CHAPTER 29

THE PULP, PAPER AND WOOD INDUSTRY

CHARACTERISTICS OF THE WASTE WATER

The basic raw materials for this industry are pine, spruce, poplar, beech, birch, aspen and other types of wood. Sometimes straws are processed, but for the manufacture of high quality paper, wood cellulose pulp alone is used. For the manufacture of lower qualility paper, waste paper can also be used in addition to pulp.

The industry included the manufacture of 1) ground wood, which is produced from spruce and aspen, 2) sulphite pulp, which is mainly produced from spruce by a sulphite cooking process, 3) the manufacture of sulphate pulp, which involves cooking with a solution of caustic soda and sodium sulphate in the ratio 4:1, 4) paper and 5) hardboard.

Table 29.1 gives characteristic analyses for the various processes.

TABLE 29.1

Analyses from the paper and wood industry (mg/l)

Waste water from	Paper manufacturing	Hardboard manufacturing	Sulphite liquor	Cellulose manufacturing
Total dry matter	600-2000	400-1500	abt. 100,000	3000-5000
Suspended matter	250-1000	100-500	1000-2000	2000-3500
BOD_5	100-250	100-200	20,000-30,000	500-1500
COD	600-1000	300-500	abt. 150,000	2000-4500
pH	6-8	6-6,5	2-3	7-9

Bleached craft-mill effluents are toxic to fish and other aquatic life.

Present information suggests that unsaturated fatty acids, resin acids and other wood extracts make up the bulk of the toxic substances (Dass et al., 1969).

As seen from the analytical data the waste water from these industries is heavily polluted. The waste water from the manufacture of sulphite and sulphate pulp, in particular, causes serious pollution problems.

The manufacture of sulphite and sulphate pulp

The sulphite and sulphate liquor is one of the most concentrated of all industrial waste (Hoesch, 1959). Assuming a yield of about 45% of completely dried cellulose, the sulphite waste liquor contains, per ton of finished product, more than 600 kg of lignin sulphonic acid, more than 300 kg of carbohydrates, about 50 kg of albuminous substances, about 75 kg of resinous substances, more than 200 kg of sulphuric acid and approximately 3 kg of potassium salts.

Table 29.2 gives the composition of the sulphite liquor. The BOD_5 is unusually high (Gaydy, 1962), (see also Table 29.1). The pH is about 3.0.

TABLE 29.2

Composition of sulphite waste liquor

Component	Concentration (g/l)
Total solid	110-140
Ignition residue	15-27
Volatile organic acid	5-7
Sulphonic acid	0.6-1.2
Acetic acid	4.2-5.2
Calcium oxide	6.5-9.5
Sulphur (total)	10-12
Sulphite SO_3^{-}	1.3-2.5
Free sulphurous acid	1.4-3.4
Organic solvent compounds	9.5-14.2
Permanganate value ($KMnO_4$)	400-4000
Methyl alcohol	0.7-1.3
Ethyl alcohol	0.15-0.23
Acetone	0.1-0.13
Furfural	0.24-0.29
Lignin	56-69
Carbohydrates	20-21
Pentoses	2.5-3.4
Hexoses	17-18

The waste water from washing and dewatering pulp is similar in composition, but is considerably more dilute. The amount from barking pulp wood is 2.5-5 m^3/ton of wood handled. This waste water is the least noxious of the effluents and contains chiefly pieces of bark or wood.

All the waste water from the pulp processing department contains cellulose fibres. Up to a few per cent relative to the final product is lost to the waste water. If the pulp is bleached the waste water will contain chlorinated, non-bleached pulp products, hemicelluloses, monosaccharides, resins and other substances extracted from the fibres.

The waste water from the manufacture of sulphate pulp includes water arising during pulp washing, evaporation of the black liquor, caustification of the dissolved sodium melt and physical treatment of the pulp such as screening and thickening. The black liquor is combusted in a furnace, which eliminates the waste water from the most heavily polluted liquor.

The composition of the mixed waste water from the manufacture of sulphate pulp is shown in Table 29.3.

TABLE 29.3

Composition of sulphate pulp waste water

Component	Concentration
Colour (Pt-Co units)	>200
pH	7.5-9.5
Suspended solid (mg/l)	200-1200
Residue after evaporation (mg/l)	350-2700
Volatile matter (mg/l)	200-1800
Ash (mg/l)	100-900
Permanganate value ($KMnO_4$),(mg/l)	600-2000
Chloride (mg/l)	50-120
Sulphate (mg/l)	100-300

The total quantity of waste water from the manufacture of non-bleached sulphate pulp is about 350 m^3/ton of product.

In most cases it is not possible to discharge sulphite liquor and it is most frequently utilized by fermenting the carbohydrates or by evaporation to produce a yellowish-brown powder, which can be used as an additive for precipitating protein, as a binder to dye-stuffs and for pelletting chicken feed.

In Norway a method is used in which the sulphite liquor is separated into lignosulphonic acid and carbohydrates. The lignosulphonic acid can be used for the same purposes as mentioned above for the sulphite liquor and the carbohydrates can be used as raw material for alcoholic fermentation. About 60 l of alcohol can be produced per ton of cellulose.

However, the sulphite liquor from bleach pulp-wood processing contains mainly pentoses, which can be used in the manufacture of fodder yeast.

The following compounds may also be produced from sulphite liquor by fermentation: acetone, butanol, 2,3-butylene, glycol, glycerol, lactic acid, butyric acid and citric acid. The lignosulphonic acid can also be used as raw material for manufacturing vaniline (Holderby, 1960).

As the cost of operation is very high, the direct use of sulphite liquor has also been investigated. It can be used for the manufacture of agricultural pesticides, for the production of dust collecting agents and for road surfacing.

In spite of all the mentioned possibilities for the utilization of the sulphite liquor, a substantial part of it must be combusted. One of the best methods is the so-called Zimmermann process in which organic compounds are oxidized in an autoclave at 270-300°C and 100 atm. The steam and gases from the reactor can be used to drive turbines.

The wet combustion method requires 30% lower investment and the energy regenerated is about 100% higher than other combustion processes.

The Zimmermann process has also found practical application in the recovery of chemicals during the process of digesting semichemical pulp with sulphite (Tanzler, 1942; Schmidt, 1957).

It is possible to reduce the pollution problem by introducing multi-stage washing of the pulp on filters or presses using weak waste water by a method described by Nepenin (Pavlinova, 1960).

In Fig. 29.1 is shown a mass balance for this process. Very dilute waste water is obtained by this method in addition to small quantities of highly concentrated liquor, which makes utilization of the concentrated liquor considerably easier.

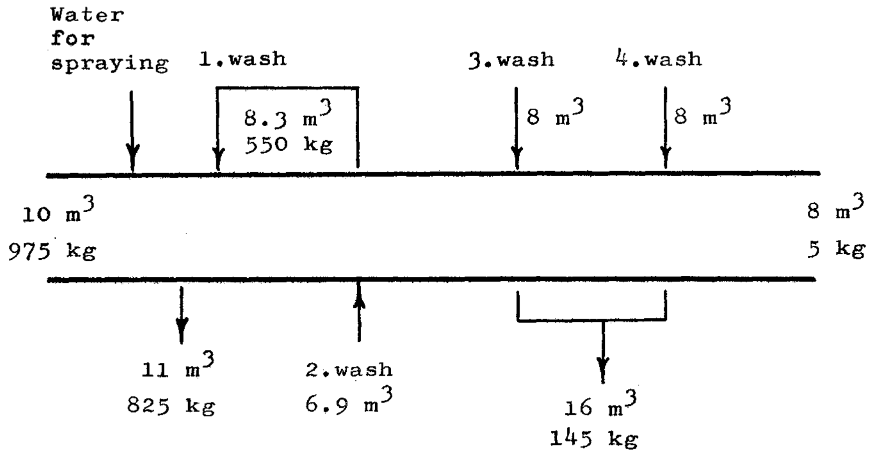

Fig. 29.1. Mass balance of liquid and dissolved organic compound. Basis: 1 ton of cellulose.

Waste water from a sulphate pulp mill does not present the same difficulties as sulphite liquor, since the compounds can to a large extent be recovered as mentioned above. According to the method mostly used, the black liquor is first concentrated in multi-stage vacuum evaporators from 17-18% to about 55% dry matter and then to about 65% in a cascade concentrator. The resulting liquor is then combusted in a sodium boiler using liquid fuel burners. The black ash obtained from the boiler contains chiefly sodium carbonate, which is called crude sodium melt. Sodium hydroxide is obtained from the sodium melt by treating with lime.

Activated carbon may be obtained as a by-product.

Decolorization of pulp mill effluents is possible with high molecular weight amines (Wung et al., 1975). The process is based on the ability of these amines to remove the coloured organic compounds present in the effluents by precipitation, but in contrast to various versions of the lime treatment process, the precipitate produced after a simple phase separation is redissolved in a small amount of strong alkaline solution.

. The amine used is thus regenerated, while the coloured organic matter is ultimately burned in the recovery furnace (Wung et al., 1975).

Simultaneously, approximately 50% of BOD_5 or COD is also removed.

Pulp-mill waste water

Full treatment of the remaining pulp-mill waste water comprises physical, physical-chemical and biological methods.

The cellulose fibres can be removed from the effluent by a settling process.

Numerous investigations have been carried out on the application of biological treatment methods to the waste water from the pulp industry (Müller, 1965). As well as activated sludge plant, trickling filters as oxidation ponds can be used (Moore, 1956; Waldmeyer, 1963; Rudolfs et al., 1953; Pearman et al., 1957).

The characteristic parameters for the design of activated sludge plants (see Chapter 11) are shown in Table 29.4.

The same parameters can also be used for treating waste water from paper-mills.

If the ratio BOD_5:N:P is adjusted to 100:16:1, it is possible to use the more favourable values in the range indicated in Table 29.4, while the more unfavourable value of the parameters should be applied when this ratio is not valid.

TABLE 29.4

Parameters for an activated sludge plant

Unit	Value
LF	0.3-0.5
K	$0.5-0.8 \cdot 10^{-3}$
a	0.5-0.85
a_1	0.4-0.9
b	0.08-0.15
b_1	0.1-0.15

The sulphite liquor has a strong brownish colour, but it seems that the colour is seldom a problem, since most streams receiving the waste water are either naturally coloured, turbid or the dilution is sufficiently high that the added colour does not alter the normal colour appreciably. Data indicate, however, that the brown colour of the effluent can make the receiving water brownish, reduce the light penetration and affect the spectrum of wavelengths which penetrate the water. This change in wavelength and reduction in intensity may affect aquatic growth.

Alum and iron coagulation of the waste water from the pulp industry removes the colour. It has been found that the dose for optimum colour removal is a linear function of the initial colour and a chemical equivalence has been found to exist between the optimum doses of alum and iron. $2.6 \cdot 10^5$ colour units were removed per rquivalent of coagulant used. The optimum pH was found to be 3.9 for iron(III)chloride and 5.3 for aluminium sulphate (Smith et al., 1969).

Paper-mill waste water

The quantity of waste water from the manufacture of paper depends on the quantity of the raw material, on the product and on the size of the plant.

The quantity of waste water is up to 1000 m^3/ton of product. A typical composition of paper-mill waste water is shown in Table 29.5.

The waste water from the manufacture of paper is milky, due to the content of loading agents and very fine cellulose fibres. (Ekemann et al., 1950). One of the major problems of paper-mill waste water is the loss of fibres. Of the raw material 15% is lost, but it can be reduced with a concomitant partial reduction in the pollution as well, by recirculating the water (Bishop et al., 1954).

TABLE 29.5

Composition of paper-mill waste water (mg/l)

Component	Concentration
Suspended matter	500-1200
Volatile suspended matter	100-250
Dissolved matter	300-400
Volatile dissolved matter	50-150
Permanganate value ($KMnO_4$)	200-500
BOD_5 (mg O_2/l)	100-500

However, recycling excessively large quantities of water affects the quality of the product, which is a problem particularly in the manufacture of high quality paper. For the production of lower quality paper up to 75% of the water can be recycled (Herrick, 1966).

The suspension of fibres in the waste water can be recovered by filtration, sedimentation or flotation (Gale, 1963), see Figs. 29.2 and 29.3.

Coagulation followed by micro-straining can remove the suspended solid and turbidity from the waste water of the paper industry (Riemer, 1971).

Biological treatment methods can be used to treat the overflow from the sedimentation process.

According to Kowanovski et al. (1968) the total effluent from paper-mills producing paper of various technical weights may contain up to 300 mg melamine/l. Since melamine is not readily attacked by micro-organisms it should be removed prior to biological treatment. It was proposed to clarify the portion of the effluent containing the maximum concentration of melamine by coagulation, sedimentation and filtration and to treat the filtrate with 13-14 g equivalents of active chlorine per mole of melamine to precipitate hexachloromelamine; the latter can be separated by filtration and used as an antiseptic or oxidizing agent.

The parameters given in Table 29.5 can be used.

Table 29.6 shows the results achieved by the three-step purification method based on a combination of precipitation (with calcium hydroxide), trickling filter and adsorption on activated carbon (see Fig. 29.4).

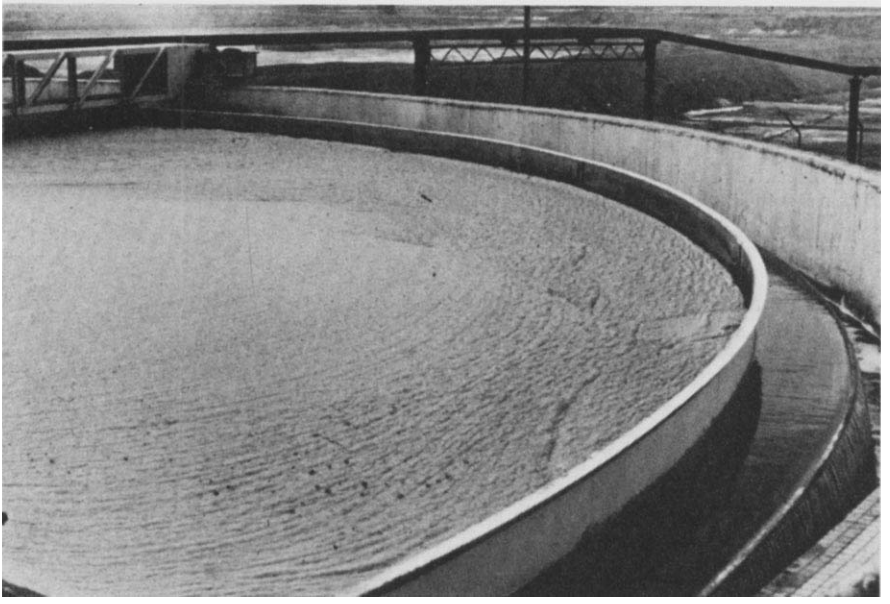

Fig. 29.2. Flotation of fibres from paper-mill waste water.

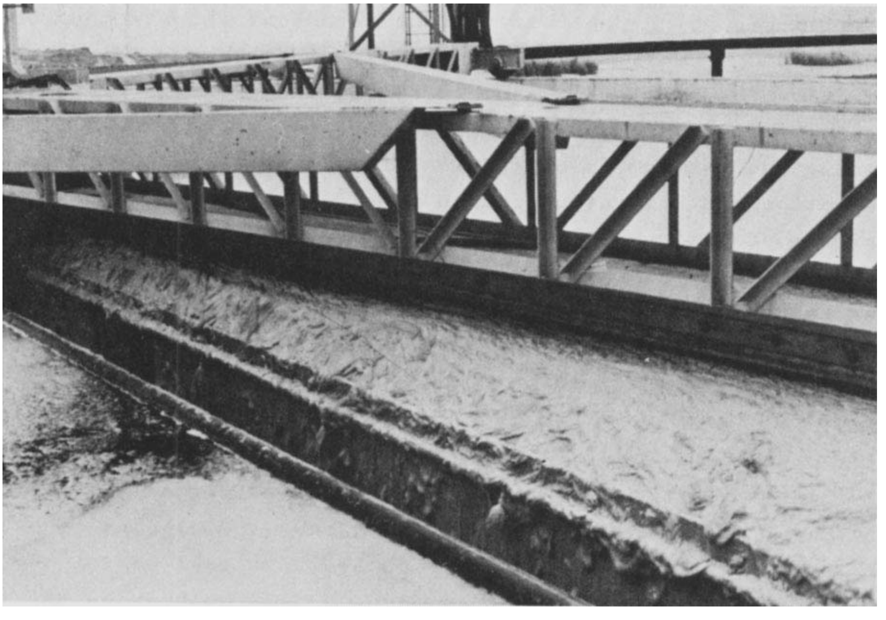

Fig. 29.3. Removal of fibres from the top of a flotation unit.

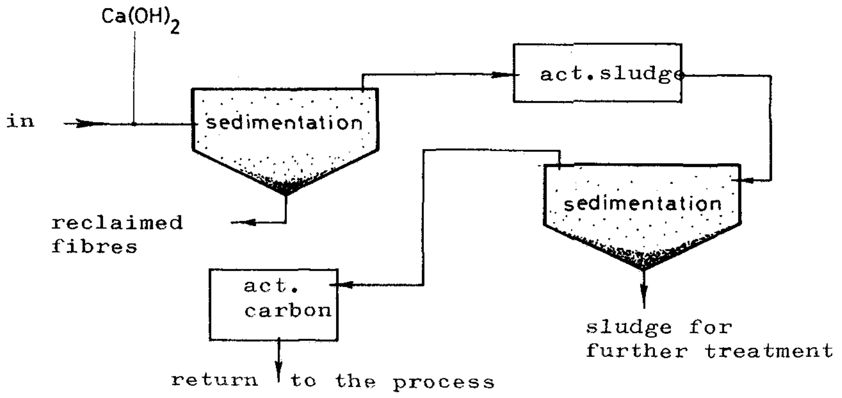

Fig. 29.4. Plant for the treatment of waste water from the paper industry. There is a possibility for complete recycling.

TABLE 29.6

Treatment of paper-mill waste water

Treatment	BOD_5 (mg/l)	Total efficiency (%)	Colour (Pt-Co)	Efficiency (%)
Raw water	723	-	5200	-
Precipitation with lime	395	45.5	358	93
Biological treatment	48	88	365	0
Activated carbon filter	23	53	13	96.5
Total	23	97	13	99.5

By use of bentonite it has been possible to recover almost 100% of the fibres and reduce the BOD_5 sufficiently to allow the water to be reclaimed (Libor et al., 1969).

The sludge produced can be used as raw material for the manufacture of corrugated paper. This solution to the waste water problem of paper-mills is used in paper-mills in Switzerland, Germany, Czechoslovakia, Hungary and Sweden, see Figs. 29.5 and 29.6.

Foam separation offers a detoxication system for the treatment of craft mill effluents.

An investigation by Moeller et al. (1975) has shown that it is possible to obtain an average detoxication of 83% by this process. The toxicity was determined as the mean survival time of juvenile rainbow trout.

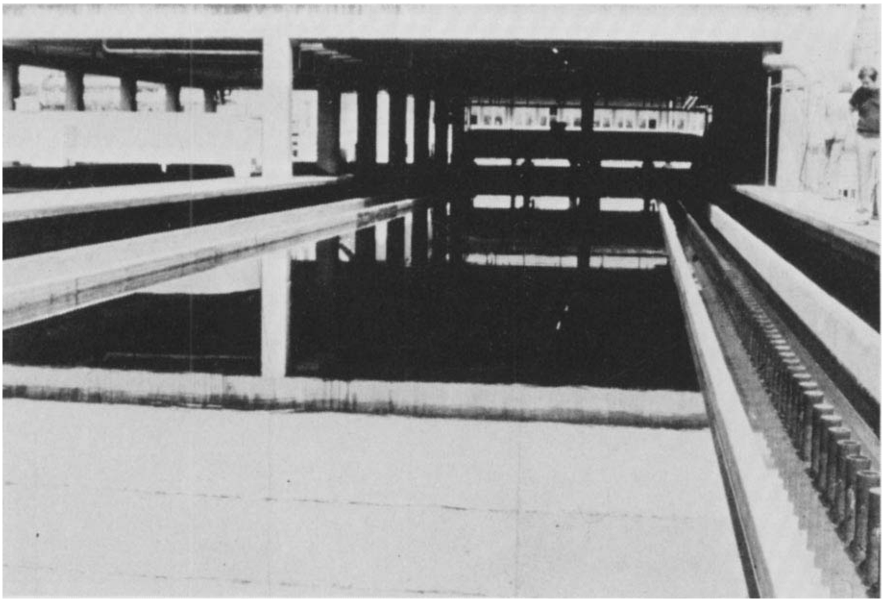

Fig. 29.5. Settling basin for treatment of paper-mill waste water after precipitation with activated bentonite and polyflocculant.

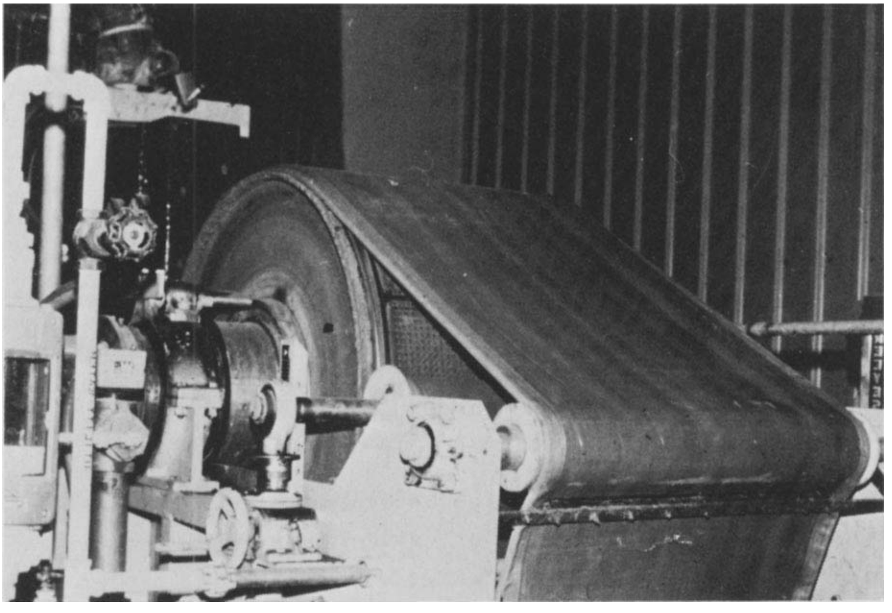

Fig. 29.6. Rotary filter for dewatering of sludge obtained by chemical precipitation of paper-mill waste water.

The principle parameters controlling the detoxication by foam separation are:

1. pH. For practical application a pH between 7 and 8 maintains the detoxication efficiency.
2. Temperature. Temperatures of 45-50°C typical of bleach craft mill effluents did not affect the detoxication efficiency.
3. Retention time. The total interfacial area required for detoxication increases with increasing initial level of toxicity.

Manufacture of hardboard and fibreboard

Waste water from the manufacture of hardboard and fibreboard contains suspended matter, but approximately 40% of the organic material is dissolved.

Biological treatment of this waste water is possible, but the nutrients balance must be adjusted or the biological treatment must be carried out on a mixture of municipal and industrial waste water (Husmann, 1970).

In some instances the waste water is evaporated and, as the sludge contains wood material, it can easily be combusted. However, this process cannot be realized from the economic point of view, unless a high percentage of recirculation takes place.

The manufacture of fibreboards produces relatively large amounts of pollutants. The specific consumption of the process water used is 20-30 m^3/ton of product.

The BOD_5 is about 2000 mg/l, corresponding to 40-50 kg BOD_5/ton of product.

It is possible to reduce the BOD_5 of waste water from fibreboard manufacture by use of phenolic resins as an aid to coagulation (Johansson, 1975). These resins form flocs in a different way from the usual coagulants such as alum, iron(III)sulphate and iron(III)-chloride. The phenolic resins are added in the form of their sodium salts which are soluble in alkaline solutions. The water is then acidified, and the resin and acid are precipitated in the very small sticky particles. The suspended solid in the waste water readily adheres to these particles.

A BOD_5 reduction of 25-30% is obtained by chemical precipitation with this coagulant.

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