sollo (17)	1,096	159	85.5	---	---
Rollag & Dornbush (18)	940	458	58.2	16.1	25
Enders et al.	1,880	350	87.0	31.4	22-27
Wymore & White (19)	---	670	64.9	12.7	---
Hester & McClurg (27)	1,703	122	92.8	9.0	24
Dietz et at. (28)	3,000	300	90.0	---	25-26
Coerver (20)	2,070	158	92.4	---	---

established. BOD removal efficiencies of 60-90 percent (Table 4) have been consistently demonstrated at organic loadings of 10-30 lbs of BOD/1000 cu ft/day. Nuisance odors generally have not been a problem with meat wastes (17, 18, 19, 20). A thick scum layer of grease is frequently allowed to accumulate on the surface of the lagoon to retard heat loss, to ensure anaerobic conditions, and hopefully to retain obnoxious odors. Low pH and wind can adversely affect the scum layer (21, 22, 23). Some states require a cover in palce of the scum layer. Nylon-reinforced Hypalon, polyvinyl chloride, and styrofoam have been used (24). Properly installed covers provide a convenient means for odor control and collection of the by-product, methane gas.

For the best operation, the pH should be between 7.0 and 8.5. At a pH below 7.0, methane-forming bacteria will not survive, and acid formers will predominate producing noxious odors. At a pH above 8.5, acid-forming bacteria will be suppressed and lower the loagoon efficiency (25).

Advantages of an anaerobic lagoon system are initial low cost, ease of operation, and the ability to handle large grease and shock waste loads while continuing to provide a consistent quality effluent (26). Disadvantages of an anaerobic lagoon are the hydrogen sulfide generated from these sulfated-containing-waste waters and the typically high ammonia concentrations in the effluent of 100 mg/l or more (24). If low pH conditions develop, sulfide odors result. Sulfide odors can be removed by adding iron filings to remove sulfides (20).

Oxidation Ponds

The meat packing industry has made extensive use of oxidation ponds. Because of the high suspended solids and high BOD in packing house waste they are usually preceeded by anaerobic lagoon. The loading

rates of oxidation ponds range from 60 lbs BOD/acre/day to 214 lbs BOD/acre/day (16, 25). BOD reductions of 53-96 percent can be attained by oxidation ponds in treating meat packing plant wastes (16, 25). Table 5 shows the median values of the BOD loading rates, removal efficiencies, as well as depth and retention periods for various industrial oxidation ponds.

The advantages of oxidation ponds are that the capital cost is lower than for mechanical systems, they require less maintenance, and they also permit flow control and wastewater storage. Disadvantages are the limited and inconsistent removal of pollutants; the algae growth problem which increases the suspended solids concentration and the pH frequently to greater than 9.0 for several months of the year; and the large land requirement (25).

Table 5. Median Values for Industrial Oxidation Ponds (29).

Industry	BOD Loading (lbs/acre/day)	% BOD Reduction	Retention Time (days)	Depth (feet)
Canning	139	98	38	5.8
Meat & Poultry	72	80	70	3.0
Petroleum	28	76	25	5.0
Dairy	22	95	98	5.0
Paper	105	80	30	5.0
Rendering	36	76	48	4.2

Aerated Lagoons

Aerated lagoons have been used successfully for many years in a small number of installations treating meat packing wastes. The aerated lagoon

has been used for pretreatment prior to discharge to a municipality or as a process between an anaerobic lagoon and an aerobic lagoon.

Aerated lagoons use either fixed mechanical turbine-type aerators, floating propeller-type aerators, or a diffused air system for supplying oxygen to the wastewater (31, 32, 33, 34). The lagoons usually are 8 to 15 feet deep, and have a detention time of two to ten days. BOD reductions range from 40 to 60 percent, with little or no reduction in suspended solids (30, 31, 34).

Advantages of this system are ease of operation, and low capital cost. Disadvantages include the power requirements and the fact that the aerated lagoon, itself, usually does not reduce BOD and suspended solids adequately to be used as the final stage in a high performance secondary system (32, 33).

Activated Sludge and Extended Aeration

In 1916 a study by the Chicago Sanitary District with its then large complex of packing plants recommended the activated sludge process for joint treatment with municipal sewage (35). This process can reduce BOD_5 and Suspended solids up to 95 percent (36). However, it cannot readily handle shock loads and widely varying flows common to meat processing wastewaters without flow equalization.

Various modifications of the activated sludge process have been developed, such as the tapered aeration, step aeration, contact stabilization, and extended aeration. Of these, extended aeration processes are most frequently being used for treatment of meat processing and meat packing wastes (16, 37, 38).

Treatment capabilities of an extended aeration system were investigated by Wells, et al. (38). The study showed that a treatment system consisting of anaerobic lagoons followed by an extended aeration system is capable of

accomplishing BOD reductions in the range of 95 to 98 percent, with an average of 97 percent. The corresponding suspended solids reductions range from 72 to 97 percent, with an average of 89.5 percent. The extended aeration system itself accomplished BOD reductions of 76 to 86 percent, with an average of 82 percent. The corresponding suspended solids removal range from 35 to 81 percent, with an average of 62 percent.

The advantages of the extended aeration process are that it is less susceptible to shock loading and flow fluctuations because the incoming raw waste load is diluted by the liquid in the system to a much greater extent than in the conventional activated sludge. Also, because of the long detention time, high BOD reductions can be obtained (38). Other advantages of the system are the elimination of sludge digestion equipment and the capability of producing a nitrified effluent (24). The disadvantages are the increased power and equipment cost for aeration. Other disadvantages of this process are that large volume tanks or basins are required to accomodate the long detention times and operating costs for aeration are high (24).

Trickling Filter

Trickling filters for the treatment of meat processing wastes must be preceded by primary treatment to prevent clogging the filters with grease and solids. The high rate trickling filter is used for treating meat industry wastewaters as a roughing filter, preceding conventional secondary treatment such as activated sludge, or as a complete secondary treatment in several stages (36). Hydraulic loading for high rate trickling filters is generally in the range of 10 to 20 mgd/acre (39). BOD loading rates are reported to be as high as 150 lbs BOD/day/a000 cu ft, yielding removal effi-

ciencies of 40 to 50 percent (40).

Advantages of the roughing trickling filter are that it can smooth out hydraulic and BOD loadings and provide some initial reduction in BOD_5 (40 to 50 percent) (36). Another advantage of the roughing filter is its reliability with mininum care and attention. Disadvantages of the trickling filter system include high cost of installation, the possible necessity to cover the filters in winter to prevent freezing, and effluent concentration fluctuation with changes in incoming waste load (24).

Rotating Biological Disks

The use of biological disks is a new approach to the treatment of meat processing wastes. The disks were first developed in Europe in 1955 for the treatment of domestic waste (9).

Although the rotating biological disks system is a proven biological wastewater treatment process in Europe, its capabilities have not been widely accepted in America. Development work on the rotating biological disks in the United States began in 1965 (10). Use of the disks in the treatment of meat processing wastes is recent, and to date, no operational data are available except on a pilot-plant scale.

Chittenden and Wells (41) presented the results of a pilot-plant study of rotating biological contractors for stabilizing the effluent from an anaerobic lagoon system at the Iowa Beef Processors plant in Dakota City, Nebraska. This pilot-plant had three stages of rotating disks (4 ft. in diameter, 0.5 in. thick, spaced on 1-in. centers with 50 disks/stages, 1,257 sq. ft. of disk area/stage) followed by a circular final clarifier. At an effluent flow rate of 5,000 gpd or 4.0 gpd/sq. ft. of disk area/stage, the dissolved oxygen concentrations ranged from 0.9 to 1.5 mg/1 in the first

stage, which was maintained throughout the unit. Reductions in BOD were 79.5 percent for the first stage and 83.2 percent overall. Lower BOD reductions were obtained at higher flow rates.

Rotating biological contractors could be used for the entire aerobic secondary system. The number of stages required depend on thd desired degree of treatment and the influent strength. Typical applications of the rotating bilogical contractor, however, may be for polishing the effluent from anaerobic process and from roughing trickling filters, and as pretreatment before discharging wastes to a municipal system. A BOD reduction of 98 percent is reportedly achievable with a four-stage rotating biological contractor (26).

Land Application

Liquid wastes with a wide spectrum of physical and chemical characteristics have been treated successfully by soil application, including municipal sewage, cannery wastes, pulp and paper mill waste, dairy wastes, vegetable and food processing wastes, distillery wastes, poultry wastes, and many others (42, 43).

Food processing wastewaters have been applied to the land through engineered systems for more than 25 years. Major interest began in the late 1940's with the primary objective being waste disposal. In 1934, corn and pea canning wastewater was applied to the land using the ridge and furrow method at Hampton, Iowa (44). Bolton (44) reported that in a 1942 study, the treatment capability of this soil system was investigated for the first time and was on the order of 50 to 80 percent removal of BOD at a BOD loading of 650 lb/acre/day.

Land application systems for treatment and disposal of food processing wastes are normally categorized into three types of systems. These categories

are based on differences in liquid loading rates and the resulting land area requirements, as well as differences in the interaction of the wastewater with vegetation and soil. The three treatment processes are infiltration, irrigation, and overland flow. Selection of a process is primarily governed by the drainability of the soil at the available site, which largely determines the hydraulic loading and the required land.

Spray runoff irrigation is an alternative technique which has been tested on the waste from a small meat packer and on a cannery waste (45, 46). With this technique, about 50 percent of the wastewater applied to the soil is allowed to run off as a discharge. The runoff or discharge from this type of irrigation system is of higher quality than the wastewater as applied, with BOD removal of about 80-90 percent; total organic carbon and ammonia nitrogen are reduced by about 85-90 percent, and suspended solid by approximately 85-90 percent (16, 47).

Potentially, the greatest concern in the use of irrigation as a disposal system is the total dissolved solids content, particularly the salt content of the wastewater. A maximum salt content of 0.15 percent is suggested by Eckenfelder (48). Some plants or some locations may require treatment in an ion exchange system upstream from the irrigation system to reduce the dissolved solids and the salt content to acceptable levels for continuing application of the wastewater on land (24).

Tertiary and Advanced Treatment

Ammonia Removal Process

Ammonia removal is becoming more important because stream standards are being set at levels as low as 1 to 2 mg/l (49). Ammonia stripping and nitri-

fication-denitrification processes show potential of removing ammonia to meet the stream standards.

Ammonia stripping is a modification of the simple aeration process for removing gases in water. Following pH adjustment, the wastewater is fed to a packed tower and allowed to flow down through the tower with a counter-current air stream introduced at the bottom of the tower. Ammonia-nitrogen removals of up to 98 percent and concentrations of less than 1 mg/l have been achieved in experimental ammonia stripping towers for treating municipal wastes.

The two-step process of nitrification and denitrification is a system to remove the ammonia nitrogen in treated meat packing wastewaters, and it is of primary importance for removal of the ammonia generated in anaerobic secondary treatment systems.

The nitrification-denitrification process has been carried out successfully in both bench and pilot-scale systems at the Cincinnati Water Research Laboratory of the EPA, and a full scale system has been built at Manassas, Virginia (51, 52). Although direct applications of this process has been limited, observations of treatment lagoons for meat packing plants give some indication that the nitrification-denitrification reactions are occurring in present systems. Also, Halvorson (24) reported that Pasveer is achieving success in denitrification by carefully controlling the reaction rate in an oxidation ditch, so that dissolved oxygen levels drop to zero just before the water is reaerated by the next retor.

Recovery of Proteins

A new approach to the treatment of many organic wastes has been provided by the development of chemical processes capable of selectively precipitating certain organic compounds. These processes now represent an alternative to physical and biological processes.

Various chemicals have been used to precipitate protein from the food processing wastewaters. These precipitants contain one of the following groups: lignosulfonic acid, sugar sulfate esters, sulfonates or sulfates of fat or fatty alcohols, inorganic coagulants, and organic polyelectrolytes.

The physical-chemical combining of lignosulfonic acid and protein in an aqueous system has been known for over 30 years (53, 54). Wallerstein (53) in 1944 described the recovery of protein from dilute solutions using spent sulfite liquor at a pH of 2 to 4. The precipitation agent in the sulfite liquor was identified as lignosulfonic acid and a ratio of 2 parts lignin to 5 parts protein was observed to optimal.

Pearl (56) discussed the uses of lignin in a survey paper in 1957 and mentioned the reaction of lignosulfonic acid with a protein to form insoluble complexes. He indicated this reaction can be used to remove proteins from effluents of canneries or fish processing plants.

In 1968 a U.S. Patent (57) was issued to Lief Jantzen of Oslo, Norway, and assigned to Arthur C. Trask and Sons, Chicago, that described a method of purifying an aqueous protein-containing liquid by adding lignosulfonic acids to effect precipitation of combined protein-lignosulfonic acid complex.

Several investigations reported that lignosulfonic acid had been used for treating various food processing wastewaters in both pilot plant and demonstration studies (4, 58, 59, 60, 61, 62, 63, 64). BOD, TSS, oil and grease, and nitrogen contents were lowered markedly and proteins and fats were recovered by adding lignosulfonaic acid to the wastes at a pH of 3 or below. The precipitated protein was removed by dissolved air flotation (58, 62, 63, 64). The resulting sludge had a protein content of up to 52 percent, and had protential use as an animal feed component (58, 62, 63, 64). Results of the studies are summarized in Table 6.

Table 6. Summarization of the Removal Efficiency of Lignosulfonic Acid Process.

Investigators		Waste	BOD	COD	Org-N	TSS	O&G
			Removal Efficiency (%)				
Tonseth & Berridge	(58)	slaughterhouse	60-88	73-86	73-95	76-90	--
Jorgensen	(4)	slaughterhouse	58	56	52	--	--
Felicetta & Peacock	(59)	fish	--	--	94	--	--
Rosen	(60)	poultry	80	--	--	--	--
Foltz et al.	(63)	slaughterhouse	84	--	87	96	95
Hopewood & Rosen	(62)	slaughterhouse	88	75	95	82	--

Several investigators have explored and utilized sulfated organics for recovery of protein from the meat processing wastes. A German Patent by Thorn and Simonsen (65) claimed that substances of high molecular weight having basic groups, such as proteins, polypeptides, nucleic acids, or aminopolysaccharides, are precipitated from solutions of wastewater by addition of a 1-20 percent solution of mono- or polysaccharide which is partially or completely esterified with sulfuric acid.

Several patents based on Norwegian investigations describe a process for treating meat packing wastes based on either the use of salts and mineral acids to reduce the pH to 2 and precipitate the complex or the use of sulfuric acid esters of sugars such as sucrose or lactose as precipitants (66, 67, 68). In the latter case, esters having a molecular weight equal to or greater than 200 gave BOD reductions as high as 80 percent, depending on dosage. The precipitated material could be used as cattle feed.

Jorgensen (4) examined different chemicals for precipitation of protein in wastewater. The results of his tests are tabulated in Table 7.

Table 7. Effect of Chemical Precipitants.

Precipitants	BOD (mg/l)	Protein (mg/l)	% Removal	
			BOD_5	Protein
None	1,660	728	--	--
Glucose trisulfate	750	556	55	24
Lignin sulfonic acid	700	430	58	41
Aluminum sulfate	770	572	54	21

It must be emphasized here that these removal efficiencies represent an increase over that of plain sedimentation and not the total removal efficiencies; therefore, they cannot be compared to the results reported by Tonseth and Berridge as shown in Table 6.

Jorgenson also determined the feasibility of using the precipitated materials for animal feed. He stated that protein precipitated with lignin sulfonic acid has a very low biological value. Nutrition studies using rats showed that the rats suffered from malnutrion and diarrhea when fed the precipitated materials. He further stated that protein precipitated with glucose trisulfate plus azoprotein has a normal biological value. Jorgensen analyzed the protein produced from slaughterhouse wastewater for its amino acid content and found it compared favorably with blood albumin and bone meal.

Streebin (69) developed a process using a specially prepared sulfated carbohydrate. The process consists of a proportional flow chemical feed system, a mixing basin and a modified dissolved air flotation unit. This system has been tested on wastes from chicken, turkey, beef, pork, and shrimp processing plants. Results showed that this process is both technically and economically feasible for treatment of beef processing or a combination of beef and pork processing wastes. The value of the product recovered plus the savings in the waste treatment is from 2 to 8 times the cost of the chemicals used in waste treatment. On the other hand, the cost of waste treatment may be as much as twice the value of the product recovered for pork and poultry processing.

This process reduces substantially the oxygen demand, suspended solids, and the oil and grease concentration of the wastewater. Further, the process econimically recovers a waste material which can be converted to a salable by-product. Table 8 shows the results of analyses and pretreatment studies

from one of the plant studies for a combination slaughterhouse and packing house operation that has a daily kill of 1200-1300 cattle.

Table 8. Average Wastewater Characteristics and Removal Efficiencies (69).

Parameter	Raw waste (mg/l)	Air flotation (mg/l)	Removal (%)	Chemical Treatment (mg/l)	Removal (%)	Total Removal (%)
Suspended Solids	14,378	6,115	57	470	92	97
COD	22,215	10,967	51	2,160	80	90
BOD	9,550	7,100	26	1,800	75	81
Org-N	217	281	--	99	65	65

Viscarin 402 carrageenan was used as a coagulant for pork waste, which reduced COD and BOD from 2,700 and 890 mg/l to 140 and 61 mg/l, respectively (70).

Viscarin 402 carrageenan is a refined water soluble carrageenan extracted from certain red marine plants (order Cigartinales) and reduced to a free-flowing powder by alcohol precipitation. It is composed primarily of sulfated d-galactose residues, linked together to form long chain polymers having molecular weights of several hundred thousand. It has the unique property of complexing and reacting with proteins. This property made possible its effective use at very low concentrations (71).

In 1954, Kountz (72) reported in the pilot plant study that slaughterhouse waste proteins can be physically absorbed on a bentonite floc with the pH adjusted to 4.2 by the use of sodium acid sulfate, resulting in BOD reduction of 95 percent.

Johnson and Peniston (73) described a process for recovering proteinaceous materials from shrimp, crab, and salmon processing wastes at Kodiak,

Alaska. A dilute sodium hydroxide solution is used to extract the protein in the shellfish waste. The extraction is conducted as a counter-current operation to obtain high protein concentrations in the extract. The protein is recovered from the extracts by adjusting the pH to the isoelectric point, pH 4.0 with HCl. The precipiated materials were then separated from the waste by filtration or centrifugation.

Grant and Robins (74) discussed a method of recovering fats and proteins from wastewater by acidifing with H_2SO_4 to less than pH 4 and gasifing with air at a pressure of 3 to 5 atmosphere to float the proteins. Readjusting the pH by adding $CaCO_3$ to a higher value causes precipitation of the protein which is collected by sedmmentation, and filtration.

Studies were made by Kojima et al. (75) on the recovery of protein lost by leaching in the manufacture of Kamaboko fish paste. It is reported that a high yield of the proteins from the wastewater was obtained by precipitating them either at pH 2 or 12 and readjusting it with an acid or alkali to appropriate pH's for their precipitation. The optimum pH for maximum yield differed with the raw fish materials used.

According to Young and Lawrice (76), native proteins may be extracted from offal, including bovine and sheep stomach and lungs, over a wide pH range at room temperature by using low salt concentrations (0.01M NaCl). Approximately 70 percent of the protein of rumen could be extracted at pH 3.5 or 10, and protein curd could then be obtained by adjusting the extracts to pH 4.7.

Processes have been developed in New Zealand for recovery of fats and proteins from slaughterhouse wastes which involve acidification to pH 3 to 4, followed by dissolved air flotation at pressures of three to five atm

(77, 78). The float and sediment contained protein in amounts of 12 and 60 percent; fat, 50 and 10 percent; other organic compounds, 35 and 18 percent; and ash, 3 and 12 percent, respectively.

According to Swingler (79), meat wastes, particularly offal, were used to prepare a spun protein fiber. The proteins were extracted by alkaline treatment and precipitated at pH 4.5. This protein isolate was treated with concentrated sodium hydroxide and extruded into a coagulating bath containing acid and salt to form protein fibers.

Courtial (80) reported a process for the separation and recovery of fats and proteins from meat processing effluents. The waste was filtered, and fats and proteins were separated by addition of inorganic flocculants. A 90 percent reduction in BOD was obtained by this process.

In 1961, Ryosaku (81) reported that removal of protein-colored matter from the slaughterhouse waste was successfully accomplished by the application of 75 ppm of $CuSO_4$ or $CuCl_2$. Eighty seven percent BOD as well as 88 percent total nitrogen was removed without showing the presence of Cu^{++} in the effluent.

Study at Aktiebolag Perac in Belgium (82) showed that protein constituents are removed from processing streams of the food industry additions of a cationic substance and a neutral salt. Precipitation of part of the protein occurs at pH 6-7 with a strongly cationic substance (e.g., a mixed form of an organic amide and HCHO), and by precipitation with a neutral salt (e.g., NaCl), after adjusting the pH of the remaining solution to 7-8 with a basic substance. After each precipitation step, air is introduced from the bottom of the vessel so that the air bubbles carry the precipitants to the surface from which they are skimmed.

Purifying protein-containing water by flocculation was investigated by Fontaine et al. (83). Fat and protein-containing wastewaters from a degreasing plant were treated at pH 5.5-7.0, at a temperature above 60°C with

an aqeous solution containing either $CaCl_2$, $MgCl_2$, $Al(SO_4)_3$ or $FeCl_3$. After precipitation and flocculation the protein was separated by centrifugation and dried.

A Czechoslovakian patent (84) outlined a three-step process for separating fat and protein from meat and rendering plant wastes. Air was dispersed in the waste by mechanical agitation to promote floatation of the fat which was skimmed off. The supernatant was treated with HCl or H_2SO_4 to break fat and protein emulsions, followed by addition of lime and oleic acid to obtain the resulting protein which was skimmed off.

Japanese patents describe processes for treating slaughterhouse wastes and blood-containing wash waters (85, 86). Slaughterhouse wastes were adjusted to pH 2.5 with H_2SO_4 followed by readjustment to pH 6.5 with NaOH. This treatment produced a precipitation of 62.0 and 58.2 percent of BOD and COD contributing materials, respectively. Additional protein precipitation was obtained by adding sodium hypochlorite and adjusting the pH to 4.5 giving 97.6 and 91.9 percent removals of BOD and COD, respectively. Blood containing wastewater was adjusted to pH 7, adsorbed on a cellulosic exchanger, pretreated with ethylene diamine and formaldehyde, and eluted with 0.1 N NaOH (86).

Johnson and Peniston (87) investigated alkali extraction and isoelectric precipitation for protein recovery and separation of chitin from fish and shellfish-processing operations at Kodiak, Alaska. The use of sodium hexametaphosphate, to complex and precipitate a protein reduced protein solubility to 0.07 percent from a 2.3 percent protein solution for a recovery of 96.7 percent.

In studies on shrimp cannery effluent in Louisiana, Thoma and co-workers (88, 89) developed a shrimp waste protein (SWP) recovery process involving isoelectric precipitation at pH 4.4 to 4.7 with concentrated HCl, followed by

drum drying the product at 124° to 127°C. The initial separation of the protein was improved by the addition of 0.002M ferric ion as $FeCl_3$ or $Fe_2(SO_4)_3$. Nutritional evaluation in rats of the SWP which contained 59.98 percent protein showed a protein efficiency ratio of 2.48 as compared with 3.13 for casein.

Araki et al. (90) developed a process for removal of proteins from chicken processing wastes in which the effluent is adjusted to pH 2.5 to 3.2, mixed with 0.3 percent $Al(OH)_3$, agitated for 1 to 2 minute, and settled for 30 minutes. BOD and grease contents of the waste were reduced from 1,200 and 17 mg/1 to 100 and 9 mg/1, respectively. TSS were reduced from an initial value of 320 mg/1 to a nondetectable level.

Claggett (91) presented details of the design and operation of a chemical treatment and air flotation system for treating fish processing wastes at Steveston, B.C., Canada. He found that lignosulfonic acid treatment gave a floc that was fragile and not easily removed. He further reported that alum-caustic ($Al_2(SO_4)_3$-NaOH) treatment at pH 9.2 followed by readjustment of the pH to 5.2 resulted in a curdy floc that floated readily. The COD, protein, insoluble solids, and soluble solids removals of 84, 61, 92, and 28 percent, respectively, were obtained by this process.

Claggett (91) reported that alum sludge from the fish processing plant wastewater fed to chicken up to 5 percent of the supplementary diet showed no adverse effect. When the sample was tested as a total replacement, there was a marked reduction in both growth rate and food utilization. The inclusion of alum in the diet at up to the 1 percent level had no significant effect.

Bough (92) reported that chitosan, derived from chitin in shrimp and crab wastes, could be used as a coagulant in treating wastes from meat

processing operations. For meat packing wastes, optimum conditions of pH 7 to 8, a chitosan concentration of 30 mg/1 and settling time of 1.5 hour, resulted in COD and TSS removals of 55 and 89 percent, respectively. At a chitosan concentration of 5 mg/1, COD and TSS removals from meat processing and curing wastes were 79 and 92 percent, respectively.

Bough (92) investigated chitosan in combination with 21 commercially available polymers for treating shrimp processing wastes. He found that an anionic polymer (WT-3000) was the optimum coagulant among all of the polymers tested. In a pilot scale study using 10 mg/1 chitosan and 5 mg/1 of WT-3000 and a settling time of 1 hour, COD and TSS removals were 76 and 94 percent, respectively. Coagulation combined with dissolved air flotation using 100 mg/1 chitosan and 5 mg/1 of WT-3000 reduced COD and TSS by 92 and 98 percent, respectively.

In the preliminary feeding trial with rats, Bough et al. (92) reported that the animals fed all but the highest level (5 percent) of chitosan grew as well as those fed the control diet without chitosan. The animals were healthy and vigorous and displayed no overt symptons of physiological distress due to consumption of chitosan. However, significant weight reduction was observed at the rats fed with highest level (5 percent) of chitosan.

In another study, Arai et al. (93) found that the chitosan fed to mice caused no harmful effects up to 18 grams per kilogram of body weight per day. Above this amount, toxic effects were observed.

The Vistec process uses cellulosic ion exchangers for the recovery of proteins from slaughterhouse and gelatin manufacturing wastes (94). Protein adsorption rate, inorganic salts concentration, and pH are important parameters. Protein concentrations of slaughterhouse wastes were reduced from 30 to 20 mg/1 by this process.

According to Grant (95), effluent from meat processing operations was treated effectively by adjusting the pH to 4 to denature proteins followed by lime treatment and sedimentation. The clarified effluent was then passed through an ion exchange resin based on cross-linked regenerated cellulose. A 95 percent removal of protein was achieved. The product was suitable for use in feeding chickens and swine.

According to Stopka (96), protein from fish processing plant waste are removed by treating with ozone and oxygen under pressure. The waste is mixed with these gases, and a foaming action takes place in the collection chamber. The proteinaceous impurities are carried in the foam and then are separated from the waste stream.

Tarkey et al. (97) conducted laboratory scale studies on the recovery of wastes from English sole filleting operations by enzyme hydrolysis using pepsin. A 50 percent fish processing wastewater was treated with 0.2 percent pepsin and centrifuged at 12,000 rpm for 10 minutes. The supernatant was heated to 80°C to inactivate the enzyme neutralized with 30 percent NaOH, filtered, concentrated to 30 percent solids, and spray dried to yield a fish protein concentrate containing 80 percent protein and 22 percent ash.

Arentz and Tonseth (98) treated effluent from a slaughterhouse by adjusting the pH to 3.5 with H_2SO_4 and adding 40 gpm of lauryl sulfate. Protein was reduced from 2,000 to 5 ppm and BOD from 1,850 to 120 ppm.

Aktieselskspet Apothekernes Laboratorium (99) invented a process by which protein contained in wastewater can be precipitated at a pH 3.5 using sulfonates or sulfates of fats, fatty oils, fatty acids, or fatty alcohols. The preferred precipitating agent is C_{8-20} fatty alcohols. Precipitation depends on the molecular weight and chemical characteristics of the protein.

CHAPTER III

EXPERIMENTAL METHODS

To determine the feasibility of chemical treatment of meat processing wastes, studies were performed on artificial beef processing wastes and on wastes from a nearby beef and pork processing plant. Preliminary studies of the wastewater from this processing plant indicate that the waste characteristics are comparable to those reported throughout the meat industry. The strength of the wastewater is shown in Table 9.

Table 9. Characteristics of the Meat Processing Waste

Parameter	Concentration (mg/l)
COD	4,980
Org-N	140
Total Suspended Solids	2,000
Oil & Grease	1,980

To prepare an artificial waste which had approximately the same strength as waste collected from the meat processing plant, five grams of ground beef were mixed with 250 ml of water. The mixture was blended in a laboratory blender at high speed for one minute. The mixed sample was then filtered through filterting media to remove grease, gross solids, and tissue. Paper

toweling, cheesecloth, and muslin cloth were tested as filtering media. Analysis of the filtered wastes recorded in Table 10 shows that filtering through cheesecloth produces the desired artificial waste.

Table 10. Characteristics of Artificial Wastes.

Filtered Waste By	COD	Org-N	O&G	TSS
	mg/l			
Paper Towel	2,624	116	1,205	1,400
Cheese Cloth	4,618	168	1,890	1,950
Muslin Cloth	1,200	68	290	590

Chemical Selection

The literature review revealed that protein-containing wastewater from the meat packing (beef and pork processing) plants can be treated by means of chemical precipitation using commercially available or easily preparable precipitating agents. Preliminary screening tests using artificial wastes prepared in the laboratory was used to determine the technical feasibility of protein precipitation. Wastewater collected at the catch basin from an existing plant was also used.

The following chemicals were used in the study:

Sulfuric acid-sodium hydroxide
Aluminum sulfate (alum)
Ferric chloride
Glucose trisulfate
Cellulose sulfate
Lignosulfonic acid
Viscarin 402 carrageenan
Chitosan
Kraft paper sulfate
Molasses sulfate
Starch sulfate
Corn syrup sulfate

Analytical Methods

Laboratory evaluations were conducted with a (Phipps & Bird) laboratory stirrer. The desired chemicals or combination of chemicals were added to 500 ml of wastewater while it was being stirred at 50 rpm. The stirring rate was increased to 100 rpm for a two-minute period to insure complete mixing and then reduced to 20 rpm for 15 minutes. The waste was settled for about 2 hours, after which a supernatant was drawn off for chemical analysis.

Initially, a number of tests were run using visual inspection and COD analysis to determine the performance of each chemical. Only the better precipitation candidates were selected to be extensively screened.

The screening process narrowed the candidates to eight chemicals. These chemicals were extensively studies to determine removal efficiencies and ease of solids liquid separation.

The raw and chemically treated wastes were analyzed for the following parameters:

(a) pH

(b) Chemical oxygen demand (COD)

(c) Total suspended solids (TSS)

(d) Protein

(e) Oil and grease

The pH was measured using a Photovolt pH meter. COD and TSS determinations were regularly performed on all samples using the procedure outlined in the Fourteenth Edition of Standard Methods for Examination of Water and Wastewater (1976).

Organic nitrogen and oil and grease analyses were performed regularly on

samples which had the optimum COD removal efficiency. Procedures outlined in Standard Methods (100) were followed. Based on the average percentage of the nitrogen content in protein, protein concentrations were estimated by multiplying the concentration of the organic nitrogen by the factor 100/16 or 6.25 (101).

In addition to the above mentioned parameters, iron (Fe) and aluminum (Al) analyses were also performed on the purified water which was treated with ferric chloride ($FeCl_3$) or aluminum sulfate ($Al_2(SO_4)_3$). Iron and aluminum were analyzed using a Instrumentation Laboratory Atomic Absorption spectrophotometer model 453. These analyses were performed on samples collected and acidified with 1:1 nitric acid and distilled water.

Solids-Liquid Separation

Sedimentation, flotation, and centrifugation processes were studied to determine the efficiency of separation of the precipitated materials from the treated wastewater.

Sedimentation

Laboratory settling studies were conducted in a column of the type shown in Fig. 1. Prior to settling air was sparged into the bottom of the column for a few minutes to assure a uniform concentration of suspended solids at the beginning of the test. The treated wastewater suspension was placed in the column and was allowed to settle under quiescent conditions. Samples were then drawn off at a a given depth at selected time intervals up to 120 minutes, and the concentration of suspended solids in each sample was determined.

The maximum settling velocity of suspended solids in each sample was

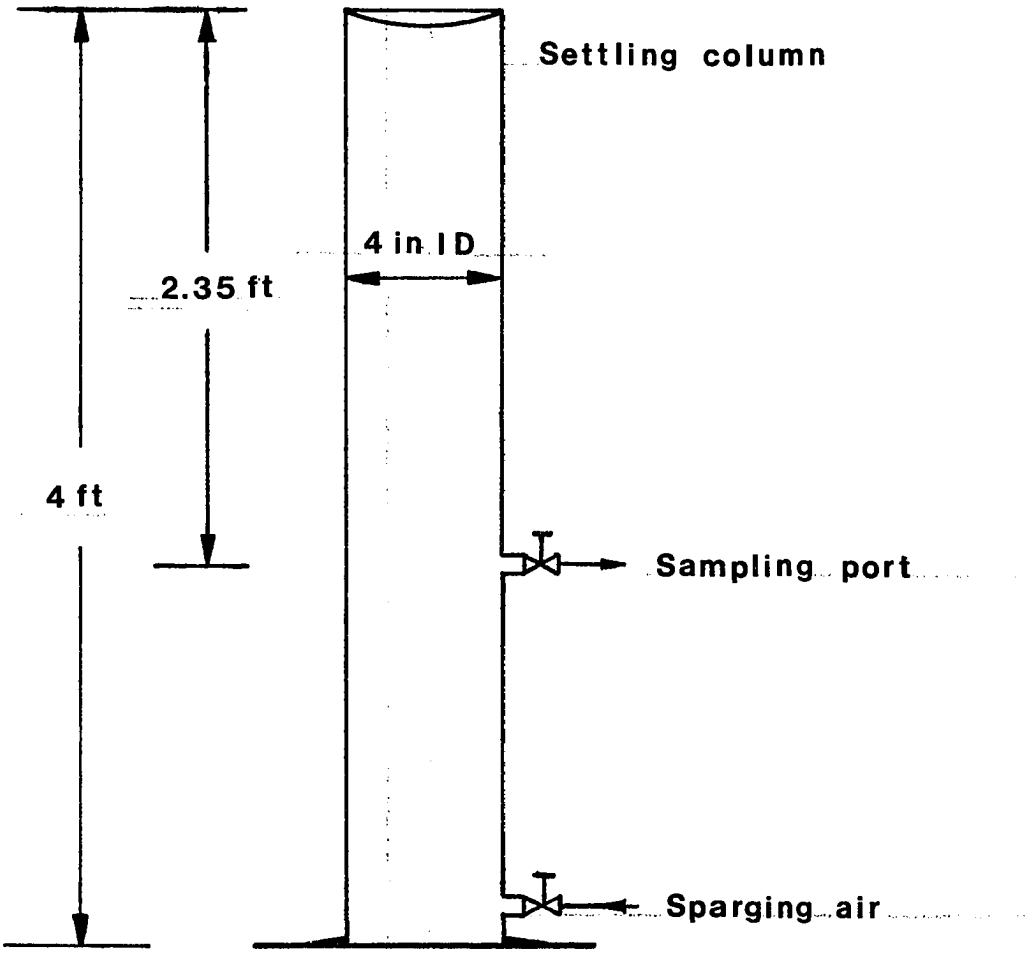

Figure 1. Laboratory Settling Column for Evaluation of Class-1 Clarification.

$$U_{tN} = \frac{Z_N}{t}$$

where Z_N = sampling depth, ft.

t = time at sampling in min.

A settling velocity curve, such as was shown in Fig. 1. was plotted for each suspension. Overall removal from the clarified liquid can be computed from the following equation:

$$X_T = (1-X_o) + \frac{1}{U_{t_o}} \int_0^{X_o} U_t dx$$

where X_T = weight fraction removed

X_o = weight fraction removed at U_o

U_o = settling velocity, ft/min

The last term in the above equation can be evaluated by graphical integration of the settling curve between the limits of 0 and X_o, i.e., across the shaded area shown in Fig. 2.

Flotation

A laboratory bench-scale test procedure was developed to simulate the dissolved air flotation process and was used throughout the study in the determination of design parameters for an air flotation unit. The primary variables for design were pressure, recycle ratio, feed solids concentration, and retention period.

The principal components of the flotation system are a pressurizing pump, air injection facilities, a retention tank, a back pressure regulating device, and a flotation unit as shown in Fig. 3.

Recycle rates of 50, 100, and 150 percent of the pressurized water were used in the flotation tests. The relationships between the air/solids ratio

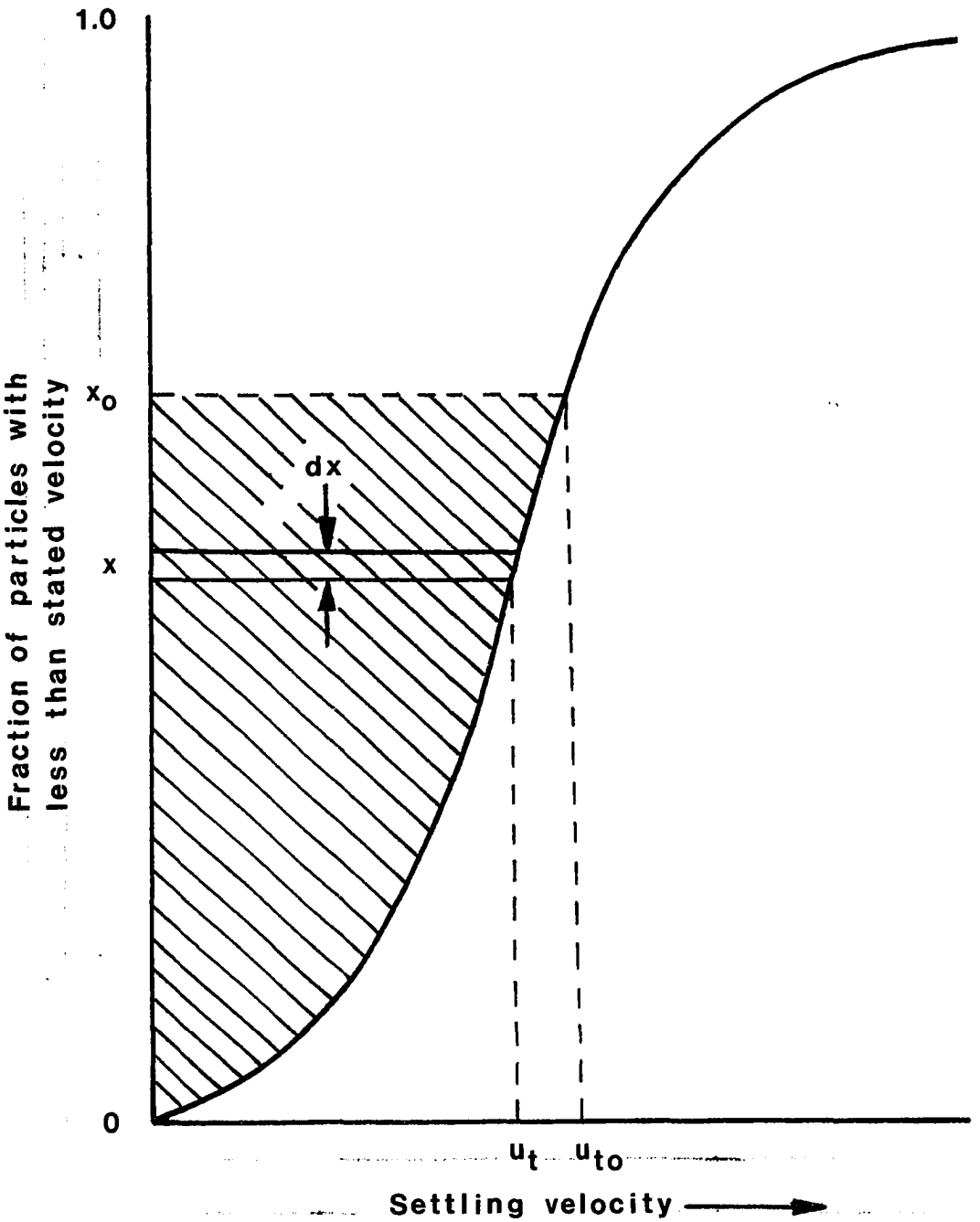

Figure 2. Settling-velocity Analysis Curve for Class-1 Clarification.

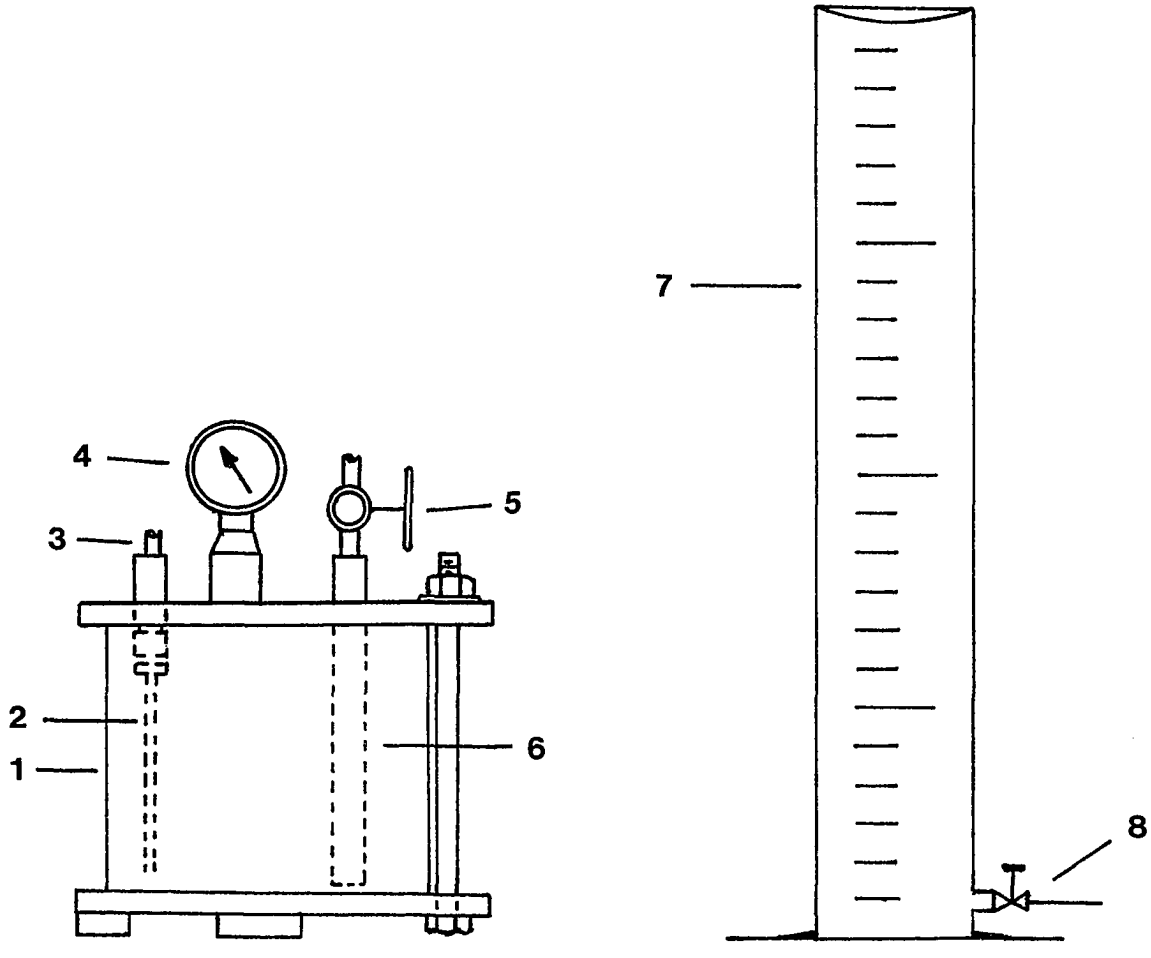

Figure 3. Laboratory Dissolved Air Flotation Unit.
1. Pressure Chamber, 2. Air Sparger, 3. Air Injection Port, 4. Pressure Gauge, 5. Pressurized liquid Control Valve, 6. Riser Tube, 7. Calibrated plastic Column, 8. Pressurized Liquid Injection and Sampling Port.

and float-solids concentration and effluent suspended solids were determined. Results of the effluent suspended solids were corrected for the percent of the recycle water used. The air/solids ratio was computed from the following equation:

$$\frac{A}{S} = \frac{1.3\, s_a f\, (P-1)R}{S_a}$$

where s_a = air saturation, cm^3/liter

f = fraction of saturation attained in the retention tank

R = pressurized volume, liter

P = absolute pressure, atm

S_a = influent suspended solids, mg/liter

The procedure used to estimate the flotation characteristics of a waste using the laboratory bench-scale model was as follows:

Select a recirculation ratio; for example, 0.50/1:

1. Place 2 liters of a representative sample of the treated waste in a 10-liter calibrated column (see Fig. 3).
2. Fill the pressure cell approximately three-fourths full of water.
3. Secure the cover gasket and cover pressure cell, making certain all the valves are closed.
4. Inject air into the cell until a pressure of 40 psi is attained, and maintain this pressure during the test.
5. Shake the cell vigorously for one minute to assure saturation of the pressurized liquid.
6. Release 1 liter of the saturated water into the calibrated column.
7. Allow the contents of the calibrated column to come to rest and observe the flotation. After a flotation time of 20 minutes, the clarified effluent and the floated sludge are drawn off through

a valve in the bottom of the column.

Centrifugation

Standard laboratory tests were developed following the procedures developed by Bird Machine Company, Inc., South Walpole, Massachusetts (102). Forty ml of the treated sample were placed in a centrifuge tube and centrifuged at 700 to 1,000 times gravity for 30-, 60-, 90- and 120-second intervals. At the end of period, the supernatant was drawn off for total suspended solids determination. The supernatant clarity was noted, and the cake or settled fraction firmness was checked with a 1/8" thick glass stirring rod approximately 6" long.

If a clear supernatant and a dense solid cake which would support the weight of the stirring rod for 30 seconds were obtained, the indications were that the solids could be easily separated by centrifugation. If, at the end of the two-minute spin period, either the supernatant was cloudy or the stirring rod settled with no resistance through the compacted cake, indications were that the solids could not be sepaprated from the liquid by centrifugation.

Total suspended solids determinations were performed on both the supernatant and the feed slurry of the treated wastewater samples. Total suspended solids removal efficiencies for all chemicals tested were calculated. The relationship between the removal efficiency of solids at various centrifugal speeds and times was plotted to establish the optimum centrifugal force and time. A Sorval automatic superspeed centrifuge model SS-3 was used for this study.

CPAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Chemical Selection

Jar tests were performed several times during the course of the study to establish the dosages necessary for coagulation. Samples of the supernatants were drawn off for analysis. Observations of floc formation, size of the floc, clarity of the effluent, and settling characteristics were made. Results of the preliminary tests including visual evaluation of the precipitate, settling rates, effluent clarity, and optimum COD removal efficiencies for all chemicals are presented in Table 11.

Based on these preliminary studies, it was apparent that cellulose sulfate was the least effective chemical among the chemicals that had been tested for the protein precipitation process. Overall performance of this chemical was poor and it was eliminated from further study.

Preliminary screening tests reduced the number of chemicals to eleven. These eleven were to be studied in more detail to determine their removal efficiencies, characteristics of floc formation, color, and settling.

Sulfuric Acid and Sodium Hydroxide

Several researchers (75, 85, 86) reported that protein could be obtained from the protein-containing wastewaters by precipitating either at pH 2 or 12 and readjusting it to the isoelectric point with acid or alkali compounds.

Table 11. Results of the Preliminary Screening Tests.

Chemical	Precipitation	Clarity of Effluent	Settling	COD	
				Effluent mg/1	Reduction %
H_2SO_4-NaOH	Fair	Fair	Fair	1,072	73
Alum dual system	Good	Good	Good	464	88
$FeCl_3$ dual system	Good	Good	Good	502	87
Starch sulfate	Fair	Poor	Fair	1,196	70
Molasses sulfate	Good	Fair	Fair	786	80
Corn syrup sulfate	Good	Good	Good	558	86
Glucose trisulfate	Good	Good	Good	518	87
Lignosulfonic acid	Good	Good	Good	668	83
Viscarin 402 carrageenan	Good	Fair	Poor	816	79
Kraft paper sulfate	Good	Good	Fair	579	85
Chitosan	Good	Good	Fair	500	87
Cellulose sulfate	Poor	Poor	Poor	1,994	50

Note: Concentration of influent for the chitosan precipitation was 4,100 mg/1.

Concentration of influent for all other chemical precipitation was 3,988.90 mg/1.

Laboratory bench tests were performed to determine the optimal removal efficiency of this protein precipitation process. In this test, sulfuric acid was used to lower the pH of the wastewater samples to the desired levels. Readjusting the pH by addition of sodium hydroxide to certain values altered the isoelectric structure of the soluble protein and aided in the separation and coagulation of the proteins.

Initially, the wastes were adjusted to pH 2 and 3 with sulfuric acid followed by readjustment with sodium hydroxide to pH 3, 4, 5, 6, and 7, respectively. Visual observations of the pH control on the protein precipitation are shown in Table 12.

Table 12. Results of the pH control tests

pH		
Initial	Final	Precipitation
3	3	Poor
3	4	Poor
3	5	Good
3	6	Poor
3	7	None
2	3	Poor
2	4	Poor
2	5	Good
2	6	Poor
2	7	None

The pH control tests indicated that optimal precipitation took place in the low pH range 2-3 and high pH value of 5. No protein precipitation occurred at a pH value greater than 6.

Table A-1 and Fig. 4 give the results of analyses showing the effects of pH on the COD removal efficiency.

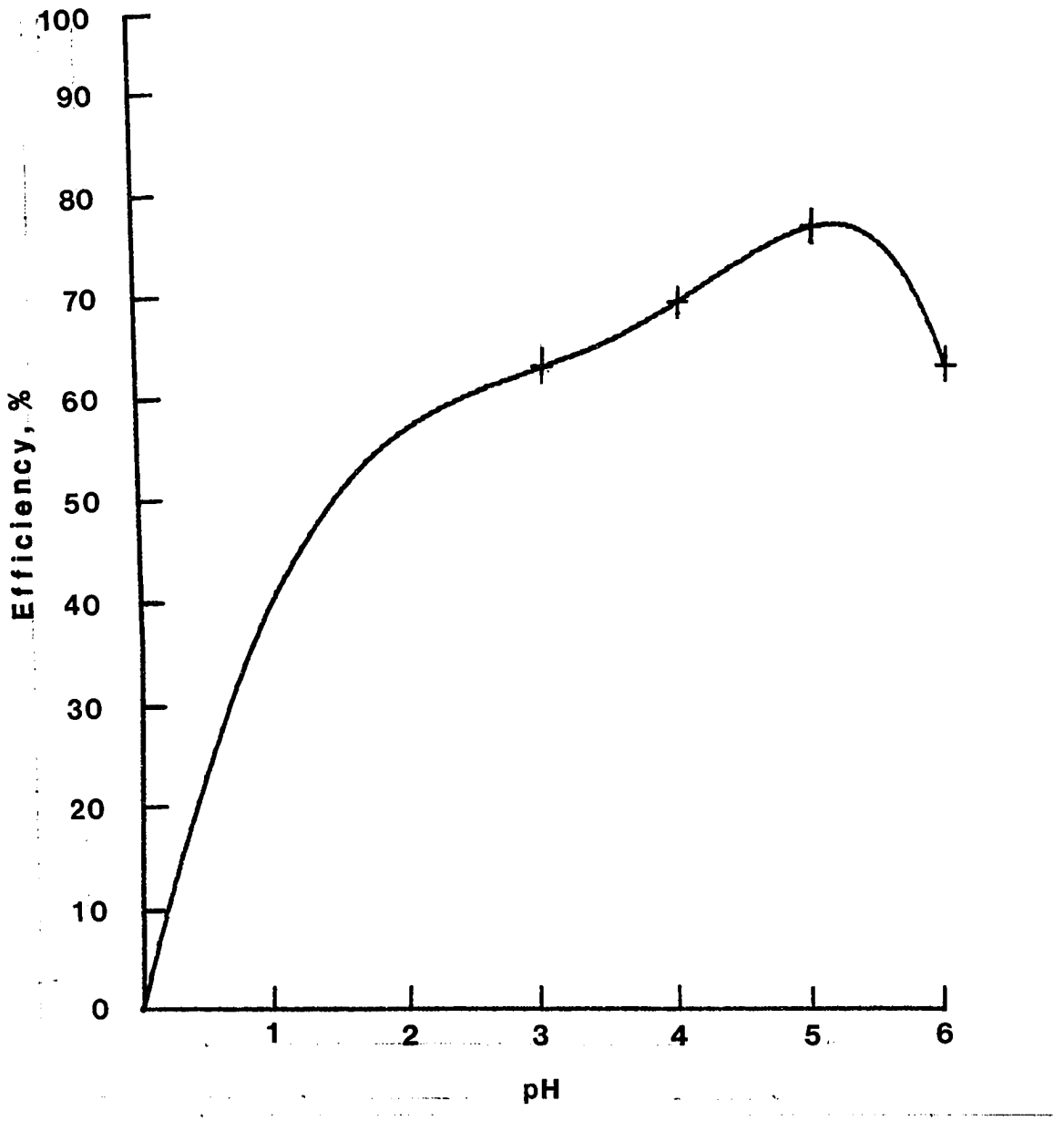

Figure 4. Effect of pH on the Efficiency in the Removal of COD.

Jar testing/visual evaluation indicated that lowering the pH to 2 or 3 produce almost equal results. The treated effluent was not clear. The floc was small, fragile, and had poor settling rate. However, efficiencies in the removal of COD, TSS, O&G, and Org-N were 77, 85, 81, and 53 percent, respectively. Comparison of the results in Table A-1 and A-2 show that the acid-alkali process increased in efficiency with an increase in waste strength.

Aluminum Sulfate

Early tests with aluminum sulfate (alum) showed some promise, but the floc was very small and slow forming. The supernatent of the treated waste was turbid and the suspended floc showed no tendency to settle. A review of the literature revealed that alkalinity must be present in excess of that destroyed by the acid released by the coagulant for effective and complete coagulation to occur. The alkalinity acts to buffer the waste at pH levels above 5 and insures complete precipitation of the coagulating ions. Jar tests indicated that large amounts of sodium hydroxide were required to raise the pH to around 9 to insure effective precipitation of alum in the pH range of 5.0-5.5.

Due to the large quantity of the chemical consumed to achieve floc formation, the precipitation was not considered comparable with that of other chemicals. Therefore, treatment by a combination of chemicals was investigated.

The proper combination of sulfuric acid, sodium hydroxide, and alum was found to be the most efficient. The wastes were adjusted to pH 3 with H_2SO_4 followed by readjustment to pH 5 with NaOH. This treatment removed 77% and 53% of the COD and organic nitrogen contributing materials, respectively. Additional protein precipitation was obtained by adding alum and adjusting the pH to 4.5-4.9. Table A-3 summarizes the relationship between the

chemical dosage, pH value, and organic removal efficiencies. The relationship between COD removal efficiency and alum dosage is presented in Fig. 5.

Results of the protein precipitation test using combinations of sulfuric acid, sodium hydroxide, and alum indicated good separation of proteins from the waste. This dual system resulted in excellent floc formation. The floc was small but compact and settled in a short period of time. The effluent was clear and color free. Using an optimum dosage of 5 ml (0.2 g/l) of alum on the 500-ml sample, COD, TSS, Org-N, and O&G were reduced by 85, 98, 67, and 96 percent, respectively.

Ferric Choride

Previous experiments using only ferric chloride for the treatment of meat packing wastes was not successful. Treatment of the waste with ferric chloride followed the same procedure as tests performed with alum. Combination treatment using acid-alkali and ferric chloride was investigated.

Acid-alkali alone resulted in a COD and Org-N removal of 77 and 53 percent, respectively. Additional treatment using different chemical dosages of 4, 5, and 6 ml (0.16, 0.2, and 0.24 g/l) of ferric chloride was studied. The data are compiled in Table A-4. The relationship between the efficiency in the removal of COD and amount of chemical added is shown in Fig. 6.

Combinations of H_2SO_4 - NaOH - $FeCl_3$ were found to be as effective as H_2SO_4 - NaOH - $Al_2(SO_4)_3$. Observations of the ferric chloride precipitation bench scale tests showed heavy floc formation, clear effluent, and good settling characteristics. This system with the optimum dosage of 0.2 g/l gave reductions of COD, TSS, Org-N, and O&G of 87, 99, 71, and 96 percent, respectively.

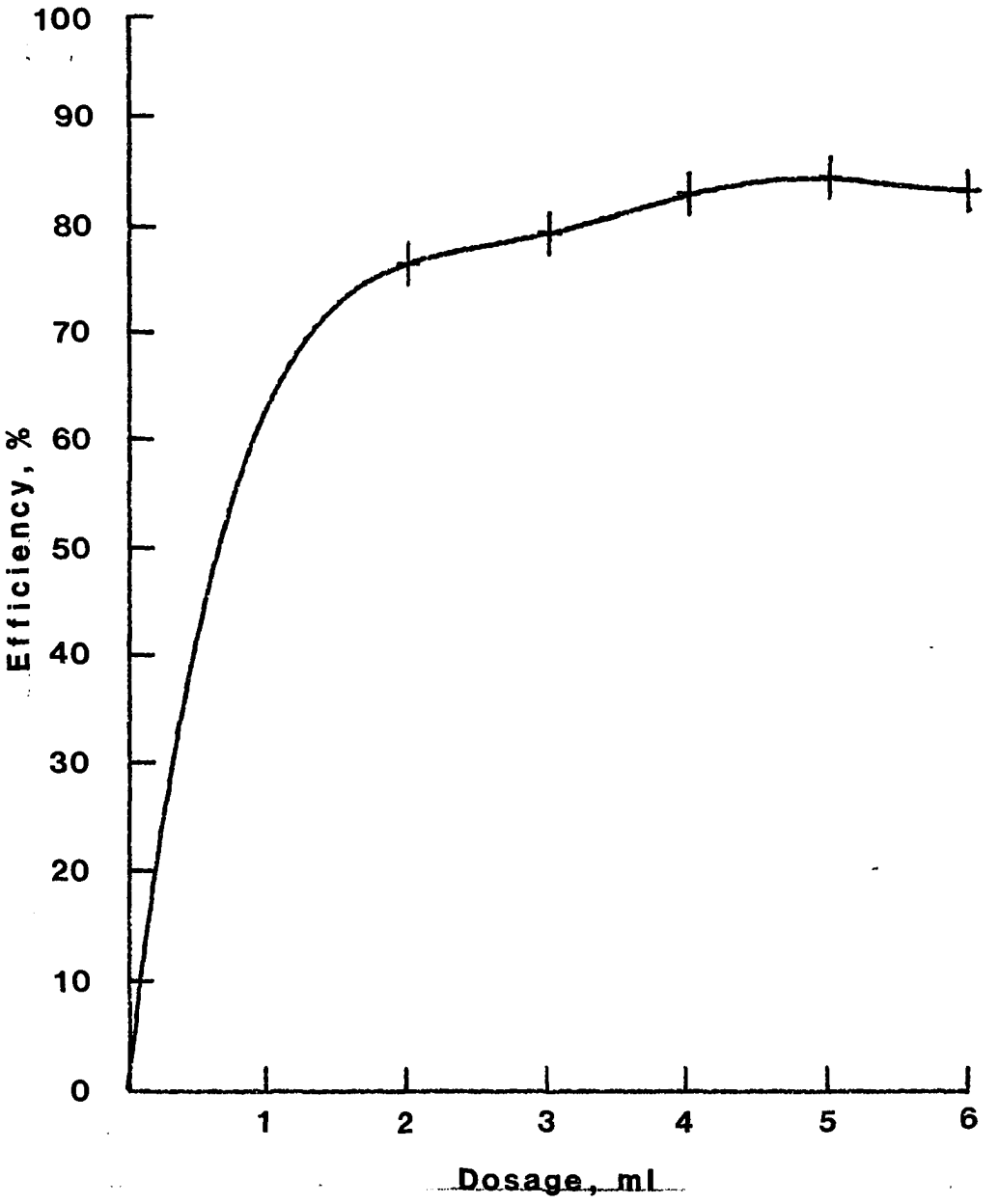

Figure 5. Efficiency in the Removal of COD by Addition of Different Amounts of Aluminum Sulfate.

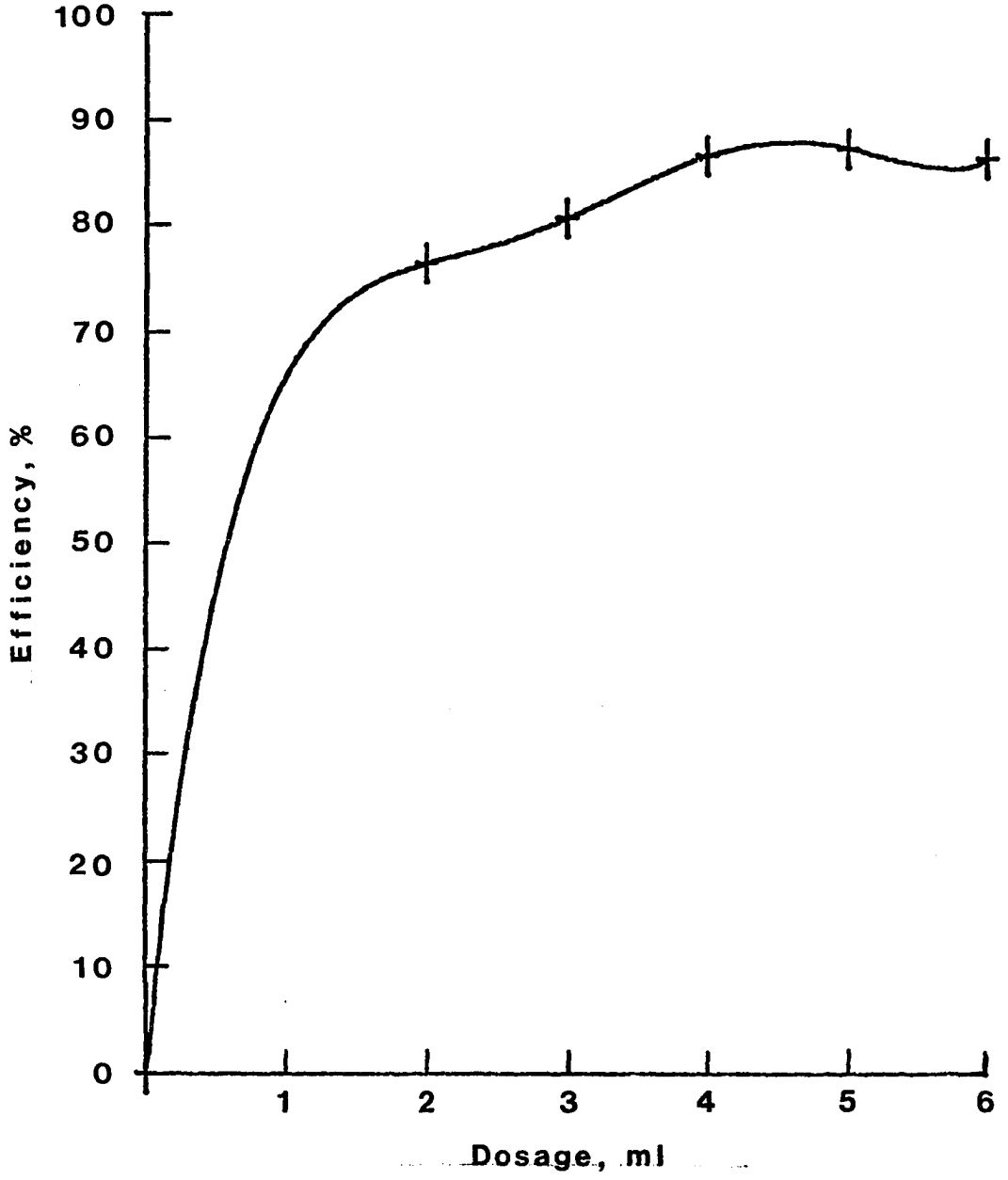

Figure 6. Efficiency in the Removal of COD by Addition of Different Amounts of Ferric Chloride.

Sugar Sulfate Ester

The sugar sulfate ester was prepared by treating a saccharide or a mixture of saccharides with an excess of concentrated sulfuric acid. The saccharides tested included glucose, molasses, corn syrup, and starch. The esters were prepared by mixing 1 volume of the saccharide material with 2 volumes of concentrated sulfuric acid at a temperature of 0-15^{o}C. The sulfation method developed by Thorn and Simonson was followed (65).

Control of pH was critical using this method. Because pH is a function of the amount of chemical added, an increase in the dosage will decrease the pH. Proteins have a certain buffering capacity which had to be overcome to reduce the pH to the isoelectric point. Isoelectric values vary with different proteins. Generally, acidification to pH 4.9 or below altered the isoelectric structure of the soluble proteins and aided in the separation and coagulation of the suspended matter.

Bench-scale tests were conducted to determine the protein precipitation efficiency of the sugar esters. Initially, a number of jar tests were run using visual inspection only to observe the precipitation and settling characteristics due to different chemical dosages. pH measurements were recorded to study the effects of pH on the protein precipitation. Influence of pH on the precipitation is shown in Table 13.

Table 13 reveals that good to excellent precipitation occurred in the pH ranges 3.8-5.0. Experimental evidence confirmed that treatment of proteinaceous waste with sugar sulfate ester is quantitative, making dosage control important. The relationship between COD removal efficiencies and different chemical dosages of starch sulfate, molasses sulfate, corn syrup sulfate, and glucose trisulfate is shown in Figs. 7 through 10, respectively.

Table 13. Influence of pH and Dosage on Sugar Sulfate Ester-Protein Precipitation.

Dosage g/l	pH Range	Precipitation
above 0.80	0-2.0	Poor
0.5-0.60	2.8-3.7	Fair
0.2-0.40	3.8-5.0	Good
0-0.12	Above 5.5	Poor

Based on these data it is evident that the maximum COD removal was achieved at the optimum dosage of 0.5 ml (0.20 g/l) within the pH range of 3.8-5.0 for all four of the esters. Chemical analysis of the effluent treated with starch sulfate, molasses sulfate, corn syrup sulfate, and glucose trisulfate were compiled in Table A-5, A-6, A-7, and A-8, respectively.

Evaluation of the sugar sulfate ester precipitation studies can be summarized as follows:

1. The COD removal efficiencies for gulcose, corn syrup, molasses and starch esters were 82, 80, 76, and 69 percent, respectively.

2. The protein precipitation efficiency was higher for the glucose and corn syrup esters than for molasses on starch esters.

3. Floc formation was good for glucose, corn syrup, and molasses esters.

4. Starch sulfate was the least effective chemical agent for protein precipitation, because most of the starch was not sulfated.

5. Increasing the chemical dosage above its optimum value did not improve floc formation but would decrease the removal efficiency of organic

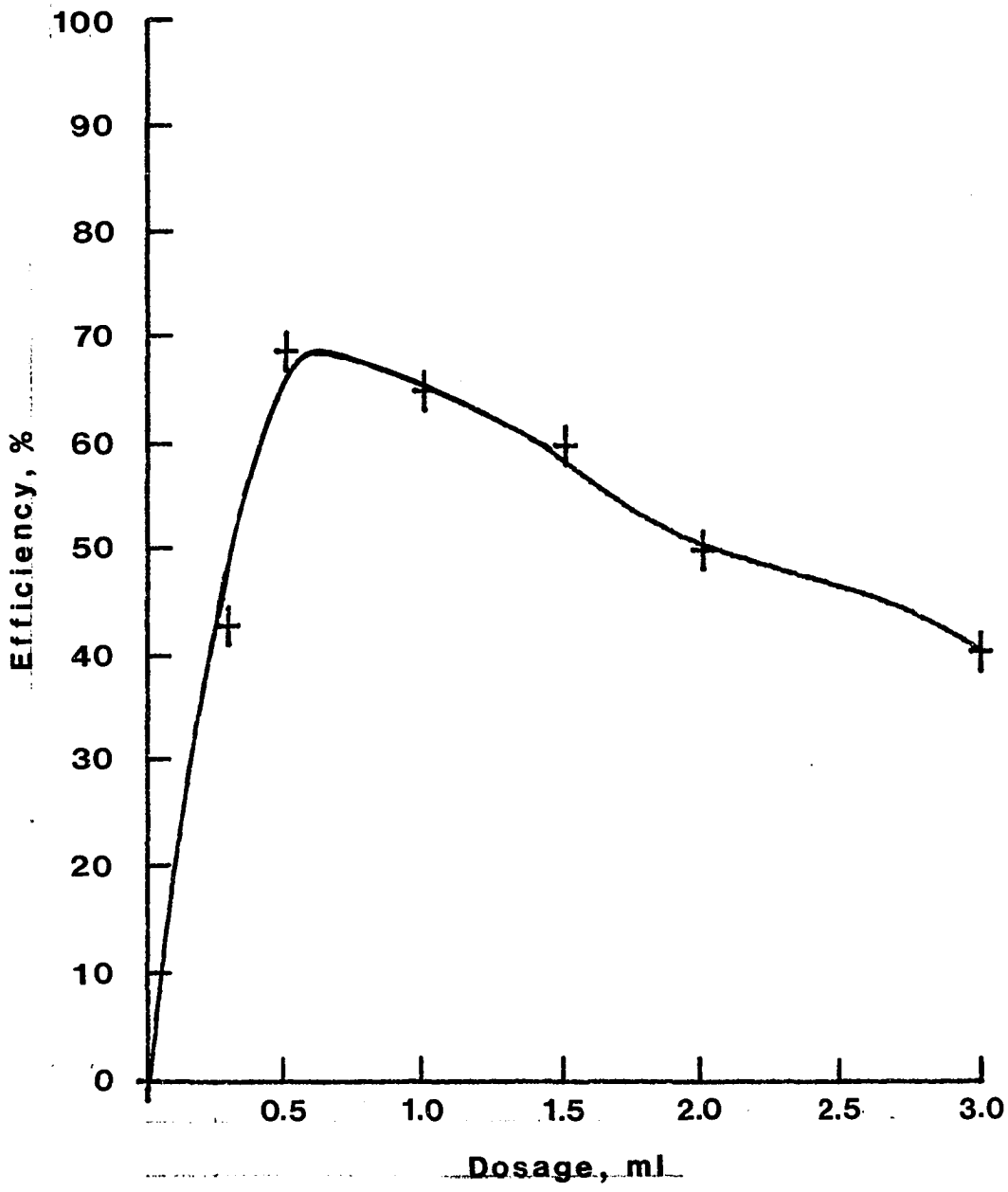

Figure 7. Efficiency in the Removal of COD by Addition of Different Amount of Starch Sulfate.

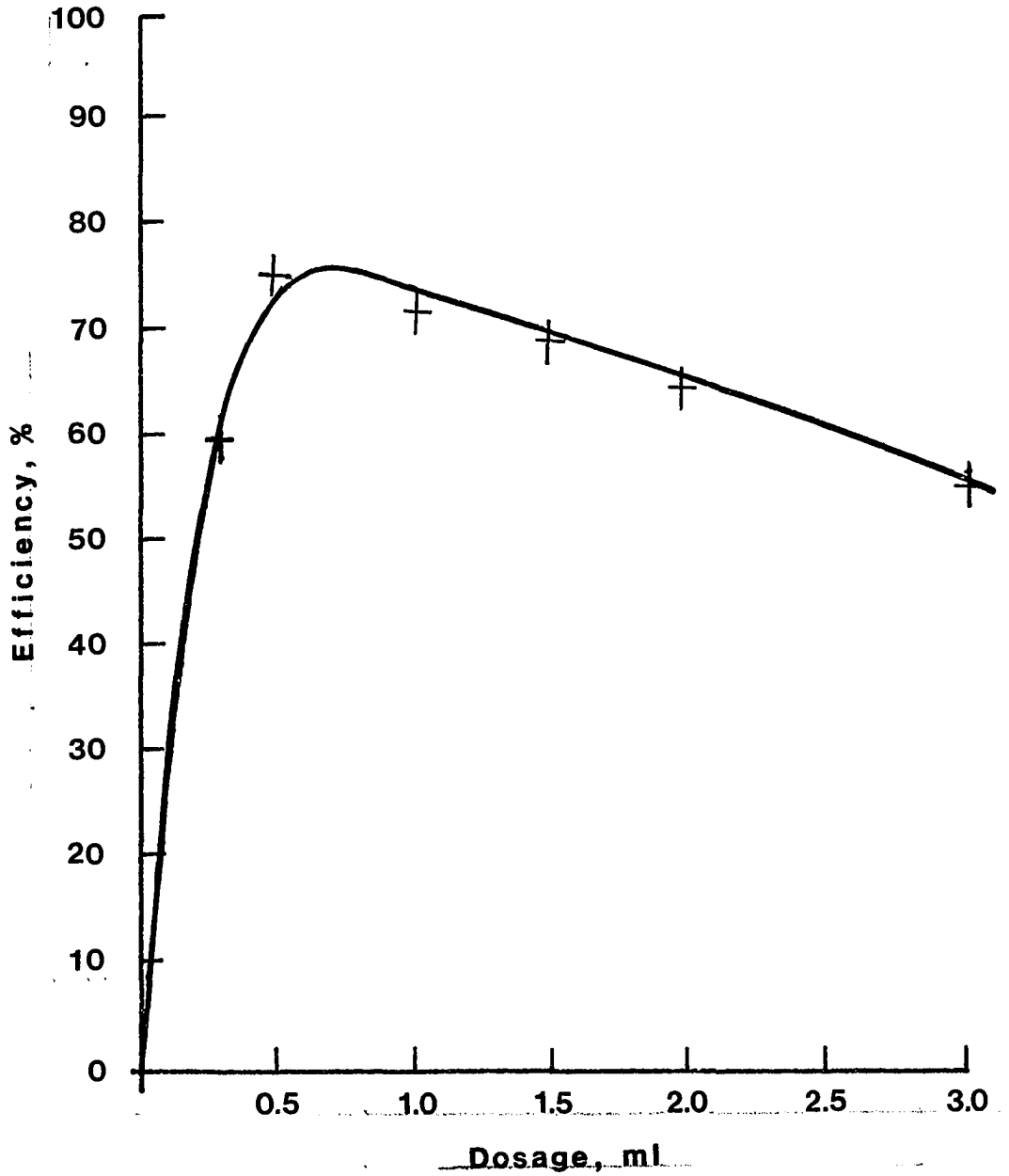

Figure 8. Efficiency in the Removal of COD by Addition of Different Amounts of Molasses Sulfate.

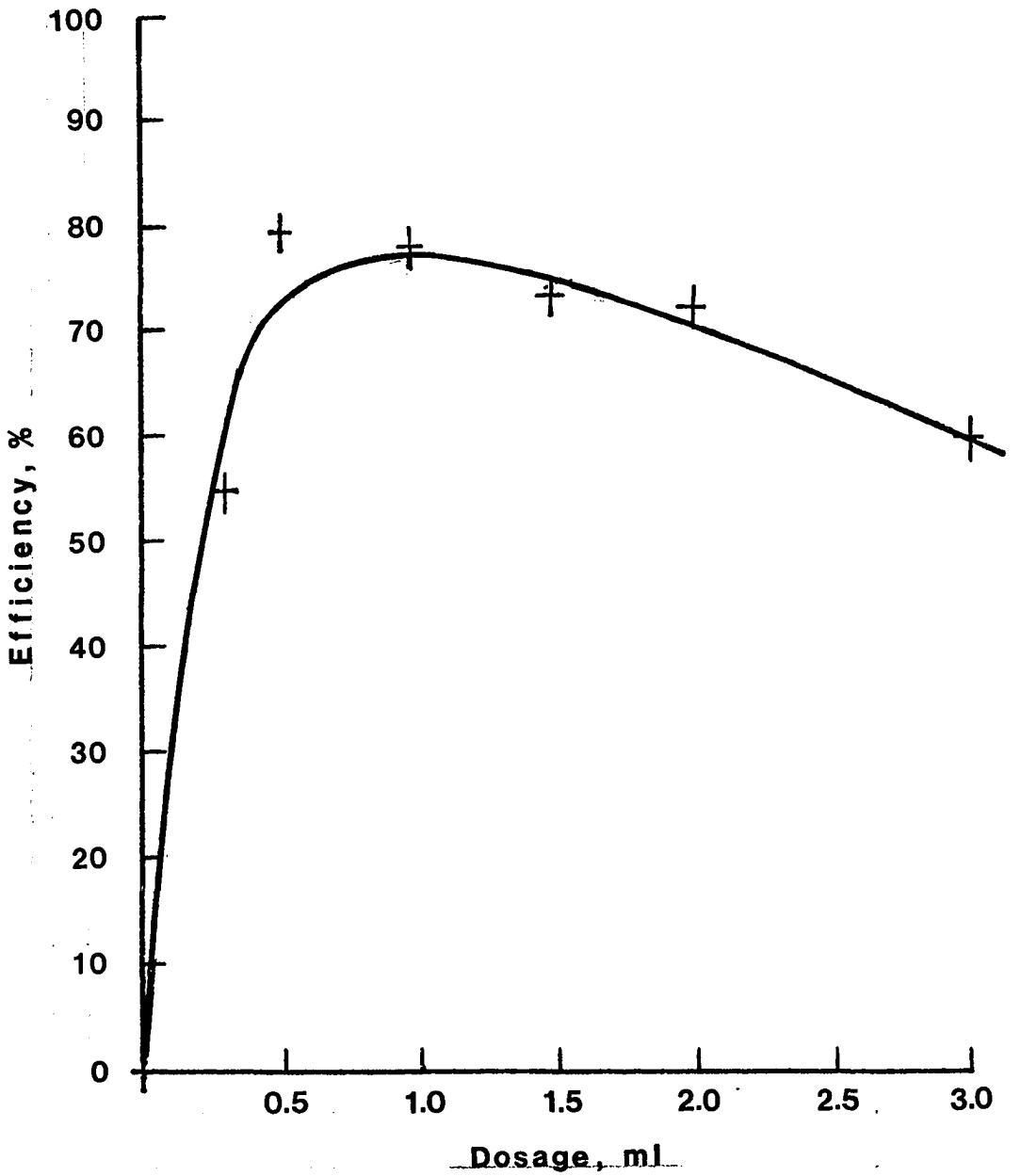

Figure 9. Efficiency in the Removal of COD by Addition of Different Amounts of Corn Syrup Sulfate.

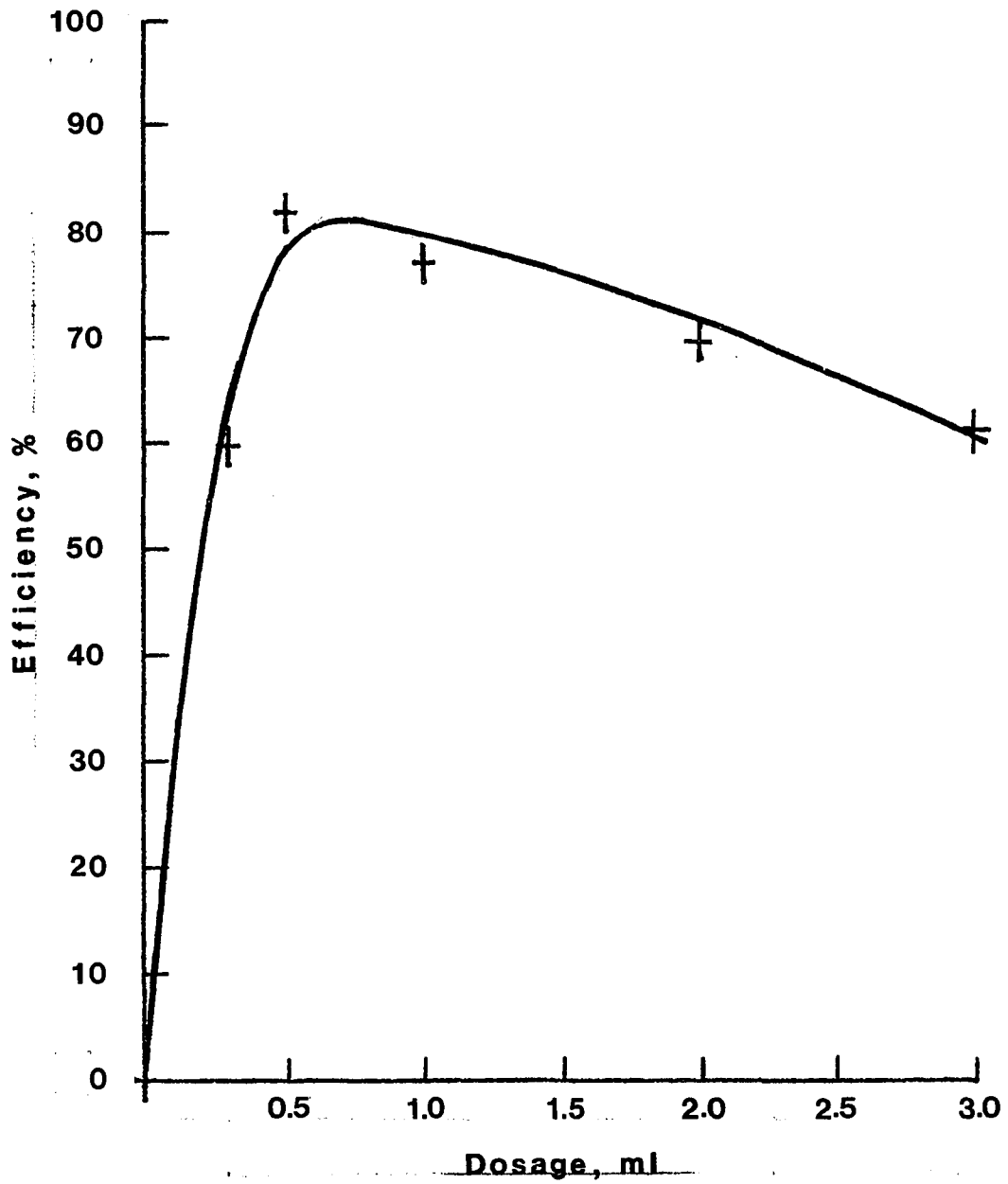

Figure 10. Efficiency in the Removal of COD by Addition of Different Amounts of Glucose Trisulfate.

matter and increase the turbidity in the final effluent. It was speculated that the floc which was initially formed was partially redissolved in the low pH solution.

Lignosulfonic Acid (LSA)

Lignosulfonic acid is a by-product from the sulfite wood pulping industry and is commercially available in a variety of forms and qualities. LSA products are available as sodium, calcium, or ammonium lignosulfonate. In applications where nitrogen removal is an objective, ammonium lignosulfonate is undesirable. Sodium lignosulfonate was used in this study.

Bench-scale studies were made using a 15 percent LSA solution for protein precipitation. Various amounts of lignosulfonic acid was added to 500 ml sample and the pH was adjusted to different levels with sulfuric acid. Results of the influence of pH on LSA-protein precipitation are shown in Table 14.

Table 14. Influence of pH on LSA-Protein Precipitation

pH Range	Precipitation
0-1	Poor
2-3	Good
3.4-4.5	Poor
Above 4.5	None

These results indicate that the pH must be in the range of 2 to 3 to obtain effective precipitation. Protein molecules contain both positively

charged amine groups and negatively charged carboxyl groups when the solution is at a pH near 7. Acidification of proteinaceous wastewater to a pH below the isoelectric point results in proteins carrying a net positive charge. Acidification to 3.5 or below insures a pH below the isoelectric point for most protein solutions.

Lignosulfonic acid in solution has a net negative charge. With acidification the LSA molecule continues to carry a negative charge down to a pH of 2. At a pH below 1 the sulfonate group loses its negative charge, resulting in poor precipitation as shown in Table 14.

Because precipitation involves the balancing of opposite ionic charges, it follows that an optimal ratio exists between LSA and proteins in order to maximize protein removal as shown in Fig. 11. Experimental evidence as shown in Table A-9 confirms that treatment of proteinaceous waste with LSA is quantitative, making LSA dosage control important.

Results from the chemical analysis of the effluent show optimal reductions of COD, TSS, Org-N, and O&G of 82, 99, 70, and 95 percent, respectively. The effluent was clear, and the solid settling rate was high. The floc was curdy and large.

Viscarin 402 Carrageenan

A one percent viscarin solution was used in this study. Initial studies on artificial waste showed that the chemical reacted with proteins under acid conditions. Table 15 summarizes the characteristics of the precipitation of carrageenan-protein at various pH ranges.

The study indicated that the pH must be in the range of 2.8 to 3.1 to achieve effective precipitation. Further experimental studies on meat packing waste confirmed that this was the optimal pH range for precipitation

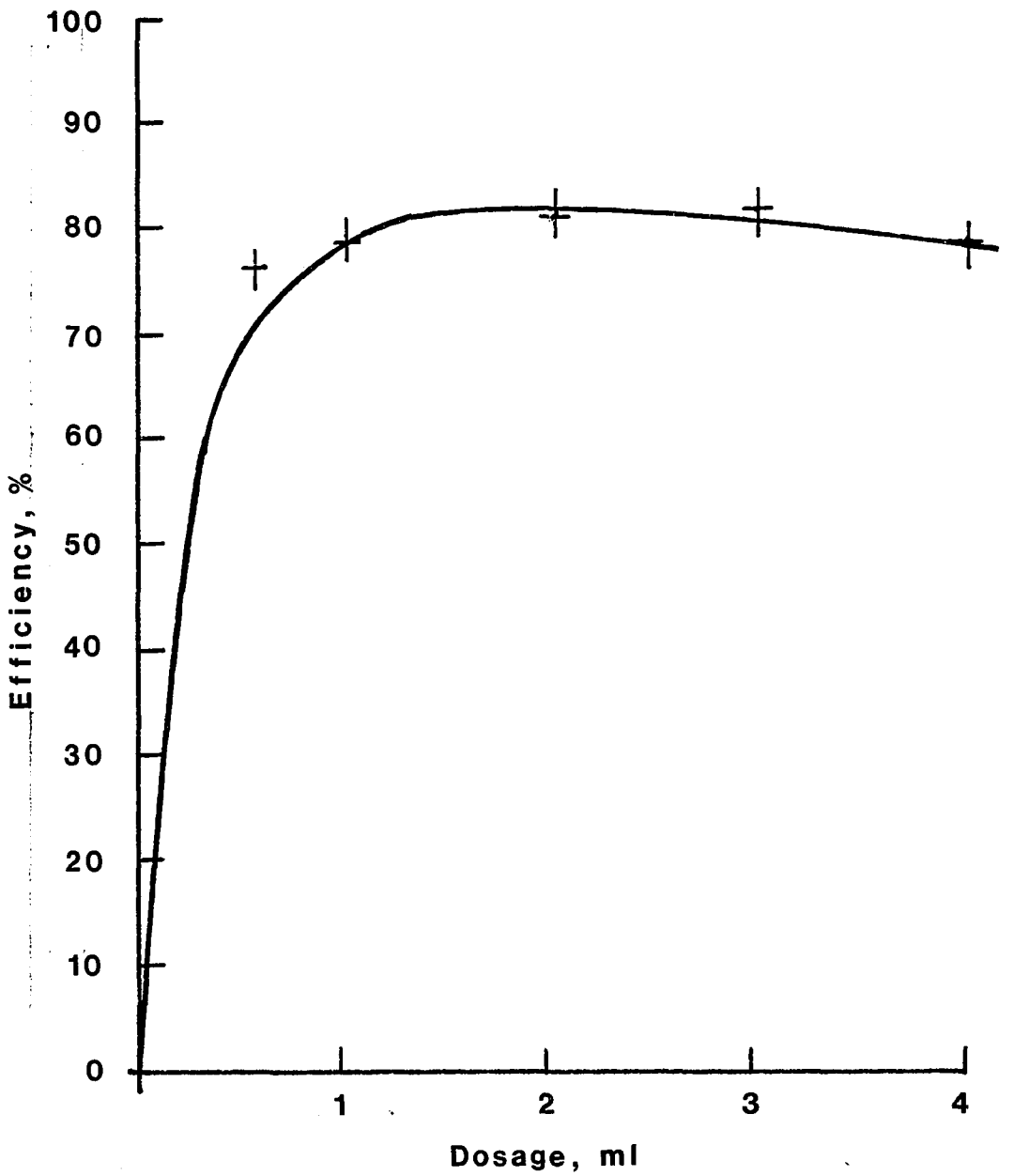

Figure 11. Efficiency in the Removal of COD by Addition of Different Amounts of Lignosulfonic Acid.

of the maximum amount of protein.

Table 15. Influence of pH on Carrageenan-Protein Precipitation

pH Range	Precipitation
0-2	Poor
2-2.7	Fair
2.8-3.1	Good
Above 3.5	Poor

Because pH is a function of the amount of chemical added, an increase in the dosage of carrageenan will increase the pH. A bench-scale study was conducted by adjusting the pH of the waste to 2.2 by addition of sulfuric acid. Various chemical dosages were added to each beaker which contained 500-ml waste samples. The supernatant of the treated samples were analyzed. Results of the tests are presented in Table A-10. The relationship between the organic removal efficiency and chemical dosages is plotted in Fig. 12.

Optimal organic removal was obtained at a pH of approximately 3 with the optimum dosage of 16 ml (0.32 g/l). This gave COD, TSS, Org-N, and O&G reductions of 79, 80, 51, and 81 percent, respectively.

The supernatant obtained from chemical precipitation was not clear. The floc was very large and fragile tended to float. Gentle stirring would break up the floc creating a cloudy effluent.

Paper Sulfate Ester

Paper sulfate ester was prepared by using paper as a starting material and a complex of sulfur trioxide and N, N-dimethylformamide as the sulfating

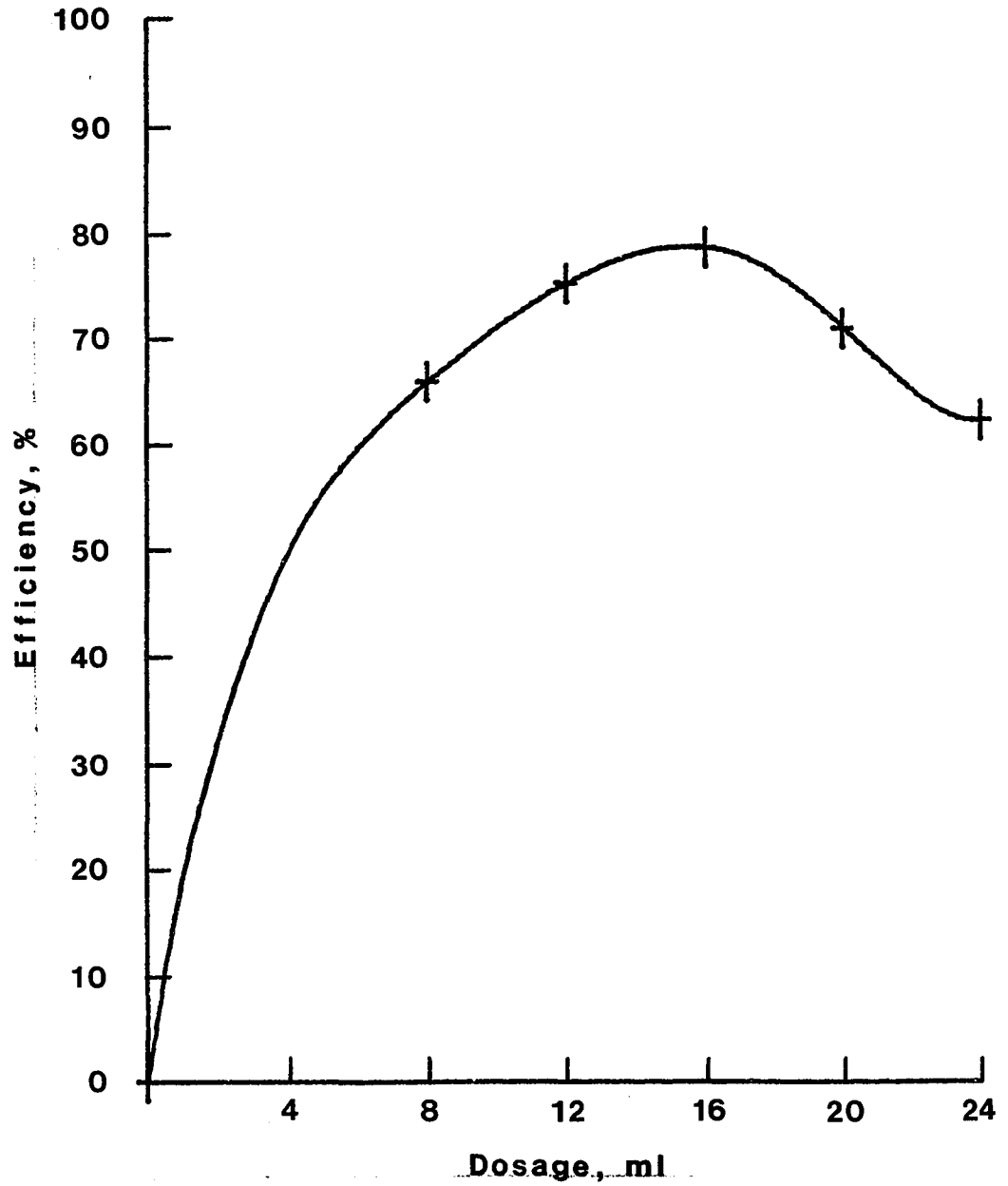

Figure 12. Efficiency in the Removal of COD by Addition of Different Amounts of Viscarin 402 Carrageenan.

agent (103).

The meat packing waste was treated with 10% kraft paper sulfate. Initially, the pH of the waste was lowered to below 3.5 with the addition of sulfuric acid. This would reduce the pH of the waste to or below its isoelectric point and enhance efficient protein precipitation.

Results of the test are given in Table A-11. The relationship between the chemical dosages and the efficiency of COD removal is shown in Fig. 13. The results show that the best floc formation with an optimum dosage of 6 ml (0.04 g/l) for each 500-ml of sample gave reductions of COD, TSS, Org-N, and O&G of 84, 98, 65, and 94 percent, respectively. The settling rate of the solids was poor, but the effluent was fairly clear.

Chitosan

Bench-scale tests were conducted on 500-ml samples of meat packing waste treated with 0.5, 1.0, 2.0, and 3.0 ml of a 1% solution of chitosan. Observations of floc formation, color, and settling characteristics were made. Results of the chemical analyses on the treated effluents are given in Table A-12. The relationship between the COD removal efficiency and the chemical dosage used is presented in Fig. 14.

Floc formation took place as soon as Chitosan was added to the waste and increased density of floc was observed as the slow mixing progressed. The effluent was clear and pink in color. The flocculated solids settled rapidly. However, upon stirring, the large floc would break into smaller suspended particles and float.

Under optimum conditions, COD, TSS, Org-N, and O&G removals of 88, 99, 72, and 96 percent, respectively, could be attained.

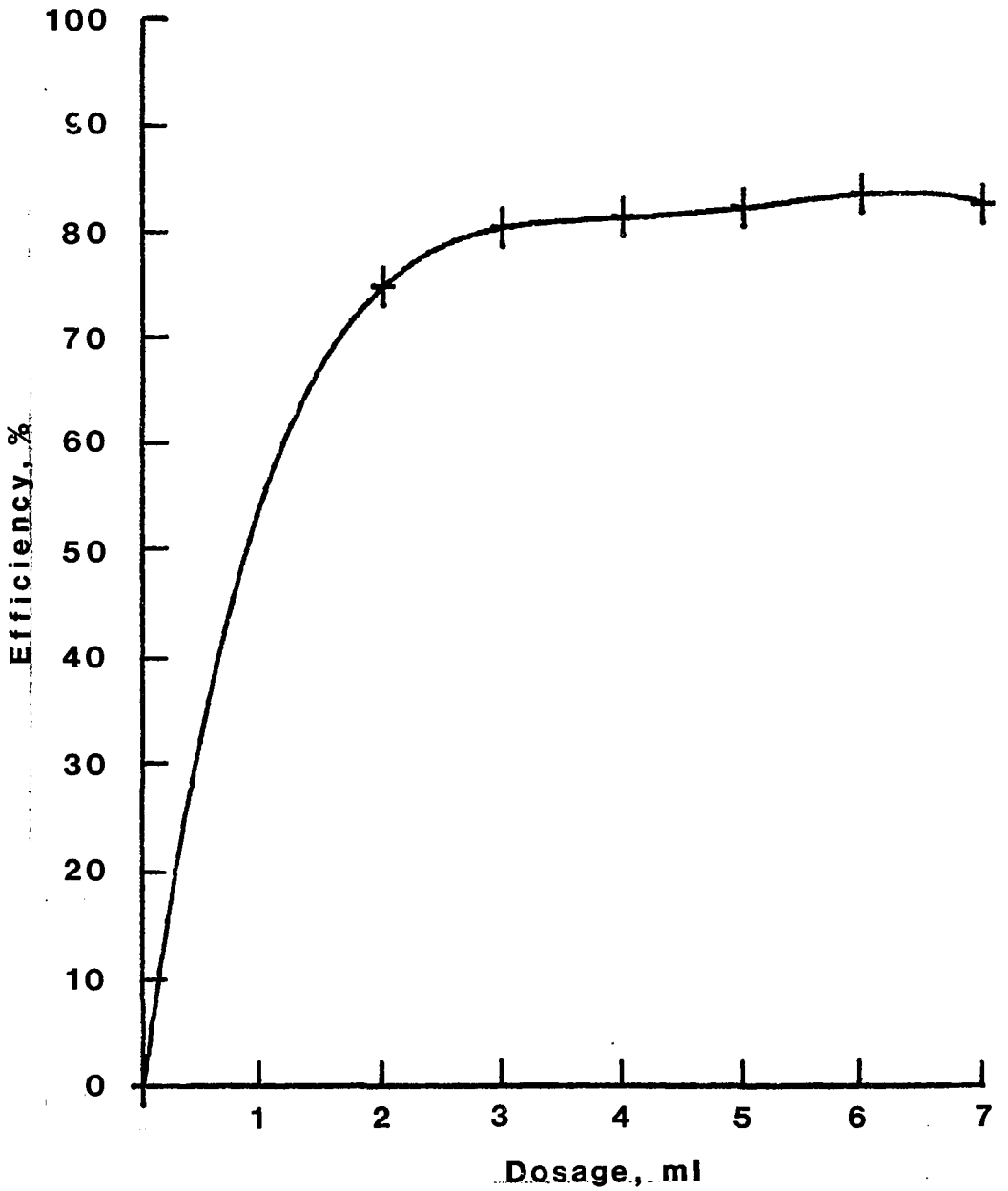

Figure 13. Efficiency in the Removal of COD by Addition of Different Amounts of Kraft Paper Sulfate.

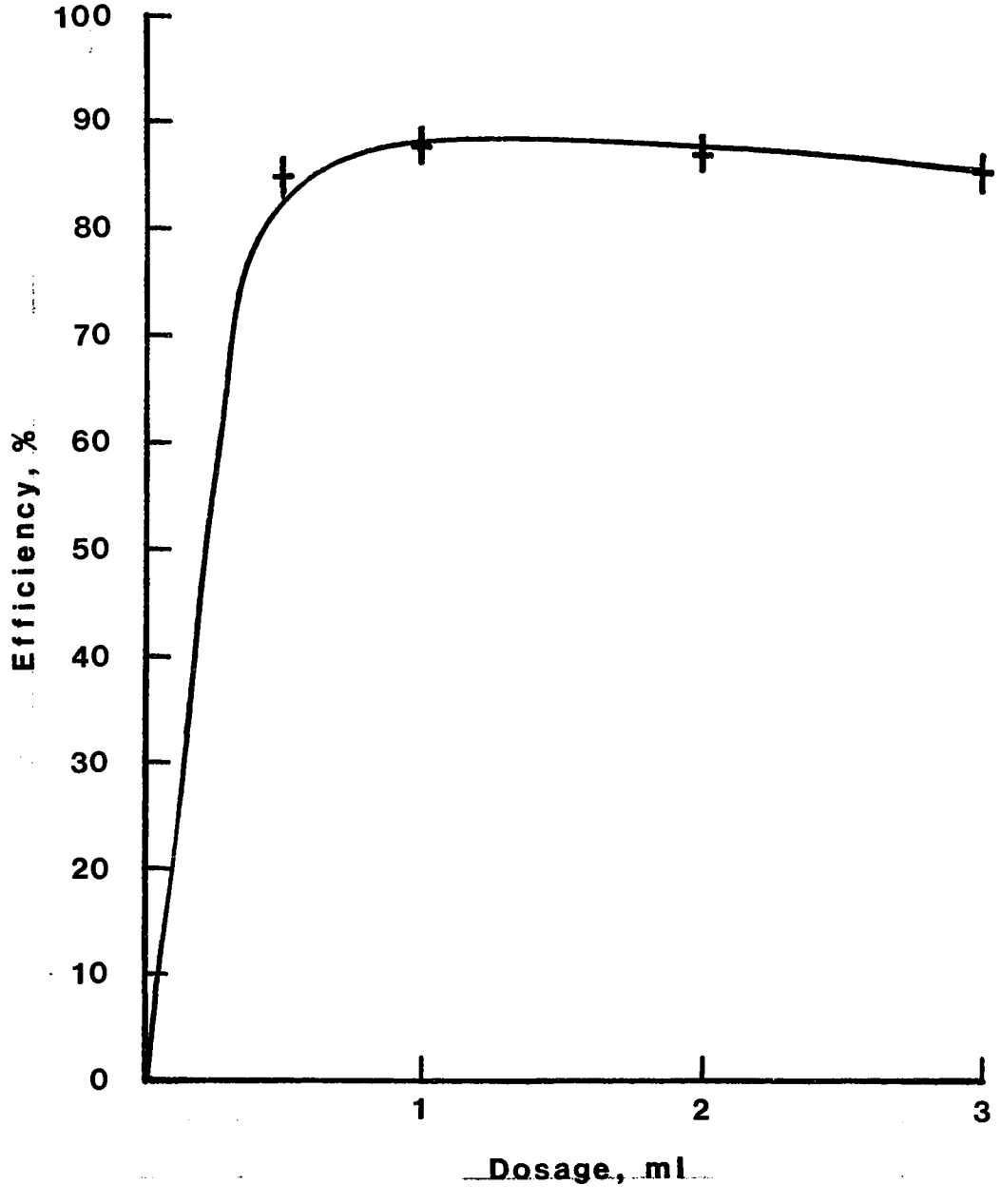

Figure 14. Efficiency in the Removal of COD by Addition of Different Amounts of Chitosan.

Optimization Studies

These studies were designed to determine optimum process efficiency and reliability using the eight different chemicals. Optimum efficiencies are dependent upon the efficiency of chemical precipitation and on solids-liquid separation. Process reliability or stability can be estimated from several replications.

Statistical significance required the testing of at least six samples. The following analysis of efficiency of glucose trisulfate in COD removal illustrates the determination of suitable sample size:

Table 16. COD Removal Efficiency of Glucose Trisulfate (From Preliminary Study).

Sample	Influent mg/l	Effluent mg/l	Y_i Removal Eff.	Y_i^2
1	5,598	1,312	76.56	5,861
1	4,044	1,081	73.27	5,368
1	6,121	1,283	79.04	6,247
1	4,802	1,574	67.22	4,519
1	5,396	877	83.75	7,014
1	4,546	1,015	77.67	6,033
n = 6			ΣY_i=457.51	ΣY_i^2=35,042

$$\text{Mean, } \bar{Y} = (\Sigma Y_i)/n = \frac{457.51}{6} = 76.25$$

$$\text{Variance, } \sigma^2 = \frac{1}{n-1}\left[\Sigma(Y)^2 - \frac{(\Sigma Y)^2}{n}\right]$$

$$= \frac{1}{6-1}\left[35{,}402 - \frac{(457.51)^2}{6}\right] = 31.22$$

$$\text{Standard deviation, } \sigma = \sqrt{\sigma^2} = \sqrt{31.22} = 5.587$$

$$\text{Coefficient of variation, } V = \frac{\sigma}{\bar{Y}} = \frac{5.587}{76.25} = 7.33 \text{ percent}$$

The error of the mean, E is given as $E = \frac{V.t}{\sqrt{n}}$ ----------(1)

To determine the sample size for this study, it is assumed that coefficient of variation, V, is the same as the previous study, 7.33 percent, for all chemicals. If V is based on a large number of tests, in the limit t = 1.645 for an infinite number of degrees of freedom; at the 10 percent level of significance. It is also assumed that the "error" in the estimated percent removal efficiencies of the chemical agent is not to exceed 5 percent in 90 percent of the tests. Equation (1) may be manipulated to obtain

$$n = \left[\frac{V.t}{E}\right]^2, \quad n = \left[\frac{0.0733 \times 1.645}{0.05}\right]^2 = 5.82$$

Chemical Efficiency

Removal efficiencies for total suspended solids, organic nitrogen compounds, oil and grease, and chemical oxygen demand have been calculated as a function of the chemical added. Results of the analyses are presented in Tables 17 through 20. Laboratory results on consistency tests of all chemicals using optimum dosages are also presented in Tables A-13 through A-20.

The relationships between the efficiency in removal of COD and Org-N, and the amount of chemical dosage used are plotted in Figs. 15 and 16, respectively. The diagrams show that the acid-alkali process gave the lowest

Table 17. Summarization of the Efficiences in Removal of Suspended Solids.

Chemical	Dosage (ml)	Sample (%) 1	2	3	4	5	6	Avg. %	Std. Dev.
H_2SO_4-NaOH	PH 3-5	85	86	84	85	88	83	85	1.7
Alum dual system	4	98	98	97	99	99	98	98	0.6
	5	98	99	98	99	99	98	99	0.5
	6	98	99	97	98	98	97	98	0.7
Ferric chloride	4	99	99	98	99	99	98	99	0.5
	5	99	99	98	99	99	99	99	0.4
	6	99	99	98	99	99	98	98	0.6
Lignosulfonic acid	1	95	97	95	97	98	95	96	1.2
	2	98	98	97	98	99	97	98	0.8
	3	99	97	95	97	98	95	97	1.4
Kraft paper sulfate	5	97	97	96	97	98	94	97	1.4
	6	98	98	97	98	99	96	98	1.1
	7	97	97	96	98	98	94	97	1.4
Corn syrup sulfate	0.5	97	97	96	98	99	98	97	0.9
	1.0	96	95	95	97	97	97	96	0.9
	1.5	95	93	94	96	97	96	94	1.5
Molasses sulfate	0.5	94	95	93	94	94	93	94	0.7
	1.0	93	94	91	93	92	93	93	1.0
	1.5	91	93	91	92	92	91	92	0.8
Chitosan	0.5	97	98	97	99	98	98	98	0.8
	1.0	99	99	98	99	99	99	99	0.5
	2.0	97	98	96	99	99	99	98	1.0

Table 18 Summarization of the Efficiences in Removal of Organic Nitrogen.

Chemical	Dosage (ml)	Sample (%) 1	2	3	4	5	6	Avg. %	Std. Dev.
H_2SO_4-NaOH	PH 3-5	53	60	54	61	64	60	59	4.2
Alum dual system	4	66	67	64	69	69	66	67	2.2
	5	67	70	66	73	74	68	70	3.2
	6	66	69	64	72	72	66	68	3.4
Ferric chloride	4	69	70	67	72	73	69	70	2.2
	5	71	74	71	77	78	72	74	3.1
	6	68	72	70	71	76	68	71	3.2
Lignosulfonic acid	1	69	67	65	68	70	64	67	2.3
	2	70	69	67	69	71	65	68	2.1
	3	70	70	67	63	70	63	68	3.0
Kraft paper sulfate	5	63	67	60	68	69	65	66	3.4
	6	65	70	69	72	76	73	71	3.6
	7	63	66	67	69	71	68	67	2.9
Corn syrup sulfate	0.5	66	68	65	68	72	68	68	2.4
	1.0	60	62	60	63	70	65	63	3.8
	1.5	58	60	58	62	69	63	62	4.1
Molasses sulfate	0.5	65	66	63	65	70	64	66	2.4
	1.0	59	60	60	63	67	62	62	2.9
	1.5	57	59	57	60	63	61	60	2.4
Chitosan	0.5	69	70	65	70	72	69	69	2.4
	1.0	72	74	69	75	78	71	73	3.1
	2.0	63	72	66	70	72	63	68	4.0

Table 19. Summarization of the Efficiences in Removal of Oil & Grease

Chemical	Dosage (ml)	Sample (%) 1	2	3	4	5	6	Avg. %	Std. Dev.
H_2SO_4-NaOH	PH 3-5	81	82	77	80	81	79	80	1.8
Alum dual system	5	96	97	94	95	96	95	96	0.9
Ferric chloride	5	96	97	95	95	96	96	95	0.9
Lignosulfonic acid	2	94	94	92	94	95	94	94	0.8
Kraft paper sulfate	6	94	94	90	93	94	92	93	1.5
Corn syrup sulfate	0.5	94	95	92	93	93	93	94	1.1
Molasses sulfate	0.5	89	91	89	92	94	89	91	2.1
Chitosan	1.0	96	98	94	97	97	95	97	1.6

Table 20. Summarization of the Efficiencies in Removal of Chemical Oxygen Demand.

Chemical	Dosage (ml)	Sample (%)						Avg. %	Std. Dev.
		1	2	3	4	5	6		
H_2SO_4-N_aOH	PH 3-5	77	80	74	80	78	77	78	2.3
Alum dual System	4	83	87	80	85	87	85	84	2.7
	5	85	87	84	90	88	96	87	2.2
	6	84	87	79	89	88	85	85	3.6
Ferric chloride	4	87	87	82	90	86	87	87	2.6
	5	87	84	82	92	88	88	88	2.3
	6	86	89	82	91	86	86	87	3.1
Lignosulfonic acid	1	79	80	73	79	80	81	79	2.9
	2	81	81	78	83	82	83	82	1.9
	3	82	81	72	82	81	81	80	3.9
Kraft paper sulfate	5	82	75	70	81	79	76	77	4.5
	6	84	78	74	84	82	79	80	3.9
	7	83	77	73	83	81	77	79	4.0
Corn syrup sulfate	0.5	80	80	75	84	75	81	79	3.5
	1.0	79	77	74	84	74	78	78	3.9
	1.5	78	76	73	81	74	78	77	3.2
Molasses sulfate	0.5	76	80	75	84	77	75	78	3.6
	1.0	72	77	75	83	75	74	76	3.6
	1.5	69	75	73	81	72	73	74	4.0
Chitosan	0.5	86	85	78	88	85	85	85	3.4
	1.0	88	87	80	91	86	86	86	3.6
	2.0	87	84	79	88	84	84	84	3.4

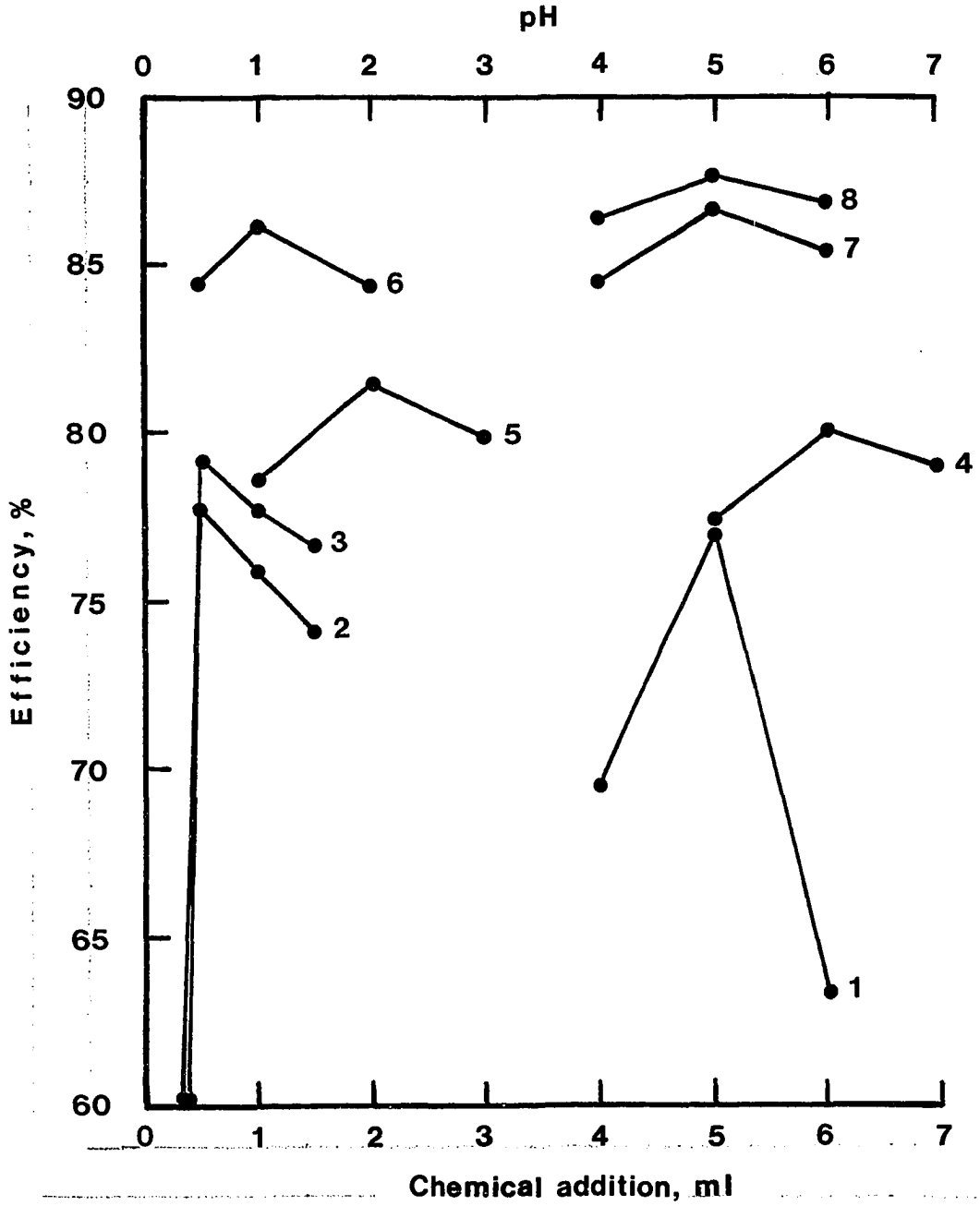

Figure 15. Efficiency in the Removal of COD by Addition of Different Amounts of Chemicals. 1. Sulfuric Acid and Sodium Hydroxide, 2. Molasses Sulfate, 3. Corn Syrup Sulfate, 4. Kraft Paper Sulfate, 5. Lignosulfonic Acid, 6. Chitosan, 7. Alum Dual System, 8. Ferric Chloride Dual System.

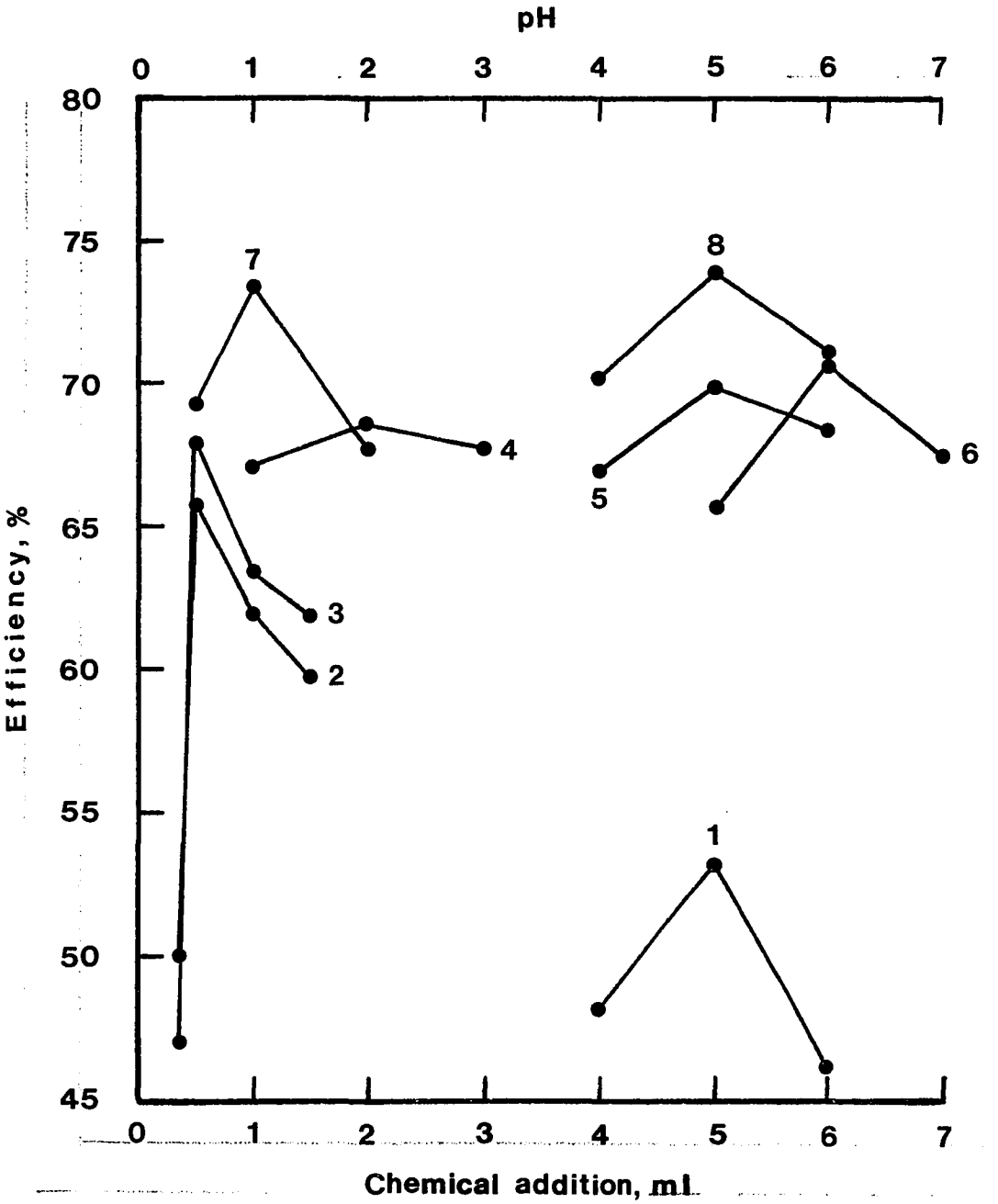

Figure 16. Efficiency in the Removal of Org-N by Addition of Different Amounts of Chemicals. 1. Sulfuric Acid and Sodium Hydroxide, 2. Molasses Sulfate, 3. Corn Syrup Sulfate, 4. Lignosulfonic Acid, 5. Kraft Paper Sulfate, 6. Alum Dual System, 7. Ferric Chloride Dual System. 8. Chitosan.

efficiency in removal of organic matter. The dual systems, acid-alkali-alum and acid-alkali-$FeCl_3$, gave about the same organic matter removal efficiency regardless of the amount of chemical used above their optimum dosages.

The amounts of solids produced from the chemical complexing reaction determined the effectiveness of the chemical. The higher concentration of the solids indicated the better performance of the chemical. The effectivenesses of all the chemicals tested are presented in Table 21.

Table 21. Effectivenesses of the Chemicals

Chemical	TSS Treated Raw Waste mg/l	TSS Produced mg/l	Performance Ranking
Kraft paper sulfate	2640	645	1
Ferric chloride dual system	2580	585	2
Lignosulfonic acid	2415	420	3
Chitosan	2385	390	4
Alum dual system	2350	355	5
Molasses sulfate	2280	285	6
Corn Syrup sulfate	2245	250	7
H_2SO_4 -NaOH	2100	105	8

Note: TSS of the raw waste is 1995 mg/l.

According to the data given in the tables above and referenced in Figs. 15 and 16, the following deductions were made:

1. Chitosan, aluminum sulfate dual systems, and ferric chloride dual system gave the highest efficiency in the removal of COD, followed by lignosulfonic acid, kraft paper sulfate, corn syrup sulfate, molasses sulfate, and sulfuric acid-sodium hydroxide, respectively.

2. Organic nitrogen compounds were removed more effectively by chitosan and the ferric chloride dual system. The efficiency decreases in the following order: ferric chloride dual system, chitosan, alum dual system, kraft paper sulfate, lignosulfonic acid, corn syrup sulfate, molasses sulfate, and sulfuric acid-sodium hydroxide.

3. All the chemicals investigated removed greater than 90 and 93 percent of oil and grease and solids, with the exception of the acid-alkali system which removed 80 and 85 percent of oil and grease and solids, respectively.

4. Ferric chloride was more successful in the overall removal of organic matter than aluminum sulfate.

5. Standard deviation values on the removal efficiencies of all the chemicals were small (4.15 and below). This indicates high process reliability.

Recovery of the Proteinaceous Sludge

Three dewatering processes, i.e., sedimentation, flotation, and centrifugation which can be used for solids-liquid separation were studied. Results of these studies for each process are presented below.

Sedimentation

It was assumed that the floc which resulted from the chemical treatment did not increase in size as it settled out of a suspension of the treated waste. This type of settling was identified as class-1 clarification.

Settling analysis was performed by adding the treated effluent to the settling column as shown in Fig. 1. As solids settled, samples of liquid were drawn off at a fixed sampling depth of 2.35 feet below the top of the column at 10 and 20 minute intervals up to a period of 2 hours. The samples

were analyzed for their suspended solid concentrations.

Settling velocity at different time intervals were calculated. Results and laboratory data of the settling analysis for all chemicals are compiled in Tables A-21 through A-27. Settling velocity analysis curves for all chemicals were plotted as shown in Fig. 17 through Fig. 23.

In order to evaluate the performances of the chemicals tested, two clarification rates of 0.13 $ft^3/min/ft^2$ and 0.07 $ft^3/min/ft^2$ were chosen. Overall removal efficiencies were determined. Results of the calculations and graphical integration of the settling-analysis curves are summarized in Table 22.

Table 22. Efficiency in Solid Removal at Different Clarification Rates

Chemical	% Efficiency in Solid Removal at Clarification Rates	
	0.13 $ft^3/min/ft^2$	0.07 $ft^3/min/ft^2$
Alum dual system	72.25	98.33
Ferric chloride dual system	80.32	96.10
Lignosulfonic acid	57.00	80.40
Kraft paper sulfate	40.37	60.59
Corn Syrup sulfate	65.08	84.92
Molasses sulfate	53.04	78.49
Sulfuric acid-sodium hydroxide	30.34	50.53

It was apparent that dewatering of the sludge by a sedimentation process could be utilized best for the alum and ferric chloride dual systems, resulting in a removal of solids greater than 96 percent. Efficiency in removal of solids at a clarification rate of 0.07 $ft^3/min/ft^2$ decreases in the

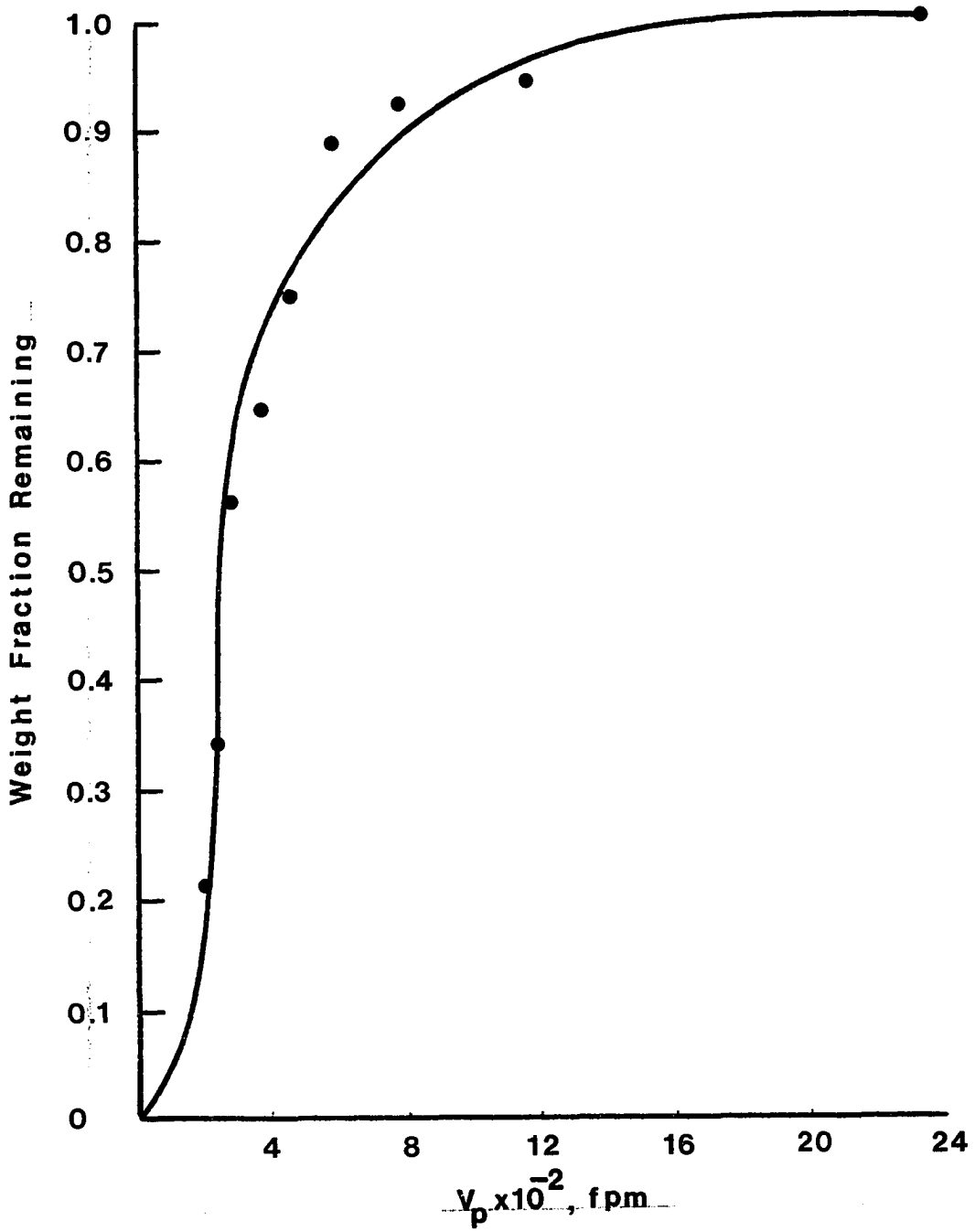

Figure 17. Settling-velocity Analysis Curve for Sulfuric Acid and Sodium Hydroxide.

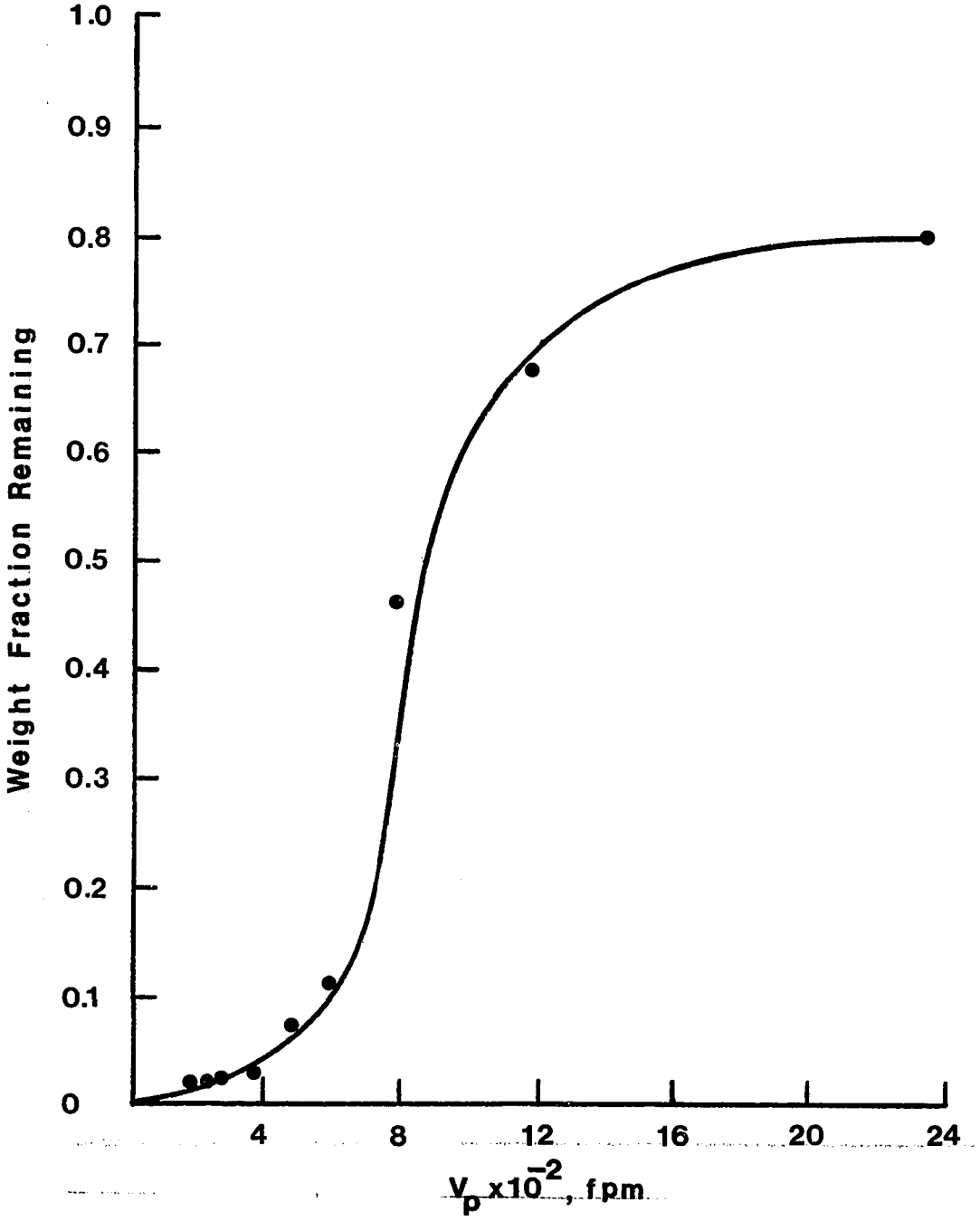

Figure 18. Settling-velocity Analysis Curve for Alum Dual System.

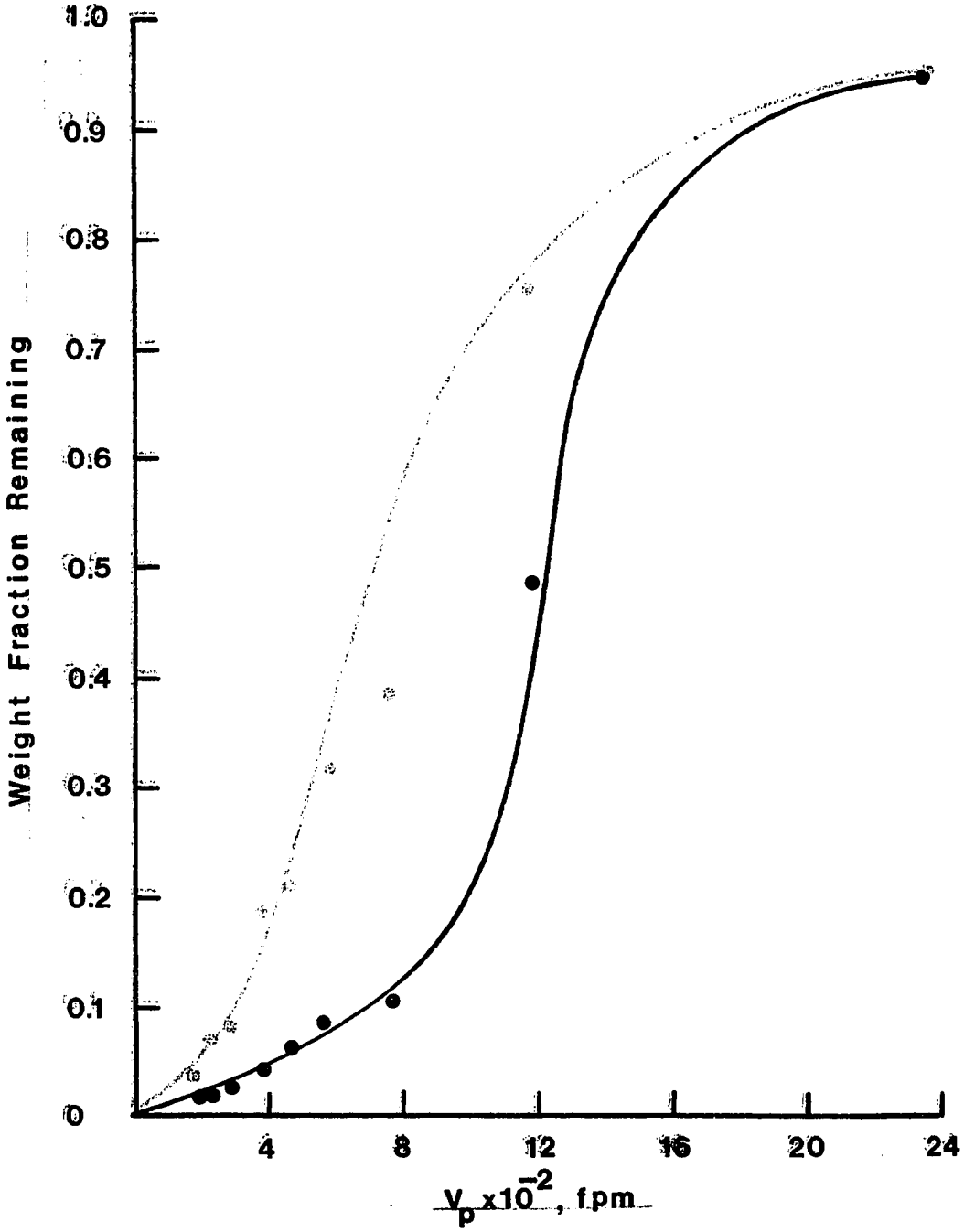

Figure 19. Settling-velocity Analysis Curve for Ferric Chloride Dual System.

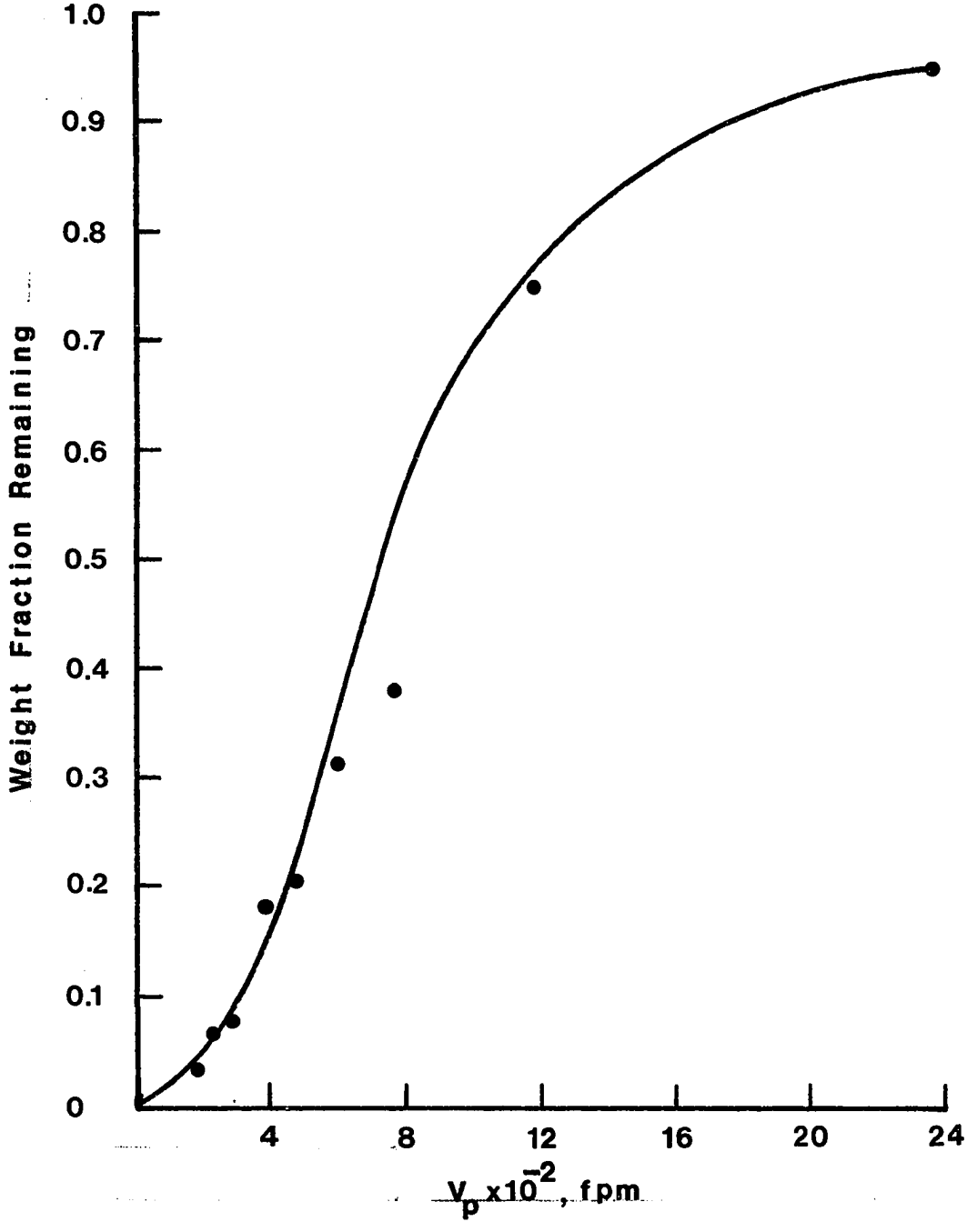

Figure 20. Settling-velocity Analysis Curve for Lignosulfonic Acid.

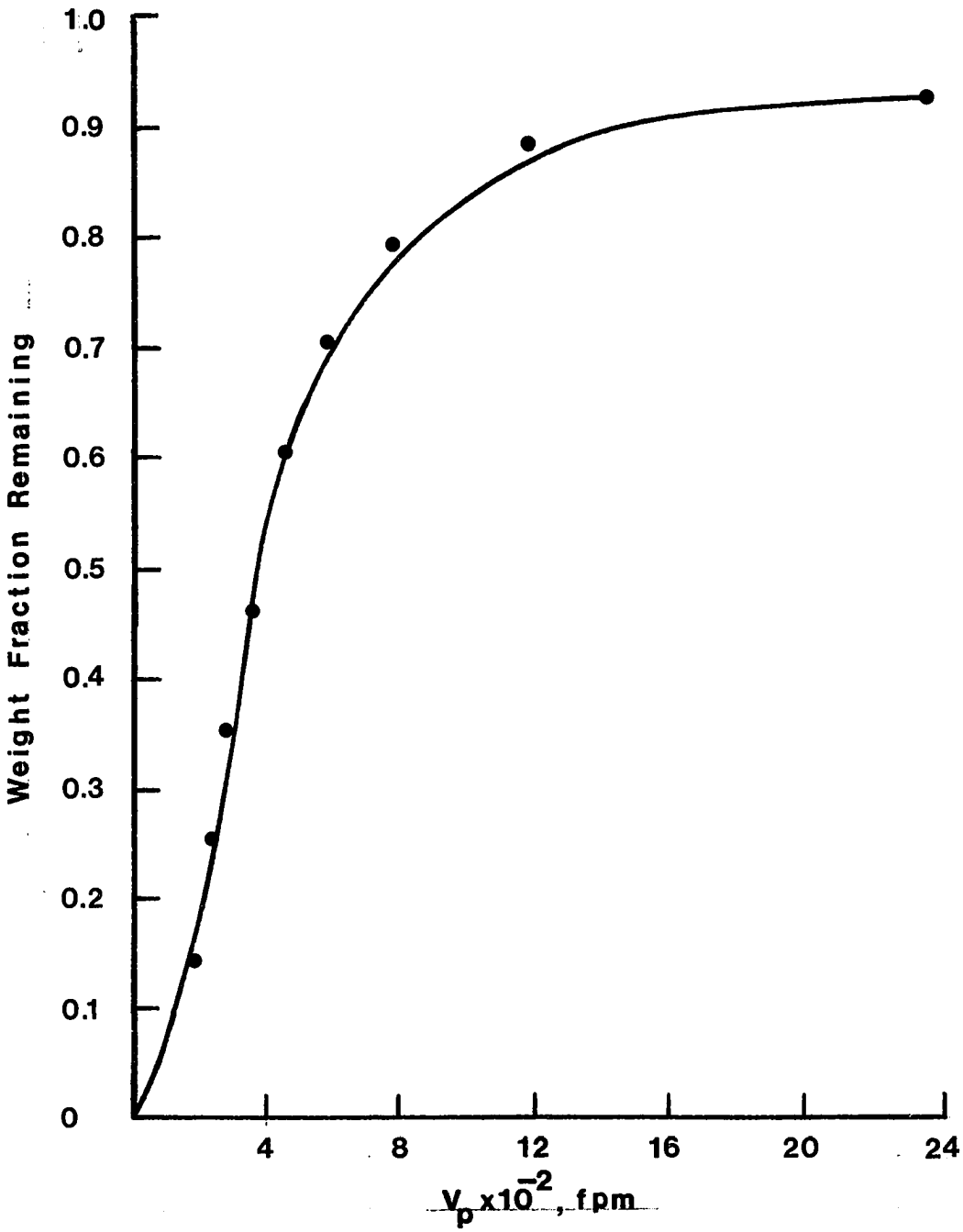

Figure 21. Settling-velocity Analysis Curve for Kraft Paper Sulfate.

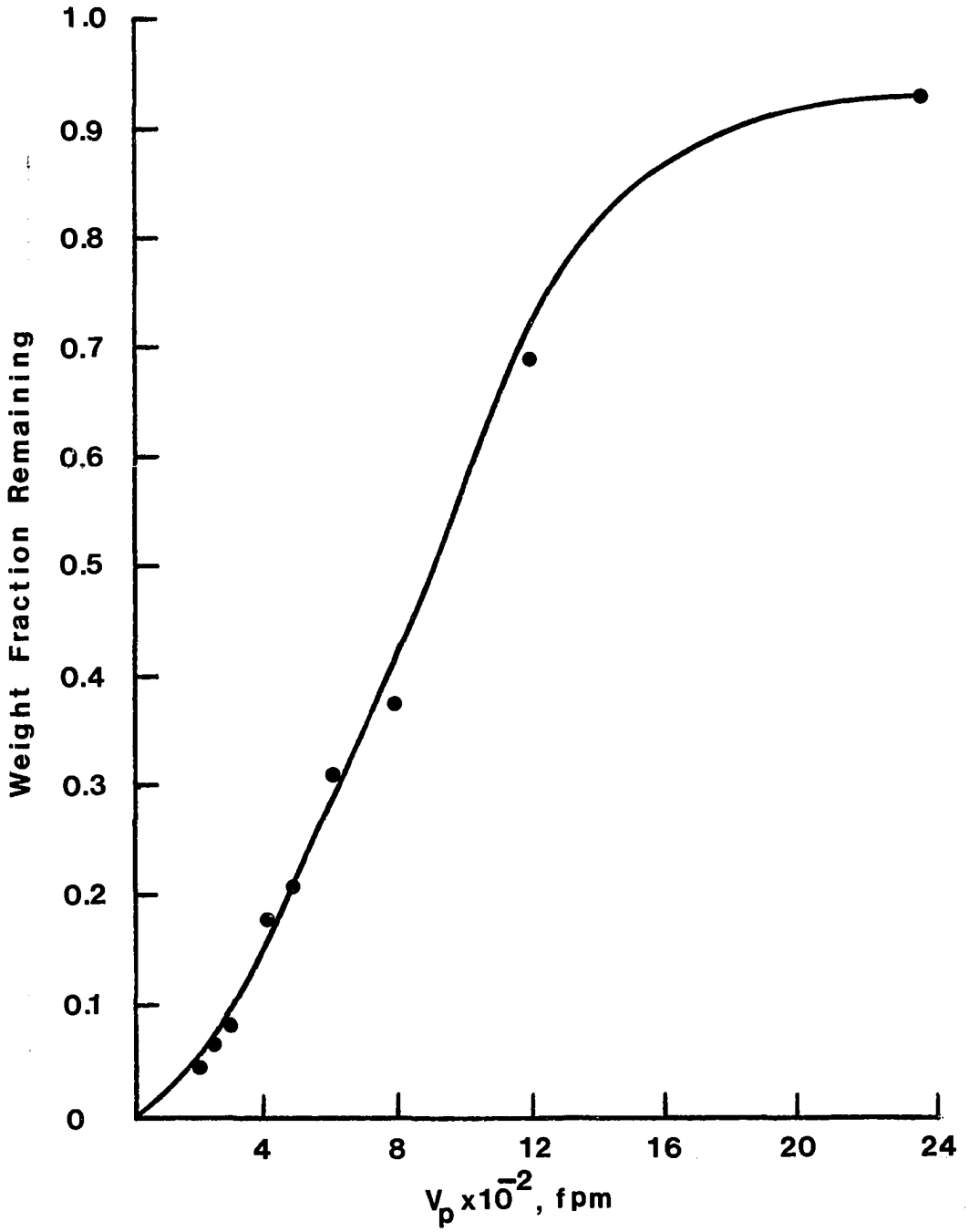

Figure 22. Settling-velocity Analysis Curve for Corn Syrup Sulfate.

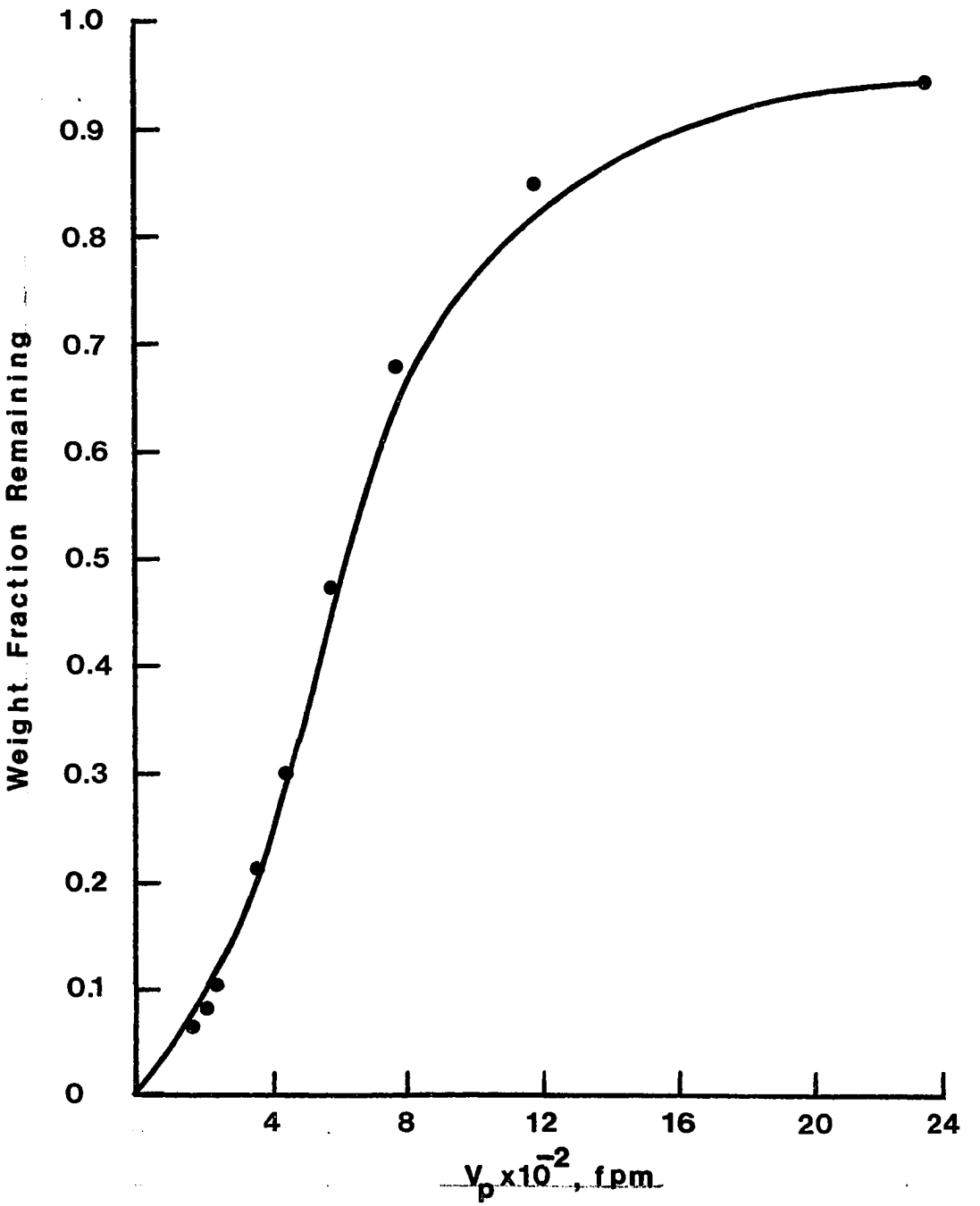

Figure 23. Settling-velocity Analysis Curve for Molasses Sulfate.

following order: alum dual system (98 percent), ferric chloride dual system (96 percent), corn syrup sulfate (85 percent), lignosulfonic acid (80 percent), molasses sulfate (78 percent), and kraft paper sulfate (61 percent). Efficiency in removal of solids at a clarification rate of 0.13 $ft^3/min/ft^2$ decreases in the following order: ferric chloride dual system (80 percent), alum dual system (72 percent), corn syrup sulfate (65 percent), lignosulfonic acid (57 percent), molasses sulfate (53 percent), and kraft paper sulfate (40 percent).

Settling tests for chitosan were unsuccessful. This was due to the fact that the chitosan floc was large, fragile, and of low density. These particles settled after flocculation was completed, but once the treated waste was disturbed, the floc would float to the surface and then showed little tendency to settle.

Flotation

A laboratory bench-scale test procedure, developed to simulate the dissolved air flotation process, was used to determine sludge removal efficiency. The laboratory air flotation unit is illustrated in Fig. 3.

Results and laboratory data of the flotation tests for all chemicals in question are presented in Table 23. The relationships between the air/solids ratios and float-solids concentration, and effluent suspended solids were plotted as illustrated in Fig. 24 and Fig. 25, respectively.

It was evident that optimum removal of solids for all chemicals was achieved within an air-to-solids ratio range of 0.020 to 0.026. The optimum air-to-solids ratio was determined by comparing the two air-to-solids ratios which gave the highest solids removal efficiency. For example, the solids removal efficiency of chitosan was 95.13 percent at an air-to-solids ratio

Table 23. Results of the Air Flotation Tests

Chemical	TSS		Solid in Sludge %	Air/Solid Ratio
	Effluent mg/l	Reduction %		
Chitosan	120	93.85	9.53	0.0080
	95	95.13	12.77	0.0156
	80	95.90	14.40	0.0230
Molasses sulfate	474	74.79	11.00	0.0080
	300	84.04	13.30	0.0160
	260	86.17	15.00	0.0240
Corn syrup sulfate	561	67.04	15.50	0.0090
	385	78.00	16.54	0.0173
	260	85.14	17.30	0.0260
Lignosulfonic acid	405	79.95	11.82	0.0080
	246	87.82	12.72	0.0150
	216	89.31	13.20	0.0230
Kraft paper sulfate	560	75.00	12.10	0.0070
	380	83.04	13.20	0.0140
	286	87.23	14.20	0.0200
Ferric chloride dual system	395	80.64	11.38	0.0070
	264	87.06	15.50	0.0150
	230	88.73	17.96	0.0220
Alum dual system	426	77.58	11.54	0.0080
	280	85.26	15.60	0.0160
	230	87.89	17.60	0.0240

Note: The concentration of suspended solids in the treated wastes of chitosan, molasses sulfate, corn syrup sulfate, lignosulfonic acid, card board paper sulfate, ferric chloride dual system and alum dual system are 1950,1880, 1750, 2020, 2240, 2040, and 1900 mg/1, respectively.

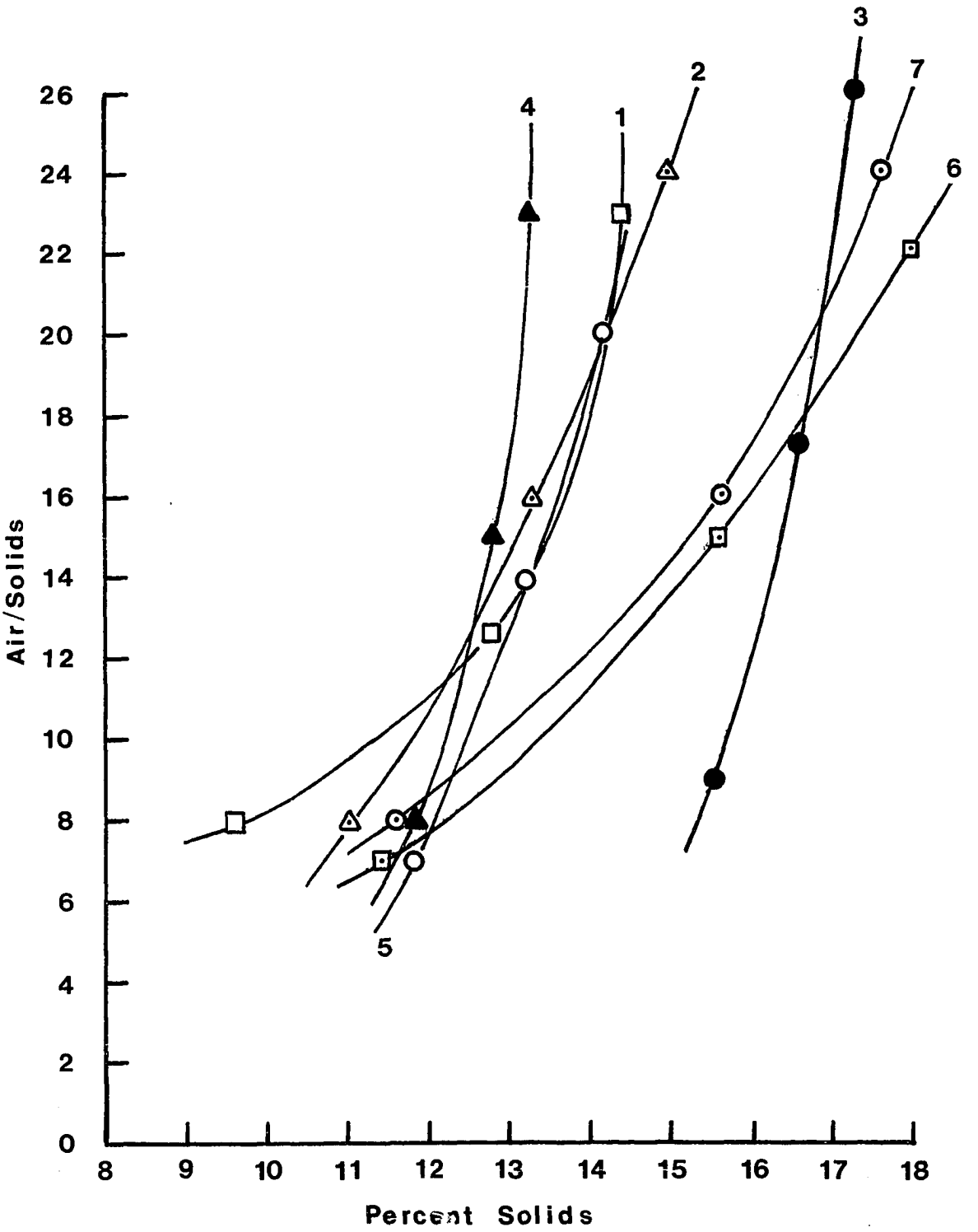

Figure 24. Relationship Between Air/Solids Ratio and Float-Solids Concentration. 1. Chitosan, 2. Molasses Sulfate, 3. Corn Syrup Sulfate, 4. Lignosulfonic acid, 5. Kraft Paper Sulfate, 6. Ferric Chloride Dual System, 7. Alum Dual System.

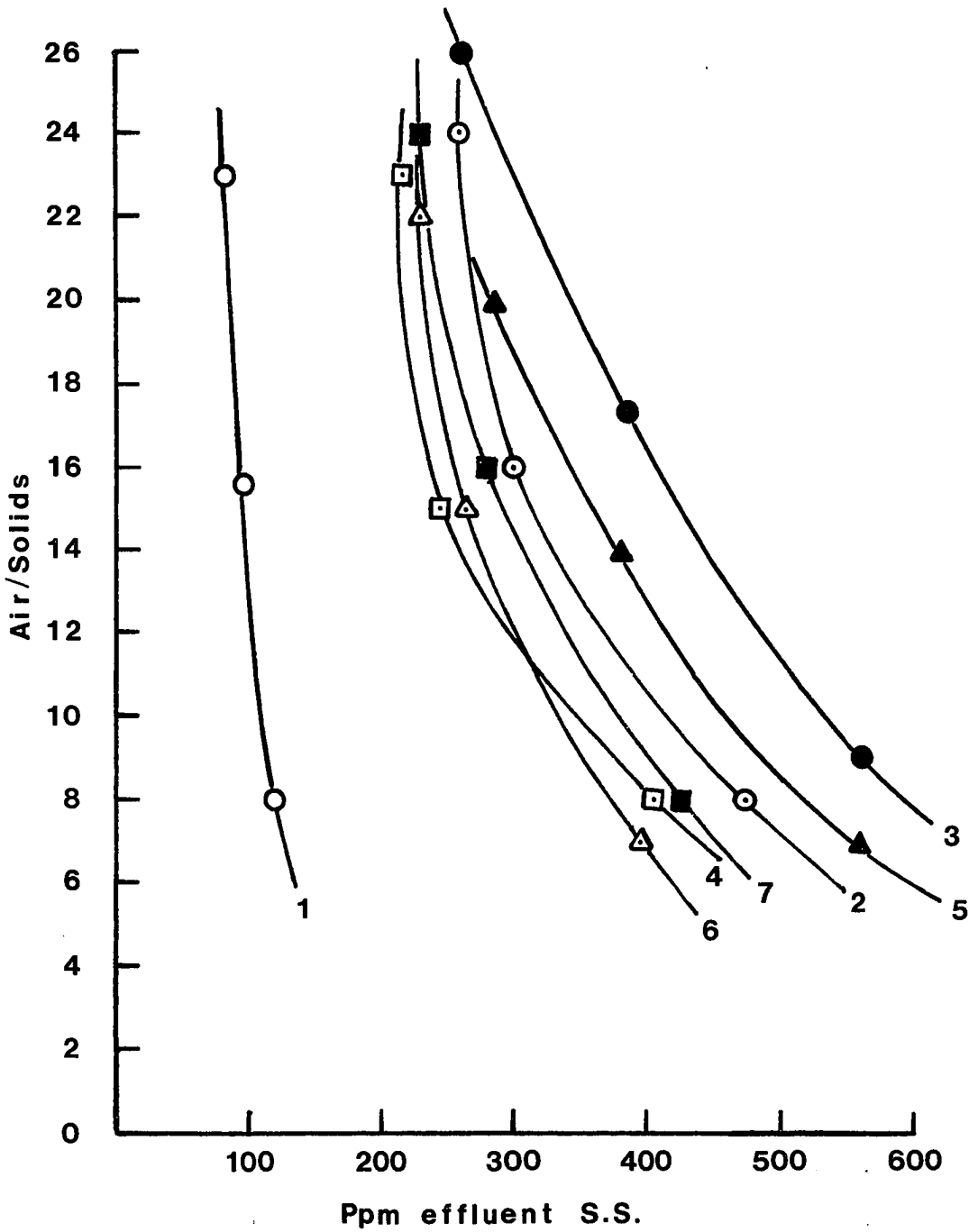

Figure 25. Relationship Between Air/Solids Ratio and Effluent Suspended Solids. 1. Chitosan, 2. Molasses Sulfate, 3. Corn Syrup Sulfate, 4. Lignosulfonic Acid, 5. Kraft Paper Sulfate, 6. Ferric Chloride Dual System, 7. Alum Dual System.

of 0.0156. By increasing the air-to-solids ratio to 0.023, 95.90 percent of the solids was removed. The difference in the efficiency of solids removal was less than 1 percent, while the difference for float solids concentration was approximately 1.6 percent. This negligible increase does not warrant increasing the air-to-solids ratio beyond the optimum value (0.0156).

The solids removal efficiency ranged from 85-89 percent for all chemicals except for chitosan which obtained about 96 percent removal. This indicates that the dissolved air flotation process could be utilized best in dewatering the sludge which resulted from treatment with chitosan. Efficiency in removal of solids decreases in the following order: chitosan (96 percent), lignosulfonic acid (89 percent), ferric chloride dual system (89 percent), alum dual system (88 percent), kraft paper sulfate (87 percent), molasses sulfate (86 percent), and corn syrup sulfate (85 percent).

Centrifugation

A literature search revealed that the precipitated proteins could be successfully recovered by centrifugation. Laboratory bench-scale tests were carried out to determine the optimum efficiency in the removal of the proteinaceous solids from the treated effluents.

Forty milliliters of the treated waste was centrifuged at 3,000-5,000 rpm for 30, 60, 90, and 120 second intervals. After centrifugation, the clear supernate was drawn off for solids analysis. The cake or settled fraction firmness was checked with a 1/8" thick glass stirring rod about 6 inches long. The relationship between the time of centrifugation and the efficiency in the removal of solids at different speeds for all chemicals are plotted in Figs. 26 through 32. Results of the tests are given in Table 24.

It was seen that the optimum efficiencies in the removal of solids were

Table 24. Results of the Centrifugation Tests.

Chemical	Retension	TSS Removal (%)			TSS Effluents (mg/l)		
		RPM			RPM		
		3,000	4,000	5,000	3,000	4,000	5,000
Chitosan	30	85	87	87	274	235	239
	60	90	95	95	179	98	92
	90	94	97	97	112	58	59
	120	96	96	97	83	68	61
Alum Dual System	30	85	89	88	286	214	229
	60	91	92	94	170	151	122
	90	93	95	95	134	97	97
	120	95	97	97	100	59	65
Ferric Chloride Dual System	30	86	90	89	266	201	213
	60	93	97	97	131	60	59
	90	95	98	98	107	33	33
	120	96	99	99	72	27	29
Lignosulfonic acid	30	83	87	96	371	281	298
	60	88	92	93	265	168	157
	90	90	93	94	220	152	127
	120	91	95	95	189	106	106
Kraft Paper sulfate	30	81	87	87	348	240	237
	60	88	91	90	219	155	182
	90	90	93	94	178	130	113
	120	92	94	94	144	110	114
Corn Syrup Sulfate	30	82	88	86	339	233	263
	60	88	94	94	222	120	113
	90	91	95	94	171	100	109
	120	94	95	96	122	90	83
Molasses Sulfate	30	80	86	86	354	251	247
	60	89	92	93	194	136	132
	90	91	94	94	165	112	114
	120	93	95	94	134	91	108

Note: The concentration of suspended solids in the treated wastes of chitosan, alum dual system, ferric, lignosulfonic acid, kraft paper sulfate, corn syrup sulfate, and molasses sulfate are 1840, 1905, 1940, 2120, 1820, 1880, and 1780 mg/l, respectively.

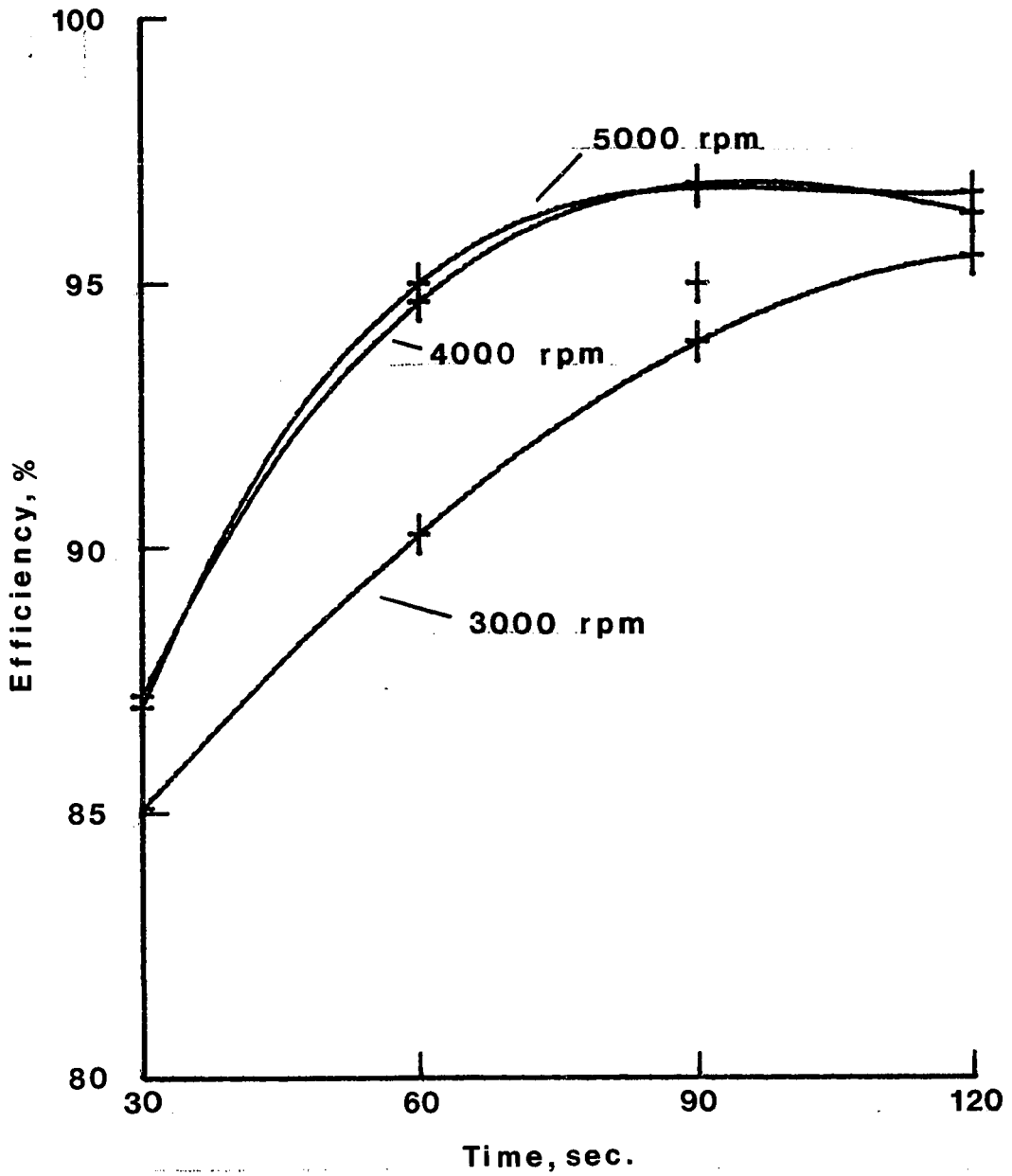

Figure 26. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Chitosan.

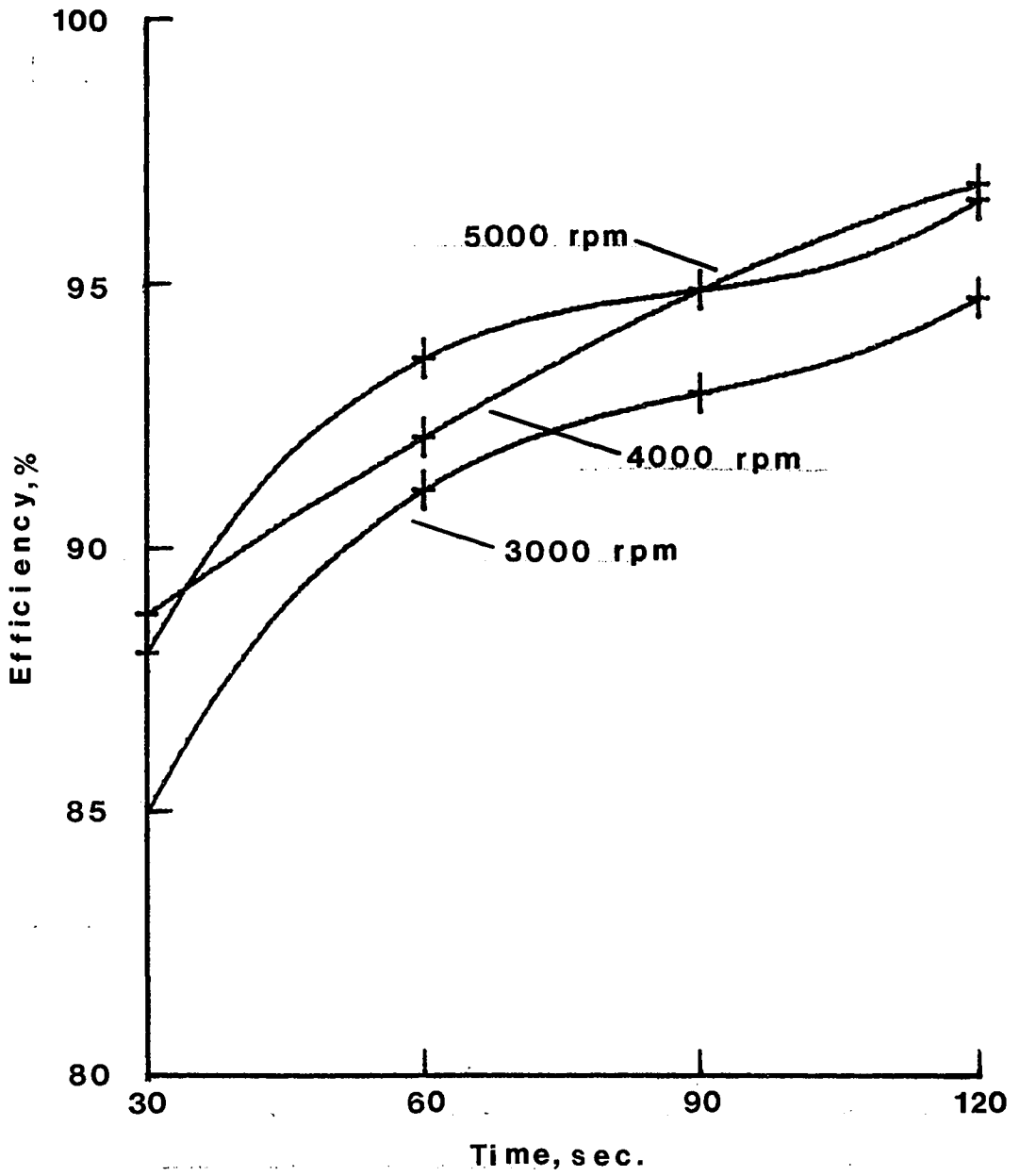

Figure 27. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Alum Dual System.

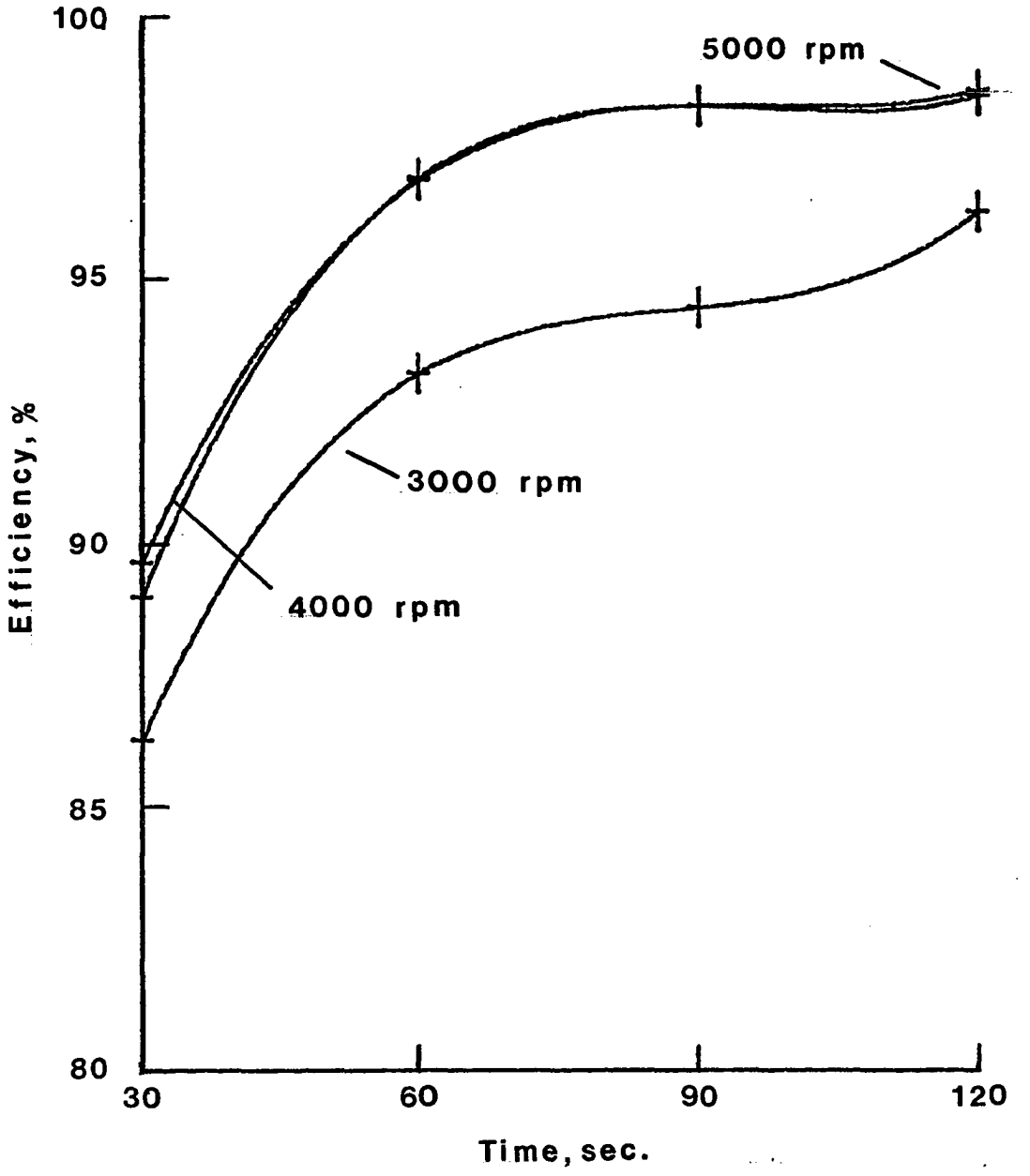

Figure 28.. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Ferric Chloride Dual System.

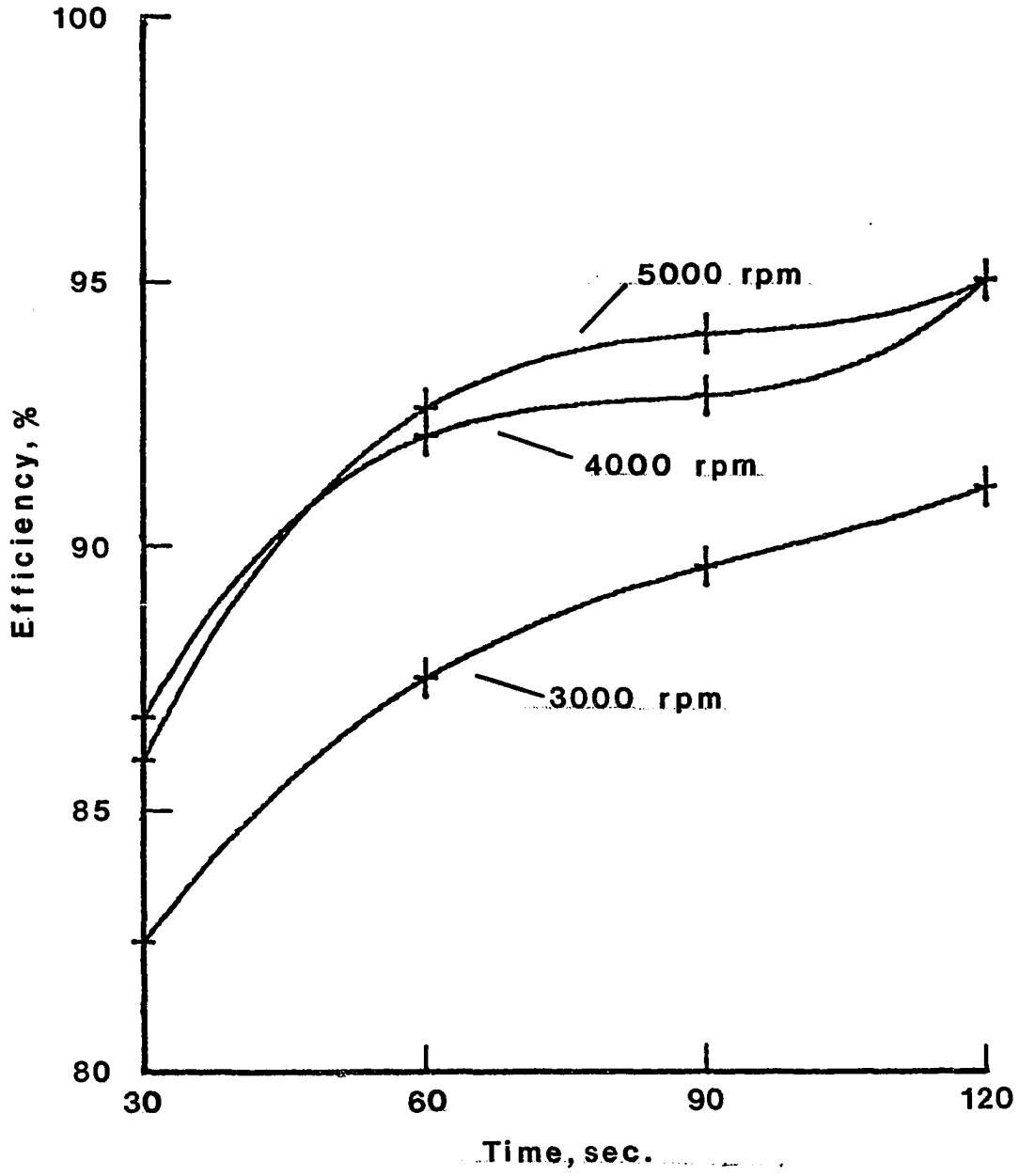

Figure 29. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Lignosulfonic Acid.

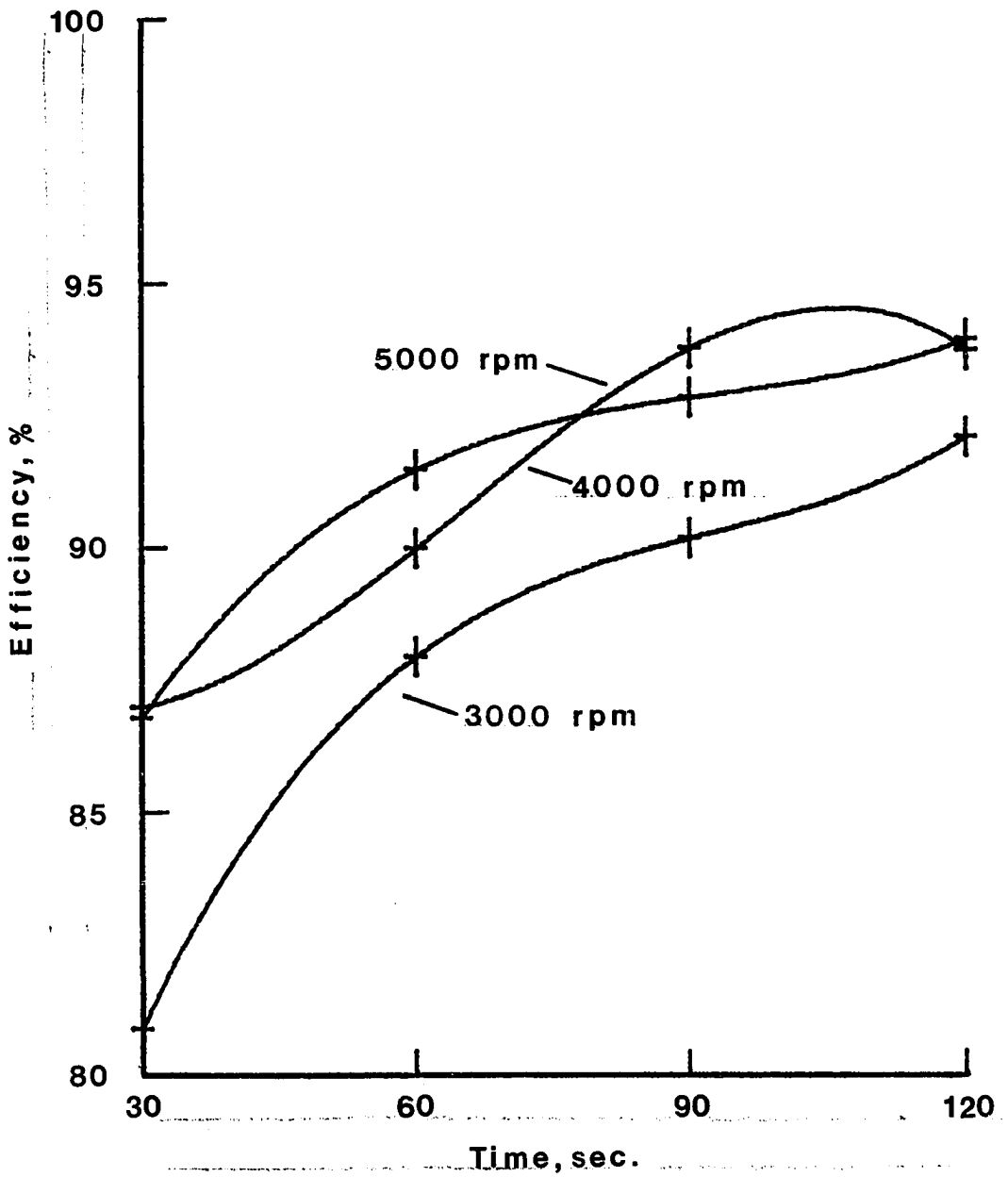

Figure 30. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Kraft Paper Sulfate.

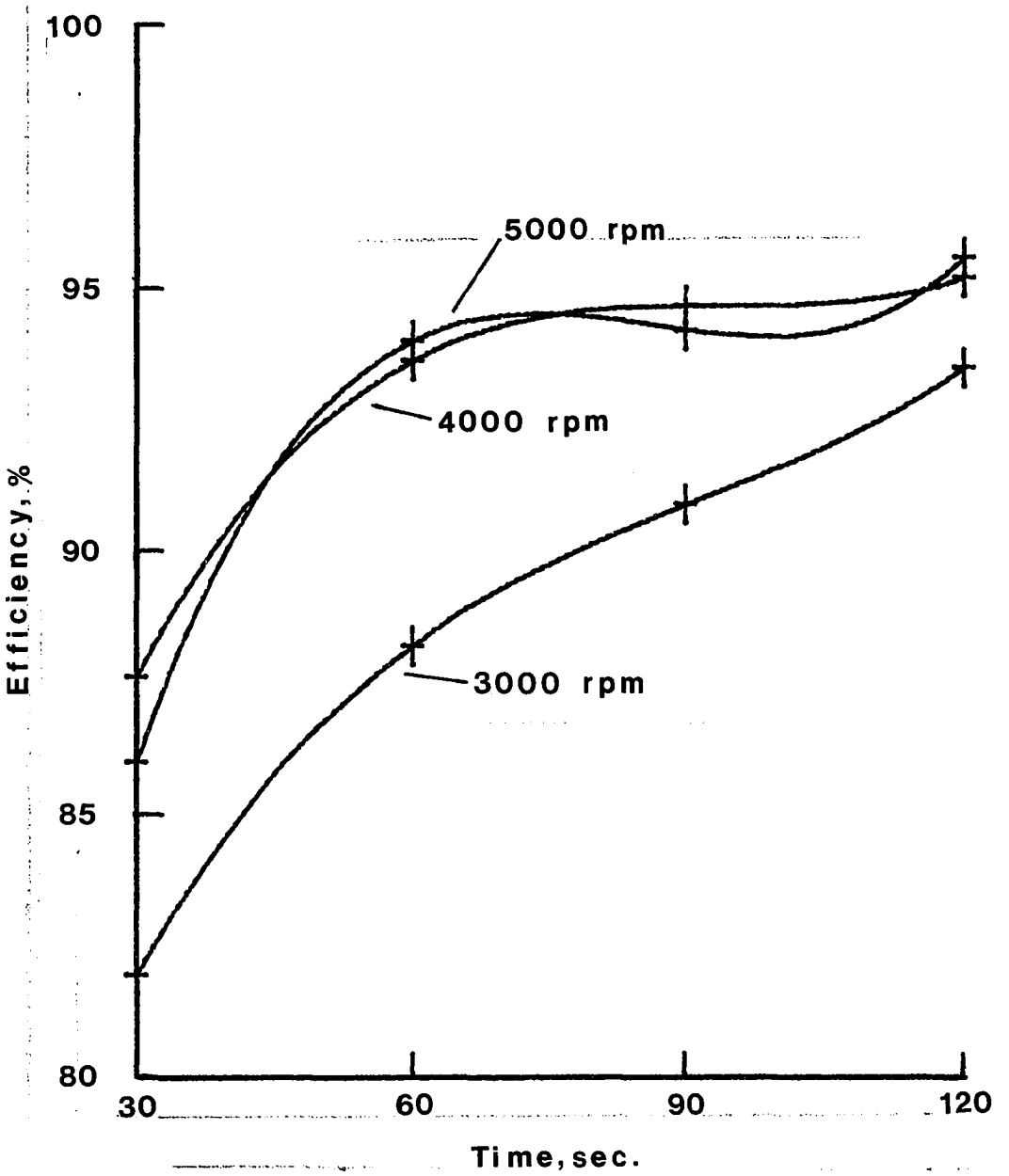

Figure 31. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Corn Syrup Sulfate.

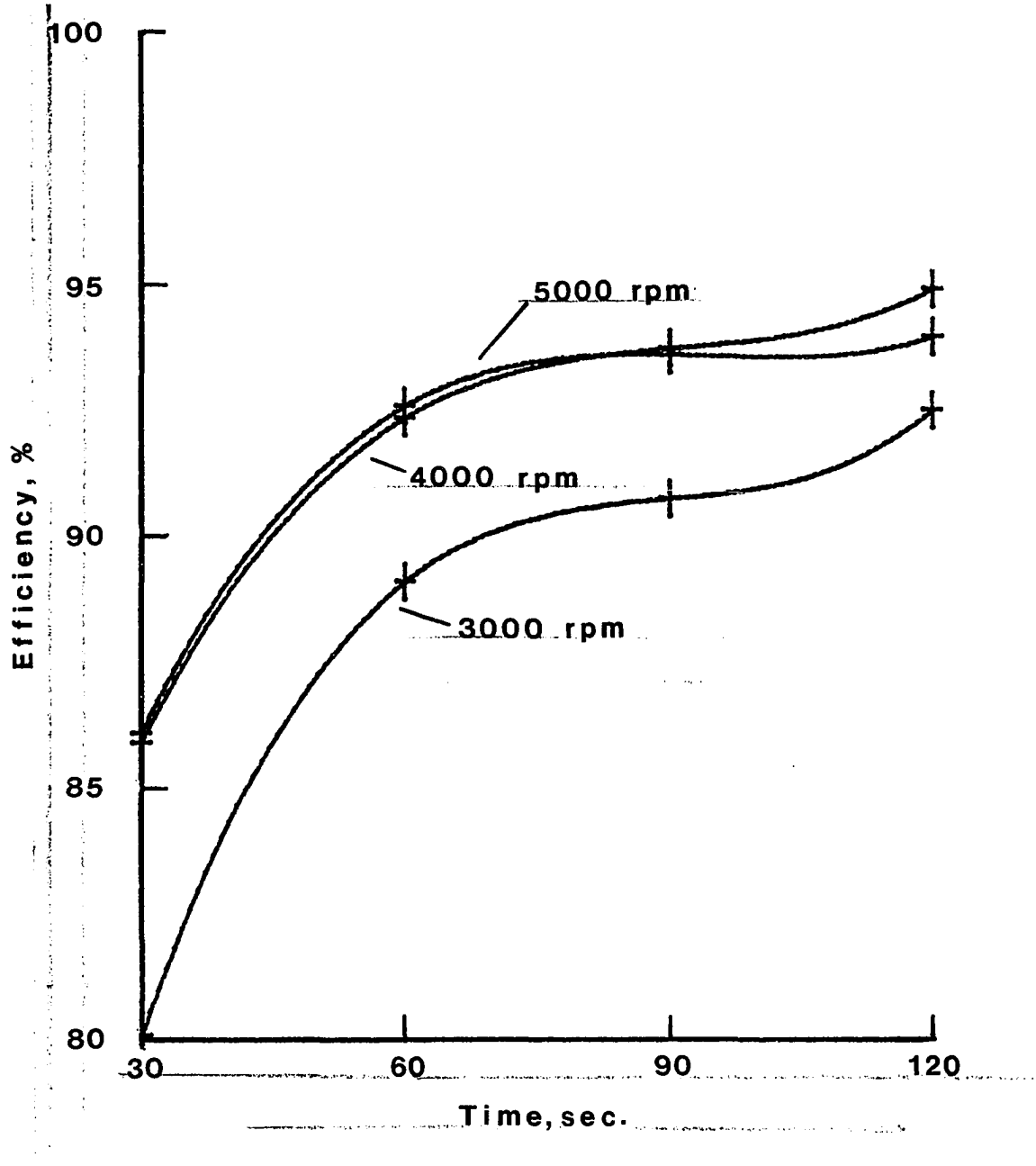

Figure 32. Relationship between Centrifugal Time and Efficiency in Removal of Solids at Different Speeds for Molasses Sulfate.

attained at 4,000 rpm with a retention time of 90-120 seconds for all chemicals. The optimum efficiency in the removal of solids was determined by comparing the highest efficiencies at two rotational speeds and retention times. Generally, increasing the rotational speed or retention time greatly increases the efficiency of solids removal. The optimum speed and retention time were determined by selecting the speed and retention time above which an increase in solids removal efficiency with an increase in speed or time was negligible.

A high efficiency in removal of solids (94-98 percent) by the centrifugation process was attained. This indicated that centrifugation could be utilized successfully in dewatering the sludge which resulted from all of the chemical treatments. Efficiency in removal of solids decreases in the following order: Ferric chloride dual system (99 percent), alum dual system (97 percent), chitosan (97 percent), corn syrup sulfate (95 percent), lignosulfonic acid (95 percent), kraft paper sulfate (94 percent), and molasses sulfate (94 percent).

Selection of the Proteinaceous Sludge Recovery Process

The efficiency in the removal of solids from the treated waste by means of sedimentation, air flotation, and centrifugation processes are summarized in Table 25. In Table 26 are listed the solids-liquid separation processes tested for each chemical. The selection of the optimum process for each chemical was based on the optimum efficiency and the economy of each process. It was assumed that the centrifugation process had the highest cost of treatment, followed by dissolved air flotation, and sedimentation.

Applciation as Feed

It is essential for this system to be economically feasible that the

Table 25. Efficiency of the Sludge Recovery Processes.

Efficiency in Removal of Solids (%)					
Sedimentation		Air Flotation		Centrifugation	
Alum dual system	(98)	Chitosan	(96)	Ferric chloride dual system	(99)
Ferric chloride dual system	(96)	Lignosulfonic acid	(89)	Alum dual system	(97)
Corn syrup sulfate	(85)	Ferric chloride dual system	(89)	Chitosan	(97)
Lignosulfonic acid	(80)	Alum dual system	(88)	Corn syrup sulfate	(95)
Molasses sulfate	(78)	Kraft paper sulfate	(87)	Lignosulfonic acid	(95)
Kraft paper sulfate	(61)	Molasses sulfate	(86)	Molasses sulfate	(95)
Sulfuric acid-sodium hydroxide	(51)	Corn syrup sulfate	(85)	Kraft paper sulfate	(94)

Table 26. Selection of Sludge Recovery Processes for Chemical Treatments.

Chemical	Process Recommended	
	1st choice	2nd choice
Kraft paper sulfate	centrifugation,	air flotation
Ferric chloride dual system	centrifugation,	sedimentation
Lignosulfonic acid	centrifugation,	air flotation
Chitosan	air flotation,	centrifugation
Alum dual system	sedimentation,	centrifugation
Molasses sulfate	centrifugation,	air flotation
Corn syrup sulfate	centrifugation,	sedimentation

proteinaceous solids recovered from the process be blended with animal feed. The concentration levels of proteins in the sludges obtained from different chemical processes are shown in Table 27.

Table 27. Concentration of Proteins in the Recovered Sludges

Chemical	Protein (N x 6.25) mg/l
H_2SO_4 -NaOH	531.44
Aluminum sulfate dual system	631.06
Ferric chloride dual system	668.38
Lignosulfonic acid	620.88
Kraft paper sulfate	655.00
Corn Syrup sulfate	628.00
Molasses sulfate	581.19
Chitosan	705.25

A high concentration of protein (greater than 531 mg/l) can be recovered. This protein is expected to have a high biological value and can be utilized as a supplementary feed for animals. However, in order for the recovered proteinaceous solids to be processed into animal feeds, it is necessary to obtain approval from Food and Drug Administration. At the time of this research, only the sludge resulting from the lignosulfonic acid treatment had been approved as animal feed from the FDA.

Because only small amounts of the chemicals were used for precipitating the protein from the wastewater, insignificant concentration of the precipitating chemical was expected to be in the recovered sludge. For example, results of the chemical analyses on 1 gm of alum and ferric chloride sludges resulted in only 9.08 mg/l of aluminum (Al), and 24.97 mg/l or iron (Fe).

The extent of the toxicity of the recovered sludge is not known. The sludge may contain toxic substances causing adverse effects on animals that are fed sludge. In order to utilize the sludge as animal feed, a study of its biological value is essential. Additional investigations determining the physiological effects of the solids on animals are needed to insure a safe valuable product.

Economics of the Protein Precipitation Process

The analysis of the economics of the processes is based on the treatment of a representative one million gallons of waste water per day. It is based upon the cost of the chemicals but the value of recovered products and reduction in waste treatment cost does not include operation and maintenance or capital costs.

Comparison of the chemical costs for treating one million gallons of meat packing wastewater is presented in Table 28. The results of assuming a sale price of $150 per ton for protein, and a surcharge of $40 per thousand pounds of COD removed are shown in Table 29.

The profit resulting from by-product recovery processes decrease in the following order: ferric chloride dual system, alum dual system, molasses sulfate, corn syrup sulfate, sulfuric acid-sodium hydroxide, chitosan, lignosulfonic acid, and kraft paper sulfate.

Table 28. Comparision of Chemical Costs

Chemical	Optimum Dosage g/l	Price $/ton	Chemical Cost $/mil gal
H_2SO_4-NaOH			72.74
H_2SO_4	0.18	46.85	35.19
NaOH	0.06	150.00	37.55
Alum-H_2SO_4-NaOH			133.16
Alum	0.20	70.00	58.42
H_2SO_4	0.18	46.85	35.19
NaOH	0.06	150.00	37.55
$FeCl_3$-H_2SO_4-NaOH			147.85
$FeCl_3$	0.20	90.00	75.11
H_2SO_4	0.18	46.85	35.19
NaOH	0.06	150.00	37.55
Lignosulfonic acid			422.45
LSA	0.60	150.00	375.53
H_2SO_4	0.24	46.85	46.92
Kraft paper sulfate			1116.3
Paper	0.04	5.00	0.83
DMF	0.26	930.00	1008.93
SO_3	0.12	142.50	71.35
H_2SO_4	0.18	46.85	35.19
Corn syrup sulfate			71.79
Corn syrup	0.07	159.40	46.56
H_2SO_4	0.13	46.85	25.41
Molasses sulfate			47.61
Molasses	0.07	76.00	22.20
H_2SO_4	0.13	46.85	25.41
Chitosan			530.75
Chitosan	0.02	6,000.00	500.71
Acetic acid	0.02	360.00	30.04

Table 29. Comparison of Total Economy

Chemical	Chemical Cost $/mil gal	Wt. of COD Removed lbs/day	Surcharge $/day	Wt. of Solids Removed lbs/day	Sale of Product $/day	Total Saving $/day
H_2SO_4-NaOH	73	36,070	1,443	15,330	1,150	2,520
Alum dual system	131	40,397	1,616	17,735	1,330	2,815
$FeCl_3$ dual system	148	40,111	1,628	17,811	1,336	2,816
LSA	422	38,182	1,527	17,633	1,323	2,428
Kraft paper sulfate	1 1,116	37,589	1.504	17,695	1,327	1,715
Corn syrup sulfate	72	37,323	1,493	17,670	1,325	2,746
Molasses fulfate	48	38,169	1,527	17,030	1,277	2,756
Chitosan	531	40,245	1,610	18,302	1,373	2,452

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This research is an attempt to select chemicals which will be technically and economically feasible for precipitating proteins from food processing wastewater. Because of the complexities of the chemical reactions, this investigation has been oriented toward acquiring an overall performance of the chemicals physically and chemically. On the basis of this experimental philosophy the following conclusions are drawn:

1. Recovery of proteins and grease from the meat industry wastewater by means of chemical precipitation is a relatively simple process. The reduction of waste loads to treatment systems, sewers, or streams through the employment of known or proven reduction methods yields, in many cases, an economic return in the form of by-product recovery which partially or totally defrays the cost of the removal process and, in some cases, may yield a profit.

   Most of the chemicals tested, reduced the chemical oxygen demand by at least 80 percent, the suspended solids by 95 percent, the organic nitrogen by 65 percent, and the grease by 95 percent for meat industry wastewaters. Chemical precipitation is suitable as a pretreatment step to final biological treatment, thereby reducing the cost of biological treatment.

Chemical treatment also has the advantage of requiring only a relatively short period for reduction of the waste load. Correspondingly, land space can be less for chemical treatment, than for biological treatment. Therefore, chemical treatment is a candidate process for both meat industry plants discharging to municipal sewerage systems or to industrially owned secondary systems.

2. Removal of protein and grease with the precipitating chemicals offers the potential of a recovered by-product that may have a value as a component in animal feed. This would eliminate a problem of ultimate disposal of materials removed. The solids concentration of the precipitated and recovered proteinaceous sludge exceeds 10 percent.
3. Results of the tests indicated that chitosan gave the highest overall removal of organic material from the meat industry wastewater. The overall efficiency in removal of organic materials for those chemicals tested decreases in the following order: chitosan, ferric chloride dual system, alum dual system, lignosulfonic acid, kraft paper sulfate, corn syrup sulfate, molasses sulfate, and sulfuric acid-sodium hydroxide.

   The alum and ferric chloride dual systems is the most economical protein precipitation process. Treatment of meat industry wastewaters with other chemicals indicated that all the chemical systems tested are economicallly and technically feasible.
4. In the process of separating the sludge from the treated effluent, three process, i.e. sedimentation, flotation, and centrifugation were used. The efficiency in removal of solids by means of sedimen-

tation, air flotation, and centrifugation is 50-98, 85-96, and 94-98 percent, respectively. Therefore, centrifugation is the candidate process for dewatering the organic solids from all of the chemically treated wastewaters. Efficiency in removal of solids by air flotation process decreases in the following order: chitosan (96 percent), lignosulfonic acid (89 percent), ferric chloride dual system (89 percent), alum dual system (88 percent), kraft paper sulfate (87 percent), molasses dulfate (86 percent), and corn syrup sulfate (85 percent). Dewatering of the solids by sedimentation can be utilized for the solids which resulted from treatment using the alum, and ferric chloride dual systems. Efficiency in removal of solids by sedimentation decreases in he following order: alum dual system (98 percent), ferric chloride dual system (96 percent), corn syrup sulfate (85 percent), lignosulfonic acid (80 percent), molasses sulfate (78 percent), kraft paper sulfate (61 percent), and sulfuric acid-sodium hydroxide (51 percent).

Recommendations

Based on the experience from the investigation of the protein precipitation process, the future studies should include the following aspects:

1. Some parameters such as dosage, volume of the waste, and the retention time of mixing were controlled, since the study of this protein precipitation process was carried on the laboratory bench-scale. In a plant, the waste flow rate and strength of the waste will vary with time. It is expected that the overall performance of the precipitating agents will be slightly lower for the plant scale operation. Thus, there is a need to perform the test on a pilot plant scale in order to determine the most desirable operating parameters in the actual environmental setting.
2. The knowledge of the chemical reaction between the protein in wastewater and the precipitating agents is not well established. The study of this research suggests that the development and application of protein precipitation process in wastewater treatment require further indepth investigations focused on the mechanism of protein reaction. Hopefully, it would result in ways to prepare more effective precipitating agents, and optimize the protein precipitating process.
3. In order to utilize the recovered sludge as animal feed, study of the biological value of the sludge is essential. Since the sludge contains some toxic substances which may result in adverse effects on animals that are fed on this sludge diet, there is a need to study the physiological effects of the recovered by-product on animals.

APPENDIX A

Table A-1. Results of Chemical Analyses of Sulfuric Acid and Sodium Hydroxide-Precipitation.

pH		Concentration (mg/l)				Removal Efficiency (%)			
Initial	Final	COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
3	3	1,822	--	--	--	62	-	-	-
3	4	1,504	478	63	--	69	76	48	-
3	5	1,139	301	57	406	77	85	53	81
3	6	1,809	551	65	--	63	72	46	-
Raw		4,922	2,001	122	2,090	--	-	-	-

Table A-2. Results of Chemical Analyses of Sulfuric Acid and Sodium Hydroxide-Precipitation in High Concentrated Waste.

pH		Concentration (mg/l)				Removal Efficiency (%)			
Initial	Final	COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
3	3	2,517	--	--	--	70	-	-	-
3	4	1,753	359	73	--	79	86	52	-
3	5	1,183	186	60	350	85	92	60	84
3	6	2,316	422	73	--	72	84	52	-
Raw		8,392	2,640	154	2,318	-	-	-	-

Table A-3. Results of Chemical Analyses of 2% Alum Dual System-Precipitation.

Dosage ml	pH	Concentration (mg/1)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
2	4.6	1,144	--	--	--	76	-	-	-
3	4.6	1,004	--	--	--	79	-	-	-
4	4.6	831	41	41	--	83	97	65.84	-
5	4.6	759	34	40	91	85	98	67	96
6	4.6	807	43	41	--	83	97	65	-
Raw	6.9	4,922	2,001	122	2,090	-	-	-	-

Table A-4. Results of Chemical Analyses of 2% Ferric Chloride Dual System-Precipitation.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
2	4.5	1,151	--	--	--	76	-	-	-
3	4.5	940	--	--	--	80	-	-	-
4	4.5	650	25	37	--	86	98	68	-
5	4.5	620	23	35	81	87	99	71	96
6	4.5	666	26	39	--	86	98	67	-
Raw	6.9	4,922	2,001	122	--	-	-	-	-

Table A-5. Results of Chemical Analyses of 20% Starch Sulfate.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
0.3	5.8	3,028	--	--	--	43	-	-	-
0.5	4.9	1,652	606	75	667	69	71	46	69
1.0	3.9	1,854	--	--	--	65	-	-	-
1.5	2.8	2,127	--	--	--	59	-	-	-
2.0	2.0	2,650	--	--	--	50	-	-	-
3.0	1.7	3,158	--	--	--	40	-	-	-
Raw	6.9	5,312	2,100	140	2,170	--	-	-	-

Table A-6. Results of Chemical Analyses of 20% Molasses Sulfate.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
0.3	5.5	2,125	--	70	--	60	-	50	-
0.5	4.9	1,296	123	48	238	76	94	65	89
1.0	3.8	1,479	--	57	--	72	93	59	-
1.5	2.9	1,625	--	60	--	69	91	57	-
2.0	2.1	1,854	--	--	--	65	-	-	-
3.0	1.7	2,340	--	--	--	55	-	-	-
Raw	6.9	5,312	2,100	140	2,170	-	-	-	-

Table A-7. Results of Chemical Analyses of 20% Corn Syrup Sulfate.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
0.3	5.5	2,125	--	74	--	60	-	47	-
0.5	4.8	1,077	60	48	130	80	97	65	94
1.0	3.9	1,156	84	55	--	78	96	60	-
1.5	2.9	1,343	115	58	--	74	94	58	-
2.0	2.0	1,487	--	-	--	72	-	-	-
3.0	1.7	2,125	--	-	--	60	-	-	-
Raw	6.9	5,312	2,100	140	2,170	-	-	-	-

Table A-8. Results of Chemical Analyses of 20% Glucose Trisulfate.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
0.3	5.5	2,130	--	-	--	59	-	-	-
0.5	4.8	956	44	47	277	82	97	66	89
1.0	3.8	1,211	--	-	--	77	-	-	-
1.5	2.8	1,301	--	-	--	75	-	-	-
2.0	2.1	1,599	--	-	--	69	-	-	-
3.0	1.7	2,045	--	-	--	61	-	-	-
Raw	6.9	5,312	2,100	140	2,170	-	-	-	-

Table A-9. Results of Chemical Analyses of 15% Lignosulfonic Acid.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
0.5	2.6	1,279	200	--	--	74	90	-	-
1.0	2.6	1,017	100	38	--	79	95	68	-
2.0	2.6	926	35	36	124	81	98	70	94
3.0	2.6	886	27	36	102	82	98	69	95
4.0	2.6	1,080	108	--	--	78	94	-	-
Raw	6.9	4,922	2,001	122	2,090	-	-	-	-

Table A-10. Results of Chemical Analyses Of 1% Viscarin 402 Carrageenan.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
8	2.7	1,678	--	--	--	65	-	-	-
12	2.9	1,222	521	66	--	75	73	45	-
16	3.0	1,056	408	57	405	79	80	51	81
20	3.1	1,433	558	71	--	70	72	41	-
24	3.2	1,858	--	--	--	62	-	-	-
Raw	6.9	4,922	2,001	122	2,090	-	-	-	-

Figure A-11. Results of Chemical Analyses of 10% Kraft Paper Sulfate.

Dosage ml	pH	Concnetration (mg/1)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
2	3.3	1,328	--	--	--	75	-	-	-
3	3.3	1,037	--	--	--	80	-	-	-
4	3.3	984	--	--	--	81	-	-	-
5	3.3	937	63	51	--	82	97	63	-
6	3.3	868	44	49	132	84	98	65	94
7	3.3	921	60	52	--	82	97	62	-
Raw	6.8	5,312	2,100	140	2,170	-	-	-	-

Table A-12. Results of Chemical Analyses of 1% Chitosan.

Dosage ml	pH	Concentration (mg/l)				Removal Efficiency (%)			
		COD	TSS	Org-N	O&G	COD	TSS	Org-N	O&G
0.5	6.5	711	69	55	--	86	97	68	-
1.0	6.4	622	25	49	97	88	98	72	96
2.0	6.3	665	70	66	--	86	97	62	-
3.0	6.2	753	--	--	--	85	-	-	-
Raw	6.0	5,100	2,360	178	2,209	--	-	-	-

Table A-13. Laboratory Results on Consistency Tests of Chitosan.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	5,100	622	2,360	25	2,209	97	178	49
2	4,156	561	2,020	20	2,100	48	136	35
3	8,219	1,684	2,560	51	2,530	164	217	66
4	4,478	425	1,800	14	2,010	70	110	27
5	5,014	702	2,150	17	2,085	56	128	28
6	6,920	941	2,430	24	2,118	105	160	46
Average	5,648	822	2,220	25	2,175	90	155	42

Notes: I = influent, expressed mg/l

E = effluent, expressed mg/l

Table A-14. Laboratory Results on Consistency Tests of Sulfuric Acid and Sodium Hydroxide.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	4,922	1,139	2,001	301	2,090	406	122	57
2	4,156	918	2,020	282	2,100	375	136	54
3	8,219	2,145	2,560	409	2,530	575	217	99
4	4,478	895	1,800	268	2,010	412	110	42
5	5,014	1,103	2,150	260	2,085	387	128	46
6	6,920	1,560	2,430	410	2,118	455	160	64
Average	5,618	1,293	2,160	322	2,155	435	145	60

Notes: I = influent, expressed as mg/l

E = effluent, expressed as mg/l

Table A-15. Laboratory Results on Consistency Tests of Alum Dual System.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	4,922	759	2,001	34	2,090	91	122	40
2	4,156	561	2,020	24	2,100	63	136	40
3	8,219	1,279	2,560	53	2,530	141	217	73
4	4,478	460	1,800	19	2,010	100	110	29
5	5,014	591	2,150	21	2,085	83	128	33
6	6,920	997	2,430	48	2,118	105	160	51
Average	5,618	775	2,160	33	2,155	97	145	44

Notes: I = influent, expressed as mg/l

E = effluent, expressed as mg/l

Table A-16. Laboratory Results on Consistency Tests of Ferric Chloride Dual System.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	4,922	620	2,001	23	2,090	81.09	122	35
2	4,156	473	2,020	18	2,100	63.21	136	35
3	8,219	1,512	2,560	48	2,530	136.62	217	62
4	4,478	376	1,800	14	2,010	98.49	110	25
5	5,014	606	2,150	17	2,085	80.90	128	28
6	6,920	833	2,430	25	2,118	109.08	160	45
Average	5,618	737	2,160	24	2,155	94.90	145	38

Notes: I = influent, expressed as mg/l

E = effluent, expressed as mg/l

Table A-17. Laboratory Results on Consistency Tests of Lignosulfonic Acid.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	4,922	926	2,001	35	2,090	124	122	36
2	4,156	750	2,020	40	2,100	126	136	42
3	8,219	1,822	2,560	72	2,530	202	217	71
4	4,478	761	1,800	33	2,010	121	110	34
5	5,041	927	2,150	19	2,085	112	128	37
6	6,920	1,179	2,430	75	2,118	137	160	56
Average	5,618	1,040	2,160	45	2,155	137	145	46

Notes: I = influent, expressed as mg/l

E = effluent, expressed as mg/l

Table A-18. Laboratory Results on Consistency Tests of Kraft Paper Sulfate.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	5,312	868	2,100	44	2,170	132	140	49
2	4,156	916	2,020	40	2,100	126	136	41
3	8,219	2,128	2,560	75	2,530	253	217	67
4	4,478	734	1,800	27	2,010	148	110	31
5	5,014	923	2,150	32	2,085	135	128	31
6	6,920	1,487	2,430	109	2,118	167	160	44
Average	5,683	1,176	2,176	54	2,168	160	148	44

Notes: I = influent, expressed as mg/l

E = effluent, expresses as mg/l

Table A-19. Laboratory Results on Consistency Tests of Corn Syrup Sulfate.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	5,312	1,077	2,100	60	2,170	130	140	48
2	4,156	835	2,020	60	2,100	115	136	44
3	8,219	2,063	2,560	99	2,530	199	217	76
4	4,478	707	1,800	45	2,010	142	110	34
5	5,014	1,232	2,150	23	2,085	106	128	36
6	6,920	1,334	2,430	58	2,118	156	160	51
Average	5,683	1,208	2,176	57	2,168	141	148	48

Notes: I = influent, expressed as mg/l

E = effluent, expressed as mg/l

Table A-20. Laboratory Results on Consistency Tests of Molasses Sulfate.

Sample	COD		Suspended Solids		Oil & Grease		Org-N	
	I	E	I	E	I	E	I	E
1	5,312	1,296	2,100	123	2,170	238	140	48
2	4,156	833	2,020	101	2,100	189	136	46
3	8,219	2,054	2,560	176	2,530	290	217	79
4	4,478	721	1,800	117	2,010	152	110	38
5	5,014	1,173	2,150	130	2,085	133	128	38
6	6,920	1,730	2,430	158	2,118	235	160	57
Average	5,683	1,107	2,176	134	2,168	206	148	55

Notes: I = influent, expressed as mg/l

E = effluent, expressed as mg/l

Table A-21. Results of the Class-1 Calrification Test of Sulfuric Acid and Sodium Hydroxide.

Settling Time Min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/1	Wt. Fraction Remaining
0	0.0	2,100	1.000
10	23.5	2,095	0.998
20	11.8	1,974	0.940
30	7.8	1,938	0.923
40	5.9	1,869	0.890
50	4.7	1,575	0.750
60	3.9	1,352	0.644
80	2.9	1,176	0.560
100	2.4	716	0.341
120	2.0	441	0.210

Table A-22. Results of the Class-1 Clarification Test of Alum Dual System.

Settling Time Min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/l	Wt. Fraction Remaining
0	0.0	2,350	1.000
10	23.5	1,866	0.794
20	11.8	1,584	0.674
30	7.8	1,081	0.460
40	5.9	259	0.110
50	4.7	165	0.070
60	3.9	59	0.025
80	2.9	42	0.018
100	2.4	35	0.015
120	2.0	31	0.013

Table A-23. Results of the Class-1 Clarification Test of Ferric Chloride Dual System.

Settling Time Min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/l	Wt. Fraction Remaining
0	0.0	2,580	1.000
10	23.5	2,436	0.944
20	11.8	1,277	0.495
30	7.8	263	0.102
40	5.9	206	0.080
50	4.7	160	0.062
60	3.9	111	0.043
80	2.9	70	0.027
100	2.4	49	0.019
120	2.0	44	0.017

Table A-24. Results of the Class-1 Clarification Test of Lignisulfonic Acid.

Settling Time Min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/1	Wt. Fraction Remaining
0	0.0	2,415	1.000
10	23.5	2,294	0.950
20	11.8	1,811	0.750
30	7.8	915	0.379
40	5.9	761	0.315
50	4,7	502	0.208
60	3.9	442	0.183
80	2.9	193	0.080
100	2.4	164	0.068
120	2.0	75	0.031

Table A-25. Results of the Class-1 Clarification Test of Kraft Paper Sulfate.

Settling Time Min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/l	Wt. Fraction Remaining
0	0.0	2,640	1.000
10	23.5	2,458	0.931
20	11.8	2,323	0.880
30	7.8	2.088	0.791
40	5.9	1,848	0.700
50	4.7	1,589	0.602
60	3.9	1,188	0.450
80	2.9	924	0.350
100	2.4	663	0.251
120	2.0	370	0.140

Table A-26. Results of the Class-1 Clarification Test of Corn Syrup Sulfate.

Settling Time min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/l	Wt. Fraction Remaining
0	0.0	2,245	1.000
10	23.5	2,083	0.928
20	11.8	1,551	0.691
30	7.8	846	0.377
40	5.9	707	0.315
50	4.7	467	0.208
60	3.9	410	0.183
80	2.9	180	0.080
100	2.4	153	0.068
120	2.0	110	0.049

Table A-27. Results of the Class-1 Clarification Test of Molasses Sulfate.

Settling Time Min	Settling Velocity ft/min x 10^{-2}	SS Concentration mg/l	Wt. Fraction Remaining
0	0.0	2,280	1.000
10	23.5	2,166	0.950
20	11.8	1,938	0.850
30	7.8	1,553	0.681
40	5.9	1,072	0.472
50	4.7	673	0.295
60	3.9	479	0.210
80	2.9	228	0.100
100	2.4	182	0.080
120	2.0	137	0.060

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