PART-II

PART -II A

REMOVAL OF COLOUR AND ORGANICS FROM EFFLUENTS

(EFFLUENT OF DYES AND DYES-INTERMEDIATES INDUSTRIES)

1. GENERAL

Colour has attracted human society from time immemorial. Ancient people were deriving colouring matters from animal and vegitable sources. The tradition continued for many centuries. It was the revolutionary contribution of British chemist W.H.Perking in synthetic dyes which changed the scenerio in 1857. It provided impetus for further research in synthetic dyes and within no time chemists synthesized hundreds of dyes which found their way in the dyeing and printing industries.

Thousands of dyes are listed in colour index and more than thousand intermediates for the dyes are known. Majority of the dyes are water soluble, however pigments are coloured compounds insoluble in water.

Dyes are numerous and they are classified based on their application [95].

Dyes are classified as under based on their application :

1. Acid dyes
2. Basic dyes
3. Direct dyes
4. Azoic dyes
5. Disperse dyes.
6. Fibre reactive dyes
7. Fluorescent brightening agent
8. Food, drug, cosmatic colours
9. Mordant dyes
10. Solvent dyes
11. Sulfur dyes
12. Vat dyes.

Currently dyes are produced in 26 countries of which only five are major producers. These five countries (W.Germany, US, UK, Switzerland and Japan) have together accounted for more than half of the world's dye production each year since 1975 [96].

It has been estimated that there are about 3000 dyes in use world-wide and that world production of dyes is about 8,00,000 t/annum. Most of these products end up on the finished fabrics but Anliker estimated that, of the 3,60,000 't' used in the textile industry, 10-20% was lost in the residual liquor. For all dye using industries, about 47,000 't' was lost to the environment even after allowing for 50% removal by effluent treatment [97,98].

Colour in water may result from the presence of natural metallic ions (Fe^{+3}, Mn^{+2}) , humus and peat materials, plankton, weeds and synthetic colours.

Colour substances (dyes) can be discharged to the environment from three major sources.

1. From Dyes and dyes-intermediate manufacturers.
2. From dye users, i.e. industrial applications.
3. From diffused or household discharge as a result of leaching of dye from manufactured products.

Based on the list of priority pollutants, industrial waste waters generated in dyestuff and dye-intermediates manufacturing, may contain compounds which are toxic to micro-organisms, compounds which inhibit biological activity or compounds which are refractory to biological treatment.

Colour imparts visible pollution, persists for long distance in flowing waters, decrease recreational capacity of streams, retard photosynthetic activity and such colour compounds may be toxic, inhibitory or refractory to biological activity - thus biological processes and productivity systems are upsetting the water body [99].

Waste waters generated from dyestuff and dyes-intermediates industries are strongly coloured having varied hue, either acidic or alkaline, have high dissolved solids, chlorides, sulfate and high concentration of organics with a high COD but considerably less BOD. In addition to this, various heavy metals such as Fe, Hg, Cr, Pb, Cu and Zn also appear in such waste waters.

In the treatment of dyestuff effluent, colour is the main culprit. Removal of BOD, COD and SS etc. sometimes do not pose a problem as serious as posed by removal of colour. High TDS, (Sulfate, Chlorides),can not be reduced by economical methods and such pollutant may not pose much problem if adequate dilution is available at the receiving body. But we must emphasise on removal of COD i.e. organics which are coloured, toxic, inhibitory or refractory in nature.

The processes that are currently available in the treatment of dyes waste water, respond differently for different types of waste products. Thus, dyes are so varied in their structure that complete treatment of the waste water is not feasible by any one single method.

Following types of treatment processes are well known for dyewastes.

1. Coagulation-flocculation, sedimentation [100-102].
2. Precipitation, filtration [103, 104A].
3. Evaporation [104 B]
4. Adsorption (activated carbon/synthetic resins)[105 - 107].
5. Chlorination [108 - 110].
6. Ozonation [110 - 113].
7. Biological processes including

   Biophysical (Powdered AC/biological i.e. PACT)[114-118].

Biological treatability was examined at several concentrations without seed, with domestic sewage and with acclimated seed, wastes generally were compatible with the biological processes but colour reduction was incomplete. No single method was effective for both colour and TOC removal. Disperse, vat and sulfur dyes were most effectively removed by coagulation and activated carbon was most effective for decolorizing reactive, basic, acid and azoic dyes [119].

Direct, reactive, acid and disperse dyes decolorize by reacting it with ozone or chlorine. The reactive and acid dyes react readily and decolorize completely, but some times metabolites formed in such treatments are likely to be more noxious compound than the parent dyes. It reduces colour completely but may not reduce complete COD.

Porter et al. (1972) stated that the dyes themselves are not biodegradable, since the same technology which imparts colour fastness and resistance to temperature, light, oxygen, hydrolysis ozone and nitric oxides, makes most dyes resistant to conventional primary and secondary waste treatment system. Thus dyewastes needs some form of pretreatment to render the dyes biodegradable.

More stringent standards of the effluent quality has compelled a number of industries to investigate a variety of treatment technologies that are capable of removing priority pollutants from their waste waters. One such industry is the dyestuff manufacturing units.

The production of dyes in India has been 1150 tonnes, in 1960, 13550 tonnes in 1970 and 30850 tonnes in 1980 [120], out of this 30850 t, 35 to 40% of it is produced in Gujarat. More than 95% of all dyes consumed in the country are now produced indigenously by organized sector and small scale units [121]. Thus it seems that the rapid development of dyestuff and its intermediate industries in India on small scale enterprises is mainly due to the excellent prospects for the market in the country as well as the brighter chances for the export. This is because many of these dyestuff and intermediates are not manufactured now in highly industrialized and developed countries due to problem of pollution, its impacts on environment and high cost of treatment. The total number of dyestuff manufacturing units in India (organised and small scale sectors) stood at 937 in 1984 as against 150 units in 1975. Export of reactive dyes was 925.1 MT in 1983-84 while import was 33 MT. Demand of dyestuff was 34950 MT in 1984-85 and demand proposed is 42190 MT for the year 1989-90 [98,122].

Export of H-acid increased from Rs. 3.6 crores in 1984-85 to Rs. 8.5 crores in 1986-87. USSR, USA and Netherlands were the major buyers [123].

It was found in the survey in Gujarat that small scale as well as large scale industries manufacturing, naphthalene based dyes-intermediates e.g. H-aicd, J-acid, K-acid etc., very important compounds used for the manufacture of a variety of dyes, were not able to treat their waste for the want of fund and proven technoeconomical method of treatment. It was also observed that such effluents carry high COD, colour, TDS, and low pH. Specially Ahmedabad, Jetpur and Surat area are mainly engaged in textile business. Jetpur area is having more than 1200 small scale units for dyeing and printing consuming large quantity of reactive dyes. All such industrial activity in Gujarat resulted high colour pollution in ground waters as well as surface waters at number of places. This is receiving more emphasis day by day due to citizens involvement with the environment quality.

Use of reactive dyes in dyeing cotton fabrics has gained popularity in recent years. Reactive dyes react with cotton, rayon and some nylons and produce goods of outstanding wash-resistance. Several reactive dyes are mutagenic in nature e.g. Lanasol Blue-3R, Lanasol Red-G, Lanasol yellow 4-G etc. [124].

Technological and environmental factors have combined to foster emphasis on development of new forms of old dyes i.e. forms such as liquid, low dusting, more concentrated powder or granular forms, in order to prevent dyes pollution.

Chemically dyes intermediates are naphthalene Sulphonic acids containing amino or amino and hydroxy groups. In the manufacture of these intermediates several unwanted isomers are also formed which being more soluble remain in the effluent along with a small amount of above intermediates. Sulfonic acid group imparts the substance, solubility and amino group being easily oxidisable gives the effluent shades of reddish brown to greenish brown colour. Naphthalene ring is a very stable ring difficult to destroy. Effluents of Dyes and intermediate industries are creating numerous problems in our country. Many such industries are small scale industry. They have limited resources for the modern treatment plants. In India there is scarcity of drinking water. Water pollution due to dyes and dyes intermediates make it coloured - the value of water for drinking is eliminated, aesthetically no body will like to drink polluted coloured water.

Number of different processes are used in the developed countries to treat coloured effluent of dyes industry. These processes are very expensive. They also consume lot of electricity supply. In the light of the problems of our country it was decided to attack this problem from different angle and with a view to find a process/treatment which should give us natural like water, without colours and pollutants in it.

2. GENERAL EXPERIMENTAL ASPECTS.

2.1 Sampling

Samples were collected from the source. Following Industries extended co-operation for the collection of effluent samples for the study.

Industry	**Product Manufactured**
M/S. Nandesari Rasayani Pvt. Ltd., Nandesari.	H - acid
M/S. Piramal Rasayan Limited, Ankleshwar.	H - acid Laurent acid Tobias acid J - acid, K - acid, Chicago acid Perry acid Gama acid
M/S. Apollo dyes, Baroda	Reactive Red H_8B
M/S. Baroda Dyestuff Industries, Nandesari	Reactive Golden yellow-HR.
M/S. Rainbow Industries, Baroda	Golden Yellow IGK

Samples were of various catagories. Mother liquor of H-acid, Grab samples were mixed to obtain composite sample and composite samples were collected. All the samples were filtered first to remove suspended matters to get uniform quality. No chemicals were used for the preservation but all the waste water samples were kept at low temperature as described in the standard methods [13].

2.2 Analysis

For analytical aspects only three parameters were considered, colour, COD and TDS. However, to correlate the results, few samples were analysed for TOC. Procedure for determination of Total Residue, Total volatile solids, Total suspended solids, COD, TC and TOC have already been discussed in the previous section.

2.2(a) Colour Measurements [13]

In the study of removal of colour from the waste water proper procedure for the determination of colour is of great significance. In case of industrial waste water measurement of "True colour" is of great concern compared to "Apparent colour" because Apparent colour is due to suspended matter and soluble substances while true colour is only due to soluble substances. In industrial waste water simply by filteration, colour due to insoluble matter can be removed but it is difficult to remove due to soluble matter.

Colour is determined by visual comparison of the sample with known concentration of coloured solution or with specially calibrated glass colour disks. Platinum Cobalt disk method is also a standard method.

The platinum-Cobalt method is useful for measuring colour of potable water and of water in which colour is due to naturally occuring materials. It is not applicable to coloured industrial waste waters as they have colour characteristics significantly different from the yellow Pt-Co standard. However in certain preliminary experiments Levibond Pt-Co Disc was used to determine colour. The colour value is pH dependent and therefore pH is mentioned while reporting colour value for comparison. In the present experiments colour values are determined, from the light transmission characteristic of filtered sample by means of spectronic-20 (B & L). This is nothing but measurement of visible spectra of effluent.

Preliminary observations for colour, by naked eye were also important for the effectiveness of treatment for colour removal.

Definite wave lengths (nm) covering wide range of spectrum (425 nm to 646 nm) were selected for the colour measurement.

As and when required accurate dilutions were made to bring solution within the range of instrument.

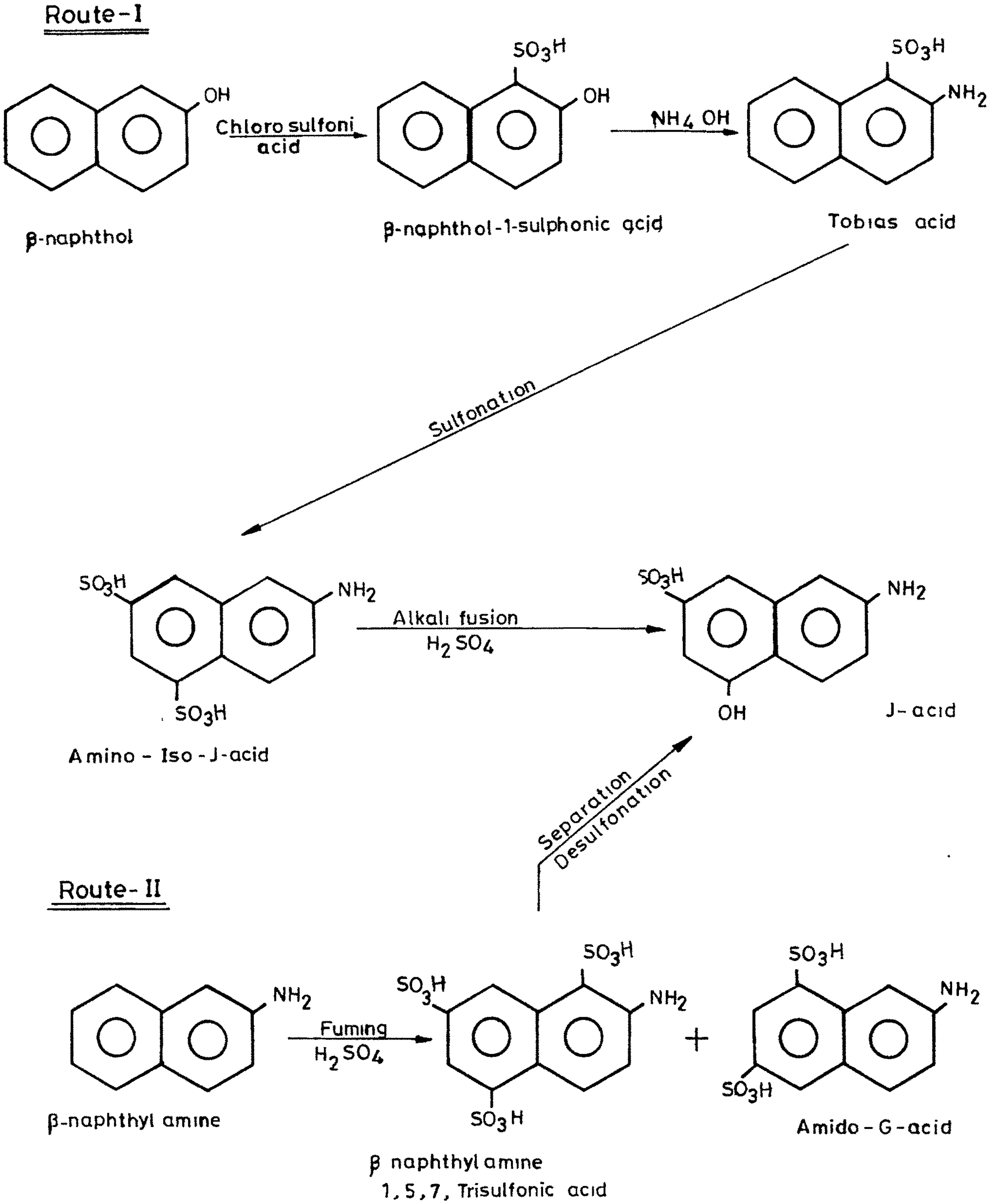
2.2(b) Procedure

Two 50 ml volumes of sample were prepared by maintaining the original pH of one aliquot and adjusting the second aliquot as required by the procedure to pH 7.6 with Sulfuric acid or Sodium hydroxide. Then filtered the samples to remove turbidity through glass fibre filter (pore size approximately 0.45 μ). Distilled water was used to set the transmittance at 100% and then transmittance was determined. This method was followed both for treated and untreated samples.

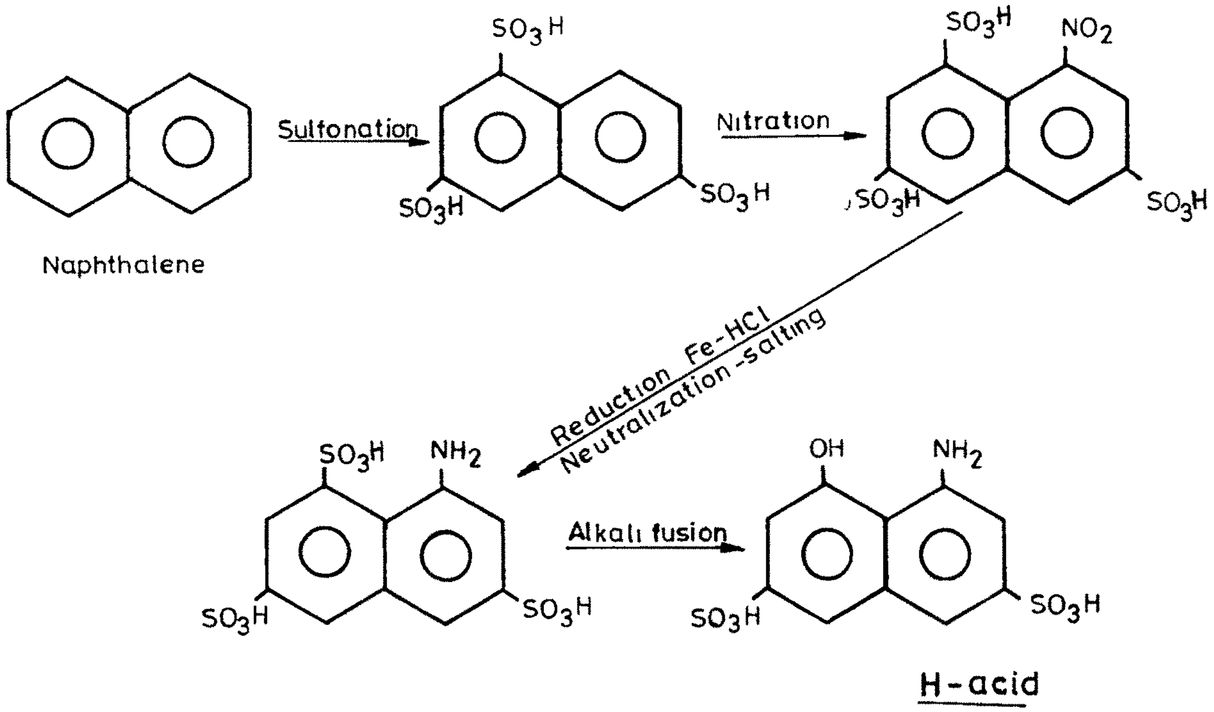
The synthetic steps involved in different dyes-intermediates are outlined in Figures 17 to 20.

This gives the idea regarding the presence of host of organics present in the composite sample of effluent collelcted from dyes-intermediate industry [125].

The synthetic steps involved in different dyes are outlined in Figures 21 to 24. The effluent reflects the presence of all these intermediates in different proportions. Colour Index number of dyes are also mentioned in respective figures [125].



J-acid Figure: 17


Naphthalene
Sulfonation
SO_3H
SO_3H
SO_3H
Nitration
SO_3H
NO_2
SO_3H
SO_3H
Reduction Fe-HCl
Neutralization-salting
SO_3H
NH_2
SO_3H
SO_3H
Alkali fusion
OH
NH_2
SO_3H
SO_3H
H-acid

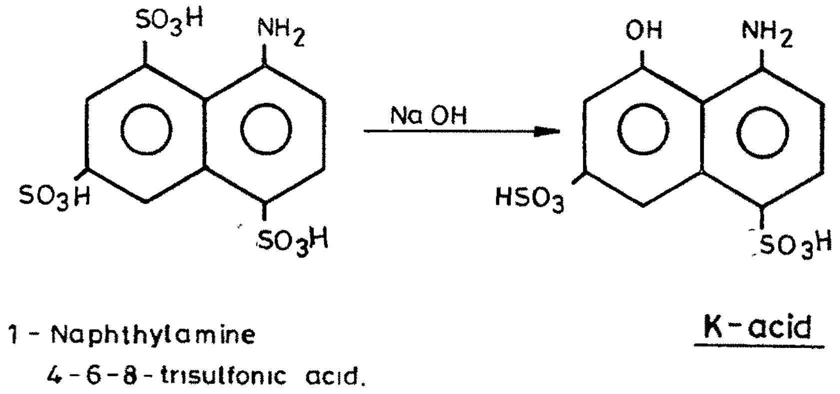
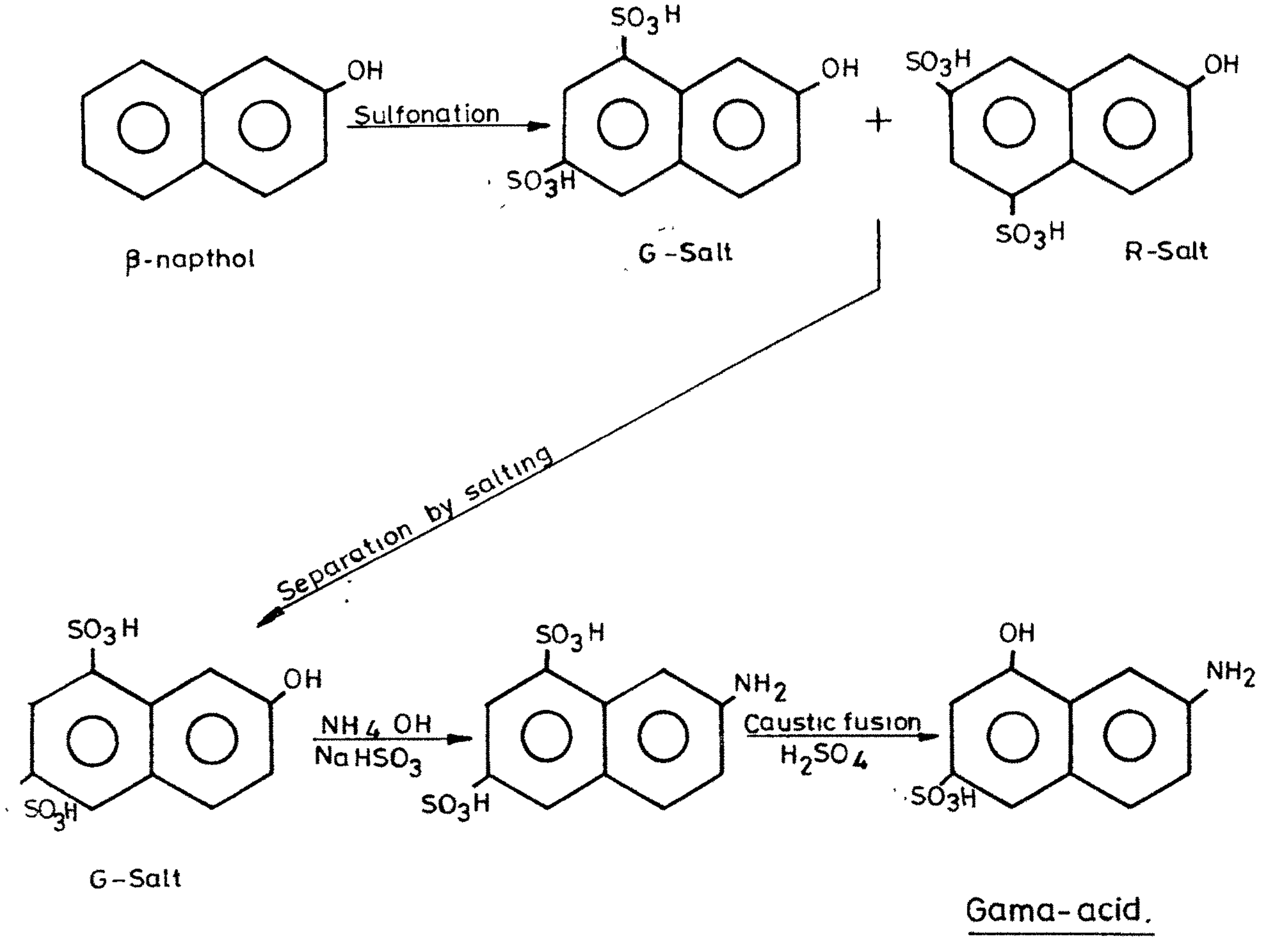
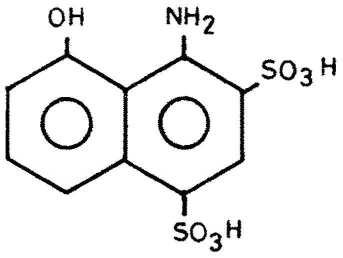

SO_3H
NH_2
SO_3H
SO_3H
Na OH
OH
NH_2
HSO_3
SO_3H
1 - Naphthylamine
4-6-8-trisulfonic acid.
K-acid

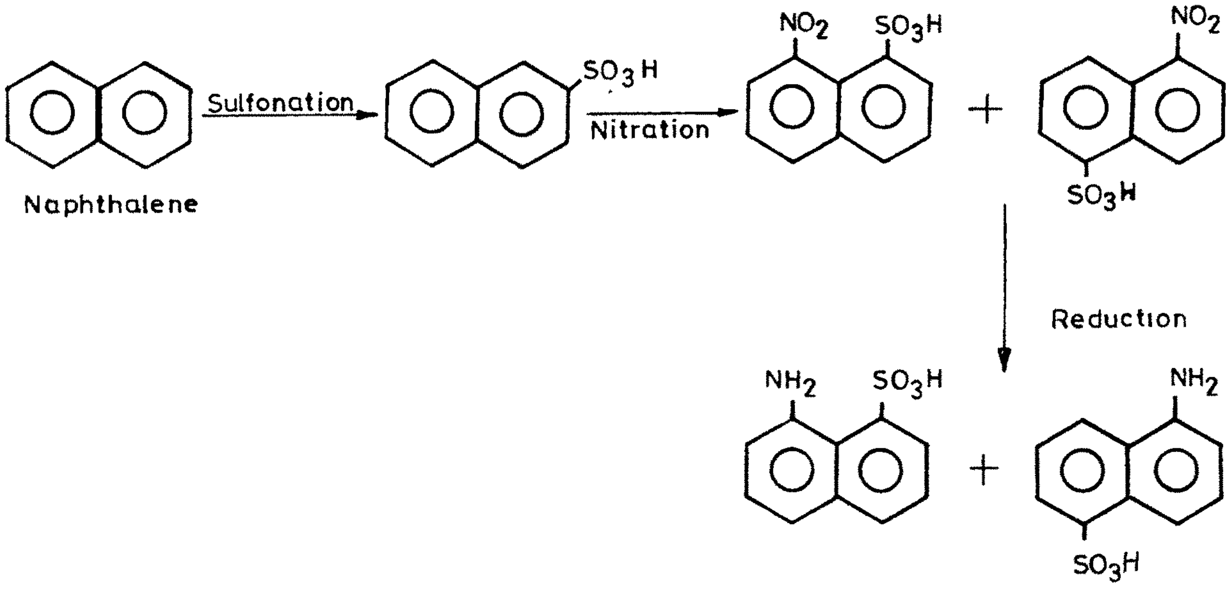
Figure: 18





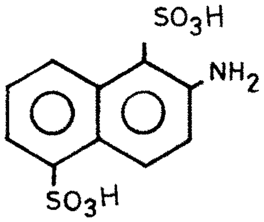
Chicago-acid

Figure : 19



Perry-acid

Laurent-acid



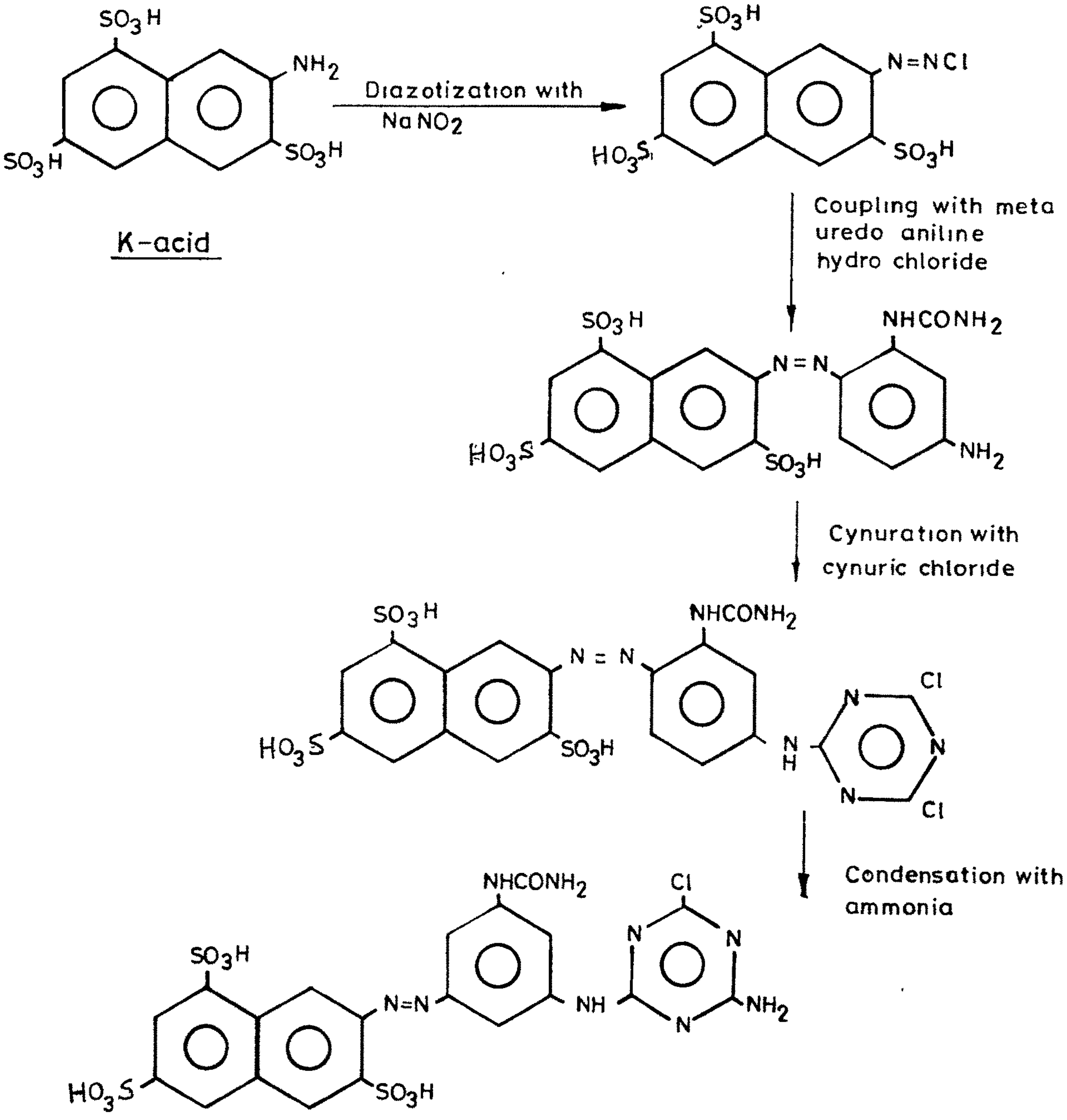
Sulfo tobias acid

Figure: 20

GOLDEN YELLOW HR

C.I.No. Reactive orange-12

REACTION STAGES



K-acid

Golden yellow HR.

Figure : 21

REACTIVE RED H_8B

C.I. No. Reactive red-31

REACTION STAGES

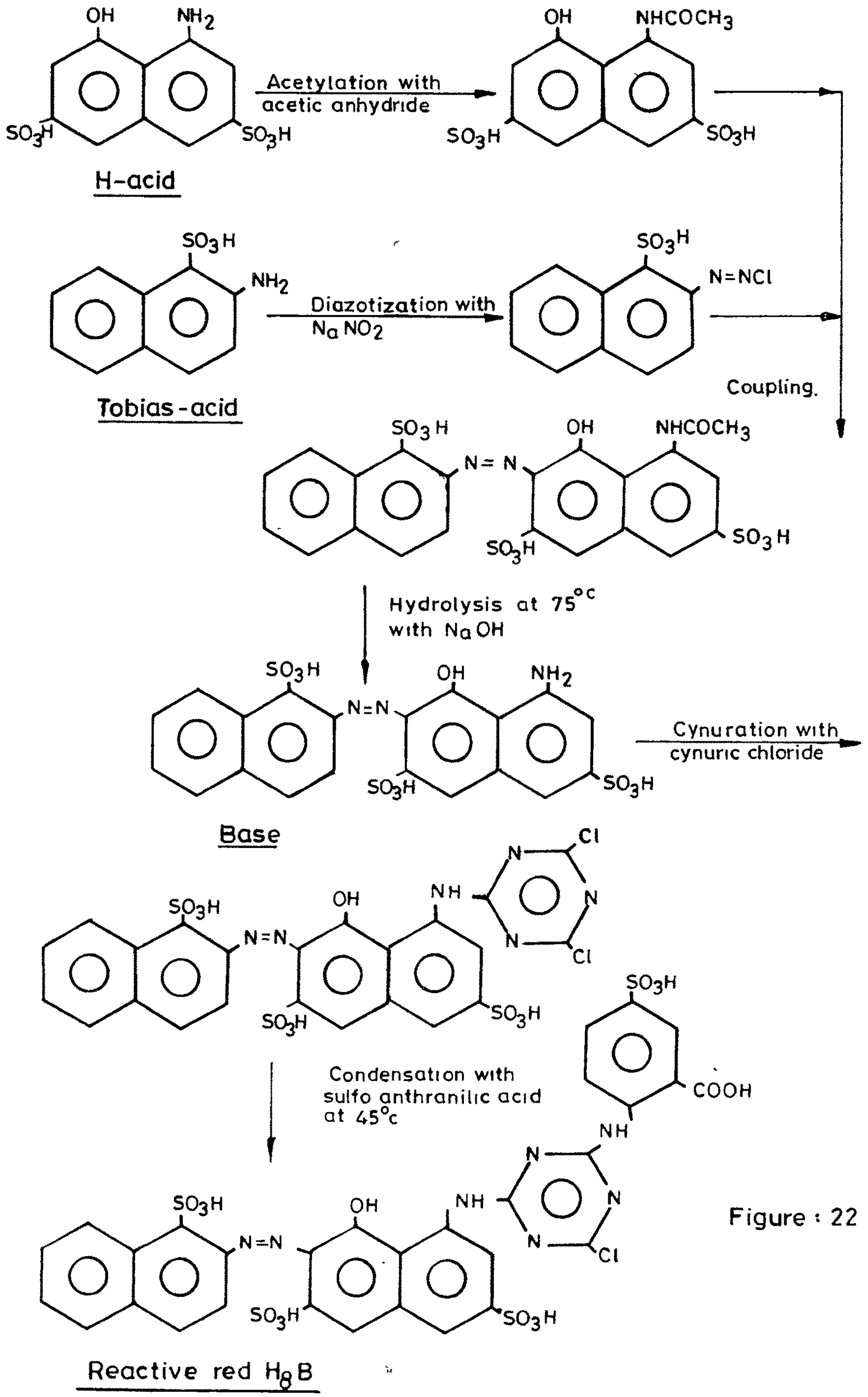
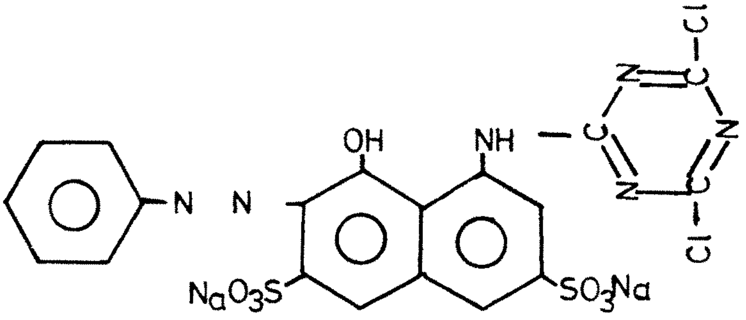


Figure : 22

REACTIVE RED M_5B. C.I.No Reactive red-2



REACTIVE ORANGE H_2R. C.I.No. Reactive orange-13

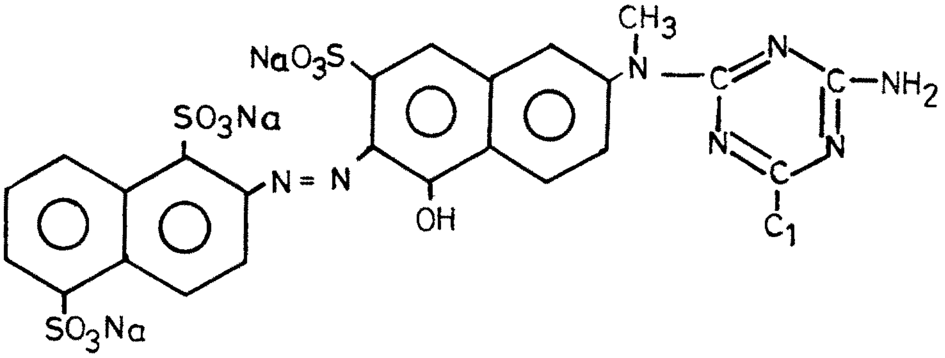


Figure : 23

INDIGOSOL GOLDEN YELLOW-IGK.

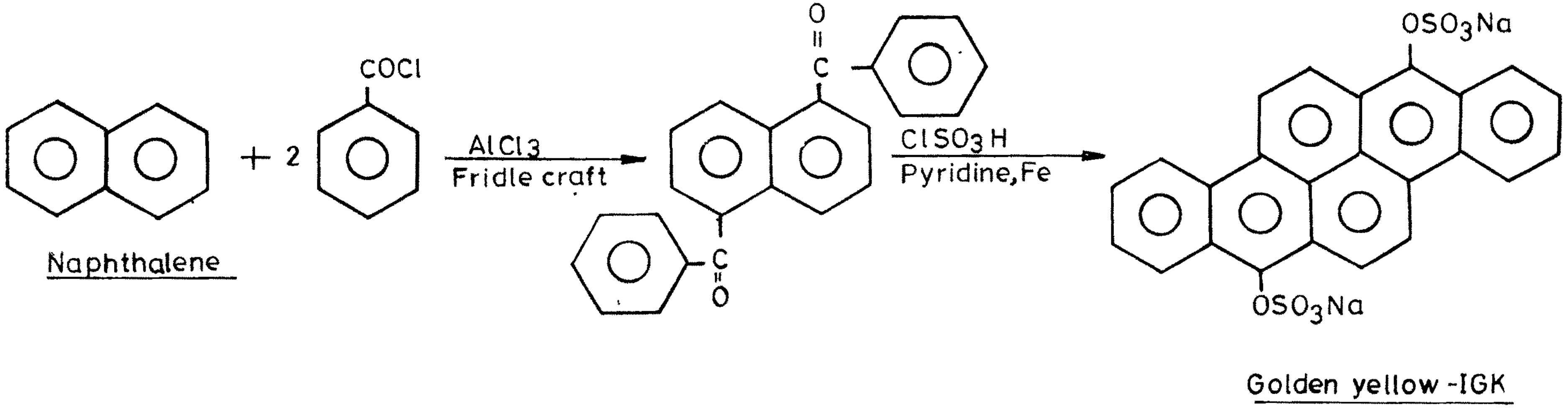


Figure : 24

3. TREATMENT METHODOLOGY

3.1 Sample collection and their characteristics

(A) Following two composite effluent samples were collected from M/s. Piramal Rasayan Ltd.

Characteristics	**Samples - I**	**Sample - II**
Appearance	Non transparent reddish black	Non transparent reddish black.
pH	2.1	2.2
Colour (Pt-Co) Unit	-	3000
Total suspended solids	Practically Nil	Practically Nil.
Total Residue (solids)	81.2 g/l	68.4 g/l
Total Volatile solids	-	9.9 g/l
COD	60,000 mg/l	10,000 mg/l

(B) A composite sample was also collected from H-acid manufacturing plant from M/s. Nandesari Rasayani Ltd.

Appearance	Reddish black and non transparent.
pH	1.2
Total suspended solids	Practically Nil
COD	22,000 mg/l

(C) Effluent from dyes manufacturing units.

Effluents of	pH	Total Dissolved solids g/l	COD mg/l	Visual colour
1. Reactive Red H_8B	6.5	230.4	8400	Red - Non transparent
2. Golden yellow IGK	9.2	117.8	2200	Golden yellow transparent.
3. Golden yellow HR	8.0	119.0	7600	Dark-Reddish orange Semi transparent.

3.2 General aspects of treatment

Number of classical approaches are being tried by the small scale industries as well as large scale industries in India.

Following attempts were made to see the effect of different materials in decreasing the colour of reddish black effluent, having COD 60,000 mg/l.

The effluent was treated with $CaCO_3$, lime, sodium dithionate, alum, ferric chloride. None of these methods gave satisfactory results.

Due to this reason it was thought to use benzidine for the reaction with sulfonic acids to obtain the precipitates of insoluble product. This method did not give positive result. It seems that concentration of sulfonic acids plays its role. This type of method is suggested for the quantitative estimation of dodecyl benzene sulfonic acid and other sulfonic acids.

Another method which is reported in literature was also tried. In this method azo dye is formed with the dissolved aromatic acids to render them insoluble. Aniline diazonium chloride was used but no apparent success was noted.

Extraction of sulfonic acids by organic solvents immiscible with water could not give good results.

Various adsorbents like activated Carbon, Activated earth, and fly ash (thermal power plant) were tried. Experiments were carried out in column and its results are given in Table-40.

TABLE - 40

Adsorption with different Adsorbents (25 ml influent of 60,000 mg/l COD).

Adsorbent 3.0 g	COD of effluent mg/l	Visual colour reduction
Activated Carbon	13,920	To some extent
Activated Earth	49,920	No change.
Fly ash	57,600	No change.

The Table-40 indicated that except activated carbon other adsorbents are not useful for treatment of such effluent.

Number of different approaches are made to treat coloured water. Looking to the vast problem and its serious effect on drinking water where drinking water is a scarce commodity lead us to develop some new methodology for the removal of colour.

Our survey of Mini River near Baroda and its surroundings indicated that river water is coloured and cannot be used for the drinking purpose. However, animals were drinking this water, moreover most of wells situated on the banks of river had also coloured water and were abandoned as the water could not be used for drinking purposes. All these pollution problems arise due to number of dyes and dyes-intermediate industries around that area. Photographs on page No.186 187, 188, designated as WP-1 to WP-6 will give the idea regarding the coloured effluents around the chemical industries manufacturing dyes and dyes-intermediates. Similar problem is faced by another complex where printing and dyeing is done by more than thousand industries in a small place.

WP - 1

WP - 2

WP - 3

WP - 4

WP - 5

WP - 6

The liquid ion exchangers are used to remove metals and metal salts from effluents. They require large quantity of solvent which can be recovered and recycled [126,127]. Recently some of the organic wastes also were treated by using liquid ion exchanger [128,129]. Large quantity of solvent is almost inhibiting factor for the small scale industries. Moreover, the data on the removal of colour or dyes from the effluent by this method is rare. It was thought to use liquid ion exchanger without solvent as flocculating agent to treat effluents. This was a novel concepts and the result would prove its worth hence present study was taken up to varify this approach. Liquid ion exchangers are different long chain primary, secondary or tertiary amines. Normally a Cationic surfactant is used which is a tertiary amine. In the present study Boramine-S (Stearyl amine), Boramine-T (Tallow amine) and Boramine-DMS (Dimethyl stearyl amine) were used as flocculants. The data regarding these (liquid ion-exchangers) Cationic surfactants is given in Table-41.

Initial experiments were carried out with Boramine-S and Boramine-T. Since waste water had very high COD value (60,000 mg/l) it was decided to dilute waste water for the treatability study. Sample was diluted 10 times to adjust COD 6000 mg/l and used for the treatment (Table-42). Treatment stretagy adopted was very simple. Variable quantity of flocculants was added to waste water (influent), and mixture was stirred for 15 minutes. This treated waste water was then filtered, filtrate was analysed for COD and colour. Findings are given in Table-42.

TABLE - 41

Characteristics of Fatty amines.

Specification	Boramine - S	Boramine - T	Boramine - DMS
Appearance	White flakes	Paste to semi-solid.	Clear liquid.
Category	Fatty primary Amine	Fatty primary Amine	Fatty Tertiary Amine
Primary Amine %	97 min.	97 min.	-
Secondary + Tertiary Amine %	3 max.	3 max.	-
Primary + Secondary Amine %	-	-	2 max.
Tertiary Amine	-	-	95 % min.
Iodine value.	4 max.	38 min.	4 max.

TABLE - 42

Treatment of 25 ml influent (COD value 6000 mg/l and pH - 2.9) with Boramine - S and Boramine - T.

Sr. No.	Quantity of flocculant gm.	COD of effluent mg/l	pH of effluent	Colour Appearance
01.	0.2 B-S	3100	5 - 6	Non transparent black liquid
02.	0.4 B-S	2230	7 - 8	Clear liquid slightly black.
03.	0.2 B-T	2100	7 - 8	Transparent yellowish.
04.	0.4 B-T	2200	7 - 8	Transparent yellowish.

B-S = Boramine - S
B-T = Boramine - T

The reference to Table - 42 shows that the fatty amines seems to be effective in three ways. The COD values are decreased, colour is decreased considerably and pH has changed from highly acidic to the neutral values. So far no reagent has shown such action. Encouraged by these results, systematic investigation was further carried out by using three fatty amines.

The quantity of effluent (pollutant) was kept fixed and the effect of variation in the quantity of three fatty amine Boramine-S, Boramine-T and Boramine-DMS was studied. Each sample of effluent after the treatment was analysed by measuring COD values and colour change was marked visually.

The data is recorded in Table - 43.

The reference to Table - 43 shows that as the quantity of fatty amines is increased, the efficiency as 'flocculants' increases except in the case of Boramine-S, which does not show an appreciable change when concentration is increased. The results are graphically represented in Fig. 25. These results indicate that upto certain limits, the increase in the quantity of fatty amines or as the ratio of pollutant/fatty amine decreases, the efficiency of fatty amines as removal of pollutants increases. The results are quite encouraging as colour is removed to great extent.

It was further thought to evaluate the effect of dillution of effluent on the efficiency of flocculants. For this purpose number of experiments were carried out (Table - 44), which indicates that the efficiency of (surfactants) fatty amines does not decrease even with variation in the concentration of pollutants.

Above results indicate that fatty amine B-DMS (Tertiary amine) is most effective compared to other two amines in the removal of colour and organics from the effluent. Naturally for the other experiments Boramine-DMS was preferred.

These experiments were repeated with 1 litre of the effluents and B-DMS gave comparable results obtained with smaller quantity of effluent. This indicates that the efficiency of B-DMS remains unchanged even in scaled-up experiments. The additional advantage of B-DMS is that it is liquid, hence mixing with the effluent is quick and uniform. This also is a factor for enhanced efficiency of B-DMS compared to other fatty amines.

Very slight tinge of colour also could be removed completely by passing it through the column of activated carbon.

This was scaled up to confirm by passing one litre of effluent (obtained by treating waste water with Boramine - DMS), in the columns containing variable quantity of carbon IC - 30/80 as under.

Activated Carbon IC 30/80 gm	COD of Influent mg/l	COD of Effluent mg/l	Visual colour
20	1,078	588	Almost colourless.
30	1,078	432	Colourless.
40	1,078	Practically Nil	Colourless.

After these experiments with the effluent of dyes intermediates, where COD was monitored and colour was mostly visually varified, it was decided to perform these experiments on the effluent of dyes and dyes intermediates and for more accurate data colour was measured by visible spectroscopic method. For this purpose number of experiments were carried out. The details of the procedure is already mentioned earlier for these experiments.

TABLE - 43

Results of treatment of 100 ml waste water, having 10,000 mg/l COD, pH - 2.2 and colour value 3000 units, with different flocculants.

Sr. No.	Type and quantity of flocculant g.	pH of effluent	COD of effluent mg/l	Effluents colour units (Pt-Co) or visual colour intensity.
	BORAMINE - S			
01.	0.7	3	8,000	1,500, Non transparent dark black.
02.	0.9	3.1	7,000	1,500, Non transparent black.
03.	1.2	3.25	7,200	1500, Non transparent black.
04.	1.5	3.3	7,000	1500, Non transparent black.
	BORAMINE - T			
05.	0.7	3-4	5,000	1000, Black colour.
06.	0.9	4-5	4,150	-
07.	1.2	5-6	3,000	600, Transparent reddish black.
08.	1.5	6-7	2,600	300, Yellow transparent.
	BORAMINE - DMS			
09.	0.935	2-3	4,116	400, Brown transparent.
10.	1.0	3-4	3,724	Brownish transparent.
11.	1.08	3-4	3,528	Brownish transparent.
12.	1.15	3-4	3,332	300, Brownish.
13.	1.25	4	2,940	200, Brownish
14.	1.33	4-5	2,548	200, Brownish.
15.	1.5	5-6	2,156	Greenish transparent.
16.	1.67	5-6	1,764	Greenish transparent.
17.	1.8	5-6	1,568	Yellowish transparent.
18.	1.9	5-6	1,764	yellowish tinge.

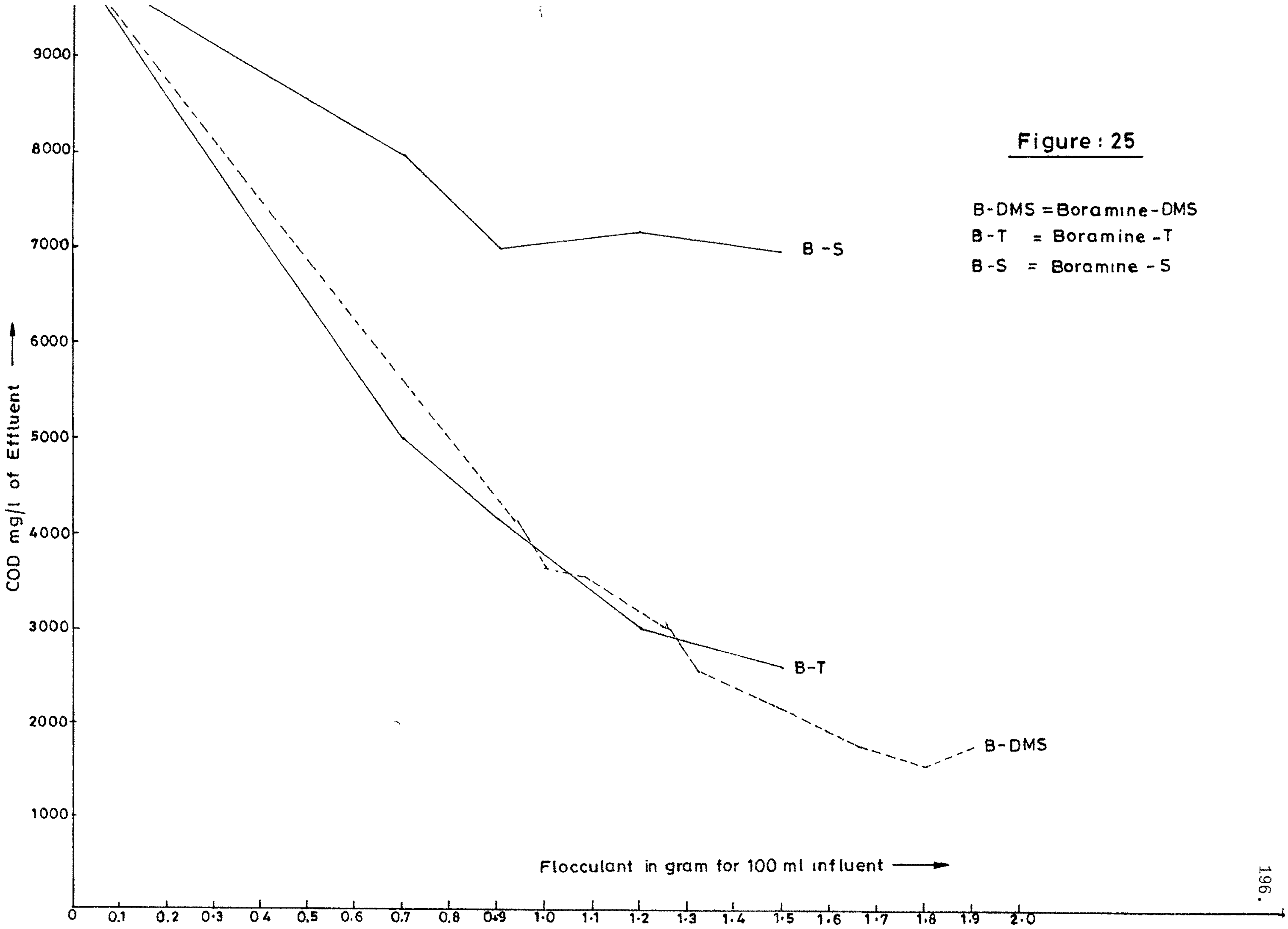


Figure : 25

B-DMS = Boramine-DMS
B-T = Boramine -T
B-S = Boramine - S
B -S
B-T
B-DMS
COD mg/l of Effluent
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0.1
0.2
0·3
0.4
0.5
0.6
0.7
0.8
0·9
1·0
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
Flocculant in gram for 100 ml influent

TABLE - 44

Variation of concentration of pollutants and its effect on the removal of COD (COD value of waste water 10,000 mg/l and colour 3000 units).

Sr. No.	Waste water ml	+	Distilled water added. ml	Flocculant added g.	Effluent COD mg/l	Visual colour intensity or colour unit (Pt-Co) disc.
				B-T		
01.	25		-	0.375	2,800	Yellow
02.	25		25	0.375	1,400	Yellowish.
03.	25		50	0.375	1,000	Slightly Yellowish.
				B-DMS		
04.	20		80	0.36	480	40
05.	40		60	0.72	760	60
06.	60		40	1.08	960	80
07.	80		20	1.44	1,280	150
08.	100		-	1.8	1,440	250

B-T = Boramine - T

B-DMS = Boramine - DMS

3.3 Experiments monitored by visible spectrophotometer

3.3(a) Samples of waste waters from dye industries.

1. Reactive Red H_8B.
2. Golden Yellow IGK.
3. Golden Yellow HR.

The treatment strategy for the experiments is as under and colour measurements were carried out as described in analysis part of this section.

Part : A

100 ml sample of influent was filtered and divided into two parts.

50 ml	50 ml
colour and pH was measured directly (1A1)	pH adjusted to 7.6 soln. filtered and colour was measured. (1A2)

Part : B

100 ml of influent sample was taken and pH was adjusted to 2. It was treated with B-DMS, and stirred. The quantity of B-DMS used is mentioned in the table. The effluent was then filtered and divided into two parts.

50 ml	50 ml
Colour and pH were measured (1B1)	pH-adjusted to 7.6, filtered and colour was measured (1B2).

Here 1A1, 1A2, 1B1 and 1B2 are for Reactive Red H_8B waste water. In this manner 2A1 to 3A1, 2A2 to 3A2, 2B1 to 3B2 and 2B2 to 3B2 samples were prepared for waste waters 2 and 3, screened through visible spectrophotometer. The results are tabulated in Table - 45. They are graphically represented in Figures 26, 27 and 28 for influent and effluent at 7.6 pH. Data of % Transmittance were converted to absorbance for graphical representation of visible spectra, using standard conversion tables. This conversion is given in Table - 46 [130]. Absorbance was selected for better graphical representation [111].

The reference to Table-45 shows clearly the effectivity of the present method. The reference to graphs give visual effect of reduction in the colour. COD values are also decreased markedly. The visible spectral measurements confirm earlier results though in those experiments colour was measured either visually or by Pt-Co method.

The important aspect of experiments is that untreated samples had to be diluted many times to bring it in the measurable range of visible spectra as they were non-transparent due to high capasity of absorbance whereas, treated samples required very little dilution.

Due to this reason the direct comparison of data between the treated samples would be misleading or may create confusion that efficiency of the system is not very good. The comparison should be viewed from the dilution point of view, as for example sample 1A1 - influent was diluted by more than sixty times even then transparancy at 544.3 nm is 0.5%, whereas treated sample was diluted by two times whereas the %T is 19 at that wave length. Now the comparative idea can be obtained. The removal of colour is quite effective hence in the treated waste water dilution was not required as many times as in the untreated effluent.

TABLE - 45

Treatment of 100 ml influent (dyes effluent) with B-DMS and colour measurement by %T at different wave length.

Sample No.	B-DMS added to 100 ml influent	pH	COD mg/l	Dilution made to measure %T ml to ml	% T Wave Length nm									
					435.5	461.2	544.3	564.1	577.4	588.7	599.6	610.9	624.2	645.9
Reactive Red H 8B														
1A1		6.5	8400	0.8 to 50	23	11	0.5	3	12	32	51	86	93	97
1B1	0.8 g	4.2	2800	20 to 50	28	25	19	29	38	48	54	67	69	73
1A2		7.6	8400	0.8 to 50	22	10	0.0	2.5	11	32	51	86	93	97
1B2		7.6	2500	20 to 50	31	31	33	40	47	53	57	68	70	75
Golden Yellow IGK														
2A1		9.2	2200	20 to 100	8	8	87	92	93	94	94	96	96	97
2B1	0.16 g	2.1	1300	No dillution.	69	75	83	83	82	82	82	83	82	82
2A2		7.6	2190	20 to 100	7	8	89	93	94	94	95	96	97	98
2B2		7.6	1300	No dillution.	86	92	99	99	-	-	-	-	-	-
Golden Yellow HR														
3A1		8.0	7600	3 to 100	0.0	0.5	35	60	73	82	86	97	98	99
3B1	1.05 g	6.7	3900	10 to 100	4	7	66	83	90	93	95	85	86	87
3A2		7.6	7400	1.5 to 100	1	3	58	78	85	91	92	99	100	-
3B2		7.6	4000	20 to 100	0.5	1	46	70	80	86	88	96	97	99

Note : A2 and B2 are at 7.6 pH (after pH correction) - A1 and A2 are untreated; B1 and B2 are treated.

TABLE - 46

Transmittance to Absorbance Conversion Table.

Trans.	O.D.	Trans.	O.D.	Trans.	O.D	Trans.	O.D.
100	0.000	73	.136	46	.337	19	.721
99	.004	72	.142	45	.347	18	.745
98	.008	71	.148	44	.357	17	.770
97	.013	70	.155	43	.367	16	.796
96	.017	69	.161	42	.377	15	.824
95	.022	68	.167	41	.387	14	.854
94	.026	67	.174	40	.398	13	.886
93	.031	66	.180	39	.409	12	.921
92	.036	65	.187	38	.420	11	.959
91	.041	64	.193	37	.432	10	1.000
90	.045	63	.200	36	.444	9	1.046
89	.050	62	.207	35	.456	8	1.097
88	.055	61	.214	34	.469	7	1.155
87	.060	60	.221	33	.481	6	1.222
86	.065	59	.229	32	.495	5	1.301
85	.070	58	.236	31	.509	4	1.398
84	.075	57	.244	30	.522	3	1.522
83	.080	56	.252	29	.537	2	1.699
82	.086	55	.260	28	.553	1	2.000
81	.091	54	.267	27	.568		
80	.096	53	.275	26	.585		
79	.102	52	.284	25	.602		
78	.108	51	.292	24	.620		
77	.113	50	.301	23	.638		
76	.119	49	.310	22	.657		
75	.125	48	.319	21	.678		
74	.130	47	.328	20	.699		

3.3(b) Samples of waste water from dyes intermediate manufacturing units.

Sample : 1

M/s. Piramal Rasayan Ltd., (original sample of 10000 mg/l COD was diluted to 2400 mg/l·COD and taken for the treatment).

Sample : 2

M/s. Nandesari Rasayani Ltd. (only H-acid manufacturing plant)

The treatment strategy was exactly simılar to Table-45. Here samples 1A1, 1A2, 2A1 and 2A2 are untreated samples. Samples 1B1, 1B2, 2B1, 2B2, 2C1, 2C2, , 2D1, 2D2 are obtained after treatment with variable quantites of B-DMS. Quantity of B-DMS used, COD, pH and %T of each sample measured are tabulated in Table - 47 and visible spectra are graphically presented in figure 29 and 30.

Reference to Table-47 shows the efficiency of B-DMS in the removal of colour as well as organic pollutants from the effluent of dyes-intermediate industry. So far no one method is found as effective as tested here for the dyes-intermediate waste water for the treatment. Looking to these facts present system is highly promising for the dyes-intermediate industry.

TABLE - 47

Treatment of 100 ml influent (dyes-intermediate) with B-DMS and colour measurement by %T at different wave length.

Sample No.	B-DMS added to 100 ml influent	pH	COD mg/l	Dilution made to measure %T ml to ml	%T → Wave Length nm.									
					435.5	461.2	544.3	564.1	577.4	588.7	599.6	610.9	624.2	645.9
Sample 1 (M/s. Piramal Rasayan Ltd.)														
1A1		2.5	2,400	20 to 100	0.5	1	5	7	8	10	11	15	17	20
1B1	0.52 g	3.0	700	No dilution	66	72	82	83	84	84	84	85	85	85
1A2		7.6	2,400	20 to 100	0.0	0.5	3	4	5	6	7	12	14	16
1B2		7.6	700	No dilution	73	83	95	96	97	98	98	99	99	-
Sample 2 (M/s. Nandesari Rasayani Ltd.)														
2A1		1.2	22,000	25 to 50	0.0	0.0	1	4	6	8	10	-	-	-
2A2		7.6	-	5 to 50	0.0	1	3	3	3.5	3.5	4	-	-	-
2B1	1.74 g	1.3	13,200	No dilution	0.0	1	20	35	44	50	55	-	-	-
2B2		7.6	-	8.5 to 50	0.5	1.5	5	5	4.5	5	5	-	-	-
2C1	3.5 g	1.4	7,500	No dilution	9	23	61	74	80	84	86	-	-	-
2C2		7.6	-	16.6 to 50	2	4	10	12	13	15	16	-	-	-
2D1	5.24 g	1.7	5,350	No dilution	18	25	59	72	76	79	81	90	91	92
2D2		7.6	-	25 to 50	3.5	6	13	13	13.5	14	14	18	18	20

Note : A1 and A2 indicate influent; B1, C1, D1 and B2, C2, D2 indicate effluent; A2, B2, C2 and D2 indicate 7.6 pH.

3.4 Synthetic Samples

3.4(a) synthetic samples of Dyes Intermediates

H-acid + K-acid + Chicago acid + Sulfotobias acid, 4 gms of each acid was accurately weighed and dissolved in 2 litres of water. This synthetic sample of 2.2 pH and 5600 mg/l COD was treated with different quantity of surfactant B-DMS and the resultant effluent was monitored by visible spectra . The treatment data are given in Table-48 and spectral data are recorded in Table-49. Spectral data are graphically presented in Figure 31.

TABLE - 48

Treatment of 150 ml synthetic sample (dyes-intermediate) with different quantity of B-DMS.

Sample No.	Amount of surfactant B-DMS gm
A	-
1A	0.39
2A	0.52
3A	0.79
4A	1.96

Sample A and 1A to 4A were divided into two parts for the colour measurements. pH of the 2nd part was adjusted to 7.6 as per the standard method followed in previous experiments. They are designated as A and 1A to 4A, B and 1B to 4B, for the convenience, respectively.

(In case of sample 4A during treatment it become turbid because of shifting

TABLE - 49

Results of treated Synthetic sample - H-acid + K-acid + Chicago acid + Sulfo tobias acid.

Sample No.	pH	COD mg/l	%T → Wave Length nm. 435.5	461.2	544.3	564.1	577.4	588.7	599.6	610.9	624.2	645.9
A	2.2	5,600	11	16	27	30	33	34	36	-	-	-
* B	7.6	5,600	7	9	26	31	34	37	39	-	-	-
1 A	2.8	4,400	71	80	89	92	93	95	95	-	-	-
1 B	7.6	-	21	24	51	58	62	66	69	-	-	-
2 A	3.2	4,010	65	73	85	88	90	93	94	-	-	-
2 B	7.6	-	24	27	53	60	64	69	72	-	-	-
3 A	6.2	3,500	6	7	38	50	58	64	67	-	-	-
3 B	7.6	-	20	21	53	60	65	68	71	-	-	-
4 A	2.4	1,100	83	83	91	93	94	94	95	97	98	98
4 B	7.6	-	52	49	67	72	75	78	80	84	89	91

Note: * Effluent of B was diluted (1:1) for the colour measurement.

of pH towards neutral as a result of addition of B-DMS. To avoid this four drops of H_2SO_4 was added to the mixture under treatment).

The reference to the tables and graphs clearly indicate the effectivity of B-DMS for the removal of colour and COD values. The experiments with synthetic samples were carried out to have comparison with the effluent of the industry to see whether the efficiency of B-DMS decrease or increases with pure samples. Results have indicated the effectivity of B-DMS comparable with both types of samples of dyes intermediates.

3.4(b) Synthetic samples of Dyes

Synthetic samples of the dyes, which were studied for the effluent of the industry, were prepared. These synthetic samples were treated in the same manner as effluents of the same dyes were treated in previous section (Table-45). 1A1, 2A1, 3A1 and 1A2, 2A2, 3A2 are the samples before treatment.

1 gm of following dye were dissolved in 1 litre of water and then these solutions were treated with B-DMS as reported in Table-50.

(1) Golden Yellow IGK (2) Reactive Golden Yellow HR .

(3) Reactive Red H_8B.

TABLE - 50

5 gm NaCl + 150 ml synthetic sample of dyes were treated with B-DMS.

Sample No.	Dye solution	Amount of B-DMS	Resultant effluent.	
			as such	with pH 7.6
1	Gy-IGK	0.14 g	1B1	1B2
2	Gy-HR	0.26 g	2B1	2B2
3	RR-H_8B	0.26 g	3B1	3B2

Note: Here pH of the solution under treatment was brought to about 2 by adding conc. H_2SO_4 (few drops).

The visible spectra of the untreated solution and treated solution, 1A2 to 3A2 and 1B2 to 3B2 respectively, where pH was adjusted to 7.6 as per the requirement of standard procedure are recorded in Table-51. Spectral data are graphically presented in Figure 32, 33 and 34.

The results of synthetic samples prepared from the reactive dyes indicate that the efficiency of B-DMS is quite comparable with the effluent. In the synthetic solution of dyes NaCl (common salt) was added to have the effect of dissolved salt, as in the effluent of dyes NaCl and Na_2SO_4 are always present in considerable quantity.

Experiments were carried out with two more reactive dyes.

Synthetic samples of following two dyes were prepared, and they were treated with B-DMS, and results are as under.

Synthetic sample of	Visual colour of influent	COD of influent mg/l	Visual colour of effluent.	COD of effluent mg/l
(1) Reactive orange H_2R	Dark Reddish orange.	1450	Almost colourless	210
(2) Reactive Red M 5B.	Dark Red	1380	Almost colourless	155

Above results indicate that B-DMS is highly effective for these two dyes. This suggests that B-DMS will remove colour and COD of the effluent of the industry manufacturing these reactive dyes.

TABLE - 51

Visible spectra of treated-untreated solutions of synthetic samples of dyes.

Sample No.	pH	COD mg/l	%T Wave Length nm.									
			435.5	461.2	544.3	564.1	577.4	588.7	599.6	610.9	624.2	645.9
Golden Yellow IGK												
1 A 1	9.5	400	1	1	86	91	93	93	93	93	93	94
1 B 1	2	160	91	91	96	97	97	97	97	97	97	97
1 A 2	7.6	-	1	1	86	91	92	92	92	98	98	98
1 B 2	7.6	-	92	93	97	97	97	97	98	99	100	100
Golden Yellow HR												
2 A 1	7.5	300	0	0	35	67	80	86	88	98	-	-
2 B 1	2	160	77	84	98	99	99	99	99	100	-	-
2 A 2	7.6	-	0	0	35	67	80	86	88	98	-	-
2 B 2	7.6	-	83	88	98	99	99	99	99	100	-	-
Reactive Red H8B												
3 A 1	7.7	425	0	0	0	0	0	1	9	56	83	97
3 B 1	2	80	92	88	73	80	88	93	96	99	100	100
3 A 2	7.6	-	0	0	0	0	0	1	9	56	83	97
3 B 2	7.6	-	90	87	70	77	86	92	95	99	100	100

3.5 Analysis of Total Carbon and Total Organic Carbon.

Previous results of COD measurements were confirmed by TC and TOC analysis. These results, recorded in Table-52, also indicate that the treatment is quite effective for the removal of organics and colours from the effluent of dyes and dyes intermediate industries.

3.6 Regeneration (Recovery) of B-DMS.

The effectivity of fatty amines for the removal of colour and especially of B-DMS is quite striking. It was thought worth while to attempt for the regeneration or recovery of fatty amines. The liquid ion-exchanger work on the principle that the complex formed by ion-exchanger is extracted in the solvent. After that by changing the pH, complex is broken, fatty amines remain in the solvent and it is recycled [128,129].

Our approach was simple, but the chemistry involved was same as in the liquid ion exchangers. The flocks obtained after the treatment of coloured water can be seperated. These flocks contain the complex formed by fatty amine and colouring matter.

The recovery of B-DMS can be made by two different methods with minor change.

(1) In the case of flocks obtained from the effluent of dyes-intermediate following method was found to be more convenient.

The flocks were taken in small quantity of dil.NaOH solution and then chloroform was added. Efficient stirring and standing gave two layers, with the help of seperating funnel both layers were seperated.

TABLE - 52

Analysis of TC and TOC alongwith COD.

Sr. No.	Sample	TC Mg/l	TOC Mg/l	COD Mg/l
01.	Effluent of M/s. Piramal Rasayan Ltd. (Table-47)	844.2	869.8	2,400
02.	Treated effluent of M/s. Piramal Rasayan Ltd. with B-DMS (Table-47).	240.9	150.3	700
03.	Treated effluent of M/s. Piramal Rasayan Ltd. with B-DMS and Activated Carbon (Table-53).	148	127.1	432
04.	Synthetic sample of 2g each H-acid + K-acid + Chicago acid + Sulfotobias acid in 1 lt. water (Table-49).	1810	1,791	5,600
05.	Effluent after treatment of above synthetic sample (Sr.no:4) with B-DMS (Table-49)	273.4	258.7	1100

Chloroform layer on the removal of chloroform by distillation gave regenerated B-DMS (Fatty amine).

Aqueous layer contained dyes intermediates. They were recovered by evaporation of the aqueous layer.

(ii) In the case of flocks obtained from dyes industry following method was found to be more convenient.

The flocks were taken in chloroform. This formed clear solution. Then the coloured matter was extracted by dilute sodium hydroxide solution. Two extractions were enough to remove dyes.

The chloroform solution, on the removal of chloroform by distillation gave B-DMS.

The aqueous solution on evaporation gave dyes. From both the experiments, recovered B-DMS was confirmed by analysis as well as by direct experiments.

Efficiency of regenerated B-DMS was confirmed by treating the effluent of dye-intermediates with recovered B-DMS as given below.

Influent ml	COD of influent mg/l	Required Regenerated B-DMS gm	COD of Effluent mg/l	Visual colour and pH of effluent.
100 ml	2400	0.68	470	Almost colourless, 6-7 pH

Thus recovered B-DMS was again used for its efficiency for the removal of colour from the waste waters. The experiments suggested that the efficiency of recovered B-DMS is quite comparable with the original virgin sample.

The aqueous coloured solution contains sodium salt of dye. Dye can be recovered by evaporation. By this method expensive dyes which has been leached in water can also be recovered.

The regeneration (recovery) of fatty amine B-DMS from the flocks is quite a positive aspect for the treatment of coloured waste water as this factor will bring down the cost of process of waste water treatment of dyes industry to a level which can be afforded or became economically viable.

4. TREATMENT WITH ACTIVATED CARBON.

Treatment of synthetic solution of dyes, dyes-intermediates and their effluents by activated carbon.

Activated carbon is known for the removal of impurities or pollutants from the waste waters [105-107]. The results of previous study are highly encouraging where fatty amines were used as flocculating agents for the treatment of effluent. However, it was thought of interest to study the efficiency of activated carbon and to compare the efficiency of both the methods for the removal of pollutants and colour from coloured waste waters.

Two types of activated carbon ICPM 8/30, IC 30/80, were used in the mixed columns. The specifications of these carbons are given in Table-14.

4.1 Procedure

The procedure of treatment is described below :

Glass columns of 2.5 cm in dia. were selected. Granular activated carbon beds were made in columns resting on support of glass wool and porous plate of silica. In each column 50% of both the types of carbons were taken, where ICPM 8/30 carbon was kept on top and IC 30/80 carbon at the bottom. Columns of mixed activated carbon were made ready using standard procedure [61].

In each case 50 ml of influent after adjusting pH-2 was passed through columns and resulted effluent was analysed for pH, COD and visible spectra using standard procedure as followed in previous experiments.

Results are tabulated in Table-53 and Visible spectra are plotted in Figure : 26 to 34.

The mixed column was used because carbon ICPM 8/30 is specially designed for adsorption of dyes while carbon IC 30/80 is designed for organics in general.

In the present experiments relatively large quantity of activated carbon was taken for 50 ml effluent having very small COD value, just to know that even with this very high ratio of activated carbon to pollutant the method shows any positive results or otherwise.

The reference to Table-53 shows that activated carbon is quite effective for the removal of colour and COD for the synthetic samples, whereas for the effluent, activated carbon fails in all the experiments but one.

In all othe effluent samples, even large quantity of activated carbon fails to adsorb dyes and dyes intermediates.

The effluent contains high concentration of inorganic dissolved solids. Naturally there will be competition for the adsorption of these dissolved solids and dyes molecules. Results indicate in this process molecules of dyes or dyes intermediate are not adsorbed.

The efficient adsorption of Golden Yellow IGK on activated carbon from its effluent may be attributed to the size of the molecule and its less solubility in aqueous phase.

TABLE - 53

50 ml sample treated with variable quantity of mixed activated carbon column.

Sample of and COD mg/l.	Experi- ment column No.	Mixed Carbon g	pH of Effluent	COD of Effluent mg/l.	Dilution made to measure %T ml to ml.	→ Wave Length nm. %T						
						435.5	461.2	544.2	564.1	577.4	588.7	599.6
Reactive Red H8B solution (425 mg/l)	1	4	8.8	105	X	73	60	18	28	50	70	83
	2	8	8.5	76	X	83	70	30	42	61	80	90
	3	12	8.0	57	X	100	98	88	92	96	99	100
Effluent of Reactive Red H8B (8400 mg/l)	4	10	8.2	2,688	5 to 10	0	0	0	0	0	1	4
	5	15	8.5	2,592	5 to 10	0	0	0	0	0	2	7
	6	20	8.6	1,920	5 to 10	1	0	0	0	1	4	15
	7	25	8.6	1,440	5 to 10	7	3	0	1	6	17	32
Golden Yellow HR Solution (300 mg/l)	8	4	3	76	X	40	51	98	100	100	-	-
	9	8	8.1	76	X	75	82	100	100	100	-	-
	10	12	8.5	38	X	100	100	100	100	100	-	-
Golden Yellow HR Effluent (7500 mg/l)	11	10	5.5	3,648	5 to 10	0	0.5	2	13	27	41	51
	12	15	8.1	3,072	5 to 10	0	0	3	16	33	46	56
	13	25	8.5	1,400	X	0	0.5	6	26	42	55	64
Golden Yellow IGK Solution (400 mg/l)	14	4	6.8	60	X	100	53	97	100	98	98	98
	15	8	8.4	60	X	100	100	100	100	100	100	100
Golden Yellow IGK Effluent (2300 mg/l)	16	10	4.0	480	X	100	-	-	100	-	100	=
	17	15	8.8	200	X	100	-	-	100	-	100	=

..Table: 53 continued...

...TABLE - 53 contnd...

Sample of and COD mg/l	Experiment column No.	Mixed Carbon g	pH of Effluent	COD of Effluent mg/l.	Dilution made to measure %T ml to ml.	Wave Length nm.						
						%T 435.5	461.2	544.2	564.1	577.4	588.7	599.6
Solution of H-acid + K-acid + Chicago acid + Sulfo tobias acid (5600 mg/l)	18	10	9.9	400	X	71	80	84	88	88	90	91
	19	20	10.0	200	X	90	94	94	96	97	97	98
	20	25	10.1	200	X	100	100	-	-	-	-	100
M/s. Piramal Rasayan Ltd., Effluent (2400 mg/l)	21	10	8.7	1,000	5 to 10	0	0.5	2	3	4	5	6
	22	20	9.7	400	X	9	11	20	24	23	25	32
	23	25	9.7	300	X	30	34	45	48	52	53	56
M/s. Nandesari Rasayan effluent (22000 mg/l)	24	10	1.5	10,200	20 to 100	0	0.5	3	2.5	2.5	2.5	2.5
	25	15	2.0	4,900	10 to 20	0	0.5	5	6	7	8.5	10
	26	20	4.5	1,000	X	4	10	30	35	39	41	44

Note : All %T measured at 7.6 pH.
X - Indicates 'No Dilution'.

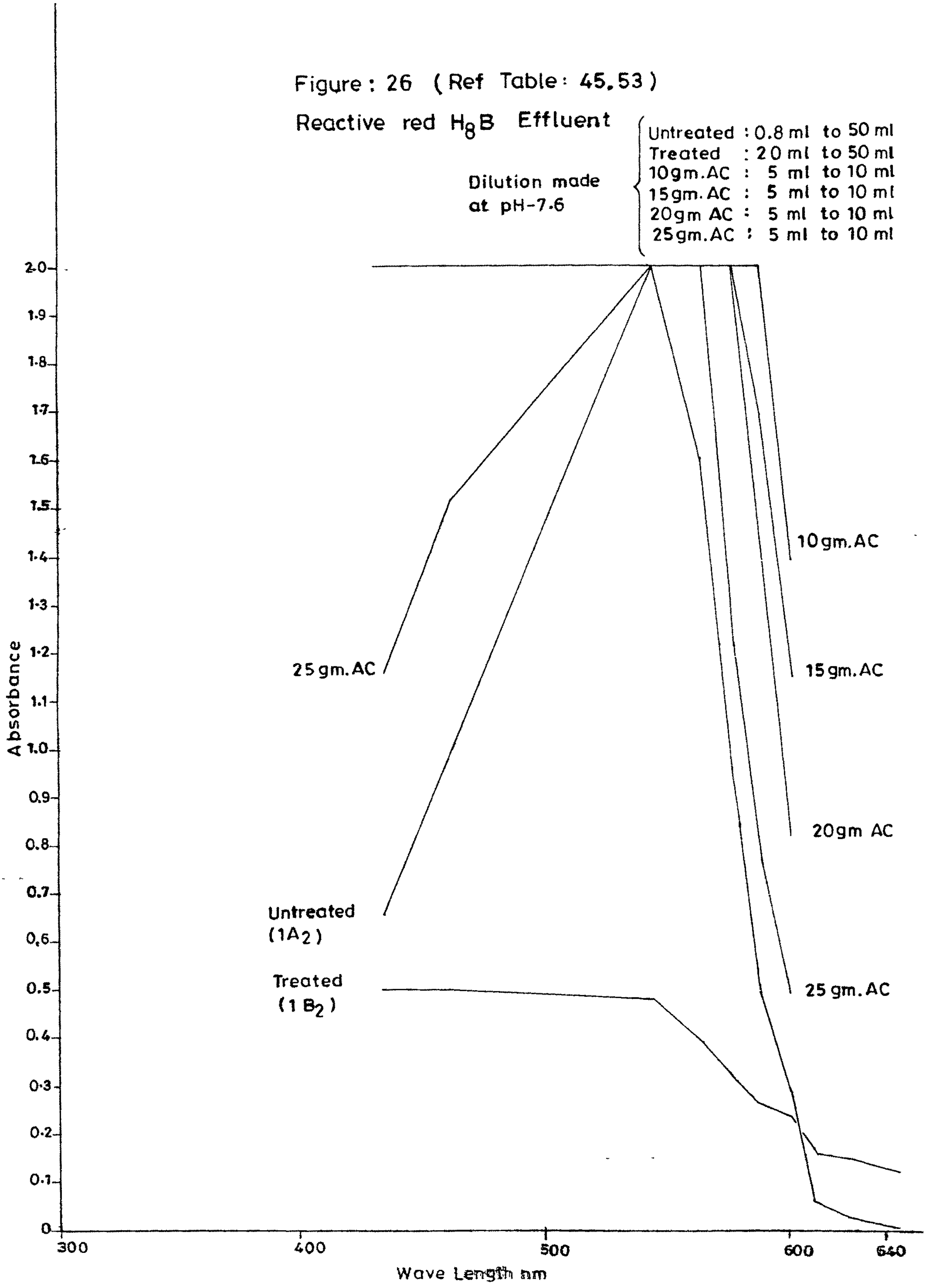


Figure : 26 (Ref Table: 45.53)

Reactive red H_8B Effluent

Figure: 27 (Ref. Table: 45, 53)

Golden yellow IGK - Effluent

Dilution made at pH-7.6 { Untreated : 20 ml to 100 ml

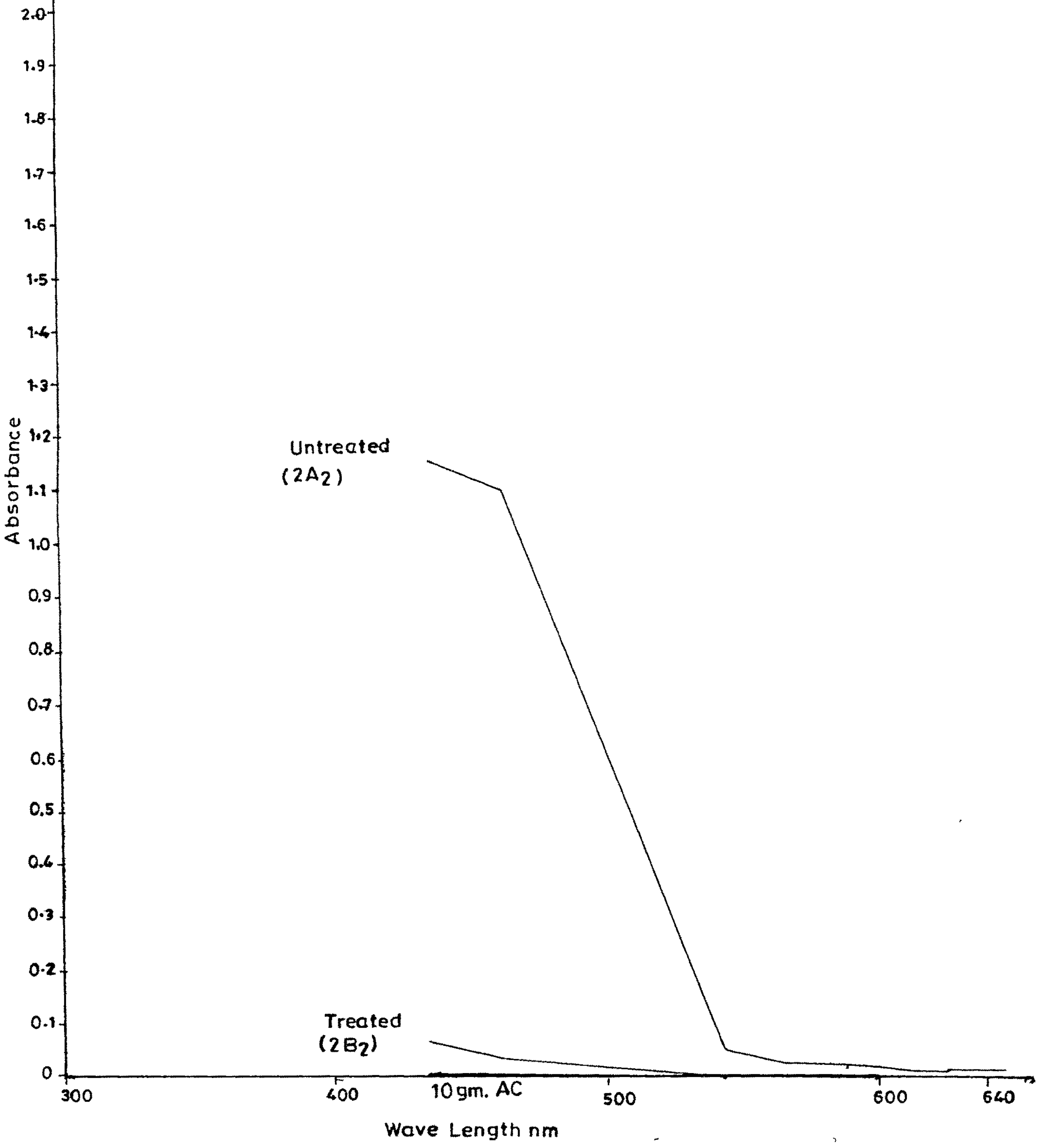


Figure: 28 (Ref. Table · 45, 53)

Golden yellow HR-Effluent

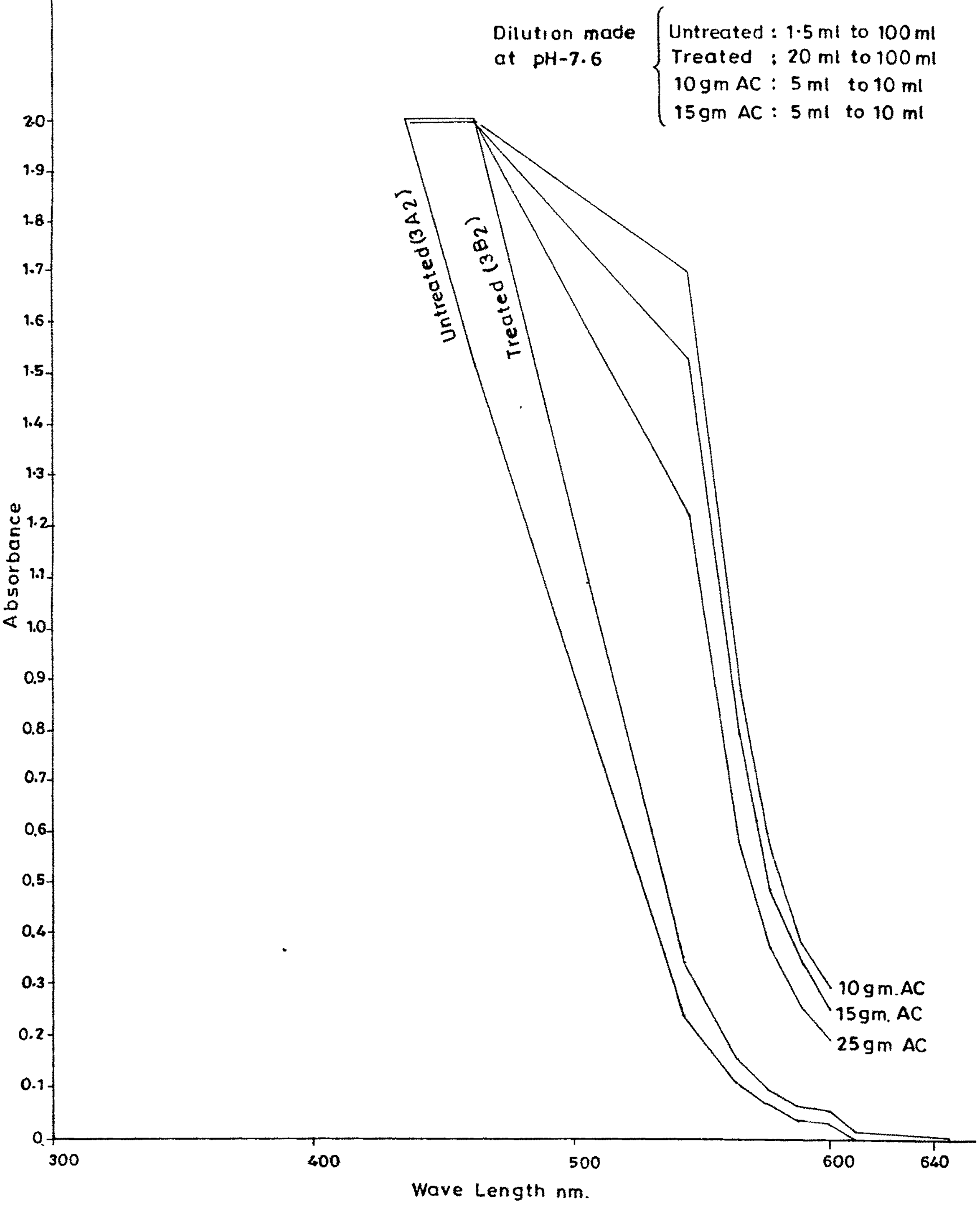


Figure: 29 (Ref. Table: 47,53)

Effluent from H-acid Plant (Nandesari Rasayani Ltd.)

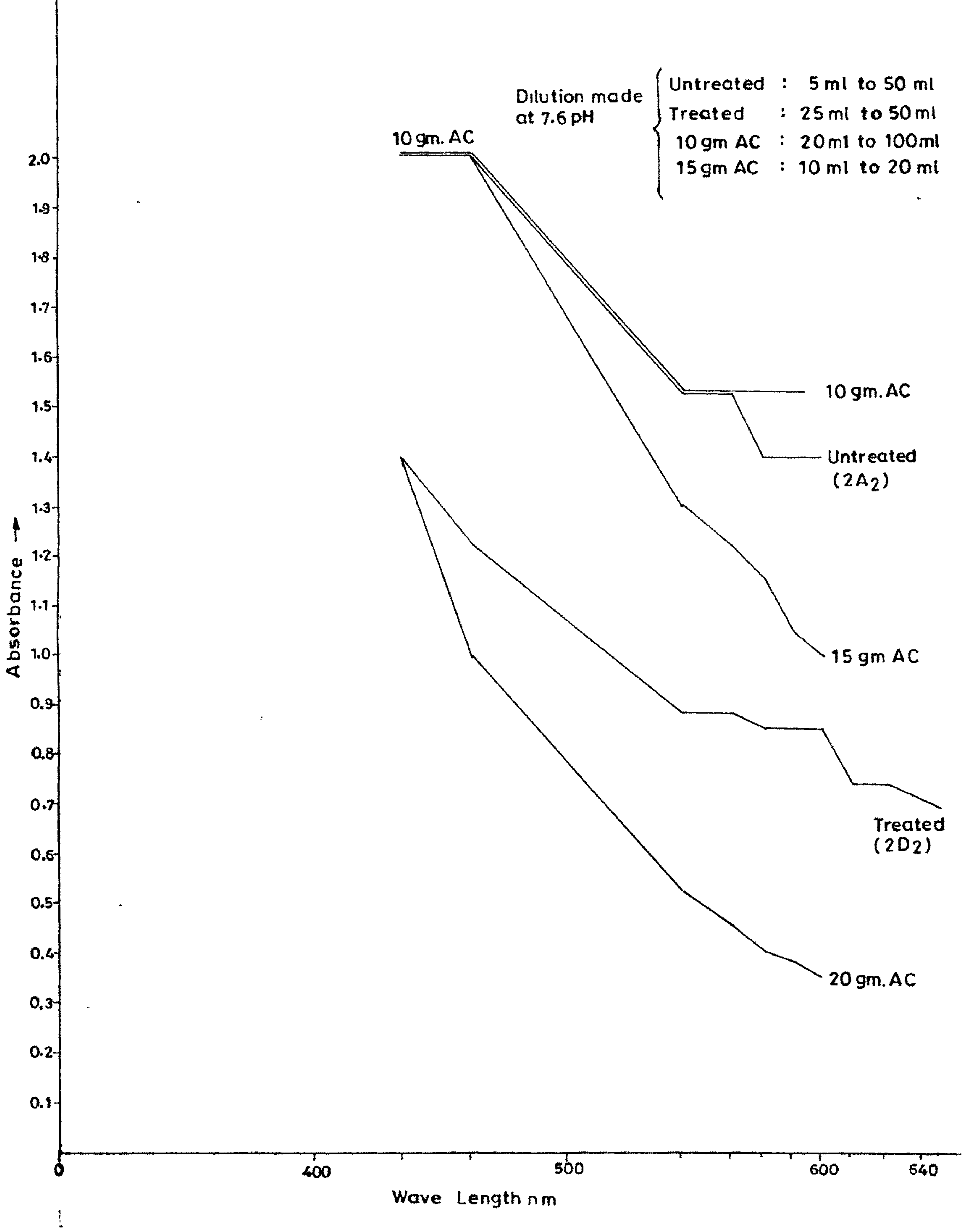
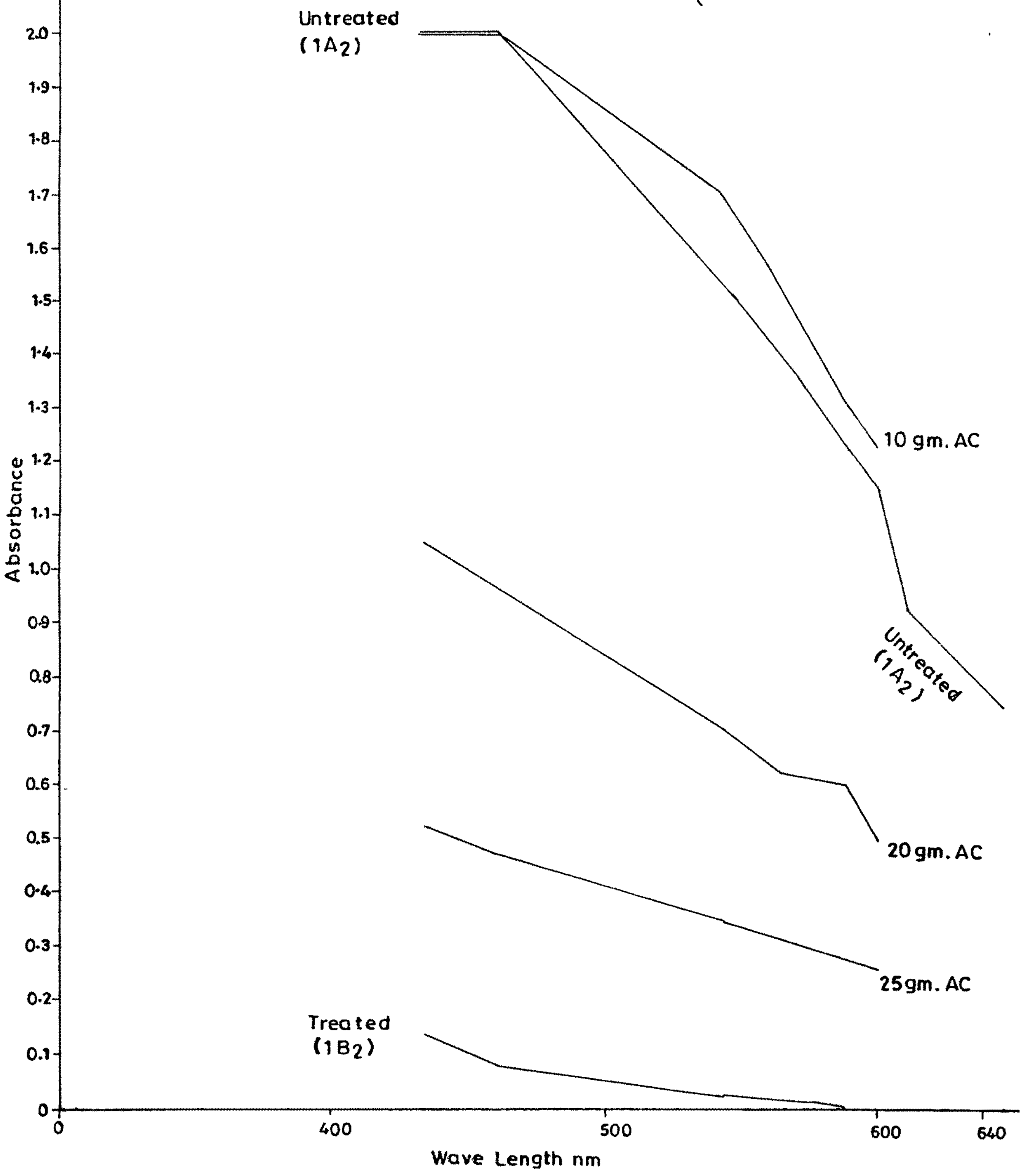


Figure : 30 (Ref Table : 47, 53)

Effluent from N/s Piramal Rasayan Ltd.



Dilution made at pH-7.6 { Untreated : 20 ml to 100 ml
10 gm. AC : 5 ml to 10 ml

Figure:31 (Ref. Table: 49, 53)

Synthetic solution H-acid+K-acid+chicago acid+S.T.acid

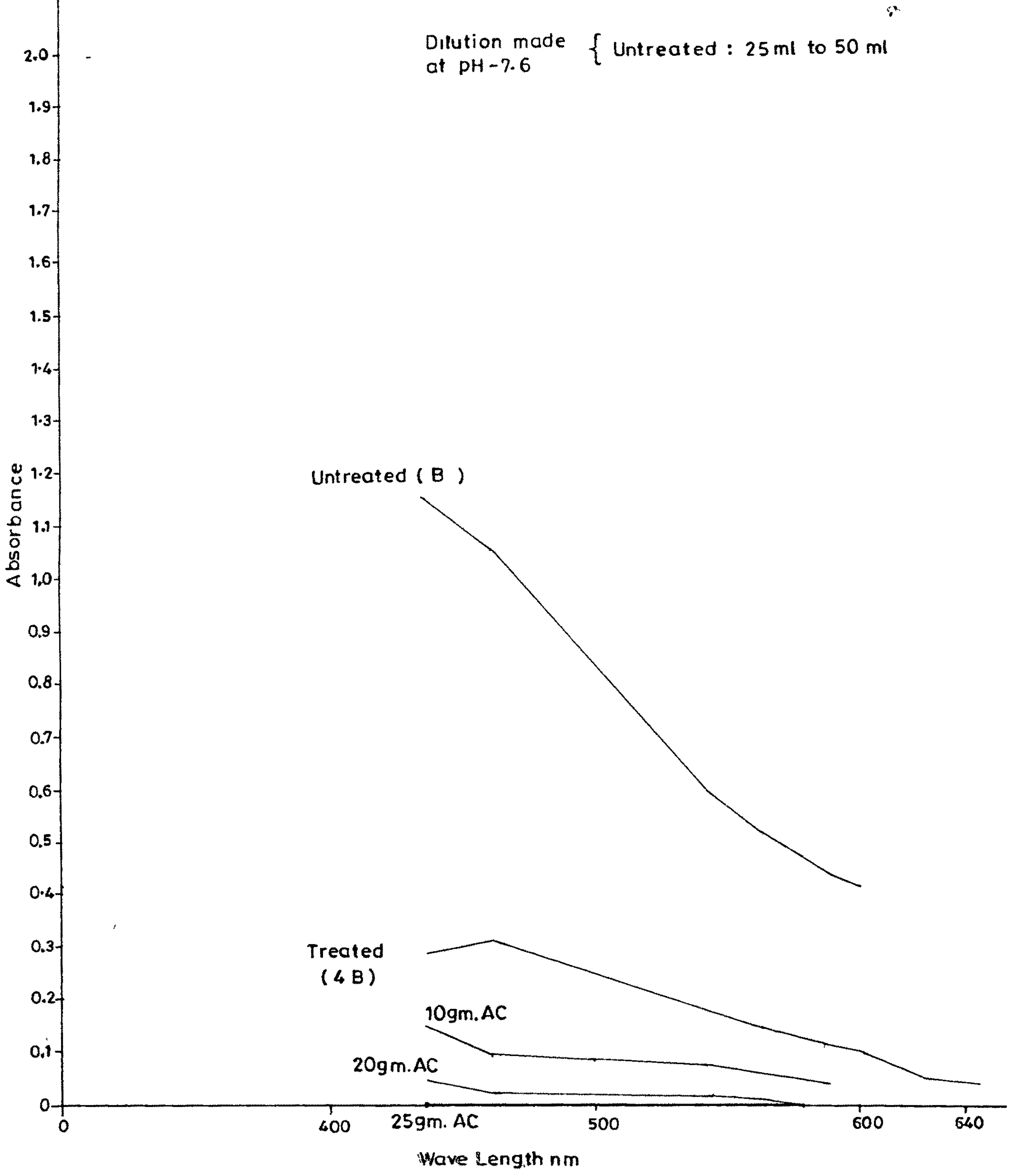


Figure : 32 (Ref. Table; 51, 53)

Synthetic Golden yellow IGK Solution

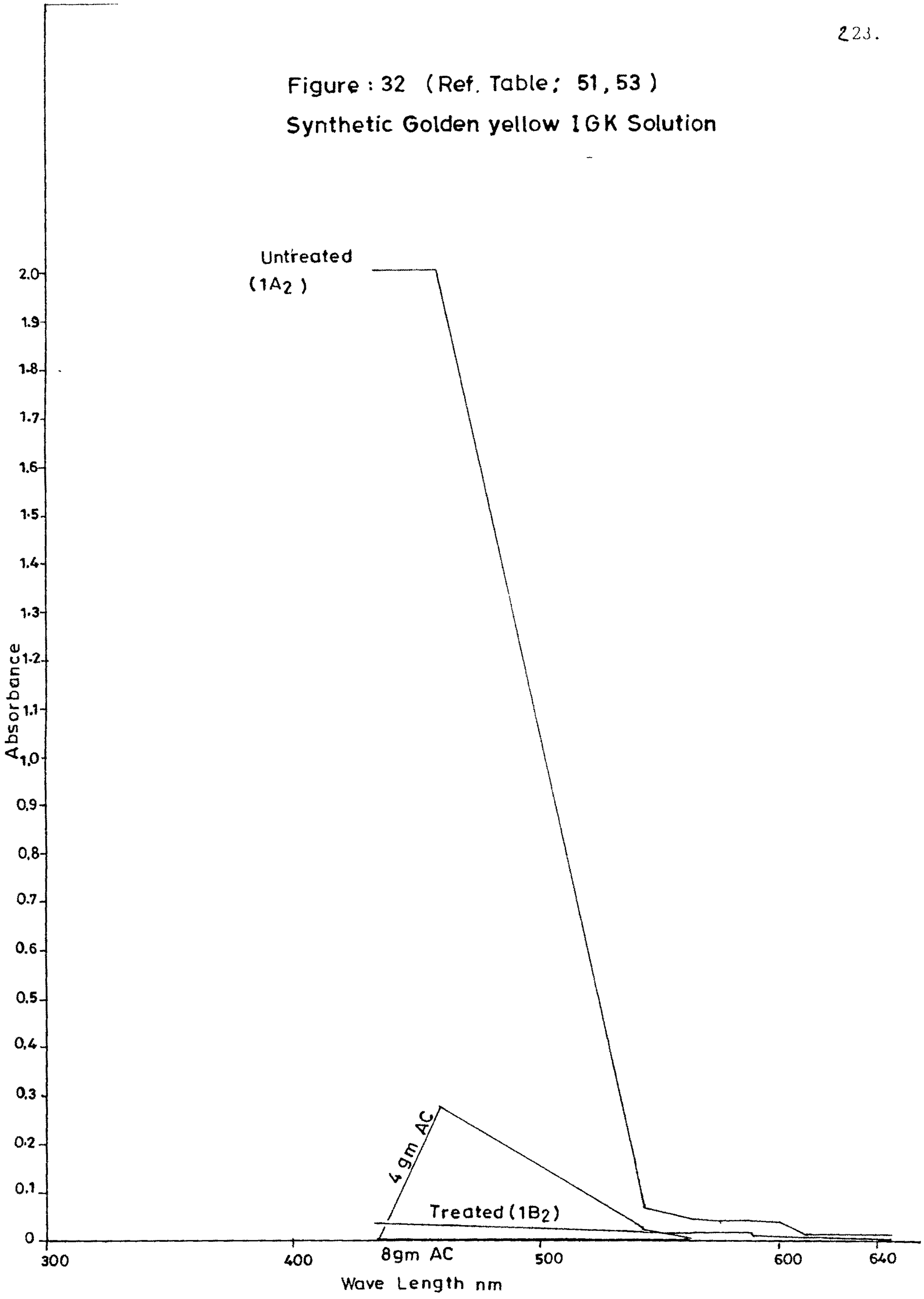


Figure: 33 (Ref. Table: 51,53)
Synthetic Golden yellow HR-Solution

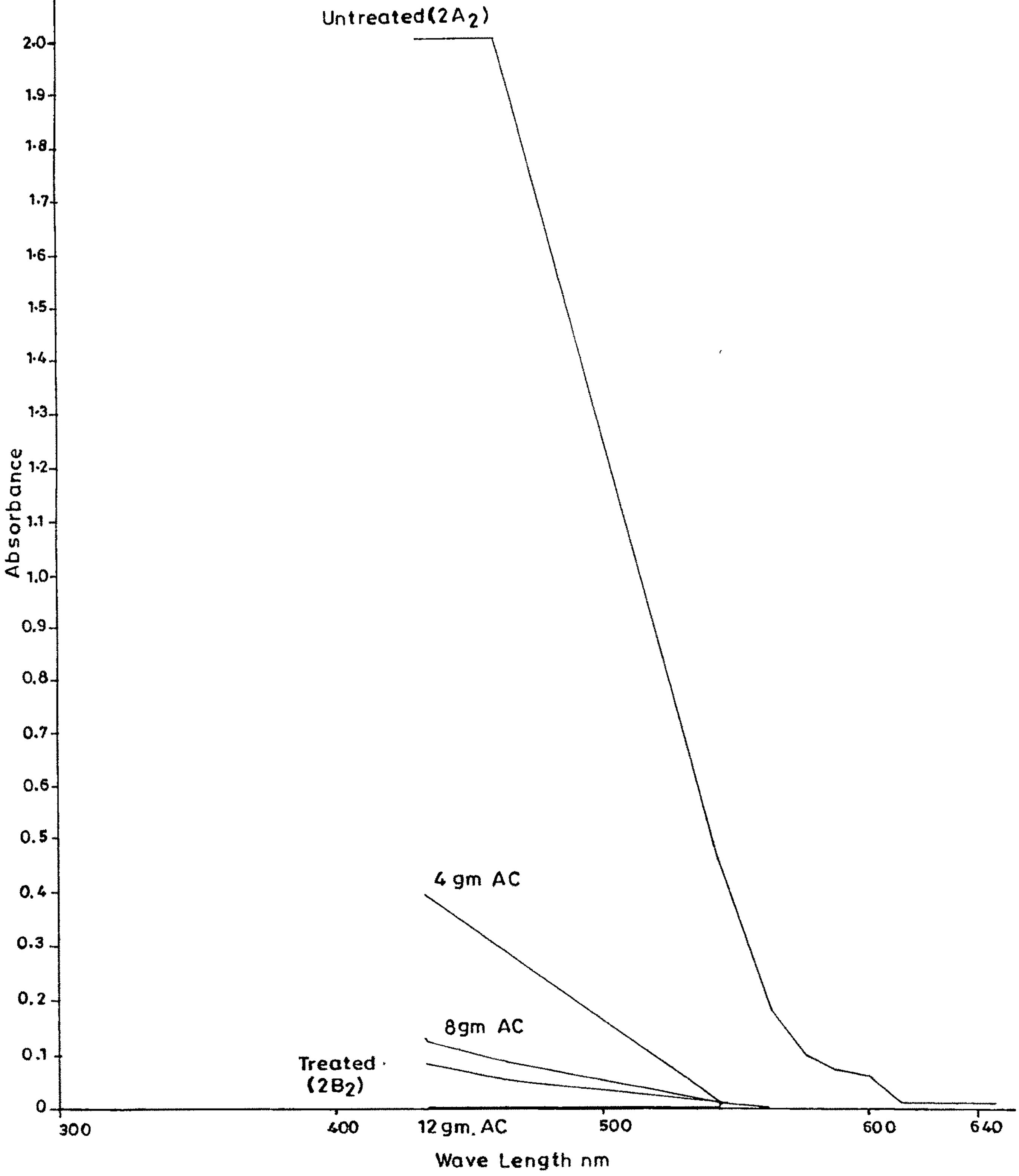
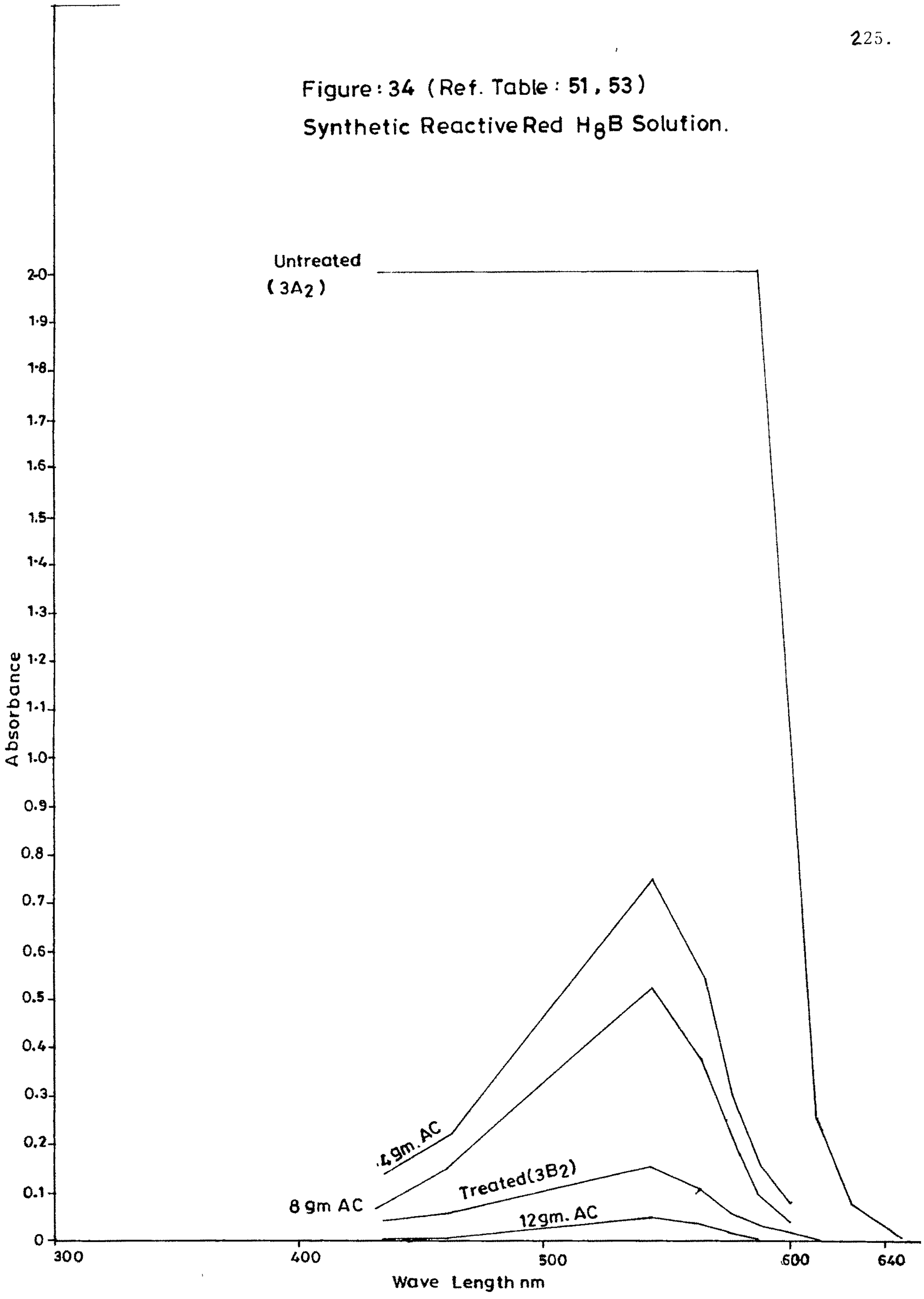


Figure: 34 (Ref. Table: 51, 53)
Synthetic Reactive Red H_8B Solution.



5. RESULTS AND DISCUSSION

Literature survey has revealed that number of researchers have tried different methods for the treatment of waste waters of dyes and dyes-intermediates. Many of these approaches have been outlined in the introduction part.

The strategy adopted in early studies is of flocculation by different flocculating agents [100-102].

Oxidation of dyes waste is very popular by different oxidizing agents like O_3, H_2O_2, Cl_2 etc. [103, 108-113]. Reducing agents are used to remove mainly the colour of azo dyes. However, both these methods are not effective on different classes of dyes. They have certain limitations. Cost factor is also quite high [131].

Electrochemical methods with different electrodes have been tried. It has given good results in the removal of colour from dyes waste [132-134]. However, they are also quite expensive on the large scale application for the countries where electricity is an expensive commodity.

Biodegradation has been tried with different variations but is not quite effective [114-117]. Some of the naphthalene derivatives are non-biodegradable [135]. EPA study has clearly indicated limitation of biodegradation for the removal of colour [118]. Another report of EPA also suggests that the adsorption on granular activated carbon (GAC) has also certain limitations in the removal of colour of waste waters [61, 105-107].

There are few references where long chain fatty amines are used as liquid ion-exchanger alone or in combination with other agents as flocculating agents [128, 136-138]. However, in most of these studies large quantity of solvents are used. The treatment is considered to be highly effective in the removal of colour.

The latest technology of reverse osmosis can be applied for the removal of colour from the dyes industry. Reverse osmosis has its own limitations [139, 140].

Overview of literature survey indicated that the removal of colour from dyes waste can only be effective by the combination of two or three different methods. Many of these methods are quite expensive. Recently there are certain reports on the removal of colour by using cheaper adsorption materials. However, these results are based on pure synthetic samples and may not hold good when applied to effluents of industry [102, 120, 141].

The treatement of effluent from dyes intermediate industry is most difficult due to non-biodegradability of naphthalene nucleus and difficulty in the removal of highly soluble coloured intermediates by adsorption. Looking to all these aspects in the present study different fatty amines were used as flocculating agents. The results have shown that Dimethyl Stearyl amine (B-DMS) is most effective (Table - 43, 45, 47, 48, 50) in the removal of colour from dyes as well as dyes-intermediate effluents. COD values are also effectively removed and pH is shifted towards neutral value. The flocks canbe separated easily.

Number of attempts were made to recover fatty amine B-DMS and recycle. A successful method has been developed for the recovery and recycle of fatty amine B-DMS.

The aqueous layer (small quantity) containing sodium salts of dye or dyes-intermediate can be evaporated to recover costly dye or intermediates or it can be incinerated . Due to small quantity of material the cost of incineration would be quite low.

The comparison of two sets of results where colour was removed by fatty amines and GAC, provided interesting information. GAC gives good results for synthetic samples (Table-53) but fails for the effluent having high dissolved solids.

The effluent after the removal of dyes contain dissolved solids-mainly NaCl, which can be disposed in a water body.

Photograph DP represents the coloured waste water before and after treatment with B-DMS.

Test Tube - 1	:	Untreated H-acid effluent.
2	:	Treated H-acid effluent with flocks, on filtration almost colourless filtrate is obtained.
3	:	Untreated effluent of Reactive Red M_5B.
4	:	Treated effluent of Reactive Red-M_5B with flocks. On filtration colourless effluent is obtained.
5	:	Untreated effluent of Reactive Red H_8B
6	:	Treated effluent of Reactive Red H_8B with flocks. On filtration colourless fitrate is obtained.

- DP -

Test Tube 1 : Untreated H-acid.

2 : Treated H-acid.

3 : Untreated Reactive Red M_5B

4 : Treated Reactive Red M_5B

5 : Untreated Reactive Red H_8B

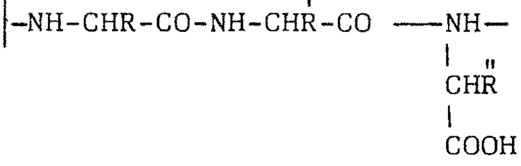
6 : Treated Reactive Red H_8B.

PART - II B

REMOVAL AND RECOVERY OF ORGANICS FROM EFFLUENT OF DETERGENT INDUSTRY

1. GENERAL

Detergents are surface active agents, developed to overcome the drawbacks of soap. The detergents have been developed by the German Scientists in the 1st world war period to allow fats to be utilised for other purposes [142]. Most prevalent hydrophobic group used in surfactant is the hydrocarbon radical having a total carbon atoms from 10 to 20 in straight chain or branched chain, and its main source is agriculture and petroleum. The most common hydrophilic groups are [143] :

Ionic	Sulfonate	$-SO_3^-$
	Sulfate	$-OSO_3^-$
	Carboxylate	$-CO_2^-$
	Quaternary Ammonium	$-R_3N^+$
Non ionic	$-O-CH_2-CH_2-O-CH_2-CH_2-O-$	Polyoxyethylene
	 $-\mathrm{NH-CHR-CO-NH-CHR-CO}-\underset{\substack{\vert\\ \mathrm{CHR}\\ \vert\\ \mathrm{COOH}}}{\mathrm{NH}}-$	Polypeptide

Detergents have been divided into following four main groups (1) Anionic (2) Cationic (3) nonionic (4) amphoteric.

Anionic surfactants are those which give negatively charged surfactant ions in aqueous solution e.g.

$RSO_3Na \rightarrow RSO_3^- + Na^+$

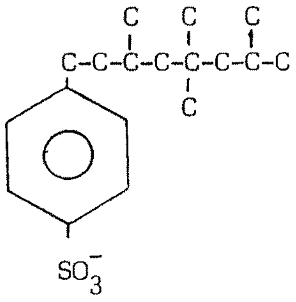
Cationic surfactants are those which give a positively charged surfactant ion in aqueous solution e.g.

$RN(CH_3)_3Cl \longrightarrow RN(CH_3)_3^+ + Cl^-$

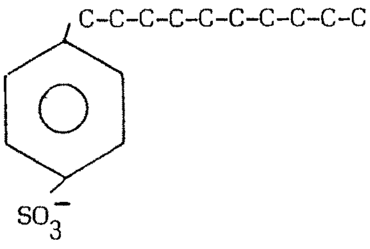
Quaternary ammonium
derivative.

Non ionic surfactant contains hydrophilic group which does not ionize apparently in aqueous solution [143].

The large group consist of anionics which are usually the Na-salts of organic sulfate or sulfonate as they are highly economical to be used [144]. During 1960s and 1970s the composition of detergents underwent rapid changes because of certain environmental considerations. The problem created by surfactants in sewage works, rivers and streams are the voluminous production of foam, the reduction in the rate of natural oxygenation and persistence of detergents in sewage pollution. Such effects were noticed in U.K., U.S.A. and Germany. In certain locks of canals in Germany, mountains of foam developed hiding ships passing into the locks. Foam contributes to unsure footing, unsightly conditions, wind can carry foam and creates nuisance in near by area. This was due to non biodegradable sodium dodecyl benzene sulfonate (DDB-Na). This resulted in the introduction of linear alkyl benzene sulfonate (LABS). Straight chain have little better detergency and slightly inferior foaming than branched chain material [142].



ABS



LABS

It is shown that enzymes do not attack branched chain readily because of steric hindrance of the branched molecule.

Commercially available detergents usually contain less than 30% by weight active detergent. Remaining 70% of the material consists of filler, water softner, fluorescent whitening agents etc. phosphate, present as Na-tripolyphosphate or tetra sodium polypyrophosphate, find its way into receiving waters and is utilized as nutrient by the algae to cause eutrophication. Arsenic in trace amount ranging upto maximum 70-80 ppm is introduced into detergent products as a constituent of the phosphate builder. This arsenic is in penta-valent form which is non toxic [145].

Derivatives of common starch were considered to be a promising phosphate substitute. However, it was found that when starch was modified to perform as detergent builder, it becomes non biodegradable [146].

The effect of synthetic detergents on water supply can be split into following two parts:

Direct effect	**Indirect effect**
1. Coagulation and sedimentation	1. Algae -Coagulation and sedimentation -filter clogging -Taste and odour -Toxicity -Colour and turbidity -Warm water -Corrosion
2. Toxicity and health hazard	2. Organism's growth
3. Corrosion	3. Eutrophication
4. Tastes and odours	
5. Chelating properties	

The water bodies can not aesthetically used for recreative purposes (swimming, fishing etc.) and population of fish also decreases due to eutrophication.

Deleterious effects of detergents have been reviewed by number of Researchers [147-149].

The toxicity to fish of anionic detergent in solution varies considerably according to the hardness of the water in which the fishes are treated. Trount and Goldfish are more susceptible to sodium lauryl sulphate (SLS) in hard water than soft water and the rate of adsorption of detergent is greater in hardwater [150].

Today over 700 surface active agents are manufactured. They are mainly used in soap-detergents. However, overall there are more than 450 different applications.

In USA alone the estimated production of surface active compounds in 1981 was 3.6 million tonnes and likely to reach 4.15 million tonnes in 1991. The total world production of soap detergents was 24.0 million tonnes in 1984 [151]. Based on this data what would be the production of such compounds in 1988 ?

The detailed aspects of anionic detergents would be reviewed as the study is mainly on anionic detergent.

ABS are the most widely used because of their excellent detergency, their low cost and the attractive physical properties of their formulations.

It has been reported by Sawyer and Bogan that removal of anionic detergents by conventional waste treatment is difficult.

Biological growth e.g. pure bacteria or activated sludge may also adsorb significant quantities of surfactant. Such adsorption may be the first step in biodegradation, but if it is not degraded significant amount may accumulate on the sludge. Structure of the hydrophobic group is a very important determinant of biodegradability. Biodegradation is promoted by increased hydrophobe linearity and deterred by hydrophobe branching perticularly by terminal quaternary branching. The nature of the hydrophilic group has only a minor influence on the biodegradability.

Increased distance between the sulfonate group and the far end of the hydrophobe group increased the speed of primary biodegradation of ABS. With 18 Carbon in chain unsaturated fatty acids are degraded more rapidly then are the 14, 16, and 18 carbon saturated fatty acids. The rate of degradation of the saturated fatty acids decreases with increasing chain length [143].

In India the drinkable water resource are meagre. The problems arising out of sodium tripoly-phosphate based detergents can be more serious as they affect the life of water body and make them useless for aesthetic purposes.

2. TREATMENT METHODS

Surfactants can be removed by precipitation, hydrolysis and oxidation. Precipitation can be in the form of Ca or Mg salts. Hydrolysis needs severe conditions like temperature and reagents. Biodegradation is rather biological hydrolysis which does not require more drastic conditions. In primary biodegradation, molecule is oxidized partly so that it does not exert its original characteristic properties while in ultimate biodegradation it is completely converted into stable CO_2 and water etc.

[143].

Cationic and anionic surfactants neutralize each other when present in same solution. The oppositely charged surfactant ions join each other to form water insoluble salt and if stoichio metrically equivalent quantities are present no surfactancy properties remain evident [143].

Fly ash is used to adsorb detergent as cheapest adsorbent [152]. In an aquatic environment however remanant concentration of LABS composition will be influenced by adsorption, flocculation and other important phenomena together with biodegradation [153]. Wayman reported that the adsorption of ABS on Clay increased with alkyl chain length [154]. Wool Charring waste was also used to adsorb surfactants. Alkaline media was more suitable for effluent containing cationic surfactant whereas anionic surfactant required acidic media.

It was found that in anaerobic conditions there was very little degradation of LABS or ABS [155]. The resistance of ABS to natural stream purification was destroyed by ozonation.

Pitter and Fuka suggested that the rate of degradation of LAB is slow and the solution after biodegradation contained biological resistant substances lacking the properties of anionic surfactants but still aromatic in nature. Hence methylene blue method should not be used to see ultimate biodegradability but COD should be used [156].

Svetlova had tried to burn the effluent from production of powdered detergent but faced problem of clogging nozzles due to oxidation product [157].

Na-DBS is degraded slowly by γ-rays 4.15 M rad/h and oil soluble material is formed during the degradation indicating that desulfonation of Na-DBS occurs [158].

Detergent manufacturing waste water having pH 9.6 to 9.8 is treated in four stage oxidation with hypochlorite in presence of $FeSO_4$ coagulant, then sedimentation using lime, followed by chlorine, removal by aeration or Na_2SO_3 and finally removal of chlorinated organics by adsorption on activated carbon [159]. 99% ABS can be removed from 5 to 100 ppm, at 10° to 60°C by chemical reaction with H_2O_2 in combination with metalic Catalyst [160-162].

For Dodecyl benzene sulfonate (DDBS) $FeCl_3$ is better coagulant than $Al_2(SO_4)_3$ in alkaline region, 85% of detergent was coagulated but high dose of coagulant was necessary and slurry was difficult to dewater. Here phosphate is not removed. Coagulation with $CaCl_2$ is more successful and can eliminate 95% of detergent, 80% of phosphate, 70% of COD and 75% BOD. Slurry is easy to dewater by filtration or centrifuging and no pH control required during coagulation. A disadvantage is the relative high cost of $CaCl_2$ [163].

Using electro-coagulation, anionic surfactants are removed. Fe electrode at 0.01 A/cm^2 d.c. flow, 0.8-1.0 gm/l were used. The anionic surfactant in waste water was decreased from 255 to 21 mg/l and all PO_4^{+3} were removed [164].

Water having ABS is mixed with solvent like benzene, Naptha or Kerosene. ABS collected at the interface of two layers. (Sulfonate portion in water and organic part in Solvent.) The organic layer was separeted containing ABS was treated with lime to precipitate the Ca-salt of ABS and is then filtered to recover solvent [165].

Na-DDBS can be removed by foaming with air after addition of $MgCl_2$, $CaCl_2$, $FeCl_3$, $Al_2(SO_4)_3$ or $ZnCl_2$ and separation of foam containing surfactant. Solution of 345 ppm Na-DBS and 0.1 gm $MgCl_2$ gave foam of 20,000 ppm DDBS and treated waste water containing 5 ppm DDBS, while 100 ppm DDBS in treated waste water without $MgCl_2$ [166].

Few Researchers have tried to separate foam and then live steam stream is passed to collapse the foam bubbles [167].

Detergents are also removed from industrial waste water by adding readily soluble alkali or alkali earth metal salts and separating the supernatant detergent containing layer. Thus adding 10 gm NaCl to 100 ml 5% detergent solution containing 3% surfactants at 65-70° results in complete separation within 20 minutes. After cooling the surfactant forms a gel on the surface [168].

Surfactants are removed from waste water by extraction with $CHCl_3$ at pH 2-3 and $CHCl_3$ waste water ratio of 1 : 10-20 by volume [169].

Phenol-formaldehyde weak base resin and many other resins are effective to remove DBS, ABS, LABS etc.. Thus resins remove pollutants and regeneration of resin helps to recover the pollutants without any chemical change to enable us to reuse it [170, 171].

ABS can be removed by weakly or strongly basic anion-exchange resin such as duolite A-7, A-30 B, A 101D, A-102 D. ABS and LABS can be removed by liquid cationic melamine-formaldehyde resin or polyamine modified urea - formaldehyde resin [172].

In review paper it is shown that foam separation, coagulation, adsorption on activated carbon and complexing and precipitation methods, are used to remove surfactants. The most economical method is complexing with quaternary ammonium salts followed by alum flocculation and final filtration [173].

The most economical method of treatment studies involved complexing the ABS with quaternary ammonium salt such as alkyl DIMETHYL BENZYL AMMONIUM CHLORIDE followed by coagulation with alum and final filtration. in some cases it may be advantageous to acidity the aqueous solution of anionic material to a pH value below 6.0 before extraction with the amine [174, 175].

Single stage extraction with a liquid Ion exchange material to remove ABS is developed, where LIX reagent is cationic high molecular weight fatty amines. In the treatment process, the waste water, 50% H_2SO_4 and LIX is mixed. LIX sorbs anionic ABS and form upper layer while lower layer is discharged, spent LIX is regenerated by stripping with 10% NaOH. Thus detergent concentration can be reduced to 1 ppm [176].

Ionic surfactants are removed from waste water by flocculation with addition of an opposite ionic surfactant in vertical and cylindrical agitator, then treated it to remove flocks. This is very quick treatment. Thus waste water containing 100 ppm Na-DDBS was treated with 100 ppm stearyl trimethyl ammonium chloride (112-03-8) and then sand filtered. The surfactant removal was 91.5% [177].

3. TREATMENT OF EFFLUENT OF SURFACTANT Industry Manufacturing LABS.

The scope of present study was limited to the treatment of waste water (effluent) of anionic surfactant manufacturing industry.

The review of literature indicates that number of methods are tried for the removal of surfactant from the effluent.

The two methods seem to be quite attractive. One of the method is using liquid ion - exchange method for the removal of anionic surfactant. In the second method quaternary ammonium salt is used as flocculating agent. [174, 175].

In the present study it was thought proper keeping with the work of previous chapter to use B-DMS as flocculant. The detail of above Japanese patent is scanty.

It was planned to use tertiary amine instead of quaternary ammonium salt. Effluent was collected from M/s. Whitco Ltd., Halol, which is manufacturing synthetic detergents.

The number of experiments were carried out and the results are highly encouraging.

3.1 Procedure

Analysis of effluent sample:

Appearance :	Soapy liquid, without suspended solids.
pH :	2.2
COD :	9750 mg/l.

3.2 Treatment Methodology

To the acidic effluent B-DMS was added stirred for 15 minutes and filtered to get treated effluent.

The quantity of B-DMS was varied to achieve stoichiometric amount. When the stoichiometric amount of B-DMS was reacted, the best results were obtained.

Quantity of B-DMS and waste water (COD 9750 mg/l, pH - 2.2) taken for the treatment are given in Table - 54.

TABLE - 54

Treatment of detergent waste water with B-DMS.

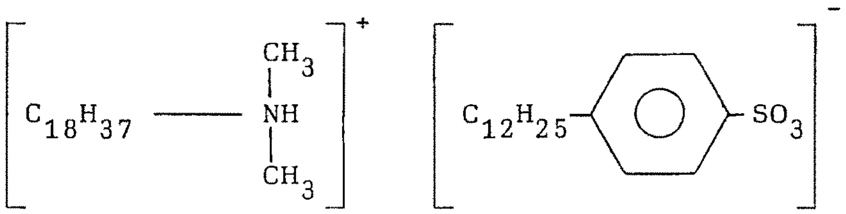
Sr. No.	Influent Quantity ml	B-DMS added g	COD of Effluent mg/l	Appearance of effluent
01.	50	0.14	-	Soapy liquid *
02.	50	0.21	576	Clear filterate like water.
03.	50	0.28	-	Soapy liquid*
04.	50	0.35	-	Soapy liquid *

* COD was not measured as it was evident from visual observation that surfactant is not removed.

4. RESULTS AND DISCUSSION

Reference to table - 54, shows that experiment number 2 gives the best results. The removal of surfactant is more than 94%.

Over and above the removal of organics, the flocks of ampholytic surfactant or the mixed surfactant separates out. It is easy to remove and recover. This anionic-Cationic surfactant or mixed surfactant can be used directly for its surface active properties. The structure can be represented as under:



Detail study with variation in concentration of surfactant and different type of anionic surfactant would make this procedure more fruitful. However, it is proposed to takeup this study further and exploit it to the fullest extent.

PART - II C

REMOVAL OF MERCURY FROM EFFLUENT OF CHLOR-ALKALI INDUSTRY

1. GENERAL

Mercury is one of the most toxic of all heavy metals. Mercury contamination of environment has received considerable international attention recently because of its inherent toxicity to living forms. Mercury is a naturally occuring element that is normally found in minerals, rocks, soil, water, air, plant and animals. The ubiquitous nature of mercury is due, in large part to the high vapour pressure of the element and its compounds. The toxicity of Hg is also attributed mainly to its high affinity for sulfur containing compounds [178]. The Bureau of the U.S. Public Health Service has tentatively proposed a standard of 0.005 ppm for Hg in drinking water.

1.1 Epidemics

Mercury present in environment was never a threat to human health, however man's activities have made it one of the most dreaded environment pollutants. The last three decades have seen many hazards caused by mercury. The most memorable is the Minamata episode which occured in Japan. An unrecognized disease of the central nervous system appeared in "Minamata" in southern Japan in 1953. Between 1953-1970 more than 2000 cases of poisoining and 121 cases of severe neurological disorder were reported. The outbreak appeared to be restricted to a limited zone along the seashore of Minamata Bay where dead and dying fish had been observed floating in the water, due to methyl mercury (MeHg) poisoining. The average concentration of mercury investigated was about 10 mg/kg of fish weight. During 1965 to 1974 cases of disease similar to Minamata were reported from people residing along the Agano River in Niigata. These cases were also found to be due to consumption of Hg contaminated fish [179].

A serious outbreak of organomercury poisoning due to consumption of treated seed grain occured in Iraq in late 1971 and early 1972. The ingestion of treated wheat caused death and permanent disability and this was associated with alkyl mercurial compounds. In a few instances people were poisoned by eating meat of domestic animals which were fed with the treated grain. Cases of mercury poisoining has also been reported from Canada, New Maxico, and Pakistan [179]. Decreasing population of wild birds species in Sweden raised another alarm.

In India such mercury episode is not known so far. Some surveys conducted in Bombay, Calcutta and Kanpur showed presence of Hg in water-sediments and fish in rivers [179].

1.2 Source of Mercury Pollution, consumption and its effects

Mercury can be divided in to two major categories of organic and inorganic compounds. The most common forms of inorganic mercury are mercurous ion (Hg^{+}) or mercuric ion (Hg^{++}). Organic mercury includes chemical compounds which contain Carbon atom that are covalently bound to a mercury atom [180]. Inorganic or elemental mercury typically produces syndrome of dermatitis, gingivitis, stomatitis and tremor together with dysfunction of the central nervous system. Poisoning by organic compounds of mercury produce an almost neurological illness. Organic mercury compounds are absorbed by skin and more efficiently by respiratory and gastro intestinal tracts. Blood and hair are indicators of mercury exposure.

The values reported of the Hg content of ocean waters also vary greatly and even in fuels it varies between 0.03 to 3 ppb [181]. Normally rivers, lakes and oceans' sediments contain below 70-100 ppb mercury. Industrial activities are mainly responsible for discharge of mercury into environment. Such activities are manufacture of electrical apparatus, chlorine, caustic soda, industrial control instruments, paints, pharmaceuticals, cosmetics, slimicides for pulp-paper industries, agricultural fungicides, and dental amalgam etc. In addition large quantities of mercury are lost to the environment through burning or other utilization of fossil fuels as well as through the smelting of ores to recover metals such as copper, lead and zinc. The mercury content in sewage is the result of all the incidental uses of mercury containing compounds such as water based paints, paper products, cosmetics, broken thermometers, discarded pharmadeuticals, house-hold and laundry disinfectants and runoff of mercury lawn and garden fungicides. The Hg content in caustic lye varies from 5 to 25 mg/l. This goes to the users and finally finds its way out as effluent.

Maximum possible release of mercury into environment, because of solid, liquid and gaseous fuel consumption all over the world has been estimated to be 3100 Tonnes/year [180]. Early estimates of maximum possible release of mercury into the environment from smelting of Copper, Lead and Zinc ores has been about 30,000 Tonnes/year [180]. However the strict regulations of pollution control boards and economics of recovery has changed this aspect and now more and more amount of mercury is being recovered from the smelters.

The total world production of mercury and its compounds are shown as under (1984) [179].

Activity	Amount (Tonnes/year)
Agricultural use	370
Amalgamation	25
Catalyst manufacture	407
Dental	423
Electrical equipment	2578
Chloralkali plant	2908
Laboratory use	290
Industrial control	980
Paints	1343
Pharmaceutical, paper	1561
Total world production	10885

It has been reported that Hg(II) is adsorbed by oxides such as α- SiO_2, α-Al_2O_3 and δ- MnO_2 and co-precipitated with lanthanum (III) hydroxide [182].

1.3 Methyl mercury

Any kind of mercury released into environment can be directly or indirectly converted into mercuric ion for chemical or biological methyl transfer reaction. Methyl mercury has a high affinity for organic material and is retained by organisms efficiently. Low concentration of mercury favours formation of dimethyl mercury and high mercury concentration favours monomethyl mercury. Moreover neutral and alkaline environment favours the formation of dimethyl mercury which readily decomposes to monomethyl mercury in mildly acidic environment [183]. Aquatic organisms are able to concentrate MeHg either directly from water through skin or gill membrane or food chain, thus it enters into food chain as a result of bio-accumulation. This bio-accumulation of mercury in organisms at the top of the food chain results in high level of mercury and endanger the life [184].

The mercury deposition in sediments may continue to release Me-Hg for a very long time unless they are removed or inactivated. Methanobacterium convert insoluble Hg into soluble Me-Hg in aerobic and anaerobic conditions.

$$Hg^{++} + 2R\text{-}CH_3 \longrightarrow CH_3\ Hg\ CH_3 \longrightarrow CH_3\ Hg^{+}$$

$$Hg^{++} + R\text{-}CH_3 \longrightarrow CH_3\ Hg^{+} \xrightarrow[R\text{-}CH_3]{} CH_3\ \ Hg\ \ CH_3$$

Mercury concentration greater than 10-20 ppb can be toxic to aquatic organism, sublethal level are also absorbed and biologically magnified. Since mercurials are atleast one thousand times more soluble in lipids than in water they are easily extracted from water or food by contact with the lipid portions of the tissues [185]. It was established that rainbow trount exposed to 60 ppb of ethyl mercury for one hour a day over 10 days contained Hg levels of 4000 & 17,300 ppb in their muscle and kidney tissues and 10 ppm of $HgCl_2$ killed rainbow trout in only 15 minutes [180]. The concentration of Hg^{+2} from $HgCl_2$ that were required to kill stickle backs and Guppies have been found to be 0.008 and 0.02 mg/l respectively [186].

The acute toxic action of Hg results from damage to the gill tissues and/or the formation of a film of coagulated mucus which prevent the normal movement of the gill filaments and hence interrupt gas exchange and hence fish die from asphyxication. It also inhibits uptake of sodium through gill which is very harmful to fish. Relative toxicity of Hg to organisms varies widely with the species, its life stage and state of adaptation, of animals acclimation to the environmental conditions [180].

Experimental studies and field observation have shown that biological methylation rate and mercury movement in environment is influenced by following factors.

1. General microbial activity.
2. Temperature (Increase in temperature accelerates biological methylation rate and also at elevated temperature solubility of all forms of mercury increases).
3. pH.
4. Redox potential.
5. Concentration of inorganic mercury.
6. Biochemical availability of inorganic mercury.
7. Presence of naturally occuring chelating agents [187].

Several methods have been suggested for effective arresting of methylation rate.

1. Removal of Hg deposits by dredging.
2. Conversion of mercury to mercury sulfide.
3. Binding of mercury to inorganic materials e.g. Silica materials.
4. Raising pH of a system so that biological methylation process produce volatile methyl mercury rather than mono methyl mercury [179].

More Me-Hg uptake by fish was found using mercuric chloride than mercuric sulfide as a source of Hg [188].

1.4 Chlor-Alkali Industries

In Chlor-alkali industry Hg acts as a flowing cathode and graphite is used as anode. In India in 1976 for the production of about 400,000 tonnes of caustic soda, about 90,800 kg of mercury was lost when the 80 percent capacity was utilized. This quantity is let out either to air or to water [189]. In short in India Chlor-alkali industry has 0.34 kg/ton of caustic, loss of Hg occurs in solid, liquid or gaseous wastes letout into environment. There is also physical losses due to spillage. More than 80,000 tons of mercury was consumed in U.S. last century and major contribution is from Chloralkali industries having 0.1 kg per ton of chlorine production [190].

In Chlor-alkali plants soluble and insoluble mercury, present in brine sludge is removed by washing the sludge which result into effluent form. Liquid waste are from [191],

(a) Call house effluent resulting from floor washings, and box cleaning, primary cleaning of the cell, graphite sludge, and Hg-butter washings.
(b) Effluent from Cl_2/HCl plant.
(c) Effluent from brine house.

After serious episodes, in 1973, Japanese Government decided to abolish by March 1978 all Chlor-alkali plants using Hg-cells. This gave real impetus to development of the membrane cell process. World wide there are about 573 chlorine plants with total capacity of over 40 million metric ton per annum [192]. In India there are about 36 chlorine manufacturing plants. World wide a little over half the production is accounted by mercury cathode cells.

The European Commission for Social Welfare has accepted the target for reducing Hg pollution by 1987 the mercury in effluent per Tonne of caustic soda produced should be brought down to 0.625 gm. The Alkali Manufacturers Association of India has set a target of 350 gm Hg per ton of caustic soda which is too high and there is no improvement to reduce this loss of Hg into environment as per the statement of Mineral and Metal Trading Corporation India, based on purchase-sell data. Mercury is not available in India. It is imported from countries like Spain, U.S.A., Yugoslavia, U.S.S.R. and China [193]. The modern technology replaces Hg-cell by membrane cell.

1.5 Treatment for Mercury removal

Abatement of mercury pollution from Chlor-alkali industry can be done by :

(I) Adopting the technology which can lessen Hg discharge e.g. use of Titanium substrate Insoluble Anode (TSIA) in place of graphite anode. This TSIA has brought revolutionary change in Hg pollution control [194].

(II) Adopting the technology which does not employ mercury at all and such methods are Diaphragm process and membrane process.

(III) Treatment of waste water before its discharge.

Several methods have been suggested and few of them are successfully applied in the chlor-alkali industries. Available methods are described as under.

1.5.1 Electrolysis :

The mercury containing waste waters can be electrolyzed in the presence of Na_2S, K_2S or thiourea to precipitate the metal as the sulfide.

1.5.2 Magnetic ferrite process (Nippon electric Japan)

1.5.3 Carbon Treatment/Adsorption process :

Several adsorbent like activated Carbon, clays, silica gel, and microbial cells have been employed for the removal of Hg or its recovery. Depending on the origin of the clay monovalent ions like Na^+ and K^+ are set free and an equivalent quantity of Hg^{+2} is adsorbed. Agregation of microbial cells with a chemical polymer constitutes a good adsorbing material for waste water treatment.

1.5.4 Reduction of mercury salts :

Mercuric salts are easily reducible and thus converted into solid metallic form that settle down and can be purified by distillation. Several types of reducing agents are used to convert ionic Hg to metallic Hg, e.g. Hydrazine, Sodium borohydride [191,195].

1.5.5 Precipitation as Hg-Sulfur compounds :

This is an old and common method used when the concentration of mercury in liquid is fairly high (more than 100 ppm). Insoluble precipitates are further treated to recover Hg or safely dumpped [196,197].

FMC's (Division of American Viscose Corporation) clean up route includes precipitation of Hg by Na_2S and then HgS is separated and treated with Cl_2 + NaOH (Na-hypochlorite) to form soluble Hg and recycled in the sytem.

$$HgS + 4(OCl)^- \longrightarrow HgCl_4^= + SO_4^-$$

Mercury bearing waste water is adjusted to pH 3.5 and passed through column of ferrous sulfide, where H_2S is liberated which reacts with mercury to form HgS precipitates on the surface of the ferrous sulphide bed. Thus 10 ppm Hg solution at 3.5 pH was passed thorugh 350 gm ferrous sulfide column at 2 lt/hr rate and effluent came out had pH 6.0 and Hg 0.01 ppm [198].

1.5.6 Ion-Exchange methods :

This method utilizes the unique property of mercury to exist an anionic complex $HgCl_4$ which can be absorbed onto a basic anion exchanger. Amino group in natural and synthetic polymers are effective binding sites for mercuric chloride e.g. polyamines derived from cellulose or dialdehyde starch etc. [199]. In case of resins such as ALM-125 and 525 (produced by Nippon soda co.) the presence of chloride ions decreased the rate and quantity of Hg (II) removal from solution [200].

Polyethylenimine modified wool (PEI-wool) has a substantially greater ability to absorb Hg^{+2} than unmodified keratin [201]. At concentration in the range of 3.1 - 6.0 ppm, 100 mg of N-(2-Aminoethyl) aminodeoxy cellulose cotton (AEAC) removed about 90% of the Hg present in 200 ml of solution [202].

Ion exchange is versatile and extremely useful method where the quantity of Hg is reduced to acceptable levels. Different types of cation exchangers are used for Hg^{+2} and they are ' Dowex-1-x8 Dowex-50-x8, xerogel of hydrodipolysiloxane, IMA-TMR process starch xanthate, polyvinyl benzyl trimethyl ammonium chloride and polyethylamine. The process cost is high due to the resin cost, its availability as well as acid-alkali cost needed for neutralization.

Apart from the above synthetic resins, other natural resins like hair, wool, feather etc. are also used. They are composed of largely of keratins that are highly soluble protein of albuminoid type. They are soluble in strong alkali and acids forming polypeptides, keratins contain exchangeable groups like -CONH, and -SH which are responsible for their weak ion-exchange or chelate forming properties with Hg ions. Being amphoteric in nature hair can remove both cationic and anionic forms of mercury [195]. The maximum ion-exchange capacity of treated hair was 41.6 mg Hg/g of hair where as that of wool was 50.5 mg Hg^{++}/g of wool [203].

I.E..method meets better selection criteria than precipitation method but its performance is seriously influenced by fluctuation in pH, temperature, concentration of SO_4^{--}, ClO_3^-, and Cl^- . ions. It is possible to regenerate resing with a liquid that can be safely reintroduced into the electrolysis process without any detrimental effect. Resin should not contain nitrogen compounds otherwise it forms explosive nitrogen trichloride in electrolysis process which is a risk.

In Akzo Imac TMR resin process, resin is polymeric mercapton in which thiol groups are attached to a chemically and mechanically highly inert matrix. Even in saturated brine this resin can compete successfully with the very stable $HgCl_4^{-2}$ complex.

$$2RSH + Hg(Cl)_4^{-2} \longrightarrow RS-Hg-SR + 2H^+ + 4Cl^{--}$$

Capacity of this resin is 240 gm Hg/lt. of resin. Akzo Imac TMR process can produce effluent having 25 ppb Hg.

1.5.7 Liquid-Liquid Extraction :

High molelcular weight amines (both aliphatic and aromatic) efficiently remove mercury from brine solution in both acidic and alkaline ranges. The amines are regenerated by stripping the mercury with an aqueous solution of nitric acid [195]. The quaternary amines are specially more attractive because of their ability to extract Hg from acidic as well alkaline solution. Following amines are used [204].

1.	Primene JM-T	Primary amine (C_{18-22})
2.	Primene 81-R	Primary amine (C_{12-14})
3.	Amberlite LA-1 (N-dodecenyl trialikyl methylamine)	Secondary amine
4.	Alamine 336-S	Tertiary amine
5.	Aliquat 336-S	Quaternary amine chloride.

The solvent extraction method by using long chain fatty amines would be quite interesting as the recovery of solvent and mercury is possible and process can be continuous. The drawback of the procedure is high cost of operation.

The mechanism of Hg extraction with quaternary amine is as below :

$$Hg^{+2} + 4X^{-} \rightleftharpoons (Hg\ X_4)^{-2}$$

$$2(R_4NX)_o + (HgX_4)^{-2}_a \rightleftharpoons [(R_4N)_2\ HgX_4)]_o + 2X^{-}_a$$

where X= iodide or bromide; o = organic phase

a = aqueous phase; R_4NX = Quaternary amine chloride.

The quaternary amine, its salt with anionic helo complex of Hg are essentially insoluble in aqueous phase but highly soluble in organic solvent.

2. EXPERIMENTAL : Analysis of Hg in effluent.

2.1 Sampling

Four grab effluent samples were collected from M/s. Gujarat Alkalies and Chemical Ltd., Baroda, a large size caustic soda plant, based on Hg electrode. Samples were preserved with conc. HNO_3 as per the standard methods. Synthetic samples were also prepared from $HgCl_2$ (99% pure) as described in standard methods [13].

2.2 Experiments

In most of the cases, 100 ml waste water (influent) was taken, and pH was adjusted to 2 using HCl or H_2SO_4. To this sample sodium chloride was added if required to increase total dissolved solids. Then variable quantity of B-DMS was added and stirred the mixture for about 10 minutes with the help of magnetic stirrer. Thereafter treated liquid was filtered through Whatman-42 filter paper. This filtrate was monitored for Hg content, with the help of Mercury Analyser MA 5800 (Electronic Corporation of India Ltd.)

2.3 Analysis

Mercury Analyser MA 5800 is cold vapour atomic absorption spectrophotometer based on the principle that Hg vapour (atoms) absorbs resonance radiation at 253.7 nm. The analyser consists of a low pressure

Hg lamp emitting the 253.7 nm line, an absorption cell, a filter and detector, etc. Mercury measuring range (in solution) of this analyser is 20-200 ng absolute and sensitivity 3 ng absolute for 1% absorbance.

This technique is based on the absorption of UV radiation by Hg atoms, all substances which absorb UV radiation will decrease the transmittance and cause positive bias. Vapour of organics like alcohols, ketones, ester acids and water will also absorb UV radiation and hence will interfere seriously. Absorbance due to these substances is known as non specific absorbance.

Pretreatment to sample should ensure that organic vapours will not be released during reduction-aeration procedure. System of analyser is as under :

$$\text{Air} \longrightarrow R_1 \longrightarrow R_2 \longrightarrow R_3 \longrightarrow R_4 \longrightarrow \text{Absorption cell} \longrightarrow R_5$$

R_1 and R_5 : are the scrubbers filled with 20 ml 1% w/v $KMnO_4$ in 10% H_2SO_4.

R_2 : Reactor Hg vapour generator.

R_3 : Scrubber filled with 4 ml of 20% w/v NaOH.

R_4 : Scrubber filled with 4 ml (1+1) H_2SO_4.

Trap R_3 and R_4 will remove the acid and water vapour respectively and hence minimize non specific absorbance.

However to minimize further such nonspecific absorbance trap R_4 was replaced by a trap containing 4 ml 1% $KMnO_4$ in (1+1) H_2SO_4.

Samples were also boiled by adding 2 ml of conce. HNO_3 to destroy organics if any present in the sample, before analysis, as pretreatment. Finally in most of the cases samples were diluted to bring the Hg content in range of analyser, using double distilled water. Samples were analysed as per the method given in the operation manual of the Analyser using $SnCl_2$ as reducing agent. Blank reading with distilled water was also taken into consideration in calculations.

All the glasswares were cleaned with HNO_3 as described in standard methods.

The effect of filteration on the Hg analysis was evaluated by analysing the Hg content before and after the filtration. The results indicated that it does not affect the content of Hg to any appreciable amount.

2.4 Removal of Mercury from the effluent.

Literature survey indicated that liquid ion exchanger or solvent extraction by using high molecular weight fattyamines gives better removal of mercury from the effluent. The quaternary ammonium salt exhibits maximum efficiency. Ion exchange resins also are lately preferred for the removal of mercury from the effluent though quality of the influent and the load are very important factor in this process. Both these processes are very expensive.

In present work the efficiency of B-DMS has been evaluated for the removal of organics, and it is found highly efficient for the treatment of effluent hence it was proposed to evaluate the efficiency of this tertiary fatty amine for the removal of mercury as a flocculant without using solvent.

The study was divided in two parts, (1) Removal of mercury from the effluent of chloralkali industries, and (2) Removal of mercury from the synthetic samples.

The purpose of two sets of study was two fold. It would establish the efficiency of tertiary fatty amine B-DMS as flocculant for both the systems and confirm the analytical procedure adopted in the present study.

2.4.1 The results of effluent are recorded in Table - 55 and 56. In both the experiments pH was adjusted to 2 either by H_2SO_4 or HCl and varied quantity of flocculant was tried. The effect of NaCl as dissolved solid was evaluated as in the previous study it was found that, it increase the efficiency of B-DMS as pollutant removal.

The reference to Table - 55 and 56 shows the overall efficiency of B-DMS. The extent of removal of Hg ranges from 68% to 91%. The experiments also indicate that it is not necessary to add NaCl to increase the efficiency of B-DMS as the effluent does contain dissolved salts.

The variation of quantity of B-DMS between 1 to 3 drops seems to be the maximum requirement. The efficiency varies 60% to 90%. It is necessary to adjust pH 2 also. The pH of the effluent as such is quite conductive for the efficiency of B-DMS for the removal of Hg, from the effluent.

The number of these experiments suggest that B-DMS is quite effective even when concentration of Hg is quite low (4-5 ppm) in the effluent.

2.4.2 Synthetic samples were prepared and experiments were carried out with these samples. The solution and measurement showed little variation in the analysis. The calculation indicated the 5 ppm value, whereas active analysis showed 4.15 ppm value. This was attributed to the impurity of $HgCl_2$.

The data of the treatment of synthetic samples are recorded in Table - 57. The experiments indicate that very small amount (mg) ofB-DMS is required to have good efficiency. Sodium chloride was added to obtain better flocculating effects. The results are quite comparable with the results of effluent (Table - 55 and 56).

TABLE - 55

Treatment of 100 ml waste waters with B-DMS at 2 pH

Experiment No.	Nacl added g	B-DMS added g	Hg in Influent mg/l	Hg in Effluent mg/l	% Hg removal
01.	-	-	-	1.25*	-
02.	-	0.13	1.25	0.4	68
03.	-	0.26	1.25	0.3	76
04.	-	-	-	3.73*	-
05.	-	0.13	3.73	0.62	83.4
06	-	0.26	3.73	0.75	79.9
07.	-	0.39	3.73	1.05	71.9
08.	-	0.52	3.73	1.24	66.8
09.	4.0	-	-	4.12*	-
10.	4.0	0.26	4.12	0.79	80.9
11.	4.0	0.39	4.12	0.79	80.9
12.	4.0	0.52	4.12	0.54	86.9
13.	-	0.26	4.12	0.37	91.0

* Amount of Hg untreated sample (influent).

TABLE - 56

Treatment of 100 ml waste water with B-DMS at 2 pH.

Experiment No.	B-DMS added g	Hg in Influent mg/l	Hg in Effluent mg/l	% Hg removal
01.	-	-	2.07*	-
02.	0.026	2.07	0.5	75.9
03.	0.052	2.07	0.79	61.9
04.	0.052	2.07	0.87	58.0
05.	0.078	2.07	0.54	74.0
06.	-	-	2.67*	-
07.	0.026	2.67	0.95	64.5
08.	0.052	2.67	0.8	70.0
09.	0.052	2.67	0.83	69.0
10.	0.078	2.67	0.67	75.0

* Amount of Hg in untreated sample.

TABLE - 57

Treatment of 100 ml Synthetic sample with B-DMS at 2 pH.

Experiment No	Nacl added g	B-DMS added g	Hg in Influent mg/l	Hg in Effluent mg/l	% Hg removal
01. *	2	0.026	-	0.003	-
02. *	2	0.052	-	0.004	-
03.	2	-	-	4.15	-
04.	2	0.026	4.15	1.15	72.3
05.	2	0.026	4.15	1.15	72.3
06.	2	0.052	4.15	1.25	69.9
07.	2	0.052	4.15	1.45	65.0

* 100 ml tap water was taken instead of 100 ml synthetic sample to know the Hg content in B-DMS if any.

To evaluate the efficiency of B-DMS with changing concentration of Hg, experiments were carried out with different dilution. Table-58 represents the data. The concentration of Hg was about 0.3 to 0.4 ppm. The results indicate that the efficiency of B-DMS is quite good even with decreased concentration (10 times) of pollutant.

The standard of Hg in milligram, for disposal, is much lower. It was thought to try repeated treatment strategy to evaluate the effect of B-DMS on the removal of Hg.

Two different concentrations were tried and overall three times treatment was given and the resultant effluent was analyzed.

2.5 Results and Discussion

The results (Table-59) indicate that with four times treatment, the concentration changes from 4.33 ppm to 0.05 ppm and from 0.36 ppm to 0.025 ppm.

These results indicate that the efficiency of B-DMS does not change appreciably, eventhough concentration of Hg, goes to very low level.

However, in the present experiments, the Indian limit for pollution control i.e. 0.01 ppm could not be achieved by the treatment of B-DMS of effluent.

It is known that, no single treatment methodology has shown such efficiency. Hence combination of another treatment methodology (e.g. activated carbon) can be quite effective for achieving the required limit of Hg in the final effluent.

These experiments have also brought out the universality of reagent B-DMS for the removal of organic and inorganic pollutants from effluents.

TABLE - 58

Treatment of 100 ml diluted Synthetic samples with B-DMS at 2 pH.

Experiment No	Nacl added g	B-DMS added g	Hg in Influent mg/l	Hg in Effluent mg/l	% Hg removal
1.	2	0.026	0.38	0.132	65.2
2. *	8	0.026	0.38	0.174	54.3
3.	2	0.026	0.277	0.045	83.8
4.	2	0.026	0.277	0.06	78.3
5. *	8	0.026	0.277	0.091	67.2

* Influent quantity taken for the treatment was 400 ml.

TABLE - 59

Repeated treatment of treated effluent with B-DMS.

Experiment No.	Influent quantity ml	NaCl added g	B-DMS added g	Hg in influent mg/l	Hg in effluent mg/l	% Hg removal
01	400	8	0.104	4.33	2.18	49.6
02.	300 (Filtrate of Expt. 1)	-	0.078	2.18	0.93	57.3
03.	200 (Filtrate of Expt. 2)	-	0.052	0.93	0.17	81.7*
04.	100 (Filtrate of Expt. 3)	-	0.026	0.17	0.05	70.58*
05.	400	8	0.104	0.36	0.097	73.0*
06.	300 (Filtrate of Expt. 5)	-	0.078	0.097	0.046	52.5*
07.	200 (Filtrate of Expt. 6)	-	0.052	0.046	0.033	28.2*
08.	100 (Filtrate of Expt. 7)	-	0.026	0.033	0.025	24.2*

* Filtrate was not diluted to analyse Hg content.