ACIDIFICATION AND ALUM COAGULATION STUDIES ON BLACK LIQUOR

A DISSERTATION

*submitted in partial fulfilment of the
requirements for the award of the degree
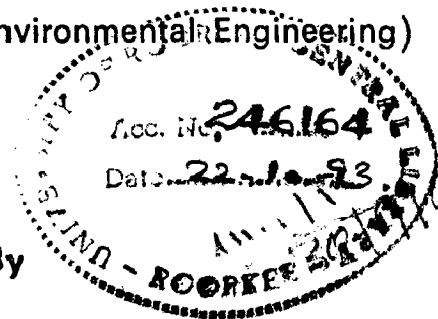of*
MASTER OF ENGINEERING
in
CIVIL ENGINEERING
(With Specialization in Environmental Engineering)

By

ARVIND KUMAR SINGH

DEPARTMENT OF CIVIL ENGINEERING
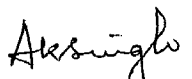UNIVERSITY OF ROORKEE
ROORKEE-247 667 (INDIA)
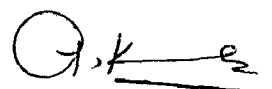JUNE, 1991

CANDIDATE'S DECLARATION

I here by declare that the work, which is being presented in the thesis entitled "ACIDIFICATION AND ALUM COAGULATION STUDIES ON BLACK LIQUOR", is partial fulfilment of the requirement for the award of Degree of Master of Enginering in Civil Engineering (with specialization in Environmental Engineering), of the University of Roorkee is an authentic record of my own work carried out during a period from 15th December 1990 to 15th May 1991 under the supervision of **Dr. A.K.Shrivastava**, Reader, Department of Civil Engineering, University of Roorkee, Roorkee.

The matter embodied in this thesis has not been submitted for the award of any other degree of diploma.

Dated 20th May 1991

(ARVIND K. SINGH)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(A.K.SHRIVASTAVA)
Reader
Deptt. of Civil Engineering
University of Roorkee
Roorkee - 247667

To my dear 'PARENTS'
and 'VANITA'

for their inspiration and moral
support leading to the successful
completion of this study

ACKNOWLEDGEMENT

ROORKEE

DATED: MAY 20th, 1991

(ARVIND KUMAR SINGH)

ABSTRACT

Multifold increase in production of industrial goods has overstrained the assimilative capacity of our waters, land and atmosphere. Pulp and Paper industry is one such ever expanding industry. Raw materials shortage and depleting forest cover has influenced the technologists to encourage the agriculture residue based small paper mills (SPM) of capacities less than 10000 tonnes per annum (TPA). A number of them has come up in western U.P. and Gujarat. Due to financial instability these SPM are unable to install a full scale chemical recovery unit, and as such they discharge very high concentrations of pollutants such as COD, BOD, Colour and Total Solids into the natural water courses or land.

Integrated methods for removal of COD, BOD, Colour and Total Solids for small paper mills have not been much explored. The methods tried and suggested are numerous, but none of them are found to be successful in case of small paper mills.

In the present study reduction in the pollution parameters of Black Liquor from small paper mills by acidification has been investigated, by lowering the pH of the black liquor to the value of 2.0, 2.5, 3.0, 3.5, 4.5 and 5.5. Percentage removal of COD, Colour and Total Solids have been observed in the range of 40-55%, 90-99% and 10-50% due to precipitation and sludge blanket formations.

Further studies were conducted on alum coagulation at pH 5.5, 6.0, 6.5 and 7.0. Reduction in COD, Colour and Total Solids were observed in the range of 40-80%, 30-97% and 5-65%.

Cost analysis indicates that the acid precipitation treatment varies in cost as a function of removal percentage of COD, Colour and Total Solids and the alum coagulation cost is much lower than acid precipitation.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

INTRODUCTION

1.1 GENERAL

First machine made paper industry started in 1832 at Serampore in West Bengal. But the major expansion has come up during the last 40 years. Excluding the closed units, today about 250 paper mills manufacture 18.5 lakh tonnes of paper and 2.8 lakh tonnes of newsprint each year. The projected demand for 1995 is placed at 24 lakh tonnes and that at the turn of the century 32 lakh tonnes. More than two-thirds of the existing paper mills are small and medium with an annual production capacity of less than 20,000 tonnes.

Primarily because of the constraints of large investments necessary for setting up of large integrated pulp and paper mills, and the reduced availability of the main raw material, bamboo, small scale paper mills have come up in recent years. Most of them are ranging between 3 and 30 tonnes per day (TPD). All mills making upto 10,000 tonnes per annum (TPA) of paper, boards etc., are classified under small paper mills (SPM). Rice Straw, Wheat Straw, bagasse, gunny and jute cuttings, Kenaf (Hibiscus Cannabinus), Sarkanda grass etc have proved suitable as raw material for manufacture of normal grades and paper boards.

Small Paper mills, using chemical process do not recover chemicals, as it is uneconomical (Chaudhuri Nilay,

1982). This leads to pollution problem of significant magnitude. In parallel, The Government of India is encouraging enterpreneurs for setting up small paper mills based on agricultural residues. In turn it saves the primary forest resources and encourages regional development.

As on march 31, 1983, there were 179 small paper mills with an installed capacity of 712,340 TPA constituting 35 percent of the total installed capacity for paper and boards in the country. Gujrat has the maximum SPM (30), accounting for 18.06 percent, followed by U.P. with 15.1 percent (Ganga basin having the maximum of 82 mills) .

Majority of SPM use chemical pulping, i.e., they employ mostly caustic soda, and to a limited extent, lime for pulping the raw materials.

Waste water from small bagasse based paper mills in Western U.P., is relatively very strong in characteristics, such as COD, BOD, and SS apart from colour. As for these SPM, chemical recovery is not economically viable, each of them is facing a great problem to discharge the Black Liquor generated from digestion of raw materials. So the strategy behind treating Black liquor is to reduce it's pollutional parameters at first and then mixing it with total mill effluent for final treatment.

A review of literature available on the treatment plants being run by Indian Pulp and Paper Mills reveals that some of the large paper mills have waste water treatment units

comprising of primary clarifiers and activated sludge process. An integrated treatment system removing colour, BOD, COD, T.S. S.S. from concentrated Black Liquor discharged from SPM has neither been installed nor been explored in the laboratory. So the present study aims to investigate the possibilities of colour, COD and solids removal at low pH ranges by acidification. Apart from it studies on Alum Coagulation done at varying pH to explore the possibilities of COD, colour and solids removal from Black Liquor.

####

TABLE 1.1

CHARACTERISTICS OF INDIVIDUAL WASTEWATERS FROM A MILLS EMPLOYING BAGASSE AND CHEMO-MECHANICAL PULPING

(COMPREHENSIVE INDUSTRY DOCUMENT, SPM, 1986)

CAPACITY: 30 TPD

Parameters	Black liquor	Pulp wash	Paper machine (from W.W tank)	Paper machine (after B/W tank)	Boiler house drains (inc.plant leakage)	Combined effluent
pH	10.2-10.6	7.8-9.9	6.0-6.4	6.7-6.7	7.0-7.4	7.5-9.3
Suspended solids	-	310-1,058	2,080-2,370	550-840	174-477	560-640
Total solids	8,134-8,702	2,682-2,711	2,790-3,496	908-1,320	922-1,090	2,032-3,76
Total volatile solids	3,892-7,458	1,999-2,070	2,068-2724	538-894	696-716	1,320-2,81
COD(total)	8,424-14,256	2,484-2,808	2,592-3,348	691-1,188	540-864	1,915-3,13
COD(soluble)	7,344-7,560	1,555-1,728	281-346	108-130	173-302	1,037-1,74
BOD(total) ?	-	1,100-1,134	680-743	181-194	100-240	717-1,067
BOD(soluble)	-	700-773	112-139	54-58	-	-
Lignin	-	-	-	350-500	-	475-500
Na	1,500-1,800	-	-	-	-	-

(All values except pH are in mg/l)

CHAPTER - 2

PROBLEMS WITH BLACK LIQUOR

2.1 GENERAL

The Black Liquor generated from pulp wash is generally very high in characteristics such as COD, BOD, Total Solids and Colour. Which makes it very difficult to treat. Hence, by providing a separate treatment its pollutional parameters could be brought down and then it would be wise to treat the combined total mill effluent.

2.2 CHEMICALS,RAW MATERIALS AND PROCESS OF MANUFACTURE

(a) Chemicals Used; For manufacture of pulp and paper, Chemicals used depend upon type of process e.g. caustic soda, soda ash, sodium sulphide, sodium sulphate, bisulphate, bisulphite of calcium and magnesium, lime, lime-stone, chlorine, chlorine dioxide, hypochlorite of sodium and calcium, hydrogen peroxide, sodium peroxide, zinc hydrosulphite, china clay, talc, rosin, starch, dyes and guns (I S: 5061-1968).

Sodium hydroxide is required essentially for agriculture residue based industry and it's quantity varies with raw material. Normally 5 to 10% of NaOH is used for most of the raw materials, however when baggasse is used, the requirement for alkali becomes as high as 12% of the raw material used.

(b) <u>Raw materials</u>:   About 34% of total installed capacities of SPM in India exclusively employ agriculture residue.,18% employ waste paper as their raw material. The rest of the capacity, 47.5% utilises combination of rice straw, wheat straw, bagasse etc.

(c) <u>Process of Manufacture</u>:   At first, digestion of raw materials like agricultural residues, gunny, jute, etc. at high temperature and pressure in the presence of chemicals like sodium hydroxide and/or lime is done. Specially designed spherical digestors with capacity around 25 cu.m are employed for this purpose. Steam pressure is maintained between 5 and 6 kg/sq.cm. Temperature of digesting material is maintained around 150 °C.

The process dissolves the lignin in the wood and loosens the cellulose fibre; Lignin is converted to thio and alkali lignin in Kraft process and ligno-sulphonate in sulphite process. The fibres still contain   a part of lignin and hence are coloured brown and require bleaching for making white paper. The spent liquor known as Black Liquor (B.L.) from Kraft or Alkali process is either drained out or recovered for chemicals wherever chemical recovery is feasible.

The process of pulp washing gives rise to dark brown coloured waste known as brown stock wash or unbleached decker waste which is high in pH and C O D , conventionally called the Black Liquor (BL). Bleaching is performed in multistages,
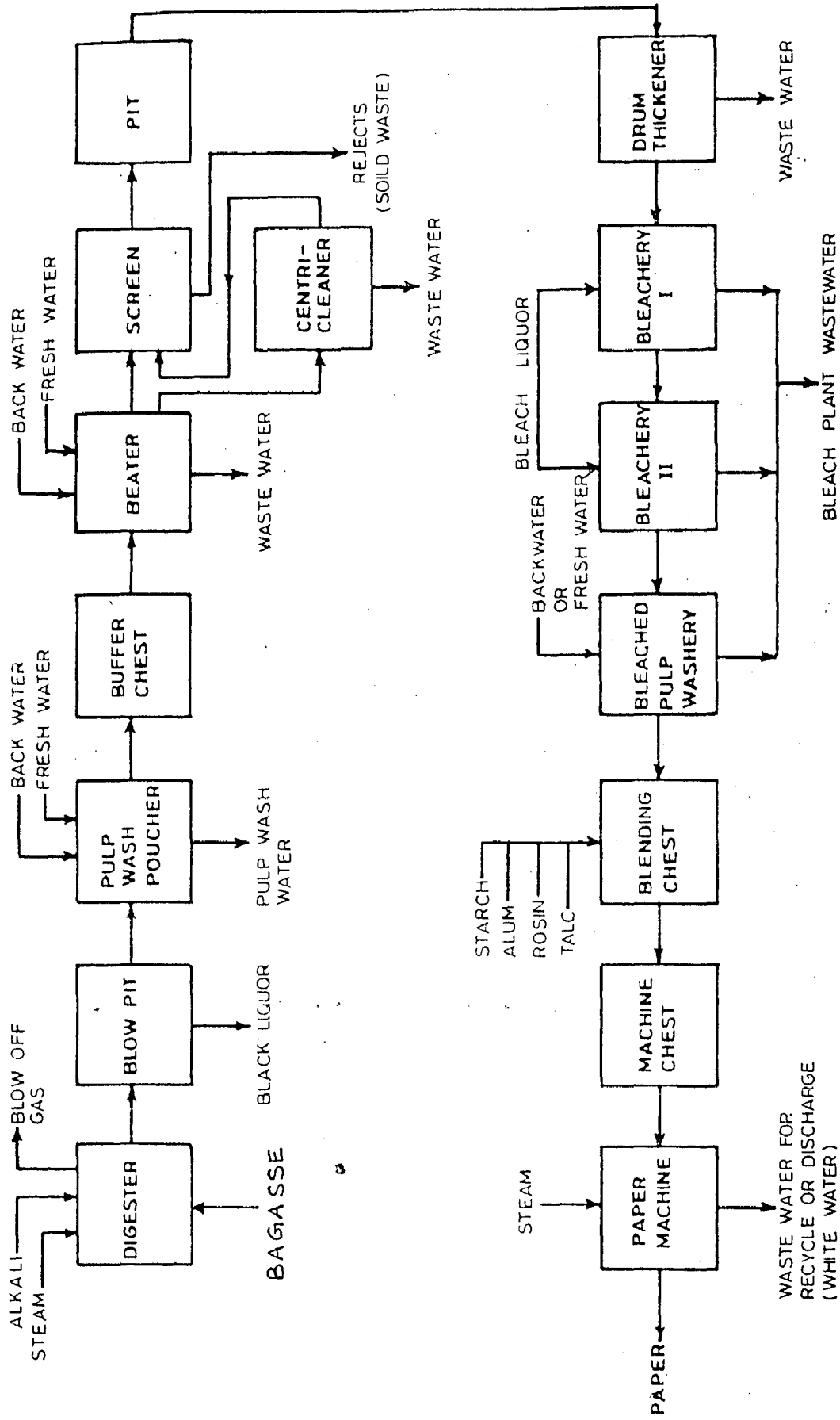
FIG-2.2.C PROCESS FLOW SHEET AND SOURCES OF WASTE WATER

using chlorine,caustic and hypochlorite. Caustic extraction effluent is highly coloured with high pH and low BOD. If chemical recovery is done, from black liquor which contains over 90% of the total lignin of the wood, the BL is first concentrated in multiple effect evaporators and burnt along with sodium sulphate in furnaces to remove organics and recover the chemicals. The smelt is dissolved in water and recausticized with lime to get black caustic soda and sodium sulphide.

The bleached pulp is converted into the paper after washing with water and adding sizing materials on a paper machine. The liquid wash water from paper machine called white water is recycled in paper machine as well as in digestion.

2.3 CHARACTERISTICS, POLLUTION LOADS AND
WASTE WATER GENERATION:

Based on weighted average characteristics of waste water for mills using agricultural residue , the pollution loads for mills of different capacity normally observed have been presented in Table 2.3 .

Further, pollution load of liquid effluent consists of:

(a)   Suspended solids like bamboo/wood or other agricultural dust, fibres, pigments, ink particles, dirt, lime sludge and similar solids.

(b)   Dissolved organic and inorganic compounds like lignin

compounds, hemicellulose, sugar, salts, acid and alkali compounds.

(c)   Colour bodies like dyes and primary lignin compounds.

(d)   Micro-organisms.

TABLE 2.3

Total Waste Water Volume and Pollution Load for Different Capacities of Mills Employing Agricultural Residue (Comprehensive Industry Document SPM 1986).

PARAMETERS	CAPACITY (TPD)		
	10	20	30
Volume, Cu m/d (90 percentile value)	3,350	6,700	10,050
Volume, Cu m/d (av.value)	2,520	5,040	7,560
pH	6.0-8.5	6.0-8.5	6.0-8.5
Suspended solids, mg/l	615	615	615
Suspended solids, kg/d	1,550	3,100	4,650
BOD, mg/l	698	698	698
BOD, kg/d	1,759	8,518	5,277
COD, mg/l	2,940	2,940	2,940
COD, kg/d	7,409	14,818	22,226

SS, BOD and COD are average values.

2.4   MINIMAL NATIONAL STANDARDS (MINAS)

The Minimal National Standards for small Pulp and Paper Mill effluent have been evolved after looking into following basic considerations.

-     Characteristics of effluent from small pulp and paper mills without chemical recovery systems.

- Achievability and Techno-economic feasibility of various waste water treatment alternatives.

- Maintained Ratio of annualised cost to the turn over of the industry.

So, based on above aspects, following tolerance limits for effluents from small pulp and paper industry are recommended.

MINAS for Small Pulp and Paper Industry

PARAMETERS	CONCENTRATION
pH	6.0 - 9.0
Suspended Solids (mg/l)	100
Bio-Chemical Oxygen Demand (mg/l) at 5 days, 20°C	50

Permissible limits for COD and lignin for which no suitable economic technology is presently available, are not prescribed at the moment; COD limits shall be introduced in MINAS as and when the suitable economic treatment systems for removal of colour/lignin would be available.

The implementation of above prescribed limits will be made in phased manner. In the first instance, the BOD and suspended solids of treated effluent should be reduced by 90 percent of the total BOD and SS load in the effluent by June 1987.

Above tolerance limits is to be achieved by all SPM by June 1988.

CHAPTER - 3

LITERATURE REVIEW

3.1 GENERAL

The cost of chemical recovery plants and its operation will prove economical only when the pulp plants are of sufficient capacity, i.e. 50 tonnes or above per day (Subramanyam 1976). Lignin is the main constituent of Black Liquor, which if effectively degraded could result in better effluent quality. Researchers have put forward various ideas for effectively treating the pulp and paper mill waste water. The treatment process could be summarized as:

3.2 BIO-CHEMICAL OXIDATION

Biological systems like aerated lagoon, activated sludge process etc. for removal of bio-degradable organic matter has been used in last few decades for pulp and paper mill wastes.

Thirumurthi (1969) has reported that aerated lagoon treatment has confirmed effective BOD removal, although colour removal was not significant.

Woodard (1974) reported that ASP sludge has the ability to reduce pollution of solution containing 1000 mg/l lignin to 90% lignin removal and 98% colour removal. Colour destroying organism development research is still undergoing. Whether these would be able to populate in lagoon or biological treatment is doubtful.

3.3 CHEMICAL OXIDATION

The chromophore formed during pulping process can be oxidised using strong oxidants like ozone, chlorine, hydrogen peroxide, potassium permangnate. Nevel et. al., (1973) reported ozone as strongest and $KMnO_4$ as weakest chemical oxidant. Ozone has gained popularity over others. Furgason (1974) reported that ozone could completely deodarize and effectively reduce the colour of Kraft pulp mill liquid effluents. Bauman (1974) studied and reported that reduction in pollutional load was dependeht on ozone dose, initial colour, COD and suspended solids in the waste water.

3.4 ION FLOATATION

Chromophoric materials possess a negative charge. Herschmiller et. al. (1973) have reported complete colour removal at a dose of 6×10^{-4} moles per litre of surfactant. Hayes et. al. (1974) obtained sifnificant colour and COD removal using alum and polyelectrolytes.

3.5 ION EXCHANGE

Synthetic resins have been reported to absorb colour by 65% to 90%, B O D 25% to 40% and COD: 40% to 60% at pH varying from 2.0 to 2.5. Resin can be desorbed by sodium hydroxide wash (I S: 5061-1968).

Bolto et. al. (1979) and Dove (1980) by virtue of laboratory studies using a magnetic ally weak basic ion exchange in two stages with contact time of 2.5 min. per stage got

colour reduced from 3000 to 250 PT-CO units.

Roberts, et. al. (1985) reported that various mixture of alum/quat removed 100% colour thus removing effectively lignin and C O D .

3.6 SOIL PERCOLATION

Dove (1982), Keenan (1981) reported that bleached Kraft Mill Effluent after having secondary treatment and settlement, if percolated through soil manifests in a colour reduction of 15 units. So soil percolation is not an effective system for colour, C O D removal, i.e. is very slow.

3.7 ADSORPTION

The most commonly used adsorbant are either granular or powdered activated carbon and pulverised carbon. It is capable of removing substantially all of the colour, C O D and B O D from Kraft Mill Effluent (KME). McGlasson (1970) and Copland (1970) have reported that substitution of granular carbon for pulverised carbon, with two hours contact time, a solution of pH 7.6 and at a temperature of 5 °C leads to removal of 98% colour and 82% COD.

Whereas granular carbon removed 64% of colour and 62% of C O D Higher capital and operating costs has limited activated carbons use. Lang et al. (1981) confirmed use of A.C. for treating caustic bleaching effluents as technically sound and achieved 94% of colour and 84% of T O C removal. Carpenter, et. al. (1980), Dove (1982) used powdered A.C. in

activated sludge treatment of pulp mill effluent at the dose of 450-1000 mg/l to remove an additional colour of 20% to 50% beyond that attained in conventional process but T.S. was found greater when using A.C. process.

3.8 MEMBRANE PROCESS

Data from League laboratory (Nelson et. al.,1968) reveals that a feed with 0.5% dissolved solids can be concentrated by reverse osmosis to 8% to 10%at 4137 KN/m^2 pressure to give a colour and colour free product. A 3-stage nominal 37.9 m^3 ultra-filtration pilot plant was operated on caustic extraction for several months (Frement, Henry A. 1980). Colour removal of 97% to 99% was obtained when calculated on a concentration basis.

Economically it is unrealistic to consider Reverse Osmosis for processing extremely large volume or produce concentration for which there is no treatment system or by-product value.

3.9 AMINE TREATMENT

Pratias et.al.(1974) carried out laboratory studies for using solution of high molecular weight amines for the removal of colour, C O D from pulp mill effluents. They confirmed high degree of decolourization (90%to 99%).

For the bleached KME, the treatment involved a capital cost of U.S. $ 600,000 and an operating cost of U.S. $ 1.4/air dried tonne of pulp. On comparison with lime treatment

capital cost of Amine treatment was found to be lower and operating cost was the same.

3.10 RADIATION

Nagai and Suzki (1979), Dove,(1980) investigated radiation-induced degradation of ligno-sulfonate in solution using gamma rays from a 60 Co source in the presence of oxygen or nitrous oxide. Colour removal was nearly complete at doses of 16.5 M. rad/hr. Addition of 60 ml of propylalcohol to nitrogen saturated solution of 200 mg/l lignin increased colour removal from 33% to 67% at a dose of 1.1 rad/hr. C O D or S S removal was not observed. Applicability of this process in field has not yet been investigated.

3.11 COAGULATION STUDIES

The aggregation of colloidal particles can be considered as involving two steps: (1) particle transport to effect interparticle contact and (2) particle destabilization to permit attachment when contact occurs. The terminology to describe these process is controversial. Some authors use the term coagulation to describe the destabilization produced by compression of electrical double layer, surrounding all colloidal particles and use floculation to describe destabilization by the adsorption of large polymer and the subsequent formation of particle-polymer-particle bridges (Lamer V.K. - 1964). Whereas others use the term to describe aggregation, including both i.e. particle destabilization and particle transport and use 'flocculation' to describe only the

transport step (Weber-1971). However, Manual of Water supply and Treatment - 1977' describes 'Coagulation' as the effect produced by addition of a chemical to a colloidal dispersion, resulting in particle destabilization. This is achieved by adding a chemical and mixing it rapidly. 'Flocculation' is the 2nd stage of formation of settleable particles (flocs) from destabilised colloidal size particles and is achieved by gentle and prolonged mixing.

For industrial waste water treatment, coagulation is dependent on dosage of coagulants, coagulant aid, pH, temperature, nature of particles and their size and concentration. Extensive laboratory studies are required to find the optimum conditions for any coagulation process.

The mechanism of removal of C O D , colour, total solids can more properly be regarded as a process of chemical precipitation rather than coagulation (water quality and treatment - A hand book - 1971). Thus removal is always accompanied by the formation of chemical sludge. Hence sludge characteristics also form the integral part of this type of studies.

The use of coagulation as a physico-chemical process for waste water is gaining popularity. It is a promising, rapid, predictable, economically more feasible and amenable. automatic control.

3.11.1 Lime Treatment

Massive lime for colour, C O D and solids removal, has been developed recently and being widely used due to its low cost. NCASI (Oswalt-1970) found that large dose (as high as 20,000 ppm) has been able to remove B O D in range of 35% to 57% and colour in the range of 92% to 97%. Heavy dose of lime also adds sufficient weight for settling and filtration of the hydrated lime and colour bodies. Economic recovery can be justified only in large pulp and paper mill.

Duggal (1975) studied the effect of lime treatment on molecular weight distribution of colour bodies from kraft linear board decker and observed that molecular weight above 5000 are completely removed whereas molecular weight <400 are not removed by lime treatment. Schmidt and Joyce (1980) suggested that by using the enzyme, 'horse raddish peroxide' which catalyze the polymerization of low molecular weight colour bodies prior to precipitation .   Increases the colour, C O D removal, by over fifty percent. I S: 5061-1968 has recommended a modified lime treatment with a dose of 1000 mg/1 only for the unclarified Kraft pulp and paper effluent. This method has helped in removal and disposal of suspended solids in the combined effluent.

Spruil (1970) found that by adding a quantity of lime several gm/litre above saturation level, rapid clarification could be realised. Resulting sludge could be thickened to satisfactory concentration and filtered at acceptable rates.

Spruil . Edgar (1973) again reported that total mill effluent when treated with 1000 ppm of lime yields colour reduction of 80% to 90%. Good dewatering and lime kiln incineration of sludges have been recorded.

Olthoff and Eckenfelder (1975) observed from their experiments that lime produces an effluent with high pH, pale residual colour and alkalinity. Neutralisation of this alkalinity involves an additional step. Recovery of residual lime may be difficult because of the tendency of the calcium carbonate to form colloids if pH is below the critical value of 11. Although colour removal is 82% to 90% with COD removal not reported by them, the whole process becomes a costly affair.

3.11.2 Ferric Chloride as Coagulant

Iron salts either in form of ferric chloride or ferric sulphate (Olthoff and Eckenfelder - 1975) are considered as economically feasible coagulant and equally competitive to lime if sludge disposal does not materially affect the cost. COD removal of 60% and, colour removal of 92% was obtained with 500 mg/l dose of iron salts. BOD removal were lower (20%-30%) in pH range of 3.5 to 4.5. Sludge volume was 200 ml/l .

Goos et al (1974), Same≈shima et. al. (1973) and Nebel et. al. (1973) have reported that ferric chloride treatment can be effectively used with pulp and paper mills effluents. It's effectiveness increases if domestic waste is combined with

pulp mill effluent.

Smith and Christman (1969) reported that soft wood water required an optimum dose of 286 mg/l, for colour removal by 85% .

3.11.3 Treatment with Magenisum Salts

Shrinivasan Iyer, M.V. (ME thesis 1983) have reported the effectiveness of magnesium sulphate as a coagulant with or without lime. Alone it is not very effective. Pulp and paper mill waste when treated with 30 mg/l of Magnesium Sulphate and 1300 mg/l of lime reveals that it removes significantly, total solids by 44%, suspended solids by 68%, B O D by 17.4%, C O.D by 52% in addition to 90% of colour removal.

Vincent (1974) showed that either 1000 mg/l CaO or 500 mg/l caO plus 30 to 60 mg/l of Mg^{+2} resulted in 90% removal of C O D from biologically treated Kraft Mill effluent. Black and Thompson (1975) found that dosages of 300 mg/l CaO plus 60 to 90 mg/l of Mg^{+2} resulted in 90% colour removal from a total pulp mill effluent. Precipitation of $Mg(OH)_2$ is the preferred mechanism because it can be accomplished at low magnesium dosages under proper conditions. Precipitation is enhanced at pH value of about 10.7, thus lime is used to raise and sustain pH during aggregation.

3.11.4 Alum Coagulation

Alum coagulation of high characteristic black liquor from small pulp and paper mills, results in a dense and rapid settling coagulum. Higher the solids or colour higher will be

the optimum dose of alum required for coagulation. Optimum pH for aluminium sulphate have been found to be 5.3. Alum as a coagulant has been gaining wide popularity because of relatively low dosage level. It requires moderate capital investment but relatively very low operating expenditure.

Electrophoretic behaviour of the colouring material reported by Black et.al. (1961) and Kawamma, S. (1967) is that good removal was at isoelectric point but removal was observed when floc particles reversed the charges from negative to positive resulting from an excess amount of alum addition. Kawamura (1976) suggested following relationship between colloid charge, alkalinity and optimum alum dosage.

Alum dosage= waste water alkalinity + 0.453

}.11.4 **Mechanism of Alum Coagulation:** When $Al_2(SO_4)_3$, a metal salt is used as a coagulant in concentrations sufficiently high to cause rapid precipitation of a $Al(OH)_3$, colloidal particle can be enmeshed in these precipitates as they are formed (Palkham, 1965). Aluminium (Al^{+3}) is found to be most effective in pH range of 5 to 6 (Weber).Different chemical coagulants can bring about the destabilization of collids in different ways. Hardy (1900) showed that destabilization of a colloid by a indifferent electrolyte is brought about by ions of opposite charge to that of the colloids (Counter-ions) and the coagulation effectiveness of these ions increases markedly with charge. For example, the concentrations of Na^{1+}, Ca^{2+} and Al^{3+} required to destabilize a negatively charged colloid

are observed to vary approximately in the ratio of $1:10^{-2}:$ 10^{-3}.

Destabilization by counter-ions is accomplished by compressing the diffuse layer surrounding the colloidal particle. Many irreversible colloids are stabilized by hydration effects in addition to charge effects. The ability of a coagulant to destabilize a colloidal dispersion is actually a composite coagulant - colloid, coagulant-solvent, and colloid-solvent interactions.

At high dosage of Alum, restabilization occur (Weber, 1964) and is accompanied by charge reversed. The initial destabilization and the subsequent restabilization are brought about by adsorption of Al^{+3} species from solution.

All metal cations such as Fe^{3+}, Al^{3+}, Ca^{2+} and H^+ are hydrated in water. Aquametal ions such as $Al(H_2O)_6^{3+}$, $Fe(H_2O)_6^{3+}$ are acidic, i.e. they are proton donors. The addition of Al^{3+} salt to waste water in concentrations less than the solubility limit of the metal hydroxide leads to the formation of soluble monomeric, dimeric and perhaps the small polymeric hydroxo-metal complexes, in addition to the free aquo-metal ion. In these cases, OH^- ions also are ligands. Ions or molecules (such as water molecules) which are bonded to a central metal atom are termed ligands.

$$Al(H_2O)_6^{3+} + H_2O = Al(H_2O)_5(OH)^{2+} + H_3O^+$$
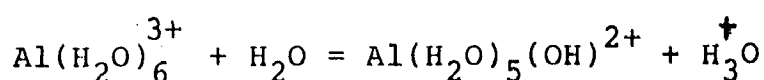
Above reaction is termed as hydrolytic reaction. When a quantity of Al^{3+} salt sufficient to exceed the solubility of

the metal hydroxide, $(Al(OH)_3$ is added to waste water, a series of hydrolytic reactions occur and finally produces metal hydroxide precipitates (Weber 1962). The dosage of Al^{3+} coagulant necessary to bring about destabilization of a colloid, depend upon the amount of colloid which is present. Adsorption in Al^{3+} cases occur at most interfaces. So, Black Liquor having higher colloid concentration is likely to produce a sweep floc depending upon pH, coagulant dose and of course colloid concentration (solids present).

Further Olthoff and Eckenfelder (1975) reported that alum as coagulant would be competitive to lime if sludge disposal materially effect the cost. The effluent from Kraft and pulping plants were treated with alum doses ranging from 250-450 mg/l at optimum range of pH between 4.0 to 6.5, the reduction in colour was attained from 85% to 92% .

Lang Edward, et. al. (1981) investigated the effectiveness of alum coagulation on total mill effluent (TME). They reported that Alum consistently removed 81% to 93% of colour, 50% to 62% of TOC, 20% to 25% of BOD and gave a product water almost free of S S and turbidity. The optimum pH was found to be 5.5 .

CHAPTER - 4

EXPERIMENTAL MATERIALS AND TECHNIQUE

4.1 EXPERIMENTAL MATERIALS

4.1.1 Waste Water Sample

Black Liquor samples were collected from a Kraft paper mill located in Muzaffarnagar (U.P.). The mill produces 10 tonnes/day and uses baggasse, an agricultural residue from Sugar Cane processing, as its raw material. Presently no effluent treatment facility exist in the mill. Characterization of Black liquor wastes from digestor house was done each time a sample was brought in the laboratory. Appendix-A shows the average values in respect of various parameters recorded for initial characterization of Black Liquor.

Experiments on Black Liquor samples were mainly carried out in two phases. First phase was aimed to observe % removal in COD colour, Total Solids (T.S.), Dissolved Solids (D.S.) and suspended solids (S.S.) by acidifcation. H_2SO_4 (concentrated) was added to coagulate the lignin compounds and pH was lowered to 2.0, 2.5, 3.0, 3.5, 4.5, and 5.5 .

In the second phase, alum coagulation was done in pH range of 5.5 to 7.0, and COD, colour, T.S. removal efficiencies were recorded. Optimum dosages of alumn at pH 5.5, 6.0, 6.5 and 7.0 were calculated and further cost analysis was done.

4.1.2 Sulphuric Acid (H_2SO_4)

Laboratory reagent grade pure H_2SO_4 (98% purity) was used. Whenever required it was diluted and used.

4.1.3 Alum [$Al_2(SO_4)_3$]

Commercially available Alum was used for coagulation studies. The stock solution of 10 gm/litre (1%) concentration was prepared in distilled water, and was used through out the investigaltion.

4.1.4 Experimental Water

Distilled water was used for dilution purposes. The pH of this water was observed to be 7.10 .

4.2 EQUIPMENTS

4.2.1 Bucchner Funnel

Bucchner Funnel of China-clay having 5.5 cm diameter was used, for sludge drainability studies.

4.2.2 Flocculators

Acidification and coagulation studies were carried out by using Aplab laboratory. Flocculator type IE-55 with six stirrers as shows in Fig.4.2.2 500ml of sample was taken in each beaker of 1000 ml capacity, to conduct experiment. The coagulant Alum dosage ranging from, 700 to 1000 mg/l at pH 5.5, 1200 to 1400 mg/l at pH 6.0, 1400 to 1800 mg/l at pH 6.5 and 1700 to 2100 mg/l at pH 7.0 were added. pH was adjusted by H_2SO_4 (Conc.) addition. The mixture was stirred at high
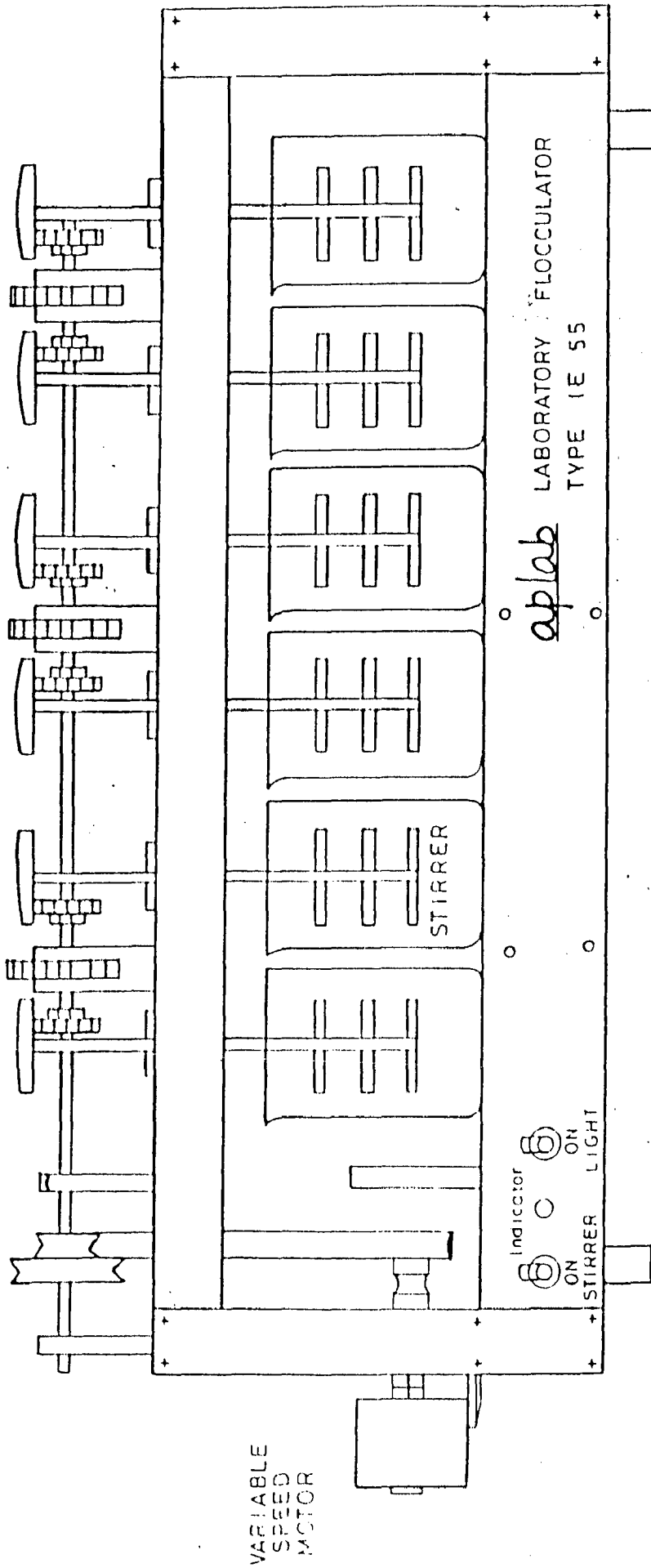
FIG 4·2·2 — LABORATORY / FLOCCULATOR.

speed (100 rpm) for two minutes and then at low speed (20 rpm) for 20 minutes. The floc was allowed to settle for 2 hrs and clear supernatant carefully syphoned from the sludge layer and analysed for physical and chemical characteristics.

4.3 ANALYSIS TECHNIQUE

4.3.1 Physical and chemical analysis of raw Black Liquor, as well as supernatant was made in accordance with the procedure detailed in standard methods, using AR grade reagents.

4.3.2 pH Measurement

A double electrode digital precise pH meter was used for pH determination. It was standardised by using Analar grade commercial buffer solution prior to recording pH of sample.

4.3.3 Colour Measurement

The "standard methods" was strictly followed. For this spectronic-20 electronic instrument was used. The procedure adopted involves simple pretreatment including the adjustment of pH of treated and untreated sample to the set pH of treatment, filtration through whatman Filter paper No.42 followed by measurement of light absorbance at a wavelength of 465nm. Colour is expressed in arbitrary colour units (C.U.) based on light absorbance by Pt-Co, standard solution at the same wave length. Procedure for colour estimation has been described in detail under Appendix-B.

4.3.4 Sludge Drainability Studies

The sludge ensuing from COD, Colour, and total solids removal by alum coagulation will ·require dewatering on sludge drying beds. Hence for measuring sludge drainability, 5.5 cm dia. Bucchuer funnel with whatman 42, filter paper was used. 50 ml of sludge from each run of coagulation was applied. Volume of filtrate collected over 2 hrs was expressed in ml drained.

CHAPTER - 5

RESULTS AND DISCUSSION

5.1 GENERAL

The data obtained from laboratory investigations conducted on the Black Liquor, obtained from a small paper mills in western U.P. for studies on acidification and alum coagulation are tabulated in Table 5.2 to 5.3 and shown plotted in Fig.5.2.1 to Fig. 5.4 . The analysis of the results is described below.

5.2 STUDIES ON ACIDIFICATION

A considerable amount of H_2SO_4 (Pure) was added to bring down the pH of black liquor from 11.36 to 2.0, 2.5, 3.0, 3.5, 4.5 and 5.5 (see Table 5.2 Figure 5.2.1). Removal percentage in COD, colour, total solids and dissolved solids were observed and are shown in Figures 5.2 .. A perusal of these plots reveal that:

(a) <u>COD removal V/S pH</u>: COD removal was maximum (53.6%) at a pH of 2.0. This was due to H^+ coalescing with solids present, and destabilising them followed by a heavy sludge blanket formation. The removal reduced rapidly and was only 7.62% at pH 5.5, where H^+ ion concentration reduced considerably (Fig.5.2.2).

(b) <u>Colour removal V/S pH</u>: Very high percentage of colour removal (98.36%) at a pH of 2.0 was observed. Even at a pH of 5.5, 93.97% colour removal was observed. Fig. (5.2.3).

This shows that colour/ COD removal is a pH dependent

less

phenomenon and is ~~more~~ at higher pH. This can be attributed to the assumptions that thio-lignin, the main colour/ COD causing compound present in black liquor is getting precipitated in lignosulphonates. The interaction between coloured/COD bodies (lignin) and precipitate (i.e. adsorption of dissolved and suspended solids and their enmeshment in precipitate as well) effectively remove colour/COD.

(c) T.S. & D.S. Removal V/S pH

Total solids and dissolved solids removal also show a similar trend (Fig.5.2.4). Total solids removal at pH 2.0 is 45.03%, following a cubic decreasing trend, it is 12.74% at pH 5.5. Similar trend is shown for dissolved solids also. Maximum removal is 51.9% at a pH of 2.0, which reduces to 26.4% at a pH of 4.5. This curve now tends to move up (see Fig.5.2.5) indicating that dissolved solids which contain lignin, is not getting oxidised/reduced by low amount of H^{+} ion concentration.

(d) Suspended Solids V/S pH: Barchart (Fig.5.2.6) show that suspended solids is increasing with pH, because the dissolved organics degraded by H_2SO_4 are also coming into suspension now. Those solids donot settle and form a blanket floating on the surface thus increasing the suspended solids in the effluent. It is 2280 mg/l at a pH of 2.0 and increases to 4440 mg/l at a pH of 5.5 .

ACIDIFICATION

Sulphuric acid (ml/l of black liquor)

PH value

Fig. 5.2.1

CODD IONITION

COD Removal (in percent)
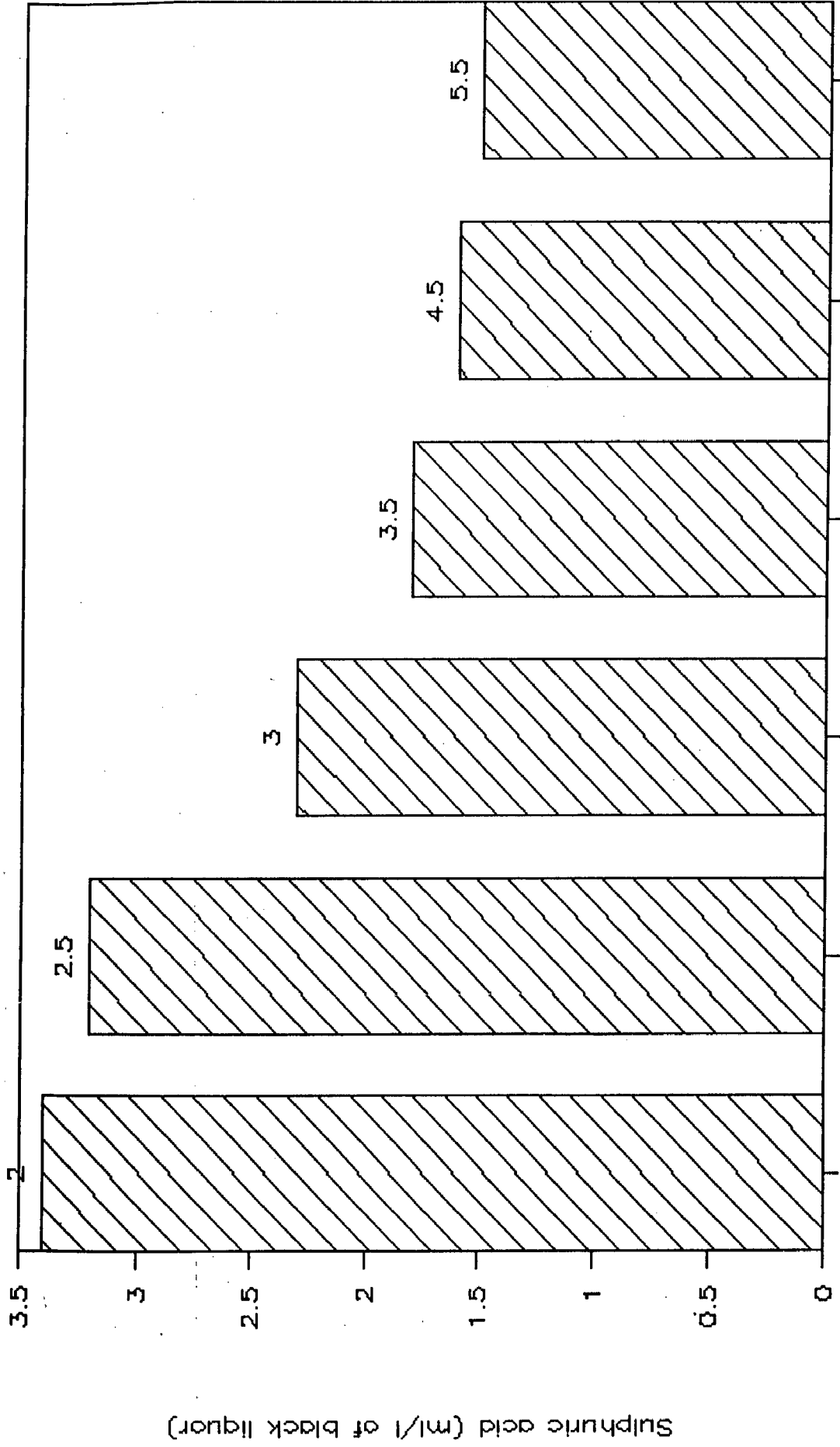
PH Value

Fig. 5.2.2

ACIDIFICATION

Colour Removal (in percent)

98.36

97.69

97.12

96.84

94.84

93.97
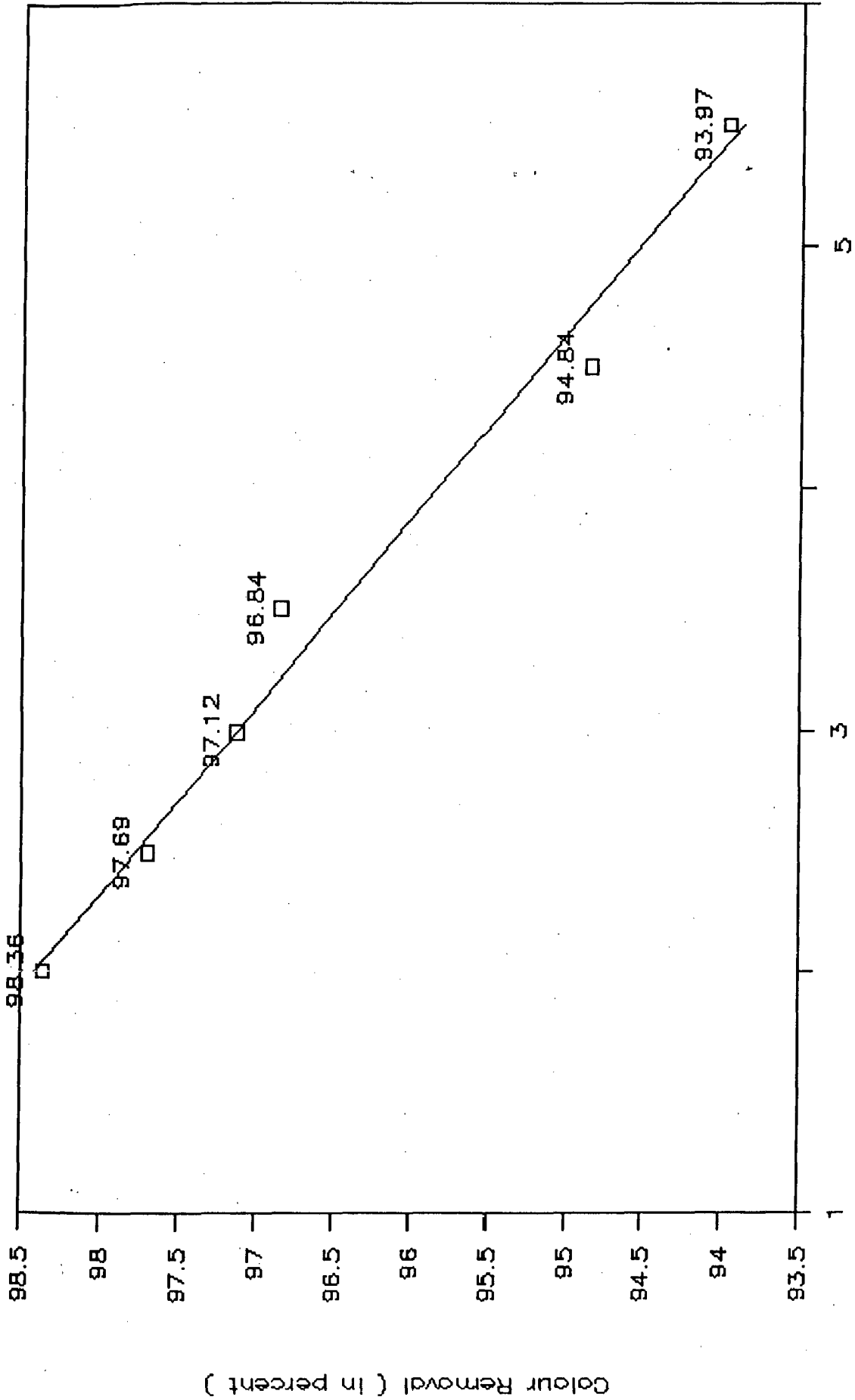
PH value

Fig. 5.2.3

ACIDIFICATION

Fig. 5.2.4

PH value

Total Solids Removal (in percent)

45.03
37.47
31.29
21.9
17.09
12.74
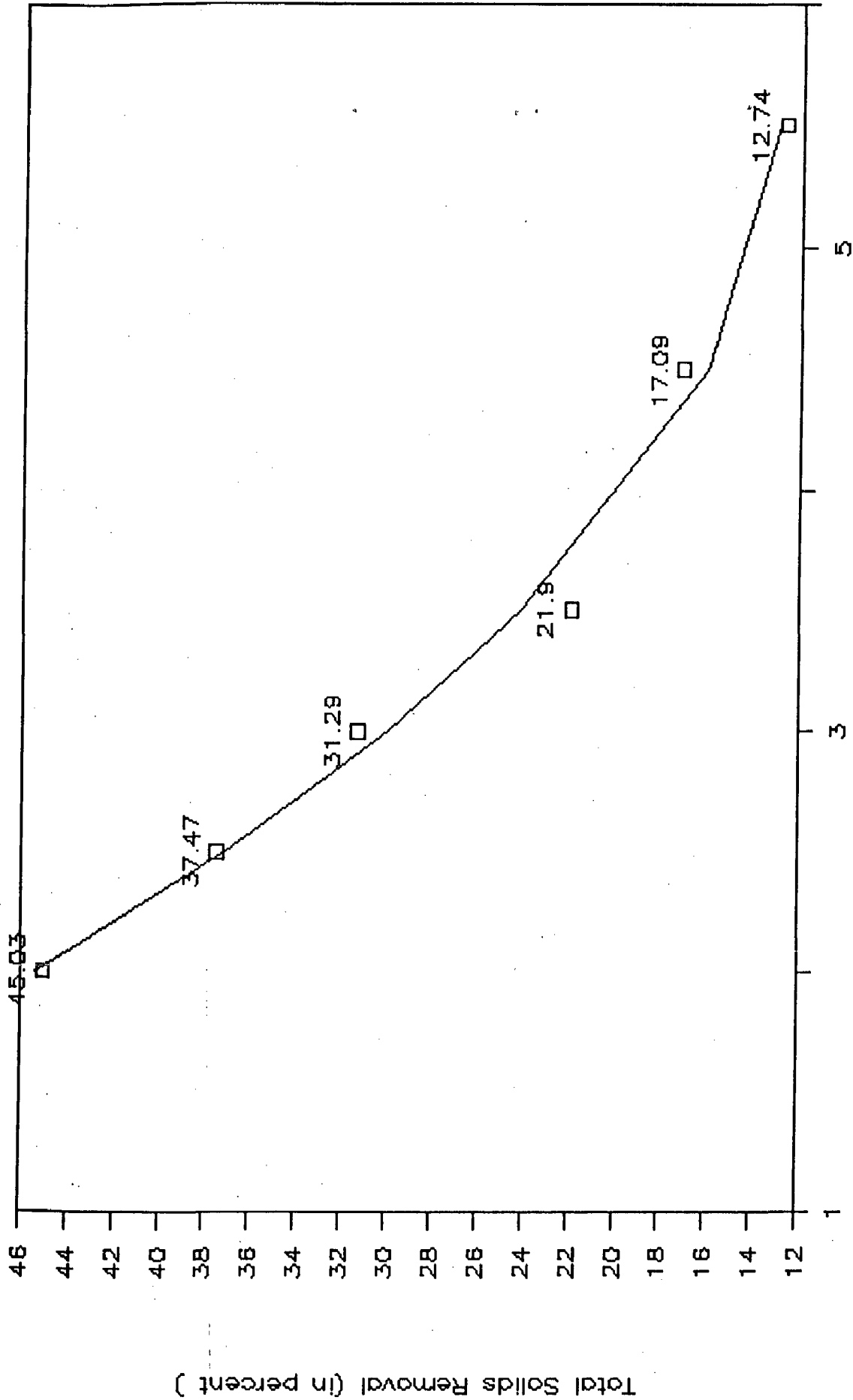
ACIDIFICATION

Fig. 5.2.5.

ACIDIFICATION

PH value

Fig. 5.2.6

Suspended Solids (mg/l of black liquor)
(Thousands)
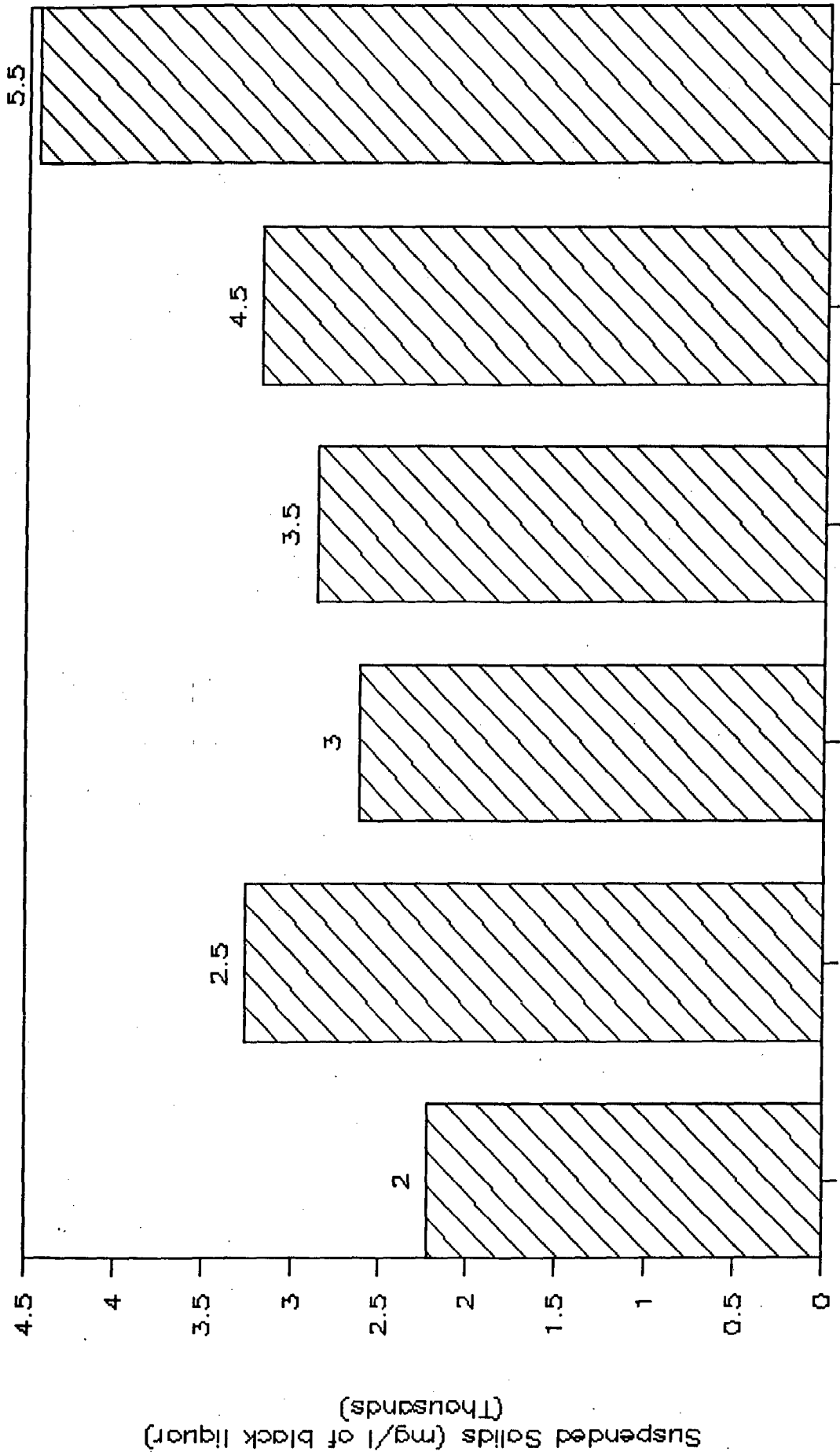
5.3 STUDIES ON ALUM COAGULATION

From literature available, Alum is bound to be very effective in the pH range of 5.0 to 7.0, with maximum at pH 5.5. So studies have been carried out at pH 5.5,6.0,6.5 and 7.0.

(a) <u>At pH 5.5</u>: The optimum alum dose (OAD) was 1000 mg/l (Fig 5.3.1 to 5.3.5) i.e. at this dose the COD, colour and total solids removal was 76%, 97% and 38.2% respectively. The graphs plotted are best fitted with the help of a computer software package.

(b) <u>At pH 6.0</u>: The OAD is found to be 1300 mg/l, with maximum COD, colour and total solids removal as 58.3%, 50% and 16.2 % respectively (Fig 5.3.4 to 5.3.6).

(c) <u>At pH 6.5</u>: The OAD is found to be 1700 mg/l, at pH 6.5. Maximum COD, colour, and total solids removal also reduces to 58.4%, 65% and 23.8% respectively (Fig 5.3.5 to 5.3.7).

(d) <u>At pH 7.0</u>: The optimum Alum Dose (OAD) is found to be 2000 mg/l, two times of that at pH, 5.5. The maximum COD, colour and total solids removal are, 56.8%, 51.8% and 64.9%. Total removal has increased. (Fig. 5.3.10 to 5.3.12).

A plot was drawn between the initial pH and the optimum alum dose (OAD). It is observed (Fig 5.3.13) that the OAD increases linearly with pH from 1000 mg/l at pH 5.5 to 2000 mg/l at pH 7.0 . A linear curve fitting gives the equation as

$$OAD \ (mg/l) = 680 \ X_{(pH)} - 2750$$

ALUM COAGULATION

(PH = 5.5)

Fig. 5.3.1

Alum Dose (mg / l)
(Thousands)

C O D Removal (in percent)

ALUM COAGULATION

(PH = 5.5)

Colour Removal (in percent)
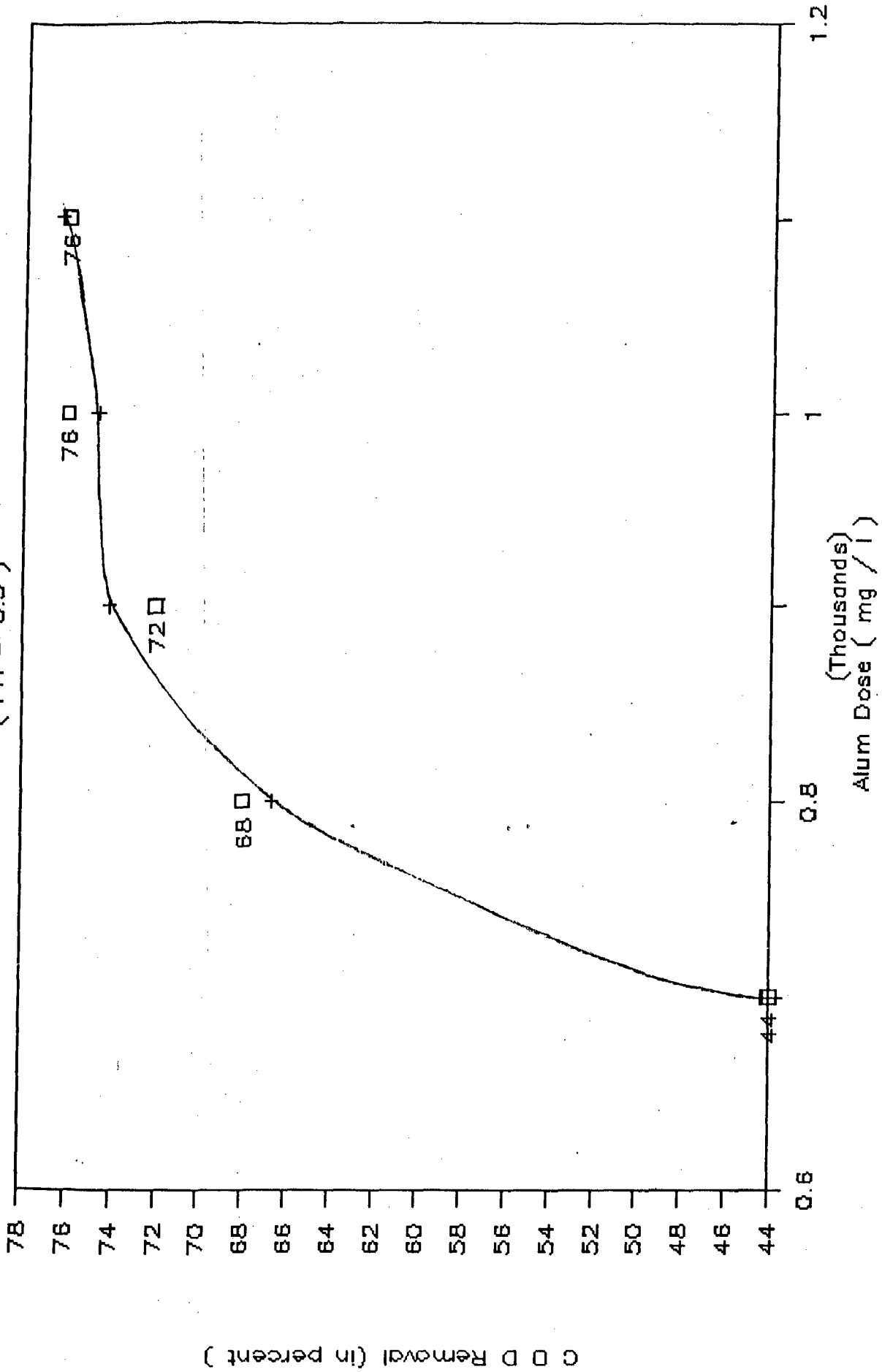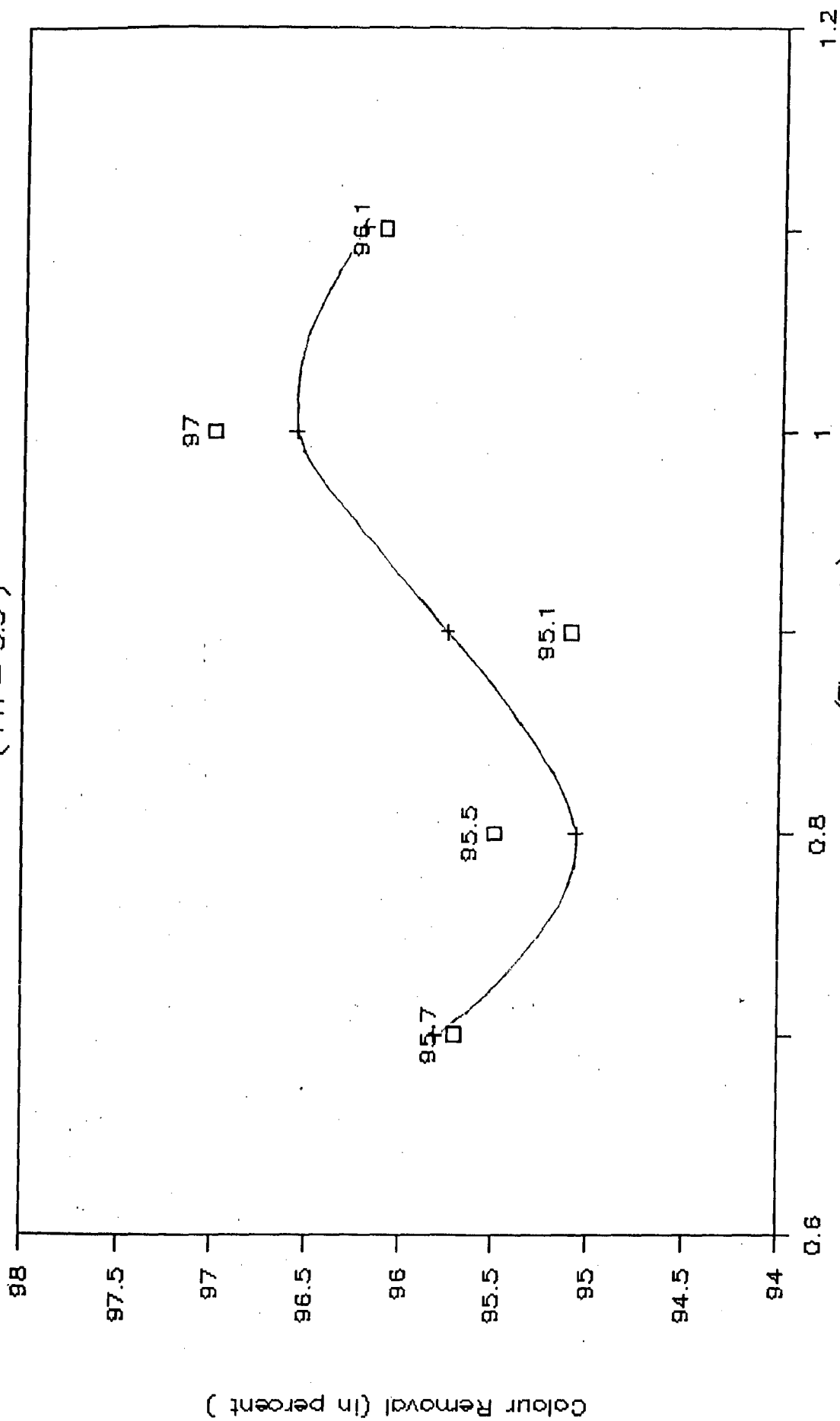
(Thousands)
Alum Dose (mg / l)

Fig. 5.3.2

ALUM COAGULATION

(PH = 5.5)

Fig. 5.3.3

Alum Dose (mg / l)
(Thousands)

Total Solids Removal (in percent)

ALUM COAGULATION

PH = 6.0

58.3   45.96

37.6

33.5

8.5

C O D Removal (in percent)
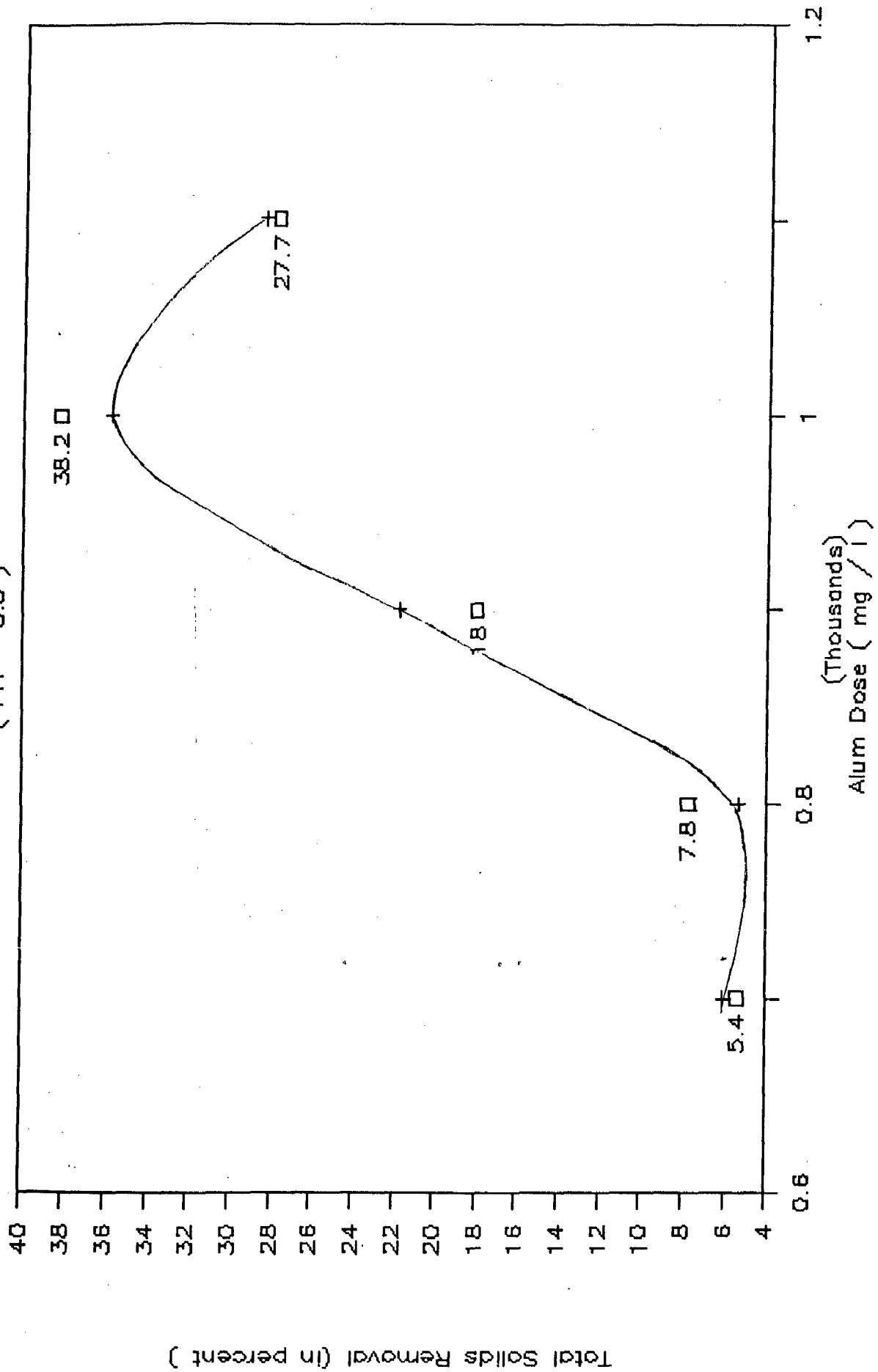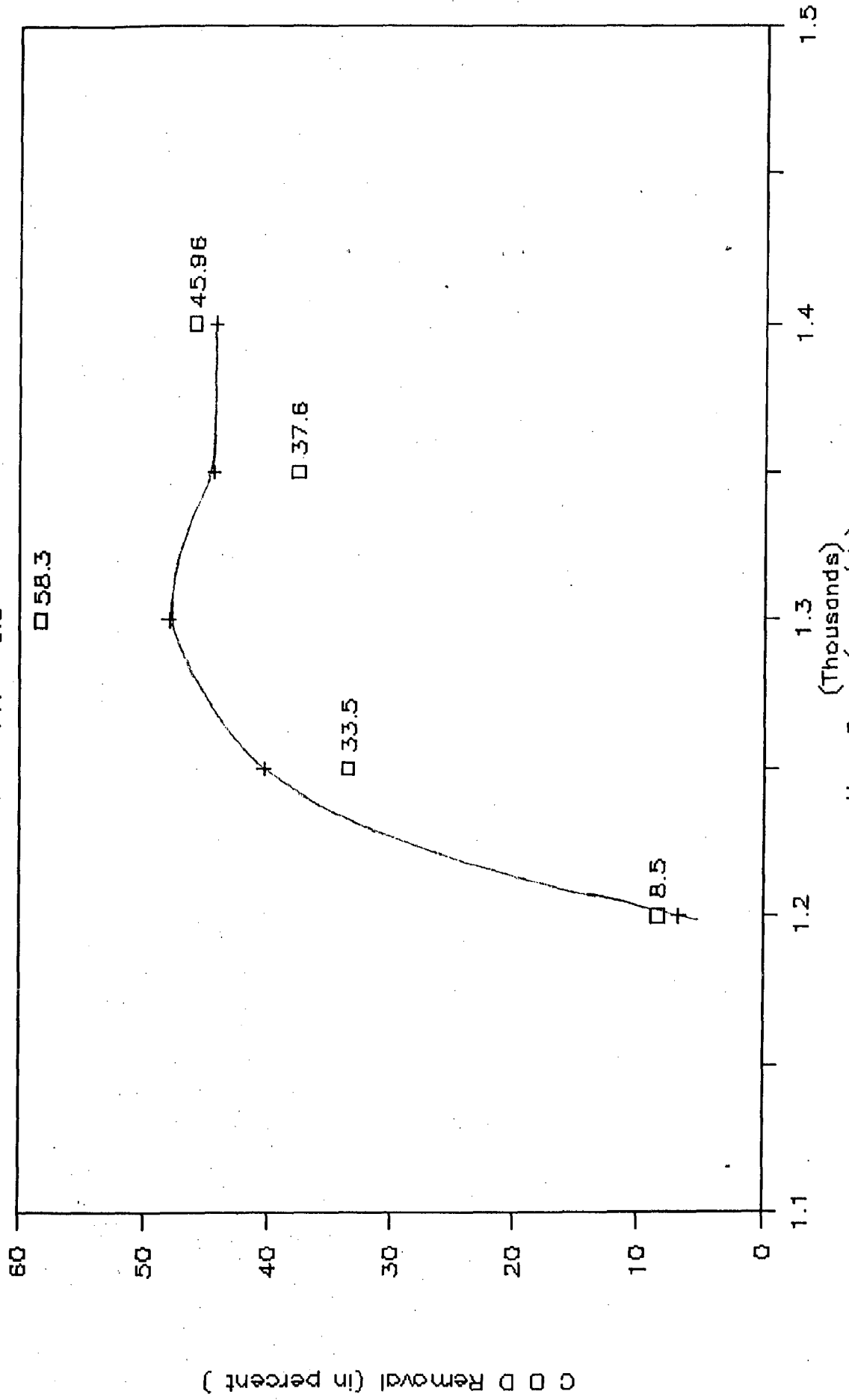
Alum Dose (mg / l)
(Thousands)

Fig. 5.3.4

ALUM COAGULATION

(PH = 6.0)

Fig. 5.3.5

Alum Dose (mg / l)
(Thousands)

Colour Removal (in percent)
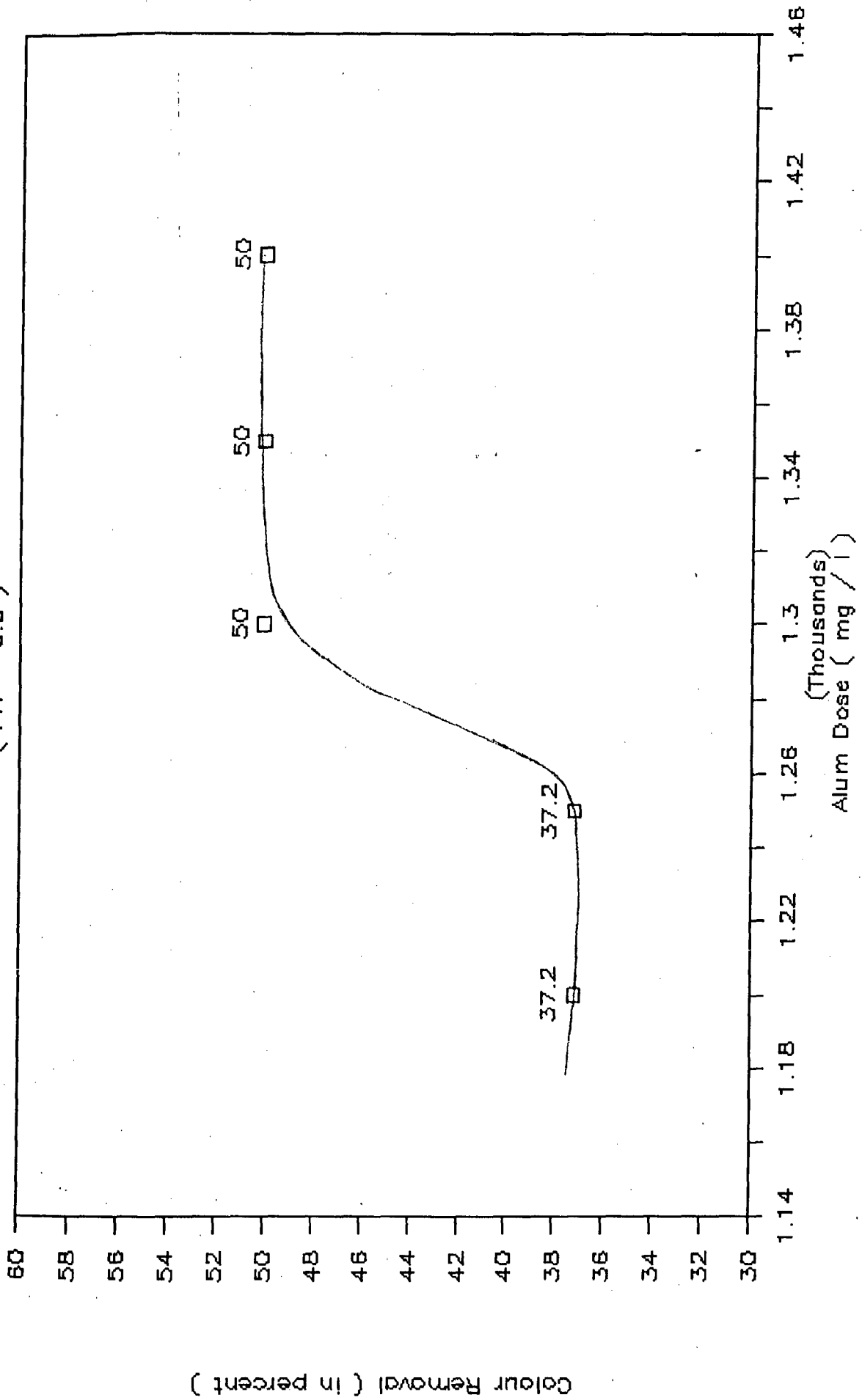
ALUM COAGULATION

(PH = 6.0)
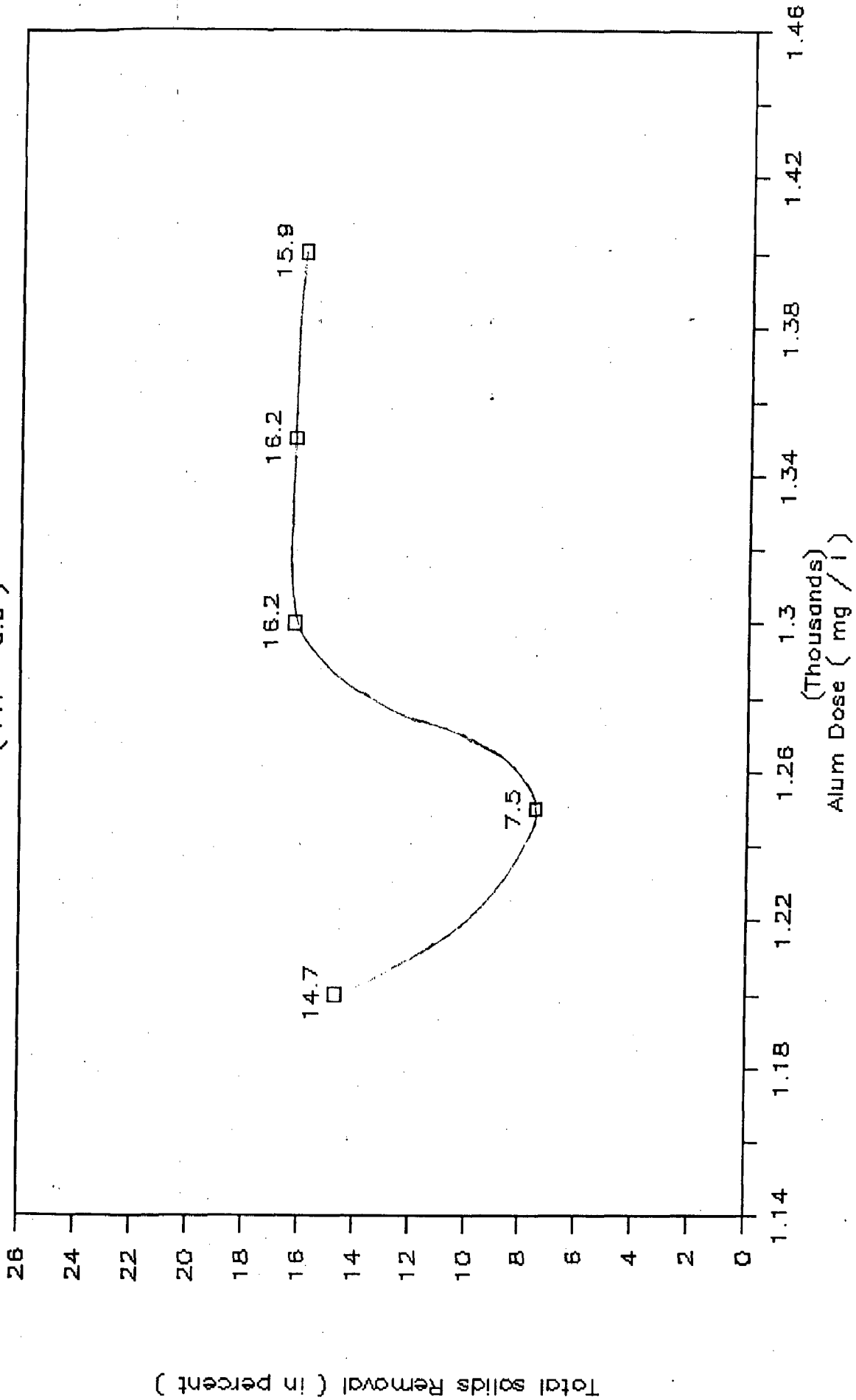
Fig. 5.3.6

ALUM COAGULATION

(PH = 6.5)

Fig. 5.3.7

Alum Dose (mg / l)
(Thousands)

C O D Removal (in percent)

ALUM COAGULATION

(PH = 6.5)

50

65

50

37.2

37.2

Colour Removal (in percent)

1.3   1.5   1.7   1.9
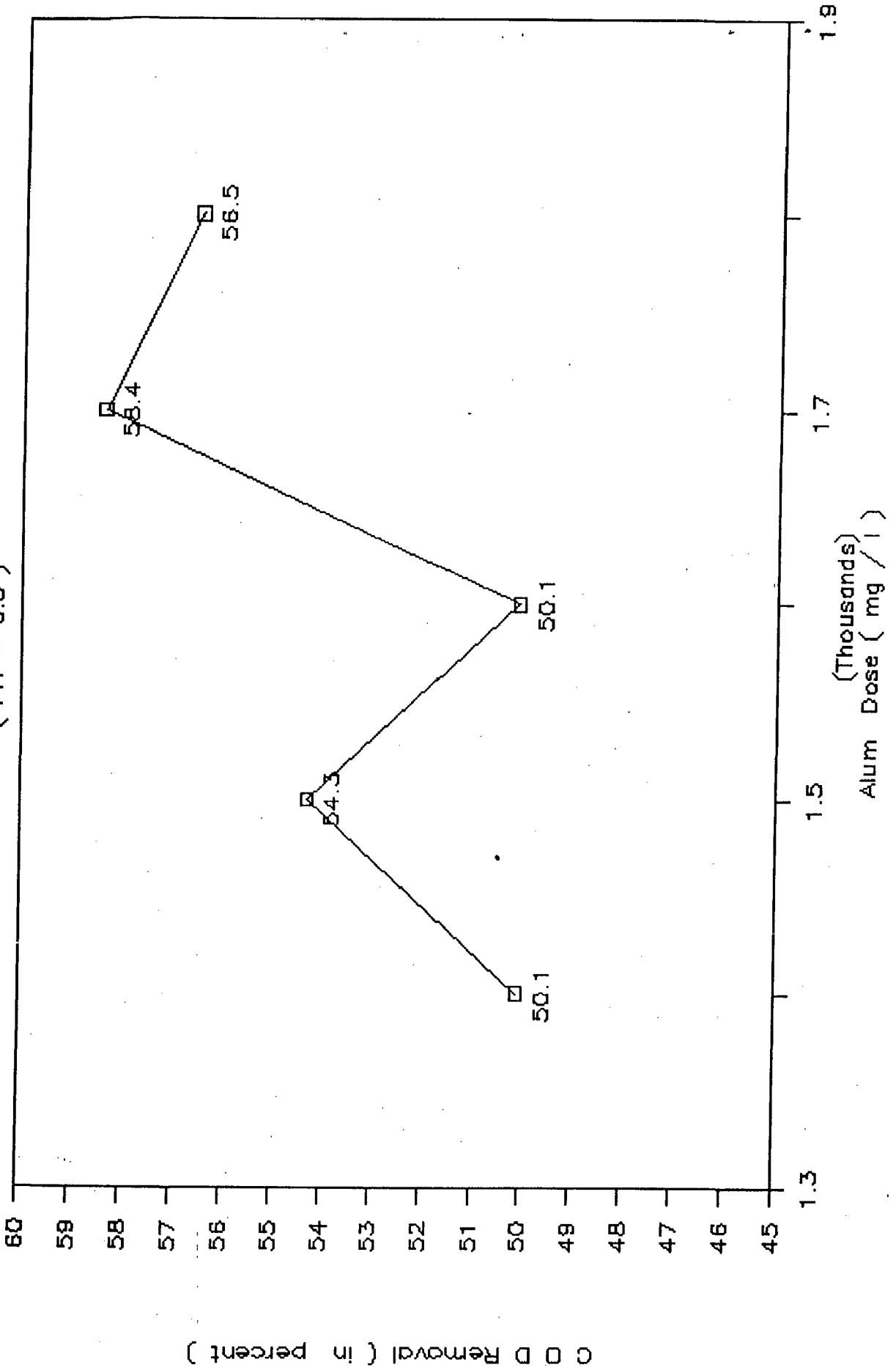
(Thousands)
Alum Dose (mg / l)
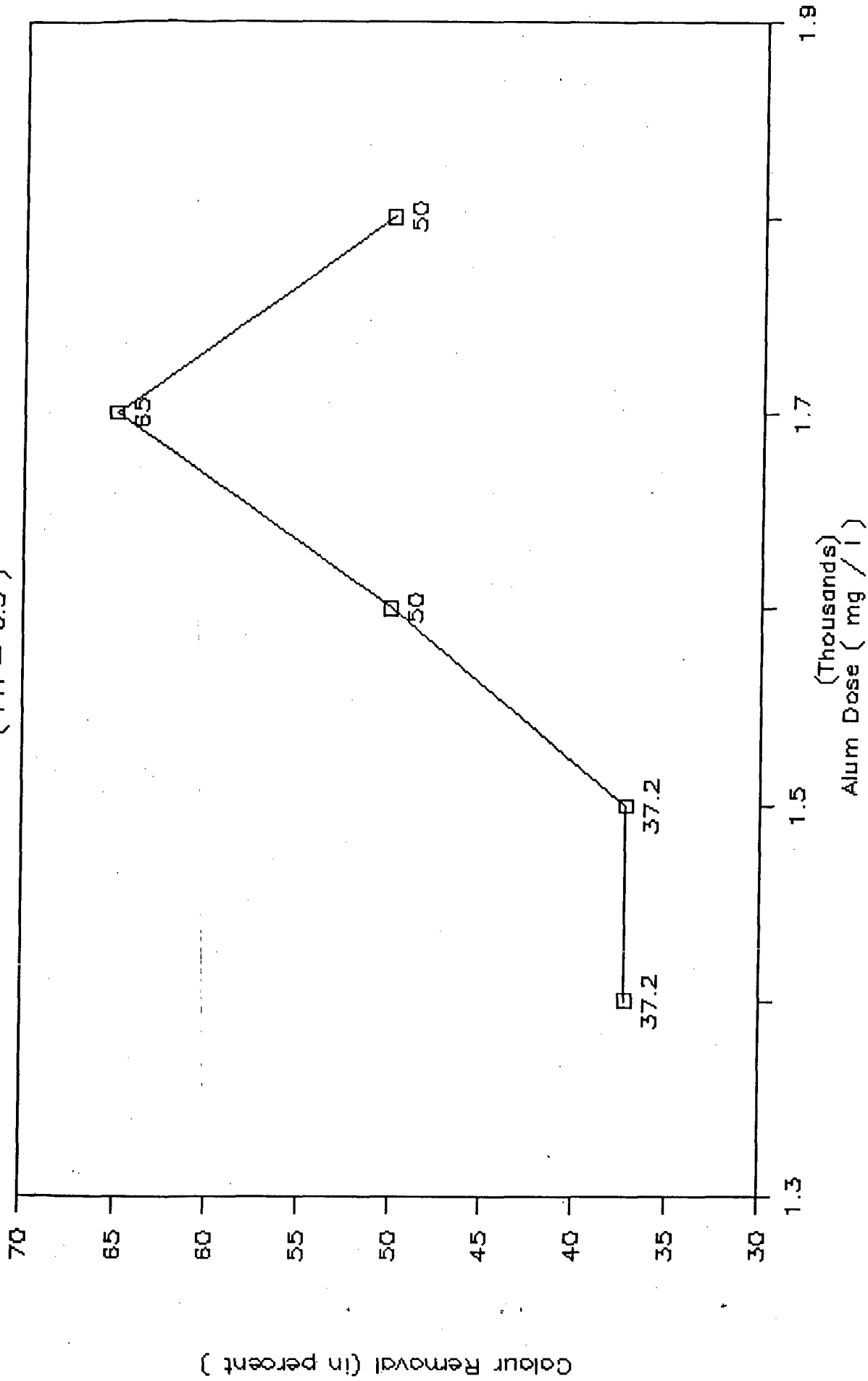
Fig. 5.3.8

ALUM COAGULATION

(PH = 6.5)

Fig. 5.3.9

Total Solids Removal (in percent)

Alum Dose (mg / l)
(Thousands)

18.9 · 19.8 · 22.6 · 23.8 · 23.5

ALUM COAGULATION

(PH = 7.0)

56.8

52.9

52.9

52.9

48.9

(Thousands)
Alum Dose (mg / l)

C O D Removal (in percent)

1.3   1.5   1.7   1.9
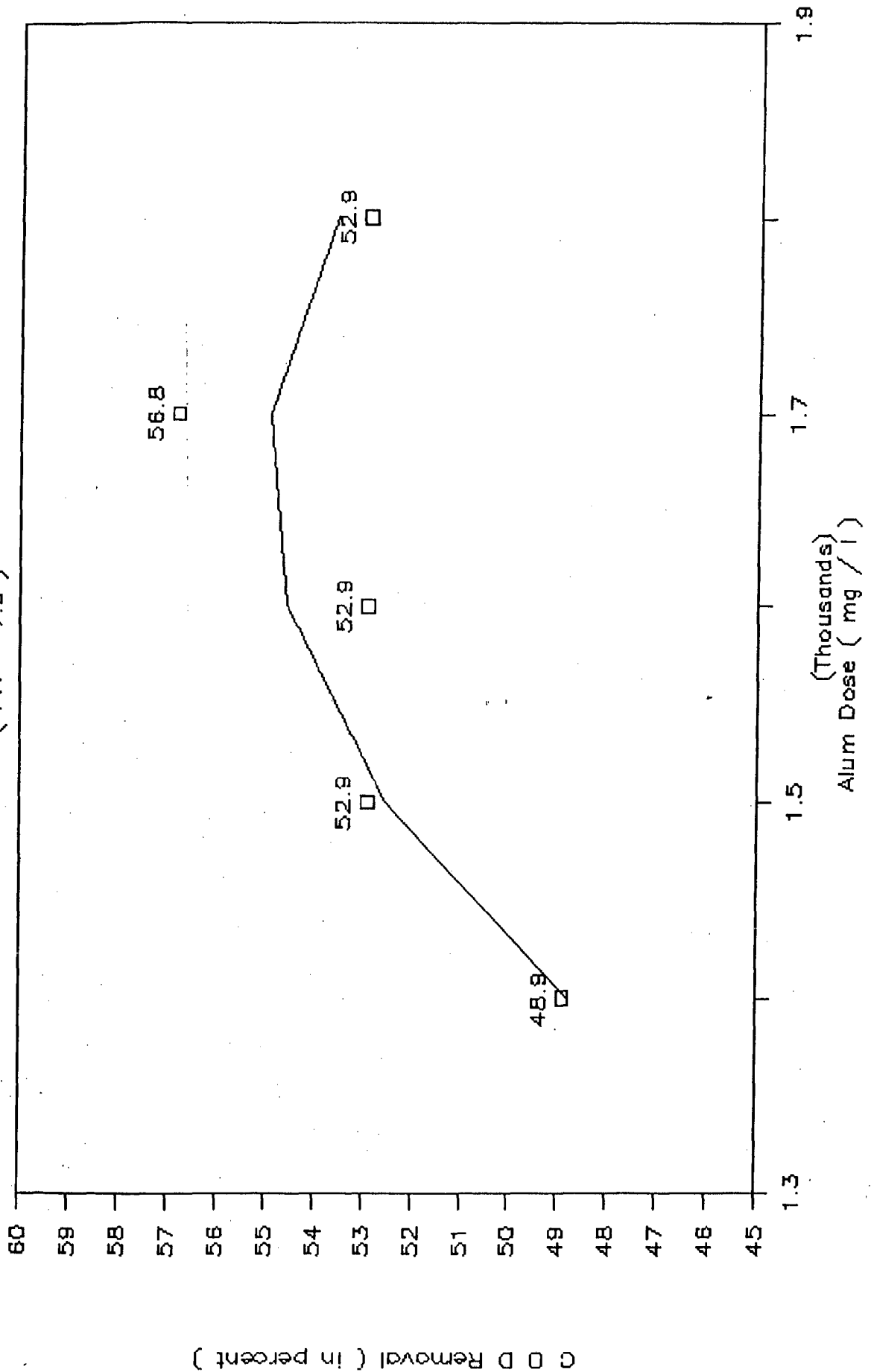
Fig. 5.3.10

ALUM COAGULATION

(PH = 7.0)

Colour Removal (in percent)

51.8

51.8

29.96

29.96

29.96

56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

1.3
1.5
1.7
1.9
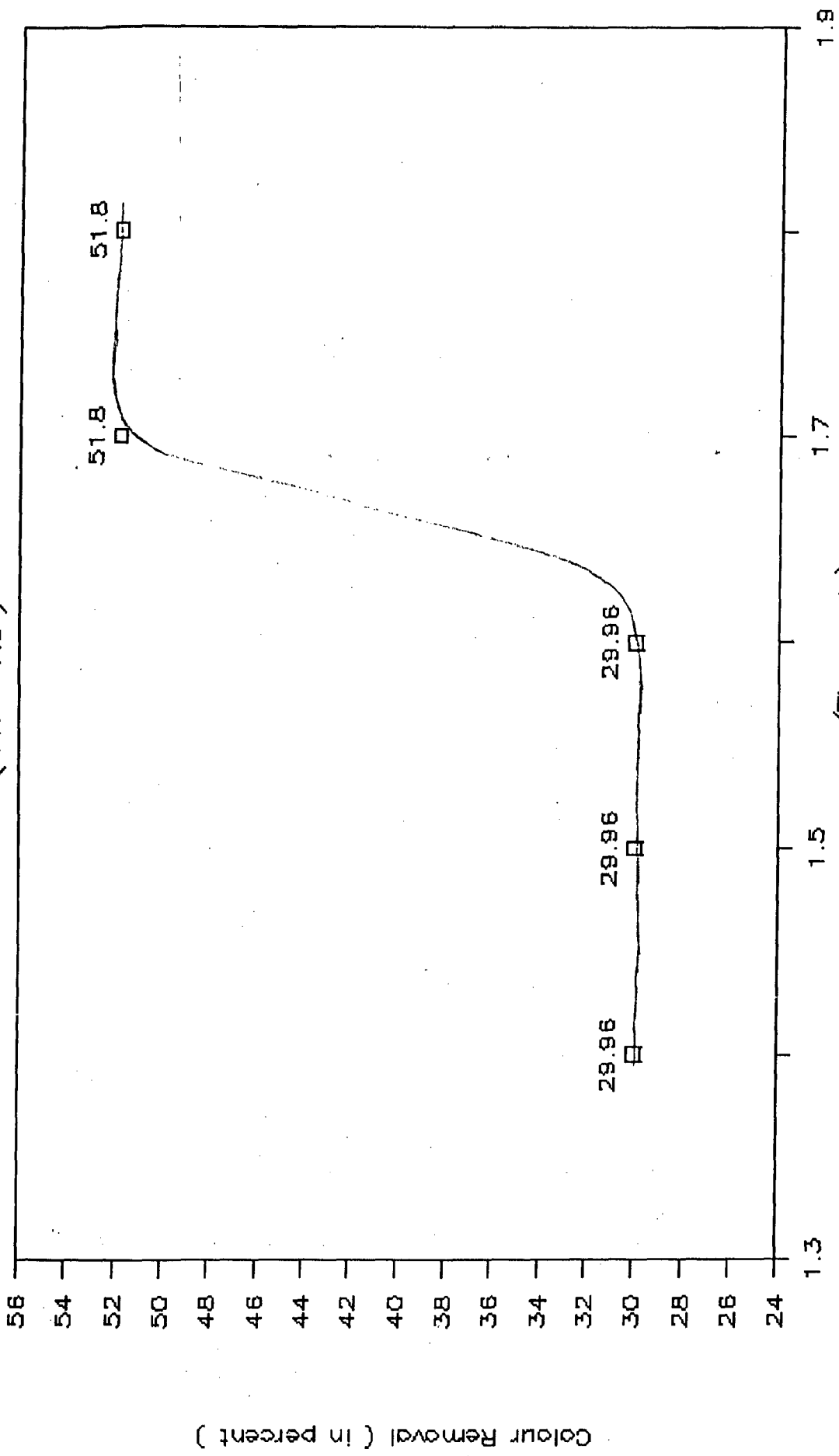
(Thousands)
Alum Dose (mg / l)

Fig. 5.3.11

ALUM COAGULATION

(PH = 7.0)

Fig. 5.3.12

Alum Dose (mg / l)
(Thousands)

Total Solids Removal (in percent)

61.6
62.5
62.5
64.9
64.9

ALUM COAGULATION

$y = 680 \, X \, -2750$
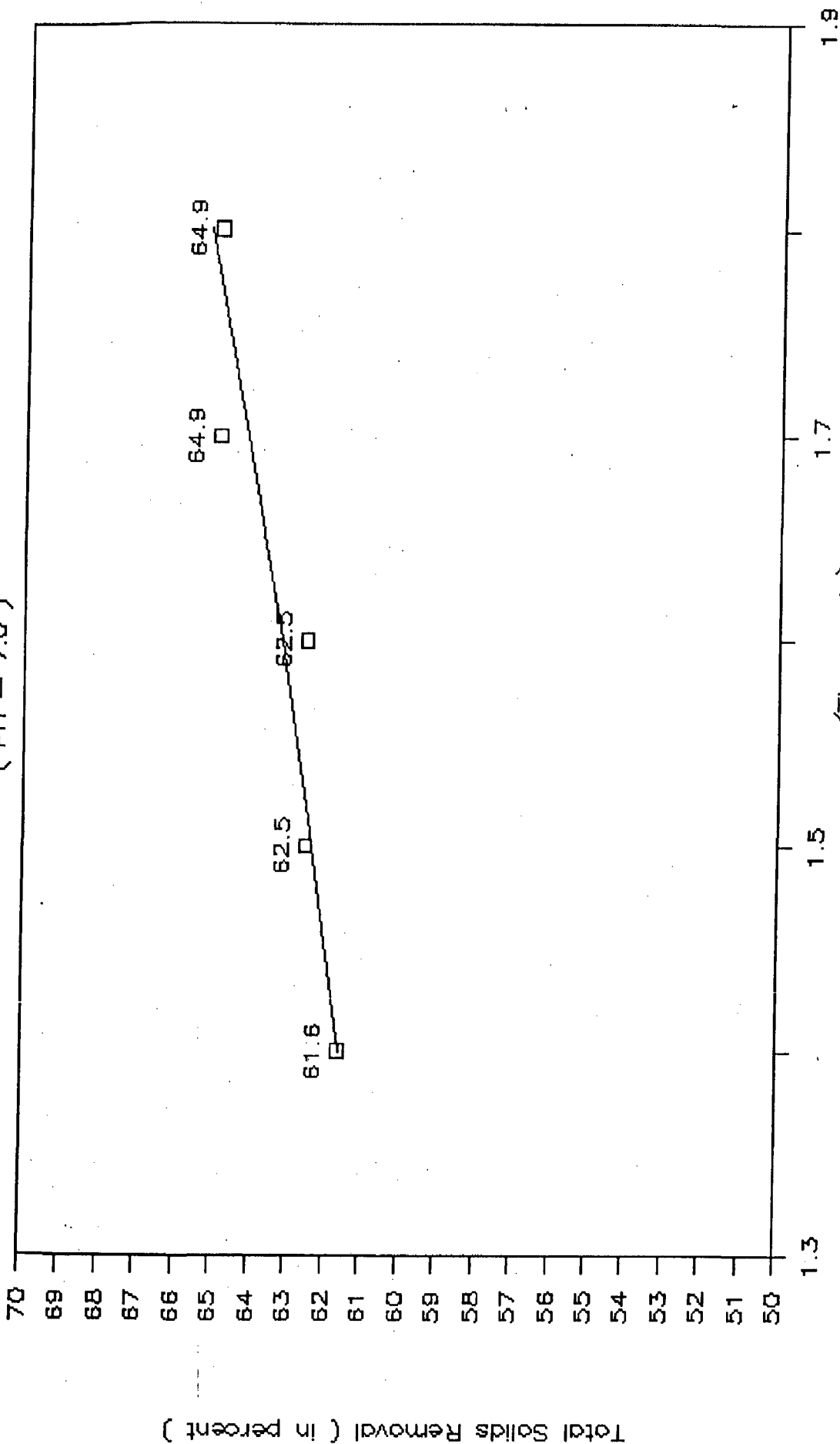
optimum alum dose (mg/l)
(Thousands)
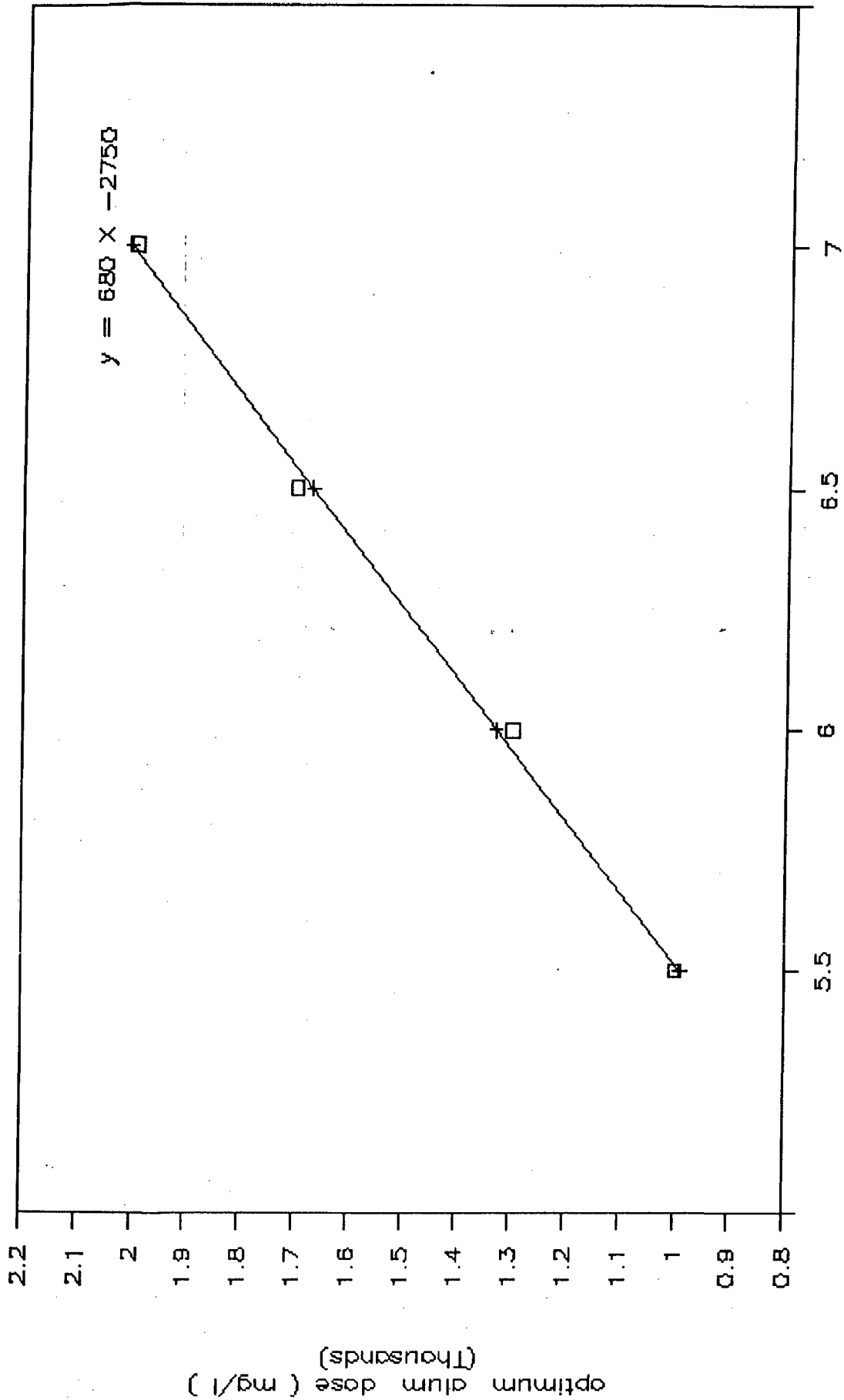
pH value

Fig. 5.3.13

ALUM COAGULATION
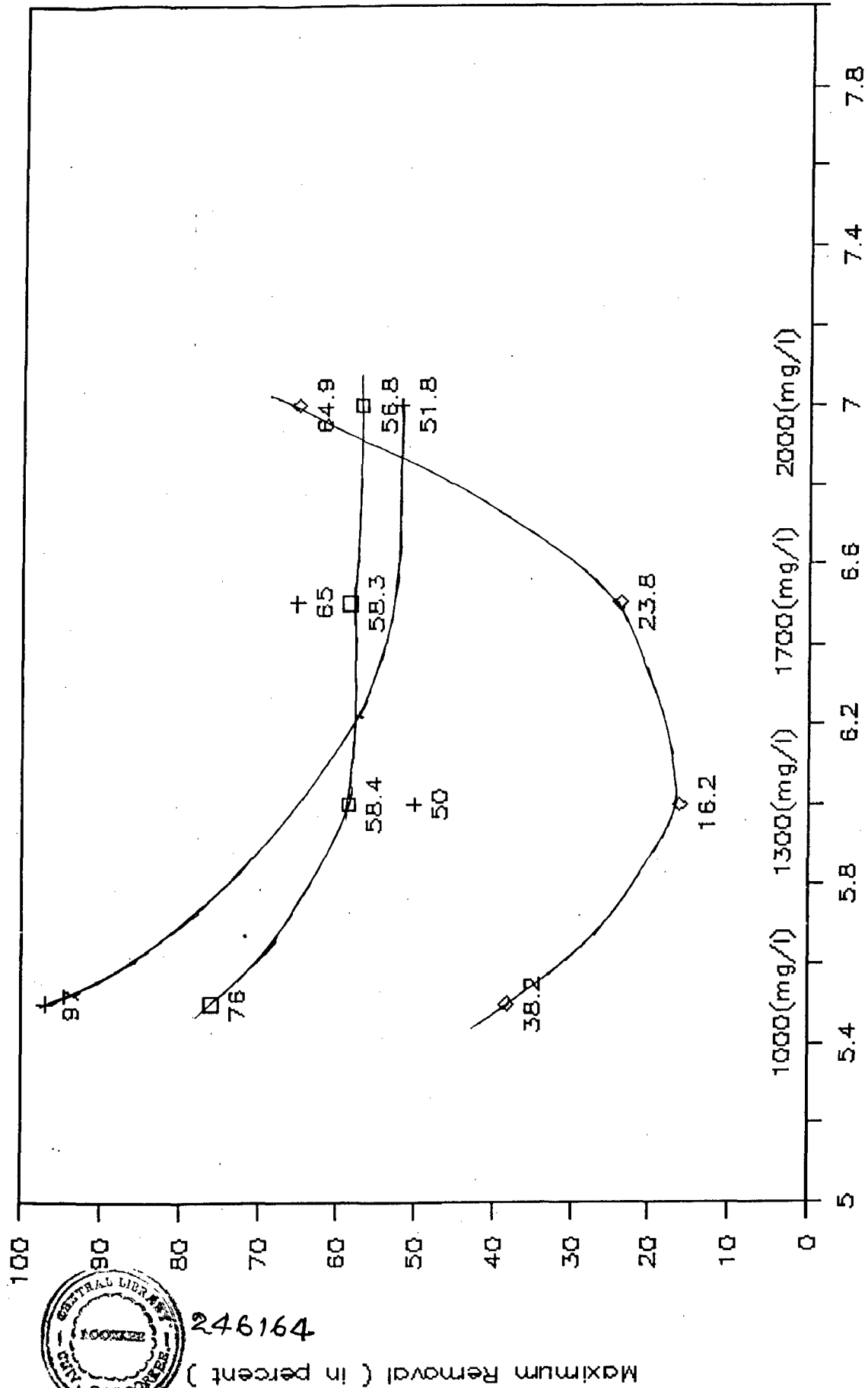
Maximum Removal (in percent)

PH Value/Optimum Alum Dose

□ COD Removal   ◇   % T.S. Removal

+   % Color Removal

Fig. 5.3.14

Further analysis was made to study the removal efficiency of various parameters at optimum alum doses at the various initial pH of the black liquor (Fig.5.3.14).

It is evident from Fig.5.3.14 that the maximum COD removal was obtained at pH of 5.5 and OAD of 1000 mg/litre, which reduces to 56.8% at pH of 7.0 and OAD of 2000 mg/litre.

The colour removal also followed similar trend giving a maximum colour removal at a pH of 5.5 and OAD of 1000 mg/litre, which reduces to 51.8% at pH 7.0 and OAD of 2000 mg/litre.

However the total solids removal observed followed a different trend. Initially at pH 5.5 and OAD of 1000 mg/litre it was 38.2% which reduces to 16.2% at pH 6.0 and OAD of 1300 mg/litre. It then increases to 64.9% total solids removal at pH of 7.0 and OAD of 2000 mg/litre. This can be attributed to the fact that at low pH Al^{+3} and SO_4^{-2} ions forms dissolved substances with the lignin , which are preciprated out at the neutral pH, giving more DS removal.

5.4 SLUDGE DRAINABILITY:

It can be observed from the bar chart (Fig.5.4.1), that sludge contains more amount of high specific gravity solids and is dense at pH 5.5 than that at pH 7.0, 50 ml of sludge at OAD drained through Bucchner funnel gives 30 ml, 26.5 ml, 25.0 ml and 22.5 ml of clear liquid in 2 hrs time. So drainability decreases with increase in optimum alum dose and increase in pH.

SLUDGE DRAINABILITY
(at optimum alum dose)

ml

PH value

Fig. 5.4.1

52
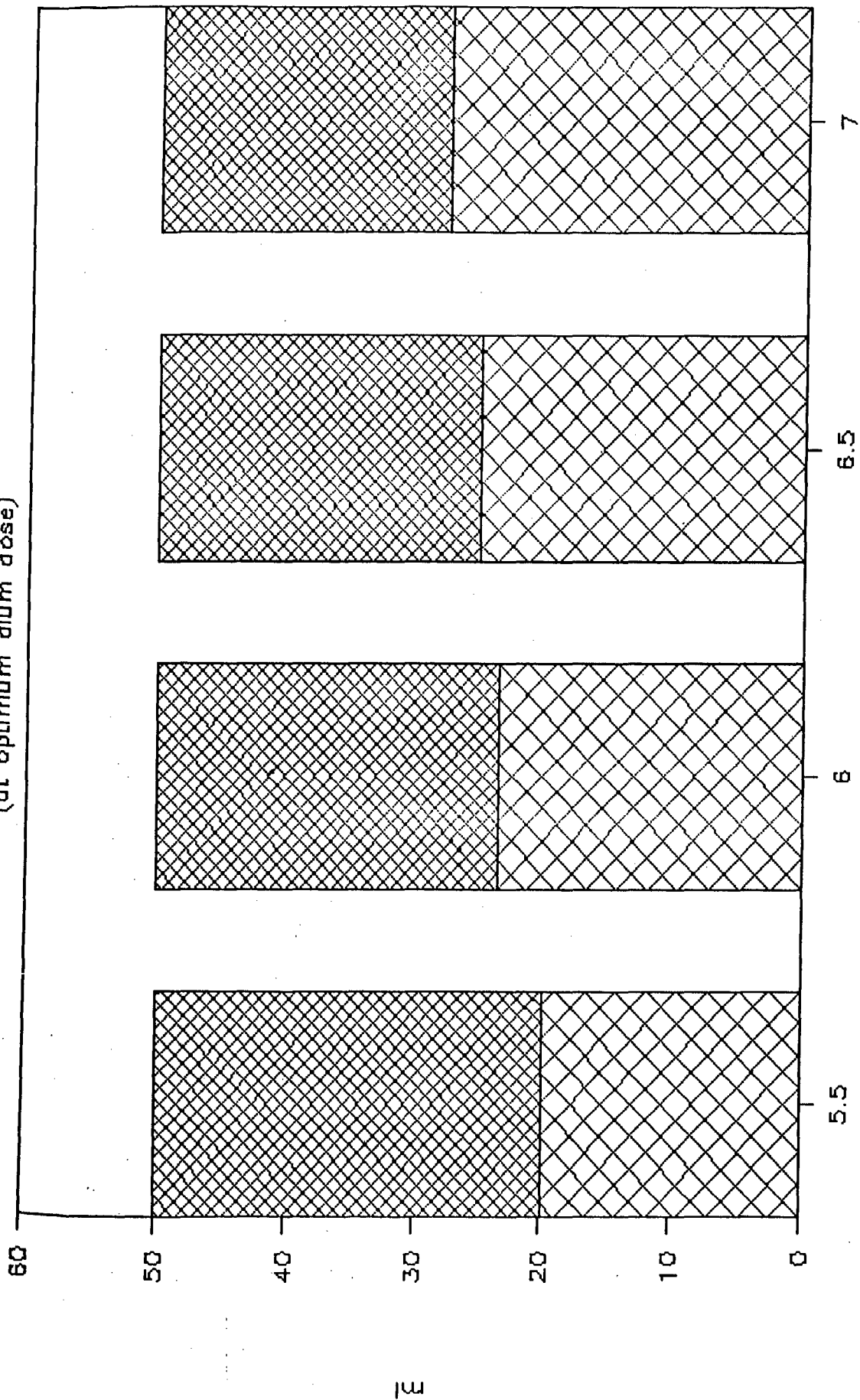
It may be that alum produces denser sludge at and around most effective pH, 5.5. So it is inferred that there is no significant advantage in using excessive dose of alum at pH 6.0, 6.5 or 7.0, where drainability is less.

5.5 COST ANALYSIS:

Cost analysis based on laboratory data for treatment of black liquor was also done, as discribed below.

5.5.1 For Acidification

The data collected from loaboratory experiments for acidification has been analysed for cost of H_2SO_4 required for a 30 TPD capacity small paper mills producing an average of 10 m^3 of black liquor per tonne of paper produced.

Cost of H_2SO_4 (98% pure) was taken to be Rs. 70.00 for 1 litre.

Cost of H_2SO_4 per 30 TPD to bring pH to 2.0,

$$= \frac{3.4}{1000} \text{ (ml/litre) x 70.00 (Rs/litre) x 10,000 x 30}$$

$$= \text{Rs } 71400$$

Also this cost reduces to Rs 67200, 48300, 37800, 33600 and Rs.31500 at pH of 2.5, 3.0, 3.5, 4.5, and 5.5 respectively. It is costly alternative although it gives higher colour and average COD and solids removal (Fig.5.5.1). Also acid handling requires more infrastructure to store large amount of acids and employ skilled labour.

So, although acidification is a lab scale treatment its

ACIDIFICATION
(Cost Analysis)

Fig. 5.5.1

Maximum Removal (in percent)

Cost of Sulphuric acid / 30 TPD
(Thousands)

□ COD   + COLOUR   ◇ T.S.
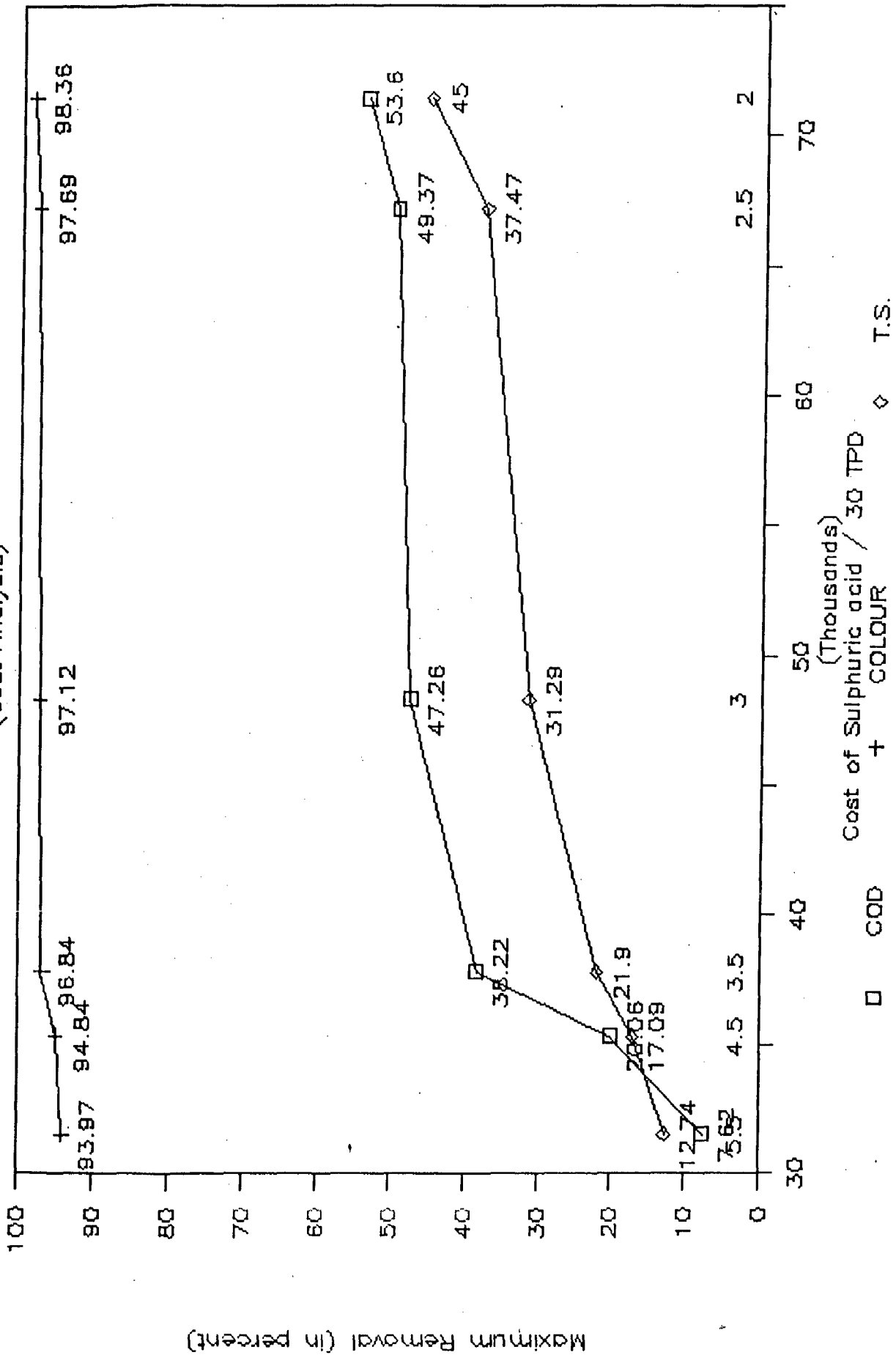
application in field is not recommended.

5.5.2 For Alum Coagulation

Rate of alum = Rs. 4.00 per kg

So cost of alum at pH 5.5 required for 30,0000 litres Black

liquor = 4 x $\dfrac{1000}{1000 \times 1000}$ x 3,00,000

= Rs.1200.00 (at 1991 cost).

Similarly it works out to be 1560, 2040 and 2400 Rs.   at pH 6.0, 6.5 and 7.0 respectively.

The figure (5.5.2) clearly gives the trend. So it can be inferred from it that alum coagulation after naturally bringing down the pH of black liquor after detention of few days and then using alum coagulation can be a very effective solution to black liquor treatment from small paper mills, wherein the black liquor COD, colour and T.S. can be brought down before mixing with the rest of the waste waters for further aerobic treatment.

ALUM COAGULATION

(Cost Analysis)

Fig. 5.5.2

□ COD   + Colour   ◇ T.S.

Cost of Alum / 30 TPD
(Thousands)

Maximum Removal (in percent)
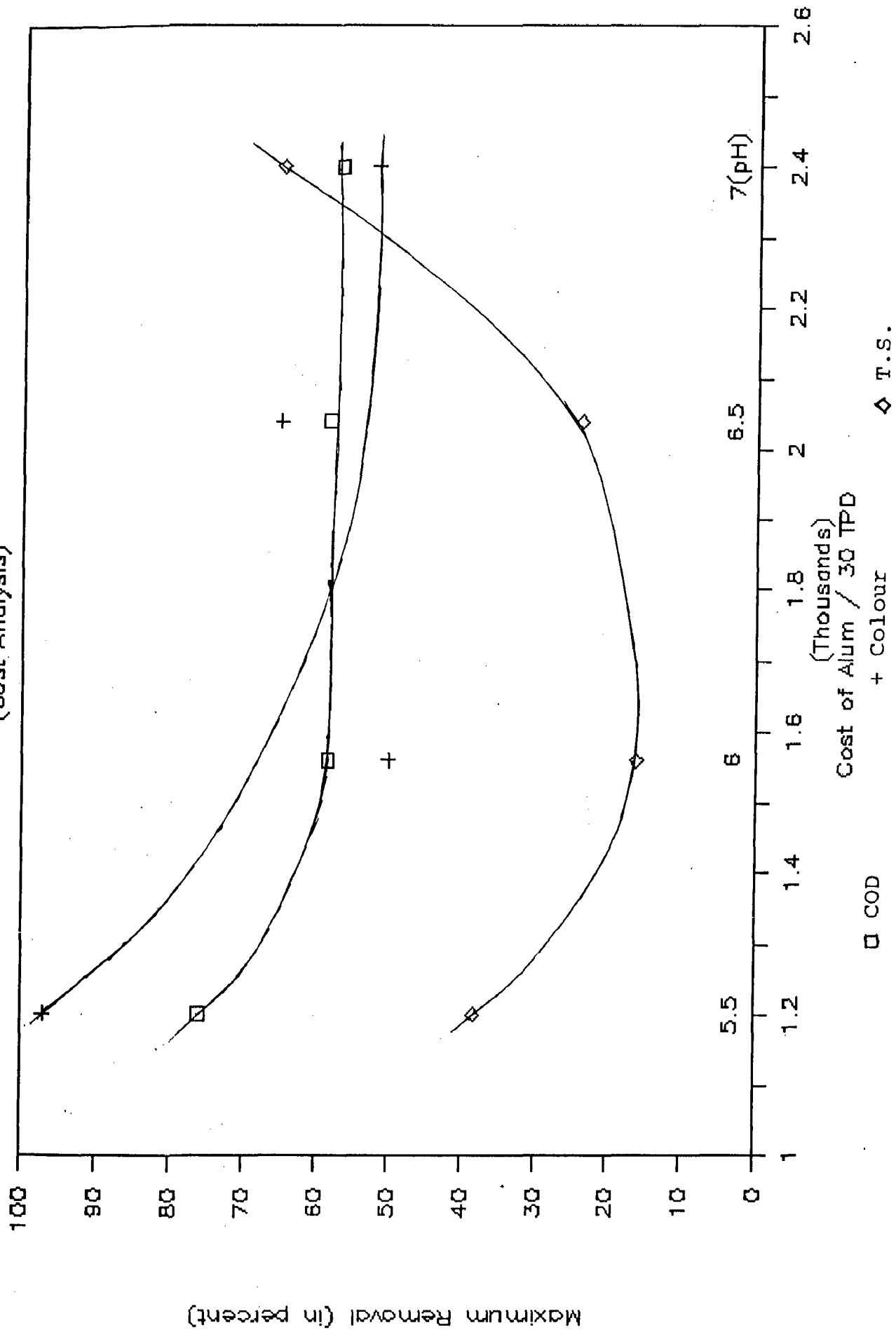
CHAPTER - 6

CONCLUSION

6.1 GENERAL

The results from acidification and alum coagulation studies on Black Liquor are the following.

** Use of sulphuric acid to precipitate black liquor at low pH gives very high colour removal (90%-99%) COD removal (40% -55%) and T.S. removal (40%-50%).

** The percentage removal of the pollution parameters colour, COD and TS is a pH dependent phenomenon Lower the pH of the effluent higher the efficiency of the removal of these parameters.

** Optimum Alum doses for the various pH of black liquor is X and also pH dependent. The OAD increases with increase in pH from 1000 to 2000 mg/litre as the pH is raised from 5.5-7.0 .

** The % removal efficiencies of COD, colour is a function of pH. At lower pH of 5.5 it is maximum, which reduces with increase in pH and OAD.

** The sludge drainability studies show that of a pH of 5.5 & OAD of 1000 mg/lit. the sludge can be drained earlier.

** The OAD of 1000 mg/l & pH of 5.5 is the best treatment for black liquor to achieve high COD and color removal, the cost being 1200.00 for a 30 TPD, small paper mill or Rs.40.00 per tonne of paper produced per day.

6.2 SUGGESTIONS FOR FURTHER RESEARCH

* Pilot plant studies for the alum coagulation of Black Liquor be conducted before recommending full scale use.

* To economise on the cost of acid, studies may be conducted to arrive at the proper D.T. in Lagoons/storage tanks where the pH of the waste can be brought down to a pH of 5.5 by natural treatment.

* Other coagulants or coagulant acids be studied for physico –chemical treatment of the Black Liquor.

#

REFERENCES

*Bauman H.D. and Luts H.R. (1974), 'Ozonation of a kraft mill effluent', TAPPI 57, 5, p.119.

Black A.P. and Th mpson (1975), 'Plant scale studies of magnesium carbonate process; EPA-660/75-006.

Black A.P. and William D.G. (1961), 'Electrophoretic studies of coagulation for removal of organic colour', Jr. A.W.W.A., 53(5), pp. 589-604.

*Bolto B.A. et al. (1979), 'Continuous process for decolourizing hardwood caustic bleach effluent using a magnetic weakly basic ion exchange resin', Appita 32, 5, 37 March 1979.

*Carpenter et al., (1980), 'Laboratory investigation of effectiveness of two colour production methods', NCASI Tech. Bul. No. 340.

Comprehensive industry document on Small Pulp & Paper Industry, Central Board for the prevention and control of water pollution, New Delhi - 1986.

Copeland, C.G., (1964), 'Water Re-use and Black liquor oxidation by container - copeland process', Proceed of 19th Ind. Waste Conf. Purdue Univ., pp. 391.

Dove, G.W. (1982), 'Pulp and paper industry waste water management', literature review JWPCF 52(6), June, pp. 1386-1415.

*Duggal H.S., Swanson J.W., Dickey, E.E., Buchman M.A. (1975), 'Effect of lime treatment on molecular weight distribution of colour bodies from kraft linear board decker effluents', TAPPI V.58n, 7,July, pp. 132-135.

* Frement Henry A., David J., Kelper Myles (1980), 'Colour removal from kraft mill effluents by ultrafiltration', Environ. Pot. Tech. Ser. EPA 2-80-D-45 Feb. p. 245.

Furgason R.R., Hardening H.L., Langeland A.W., Smith M.A. (1974), 'Ozone treatment of Kraft mill effluents - General Characteristics', A.I.Ch.E. Sym. Series no. 139, (V70), 1974.

GanczarCzyk J. (1972)', Fate of lignin in Activated Sludge treatment of Kraft mill effluents', Proced of 27th Indust. waste. Conf. Purdue. Univ., pp. 256-269.

Goos G. et al. (1974), 'Optimizing organic carbon and colour removal from board mill effluents', A.I.Ch.E., Sym. Series 144 (70), p. 213.

Herschimiller D.W. and Branion R.M. (1974), 'Ion floation for colour removal from Kraft mill effluent', Proceed. of 28th Ind. Wastes, Conf. Purdue Univ. pp. 224-233.

Indian Standard, 'Guide for Treatment of effluents of pulp, paper and board industries, I S: 5061-1968.

Kawamura. S. (1967), 'Removal of Colour by alum coagulation part I & II', Water and Sewage works, Vol.114(8), pp. 282-285 and Vol. 114(9), pp. 324-327.

Keenan W. Jr. (1981), 'Crest book Forest industries treat mill effluent with a rapid filtration system', Paper trade J. 165. 63.

Lang E.W. (1981)', Alum coagulation treatment of Kraft in plant total mill effluent', Environ. Conf. Proc. Tech. Assoc. Pulp Paper Ind. (1981), New Orleans Apr. 27-29, 1981.
Manual of Water Supply and Treatment - 1977.
Manual on Sewerage and Sewage Treatment - 1980.

* Nagai T. and Suzki, N. (1979), 'Radiation Induced degradation of lignin in aqueous solution', International Jourl. Appl, Radiation and Isotopes 29, 4/5, 255 (1978),
Ser. Water Research Abs. 12, 1, W79-00164.
Nebel. C. et al. (1973), 'Ozone decolourization of pulp and paper mill secondary effluent', Proceed. of 28th Ind. Waste. Conf. Purdue Univ., pp. 948-965.

Nelson, W.R. et al. (1968), 'A role for reverse osmosis in a neutral sulphite semi-chemical pulp and paper board mill', Proceed of 23rd Ind. Waste Conf. Purdue Univ. pp. 540-549.

Olthoff, M.G. and Eckenfelder, W.W. Jr. (1975), 'Colour removal from pulp and paper waste waters by coagulation', Water Research (9) pp. 853-856.

Oswalt J.L. (1970)', Massive lime combats colour of pulp and paper mill waste water', water and waste water engg., 7, (11), pp. F-12-F-13.

Pratias S. Pointe Claire, Wang A., Jones H.G. (1974), Amine treatment process for the decolourization of pulp mill effluent 1-laboratories studies, A.I.Ch.E.Sym.Ser.No.139 (V70), 1974, pp 11-12.

Roberts, K. Larry and Schoolfield John (1985), 'Removal of colour from Kraft pulp mill effluent', Proceed of 40th Ind. Waste Conf. Purdue Univ. pp. 305.

Saxena K.L., et al. (1979), 'Physico-Chemical and settling characteristics of wastewater from a waste paper and straw based paper mill', Indian J. Environ. HLTH, Vol.21(3), pp.205-219.

* Schmidt R.L., Joyce T.W. (1980), 'Enzymatic pretreatment to enhance the lime precipitability of pulp mill effluents', TAPPI Paper maker Conf. Proc. Atlantic, Ga Ap.14-16-1980, Published by TAPPI Atlanta Ga 1980, pp. 169-173.

* Shameshima, K. et al. (1973), 'Colour of pulp industry waste liquors interaction of chloroxylignin with metal salts', Abstract. bulletin inst. of Paper Chem. 44, p. 4020.

Shrinivasan Iyer, M.V. (ME Thesis 1983, U.O.R.), 'Removal of colour from pulp and paper mills waste by magnesium-salt.

Smith E.S. and Christman R.F. (1969), 'Coagulation of pulping waste for removal of colour', JWPCF 41-2-part 1, pp. 222-232.

Spruil, E.L. (1970), 'Colour removal from paper mill waste', Proceed of the 25th Ind. Waste Conf. Pardue Univ. pp. 761-765.

* Spruil Edgor L. (1973), 'Colour and sludge recovery from the mill effluent', TAPPI V65n. Apr. pp. 98-100.

Standard Method for examination of water and waste water 16th Edition, 1985.

Subrahmanyam, P.V.R. (1976), 'Colour in pulp mill wastes and its removal' I.A.W.P.C. convention, Vol.III, pp.16.

The Illustrated Weekly of India (1991), March 9-10, pp. 34-37.

Thirumurthi G., McKenna and Brown H.G. (1969)', BODD and colour removal from kraft mill wastes', water and sewage works 116 (12) p. 491-494.

* Vincent D.L. (1974), 'Colour removal from biologically treated pulp and paper mill effluent', Canadian pollution abatement, Research project No.210, Forestry Service Environ. Canada.

Water Quality andd Treatment (1971), 'A handbook of Public Water Supplies, prepared by AWWA Inc.

Weber W.J., "Physico Chemical Process for Water quality control-wiley interscience", New York (1971).

Woodard, F.E. and Etzal, J.E. (1967), 'Coacervation and Chemical Coagulation of Lignin from Pulp mill Black liquor' JWPCF, 36, pp. 990.

Woodard F.E., Sproul O.J. and Atkins P.F. (1974), 'The biological degradation of lignin from pulp mill black liquor', JWPCF 36(12), pp. 1401-1410.

---

* Reference not referred in original.

TABLE NO. 5.2

ACID PRECIPITATION STUDIES ON BLACK LIQUOR

Initial pH - 11.36
Initial COD - 9232 mg/l
Initial Colour - 52,800 (Co-pt units)
Initial Total Solids - 17465 mg/l
Initial Suspended Solids - 2105 mg/l
Initial Dissolved Solids - 15,360 mg/l

Sl. No.	pH	H_2SO_4 (Pure) Required (mg/l)	COD (mg/l)	Removal Efficiency (in percent)	Colour (Co-pt) Scale	Removal Efficiency (in percent)	Total Solids (mg/l)	Removal Efficiency (in Percent)	Dissolved Solids (mg/l)	Removal Efficiency cy(in %)	Suspended solids (mg/l)
1.	2.0	3.4	4312	53.6	864	98.36	9600	45.03	7380	51.9	2220
2.	2.5	3.2	4704	49.37	1220	97.69	10920	37.47	7660	50.1	3260
3.	3.0	2.3	4900	47.26	1520	97.12	12000	31.29	9380	38.9	2620
4.	3.5	1.8	5740	38.24	1664	96.82	13640	21.90	10780	29.8	2860
5.	4.5	1.6	7428	20.06	2720	94.84	14480	17.09	11300	26.4	3180
6.	5.5	1.5	8584	7.62	3180	93.97	15240	12.74	10800	29.6	4440

ALUM COAGULATION STUDIES ON BLACK LIQUOR AT pH 5.5

TABLE 5.3a

Initial pH - 11.36   Initial colour - 52800 mg/.

Initial COD - 9232 mg/1   Initial T.S. - 17465 mg/.

Sl. No.	Alum dose (mg/1)	COD mg/1	% removal	Colour (Co-pt units)	% removal	T.S. mg/1	% removal
1	700	5170	44.0	2270	95.7	16521	5.4
2	800	2954	68.0	2376	95.5	16102	7.8
3	900	2585	72.0	2587	95.1	14321	18.0
4	*1000	2216	76.0	1584	97.0	10793	38.2
5	1100	2216	76.0	2059	96.1	12627	27.7

TABLE 5.3b

AT pH 6.0

Sl. No.	Alum dose (mg/1)	COD mg/1	% removal	Colour (Co-pt units)	% removal	T.S. mg/1	% removal
1	1200	8447	8.5	33158	37.2	14897	14.7
2	1250	6140	33.5	33158	37.2	16155	7.5
3	*1300	3840	58.4	26400	50.0	14635	16.2
4	1350	5761	37.6	26400	50	14635	16.2
5	1400	4989	45.96	26400	50	14688	15.9

* Optimum Alum Dose (OAD)

TABLE 5.6c

At pH 6.5

Sl. No.	Alum dose (mg/l)	COD mg/l	% removal	Colour (Co-pt units)	% removal	T.S. mg/l	% removal
1	1400	4607	50.1	33158	37.2	14164	18.9
2	1500	4219	54.30	33158	37.2	14006	19.8
3	1600	4607	50.1	26400	50.0	13518	22.6
4	*1700	3850	58.3	18480	65.0	13308	23.8
5	1800	4016	56.5	26400	50	13360	23.5

TABLE 5.3d

At pH 7.0

1	1700	4718	48.9	36981	29.96	6706	61.6
2	1800	4348	52.9	36981	29.96	6549	62.5
3	1900	4348	52.9	36981	29.96	6549	62.5
4	*2000	3988	56.8	25449	51.8	6130	64.9
5	2100	4348	52.9	25449	51.8	6130	64.9

* Optimum Alum Dose (OAD)

APPENDIX-A

AVERAGE CHARACTERISTICS OF BLACK LIQUOR COLLECTED FROM A SMALL (10 TPD) CAPACITY BAGASSE BASED PULP AND PAPER MILLS

PARAMETERS	UNIT	VALUE
pH	-	11.36
Total Solids	mg/l	17465.0
Dissolved Solids	mg/l	15360.0
Suspended Solids	mg/l	2105.0
COD	mg/l	9292.0
BOD_5 day at 20°C	mg/l	4906.0
Colour	Co-pt	52800.0
Sodium	mg/l	325.0
Magnesium	mg/l	800.0
Calcium	mg/l	900.0
Total Nitrogen	mg/l	3.135
Phosphorous	mg/l	0.6

TENTATIVE PROCEDURE FOR COLOUR MEASUREMENT OF BLACK LIQUOR

(SPECTROPHOTOMETRIC METHOD).

INTRODUCTION

The colour of Black liquor waste is considered to be the colour of the light transmitted by the waste solution after removing the suspended material including the pseudocolloidal particles. It is recognised that the colour characteristics of some wastes are affected by light reflection from the suspended material in the waste. The term colour is used herein to mean 'true colour - that is, the colour of the water the turbidity of which has been removed.

PRINCIPLE

Colour is determined by spectrophotometric comparison of the sample with known concentration of coloured solutions. The platinum-cobalt colour is used as standard reference, the unit of colour being that produced by 1 mg/l to match the hue in special cases. Colour has to be measured at specific pH, as it is dependent on the pH of the solution.

APPARATUS

    (a) Spectrophotometer

    (b) pH meter for determining the sample pH

    (c) Filtration system, consisting of filtering flask, vacuum source, filter holder and 0.8 micron porosity membrane filter.

PREPARATION OF STANDARDS

Dissolve 1.2 gm pottassium chloroplatinate (K_2PtCl_6) equivalent to 0.5g metallic platinum and 1 gm crystallized cobaltous chloride ($COCl_26H_2O$) equivalent to about 0.25 gm metallic cobalt in distilled water with 100 ml concentrated HCl and dilute to one litre with distilled water. This stock standard has a colour of 500 units.

If the potasium chloropolatinate is not available dissolve 0.5 gm pure metallic platinum in acqua regia with the aid of heat, remove nitric acid by repeated evaporation with portions of concentrated HCl. Dissolve this product together with 1 gm crystallised cobaltous chloride as directed above.

Prepare standards having colours of 25, 50, 100, 150, 200 and 250 by diluting 2.5, 5.0, 10.0, 15.0, 20.0 and 25.0 ml stock colour standard with distilled water to 50 ml in stoppered volumetric flasks. Protect these standards against evaporation and contamination when not in use.

Transfer a suitable portion of each final solution to a 10 mm absorption cell from a 'matched set' of cells and measure the absorbance of these solutions with different colours in a spectrophotometer at 465 nm wave length. As reference, use distilled water for instrument calibration to zero absorbance.

Construct a calibration curve by plotting absorbance values against colour units similar to the one shown in Fig. B-1.

PROCEDURE

Preparation of sample: Select a 200 ml sample of waste water, adjust the pH to 7.6 with HCl or NaOH. If the colour of the sample is to be measured in the existing pH, adjustment of pH is not required. While adjusting the pH, if the overall volume change in volume is greater than one percent, discard the sample and make use of a new sample with stronger solutions of HCl or NaOH. In any event, the volume change in the final sample should not be more than one percent lest the colour will change due to dilution.

Take a 50 ml of liquor of the pH adjusted sample and filter through a 0.8 micron membrane filter prerinsed with distilled water. If membrane filter is not available. Whatman No.1 filter can be used satisfactorily. Prerinsing the filters before use with distilled water is essential in order to prevent any change in pH resulting from use of 'acid washed filters'. Transfer an appropriate portion of the filtered sample to a 10 mm absorption cell and measure its absorption of 465 nm wave length using distilled water for the blank. Read the corresponding colour units for that absorbance on the calibration curve. If the sample is having more than 500 colour units dilute it to less than 500 units and measure the absorbance. Convert the colour of the diluted sample to that of the original sample by considering the dilution ratio.
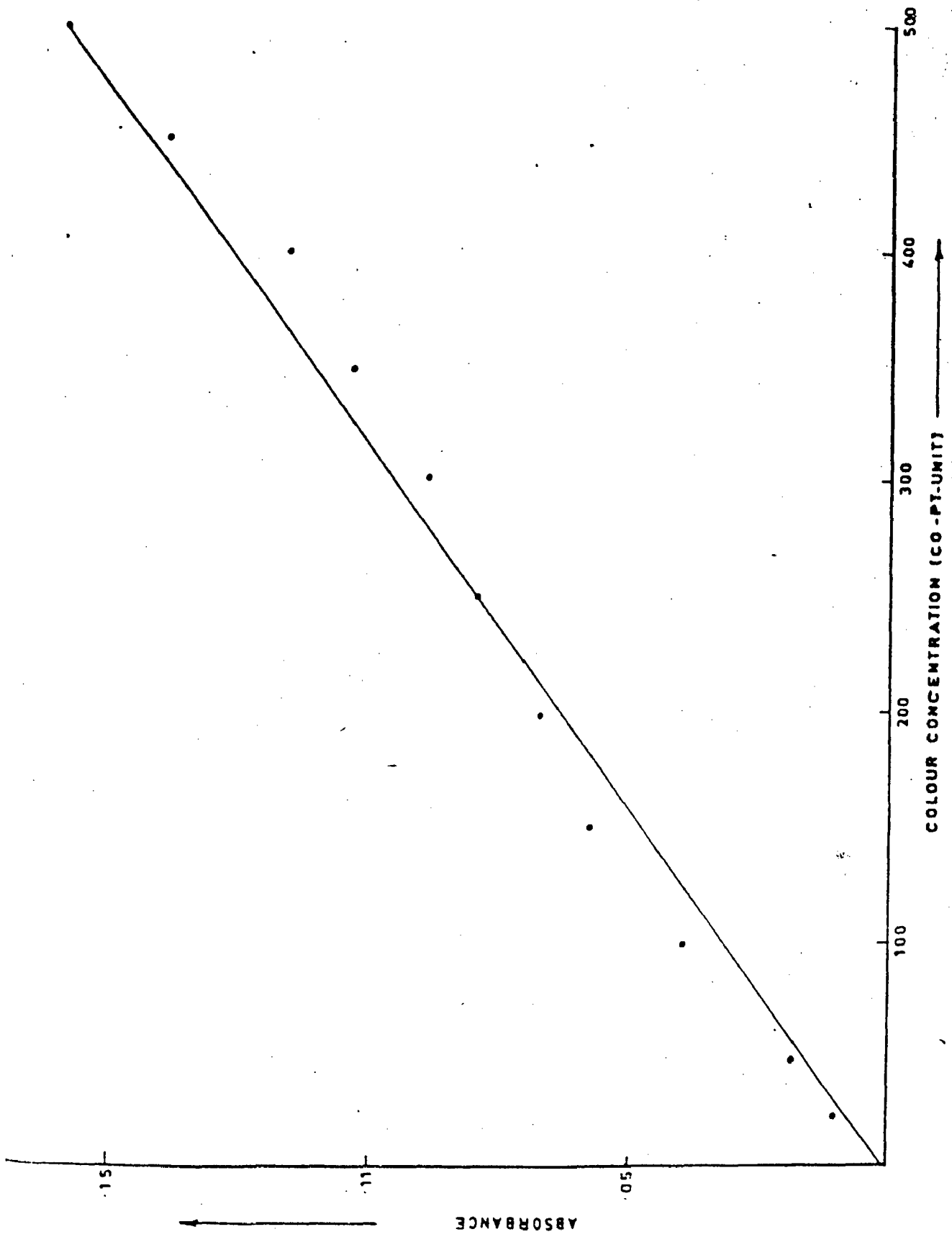
FIG. B-1 COLOUR CALIBRATION CURVE $\lambda=465$

APPENDIX - C

TOLERANCE LIMITS FOR INDUSTRIAL EFFLUENTS DISCHARGED

INTO INLAND SURFACE WATERS

Sl. No.	Characteristics	Tolerance limit (Sec 0.5)
i)	Total suspended solids mg/l Max	100
ii)	Particle size of total suspended solids	Shall pass 850-micron IS sieve (see IS 460-1962)
iii)	pH	5.5 to 9.0
iv)	Temperature	Shall not exceed 40°C in any section if the stream within 15 metres downstream from the effluent out let.
v)	Biochemical oxygen demand for 5 days at 20 °C, mg/l, max.	30
vi)	Oils and grease, mg/l, Max	10
vii)	Phenolic compounds, mg/l, Max	1.0
viii)	Cyanides (as CN), mg/l, Max	0.2
ix)	Sulphides (as S), mg/l, Max	2.0
x)	Radioactive material:	
	(a) Alpha emitters, uC/ml Max	10^{-7}
	(b) Beta emitters, uC/ml Max	10^{-8}
xi)	Insecticides	Absent
xii)	Total residual chlorine, mg/l	1
xiii)	Flourides (as F), mg/l Max	2.0
xiv)	Arsenic (as As), mg/l Max	0.2

Sl. No.	Characteristics	Tolerance limit (Sec 0.5)
xv)	Cadmium (as Cd), mg/l Max	2.0
xvi)	Hexavalent chromium (as Cr) mg/l, Max	0.1
xvii)	Copper (as Cu), mg/l, Max	3.0
xviii)	Lead (as Pb), mg/l, Max	0.1
xix)	Mercury (as Hg), mg/l Max	0.01
xx)	Nickel (as Ni), mg/l Max	3.0
xxi)	Selenium (as Se), mg/l, Max	0.05
xxii)	Zinc (as Zn), mg/l Max	5.0
xxiii)	Ammonical Nitrogen, mg/l, Max	50
xxiv)	Chemical oxygen demand, mg/l, Max	250

NOTE (0.7) Tolerance limit for colour and odour have not been prescribed in this standard but it is recommended that as far as practicable, colour and unpleasant odours should not be present in the industrial effluents.