EVALUATION OF TANNIN AS NATURAL COAGULANT FOR PULP AND PAPER MILL WASTEWATER TREATMENT

NURUL FARAHANES BINTI MOHD FADZIL

SCHOOL OF CIVIL ENGINEERING
UNIVERSITI SAINS MALAYSIA
2017

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By

NURUL FARAHANES BINTI MOHD FADZIL

This dissertation is submitted to

UNIVERSITI SAINS MALAYSIA

As partial fulfilment of requirement for the degree of

BACHELOR OF ENGINEERING (HONS.)
(CIVIL ENGINEERING)

School of Civil Engineering,
Universiti Sains Malaysia

June 2017

UNIVERSITI SAINS MALAYSIA

SCHOOL OF CIVIL ENGINEERING
ACADEMIC SESSION 2016/2017

FINAL YEAR PROJECT EAA492/6
DISSERTATION ENDORSEMENT FORM

Title:

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I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

Signature:

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Date :

Approved by:

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(Signature of Supervisor)

Name of Supervisor:

Date :

Approved by:

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(Signature of Examiner)

Name of Examiner :

Date :

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful

Alhamdulillah, all praise to Allah S.W.T, the Almighty, for the strengths and blessing in completing this study. Sincere appreciation goes to my supervisor, Dr. Mohamad Fared Bin Murshed for his guidance and constant support. His invaluable help of constructive comments and suggestion throughout the study helped me to complete this dissertation.

I would like to express my gratitude to all technicians from Environment Laboratory, School of Civil Engineering, USM for their assisting help in providing materials and technical support during the experiments was carried out.

Sincere thanks goes to these people, Kak Aisyah, Kak Nadiah, Sharizal, Nani, Munira and others who had helped me directly or indirectly, for their kindness and moral support during my study. I am also like to thank to my colleagues and friends for their useful discussion and support.

Last but not least, my deepest gratitude goes to my beloved parents, Mohd Fadzil Kassim and Roshadah Said, and also to my siblings for their kind support and prayers. This work is supported by Universiti Sains Malaysia under the Research University Grant No. 814259.

ABSTRAK

Pada asasnya, setiap tahun kilang kayu dan kertas menjana berjuta-juta tan air sisa yang sangat tercemar. Kualiti air sisa bergantung kepada jenis proses pulpa. Dalam kajian ini, air sisa kilang pulpa & kertas dari Nibong Tebal Paper Mill telah diambil dan dirawat dengan menggunakan koagulan semula jadi (Tannin) dan alum. Kesan daripada kadar dos dan pH dikaji untuk pengurangan COD, SS, kekeruhan dan warna dengan menggunakan ujian jar. Kepekatan COD dan pepejal terampai yang sangat tinggi telah direkodkan sebanyak 620-740 mg/L dan 2015-3550 mg/L. Berdasarkan keputusan ujian balang, dos optimum dan pH optimum untuk tanin yang telah direkodkan adalah 200 mg/L dan pH 3 manakala dos optimum dan pH optimum untuk alum adalah 300 mg/L dan pH 9. Dengan menggunakan koagulan alum, peratusan penyingkiran COD, SS, kekeruhan dan warna ialah 77.42-95.95 %, 87.32-96.50 %, 99.98-100 % dan 87.00-88.10 %. Peratusan penyingkiran COD, SS, kekeruhan dan warna untuk tannin ialah 47.26-74.32 %, 90.78-97.18 %, 99.29 % dan 16.67-34.00 %. Hasil penyelidikan telah menunjukkan bahawa tanin amat berkesan menyingkirkan pepejal terampai sebanyak 90.78-97.18 % tetapi tidak untuk parameter lain. Walau bagaimanapun, kajian ini membuktikan bahawa tanin tidak sesuai untuk menyingkirkan warna dalam penyelidikan ini kerana peratusan penyingkiran untuk warna ialah 16.67-34 % sahaja. Oleh itu, kajian masa depan adalah penting dalam menentukan peratusan penyingkiran warna keberkesanan.

ABSTRACT

Basically, pulp and paper mills generated million tons of highly polluted wastewater every year. The quality of the wastewater is totally depends on the different types of pulping processes. In this research work, pulp & paper mills wastewater from Nibong Tebal Paper Mill have been collected and treated by using natural coagulant (Tannin) and alum. The effects of dosing rate and pH are examined for reduction of COD, SS, turbidity and colour by using jar testing. High COD and suspended solid concentration was recorded at 620 to 740 mg/L and 2015 to 3550 mg/L respectively. Based on the jar testing results, the optimum dose and optimum pH for tannin was recorded at 200 mg/L and pH 3 while the optimum dose and optimum pH for alum are 300 mg/L and pH 9. The removal of COD, SS, turbidity and colour were 77.42 to 95.95 %, 87.32 to 96.50 %, 99.98 to 100 % and 87.00 to 88.10 % by using alum. The percentage removals of COD, SS, turbidity and colour for tannin were 47.26 to 74.32 %, 90.78 to 97.18 %, 99.29 % and 16.67 to 34 %. The results had shown that tannin can removed suspended solid which was at range 90.78 to 97.18 % but not to other parameters. However, the study proved that tannin is not suitable for the purpose of removing colour as the percentage removal of this experiment range between 16.67 to 34 % only. Thus, future study is essential in determining effectiveness colour removal percentage.

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LIST OF ABBREVIATIONS

BOD	**B**iochemical **O**xygen **D**emand
COD	**C**hemical **O**xygen **D**emand
DO	**D**issolved **O**xygen
NTU	**N**ephelometric **T**urbidity **U**nit
PPME	**P**ulp and **P**aper **M**ill **E**ffluent
Pt Co	**P**latinum-Cobalt
RPM	**R**evolution **P**er **M**inute
SS	**S**uspended **S**olids
WHO	**W**orld **H**ealth **O**rganization

CHAPTER 1

INTRODUCTION

1.1 Pulp and Paper Mill Industry

Pulp and paper are manufactured from raw materials containing cellulose fibers such as wood, recycled paper, and agricultural residues. Therefore, pulp and paper mill is a major industrial sector utilizing a large amount of lignocellulosic materials and water during the manufacturing process (Ahmad *et al.,* 2008). Pulp and paper mill can consume as high as 60 m^3 of fresh water per ton of paper produced (Thompson *et al.,* 2001). Different processes utilize different amount of water and all of these processes are water intensive. Wastewater from pulp and paper mill industry will produce from manufacturing processes which are wood preparation, digester, pulp washing, pulp bleaching and paper making process. There are 67 pulp and paper mills operating in Malaysia, out of which 19 companies are using wood fibre (Roda and Rathi, 2006).

Figure 1.1 shows the graph of pulp and paper mill industry against total capacity paper produce. Based on the graph, three company are producing paper less than 10 000 mt which are Pembuatan Kertas (Perak) Sdn. Bhd., Taiping Paper Sdn. Bhd. and Yeong Chaur Sdn. Bhd. while ten industry producing between 11 000 and 80 000 mt which are Cita Peuchoon Sdn. Bhd., Johmewah Sdn. Bhd., Nibong Tebal Sdn. Bhd., Pascorp Paper Sdn. Bhd., Kimberly-Clark Sdn. Bhd., See Hua Paper Sdn. Bhd., Theen Seng Paper Sdn. Bhd., Trio Paper Sdn. Bhd., Union Paper Sdn. Bhd. and United Paper Board Sdn. Bhd. Besides that, there are five mills can produce from 100 000 up to 300 000 mt which are Genting Sanyen Sdn. Bhd., Muda Paper (Kajang) Sdn. Bhd., Muda Paper (S. Prai) Sdn. Bhd., Malaysia Newsprint Sdn. Bhd. and Sabah Forest Sdn. Bhd.

The industry that produce maximum and minimum total capacity of paper produce are from Genting Sanyen (300 000 mt) and Taiping Paper (2400 mt). The fresh water consume depends on total capacity of paper produce.

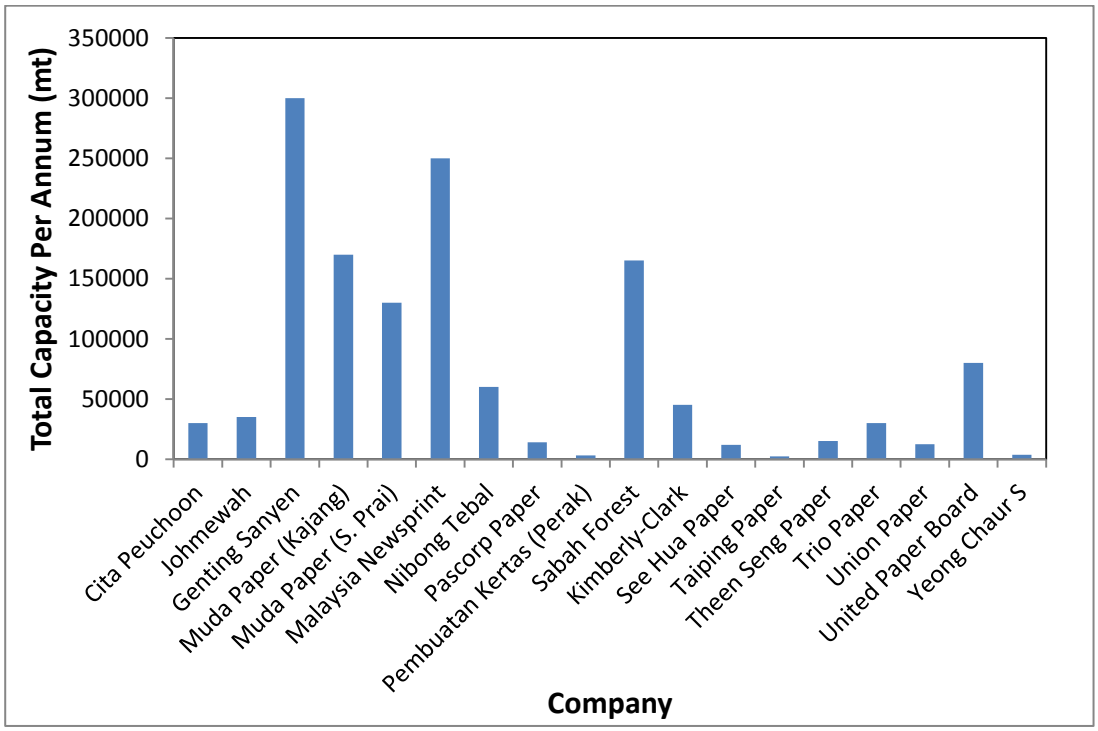

Figure 1.1: Production of Malaysian paper mills

1.2 Pulp and Paper Mill Effluent

Pulp and paper mill industry is considered as one of the most polluting industry in the world (Thompson *et al.*, 2001)**.** The effluent pulp and paper mill effluent (PPME) contains toxic substances include various chlorinated compounds and pollutants such as extractives, waxes, sterols, suspended solids, fatty acids, diterpene alcohols, tannins, lignin and its derivatives (Wong *et al.*, 2010). High level of toxicity in pulp and paper mill industrial generates large volumes of effluents with high content of biochemical oxygen demand (BOD), chemical oxygen demand (COD), colour and suspended solids (SS). According to Bajpai (2000) research, there are high content of BOD,COD, and suspended solids which are 1600 mg/L, 5020 mg/L and 800 mg/L.

If the untreated wastewater is released to the environment, it is certain to cause significant environmental problems due to its accumulation in soil and water environment (Wu *et al.,* 2013). Table 1.1 shows the limitation values of parameters and maximum allowable concentration of pollutants.

Table 1.1: Acceptable conditions for discharge of industrial effluent for mixed effluent of standards A and B (Source: Environmental Quality (Industrial Effluents) Regulations 2009)

FIFTH SCHEDULE

No.	Parameter	Unit	Standard	
			A	B
(i)	Temperature	˚C	40	40
(ii)	pH Value	-	6.0-9.0	5.5-9.0
(iii)	BOD_5 at 20˚C	mg/L	20	40
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

1.3 Problem Statement

The pollutants of wastewater from pulp and paper mill could be characterized as high content of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity and colour which have negative impact to the environment. The untreated wastewaters discharged from the industry could cause slime growth, thermal impacts, scum formation, colour problems and loss of aesthetic beauty in the environment (Pokhrel and Viraraghavan, 2004). The characteristics of raw wastewater paper mill industry at Malaysia are shown in Table 1.2. The highest value of turbidity is 4770 NTU while the highest value of COD is 28270 mg/L. Besides that, the wastewater contains high value of BOD and SS which are 5279 mg/L and 11455 mg/L.

Table 1.2: Characteristic pulp and paper mill wastewater

Author	pH	Turbidity (NTU)	COD (mg/L)	BOD (mg/L)	SS (mg/L)
(Sundaram et al., 2014)	8.20	NA	205	14	60
(ElSergany et al., 2015)	5.60 - 5.80	454	9507	5279	1747
(Wong et al., 2006)	7.30 - 8.30	4770	NA	NA	5240
(Irfan et al., 2013)	6.73	NA	28270	-	11455
(Avşar and Demirer, 2008)	7.00	NA	1275	556	7150
(Razali et al., 2011)	7.00	4585	2900	NA	6000

Note: NA: Not Available

Aluminium sulphate is commonly used as coagulants in industries all over the world. The effectiveness of this inorganic coagulant is well recognized but some disadvantages were reported by using these coagulants. The disadvantages of Aluminium Sulphate are ineffectiveness in low-temperature, negative effect on human health, high procurement cost, produce large volume of sludge, limited potential for recycling due to non-biodegradability (Xiao *et al.*, 2008).

This study is conducted to determine the performance of biopolymer which is tannin to remove turbidity, suspended solid (SS), colour and chemical oxygen demand (COD) due to the various disadvantages of alum as coagulant. The advantages of tannin are sustainable and environmentally friendly which is safe to use for human health and not endanger next generations resources, produce readily biodegradable and produce less voluminous sludge that amount only 20-30% that of alum treated counterpart (Yin, 2010). Besides that, the advantage of this biopolymer is cost effective which is the maintenance inexpensive due to the decreasing effluent conductivity, in water recycling process, the corrosion of the facilities will be avoided.

1.4 Objective of Study

1. To identify the characteristics of pulp and paper mill wastewater.
2. To determine the optimum tannin dose and pH for turbidity, suspended solids (SS), colour and chemical oxygen demand (COD) removal.
3. To determine the performance of tannin to remove turbidity, suspended solids (SS), colour and chemical oxygen demand (COD) removal.

1.5 Scope of Work

The performance of tannin as natural coagulant for pulp and paper mill wastewater treatment was pursued in this research. The wastewater samples from Nibong Tebal Paper Mill Sdn. Bhd. were collected and tested in the Environmental Laboratory, School of Civil Engineering for laboratory tests. Jar test was conducted for this research. At the first stage the characteristics of the wastewater was analyzed. Next, the tannin dose and pH for turbidity, suspended solids (SS), colour and chemical oxygen demand (COD) removal was determined.

1.6 Thesis Structure

This thesis contains five chapters. Chapter one presents the introduction of pulp and paper mill industry, pulp and paper mill effluent, problem statement, objective of the research and scope of work. Chapter two discuss the literature review of pulp and paper mill, pulp and paper mill water consumption, pulp and paper mill effluent, pulp and paper mill wastewater treatment, coagulation, effect of initial pH, effect of coagulant dosage, coagulation stage and coagulant (tannin and alum) with relevance of other research. Chapter three covers the methodology of chemical oxygen demand, colour, suspended solid, turbidity and jar test. Chapter four discuss the result of characteristic wastewater, optimum dosage and optimum pH for tannin and alum and comparison performance between tannin and alum as coagulant for paper mill wastewater treatment while chapter five conclude about conclusion and recommendation of this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Pulp and Paper Mill

Paper is a major product of the forestry industry and versatile material with a huge of applications such as writing, printing and packaging purposes. Paper can be produced from wood pulp as a primary source of fibers or from recycling waste paper as a secondary source of fibers. More than 300 million tons of wood used to produce Pulp and paper mill because of the demand for paper product increasing yearly (Singh *et al.,* 2011). There are 6 processes whereby timber is converted into paper which are wood preparation, cooking, pulp washing, pulp screening, bleaching and paper making. For the wood preparation the bark is removed from in-coming logs, and these are then chipped. Sometimes, the wood arrives at the plant already chipped, meaning that this step is unnecessary.

Then, for the cooking process, the wood chips are heated in a solution of NaOH and Na_2S in a pressure cooker, during which time a lot of the lignin (the reinforcing substance that make tree cells wood hard and 'woody' rather than soft like those of other plants) is removed from the wood. The pressure is then released suddenly, causing the chips to fly apart into fibres. The pulp is washed with water for pulp washing process to wash out the cooking chemicals and lignin from the fibre so that they will not interfere with later process steps. Besides that, for pulp screening, a sieve is used to remove knots and clumped-together uncooked fibres from the pulp. For bleaching process is done in two stages. Firstly the pulp is treated with NaOH in the presence of O_2.

The NaOH removes hydrogen ions from the lignin and then the O_2 breaks down the polymer. Then, the pulp is treated with ClO_2 then a mixture of NaOH, O_2 and peroxide and finally with ClO_2 again to remove the remaining lignin. The fibres are mechanically treated to make them bond better to each other (strengthening the paper), chemicals added to provide special properties such as colour or water resistance, and then the water is squeezed out and the pulp is rolled smooth and dried for paper making process.

2.2 Pulp and Paper Mill Water Consumption

According to Thompson studied, water consumption get as high as 60 m^3/ton paper produced during pulping process. Based on Table 2.1, bleached sulphite pulp has the highest water consumption at 40-70 m^3/ton while waste paper recycling without de-inking requires the minimum water intake which is around 1.5–10 m^3/ton.

Table 2.1: Water consumption for pulp and paper mill industries (Degremont, 2007)

Factories	Water Consumption (m^3/ton)
Pulp production (circulation per process)	
i. Unbleached kraft paper	20-30
ii. Bleached kraft paper	40-60
iii. Bleached sulphite	40-70
iv. Semi-chemical	12-20
v. Chemi-thermo-mechanical pulp	15-40
Waste paper (overall consumption)	
i. Recycling without de-inking	1.5-10
ii. Recycling with de-inking	8-20
Paper manufacture (overall consumption)	
i. Integrated factory	15-20
ii. Non-integrated factory	10-20

2.3 Pulp and Paper Mill Effluent (PPME)

Pulp and paper mill industry is the sixth largest polluter in the world (after oil, cement, leather, textile, and steel industries) discharging gaseous, liquid, and solid waste into the environment (Ali and Sreekrishnan, 2001). Toxic substances present in Pulp and paper mill effluent (PPME) include low biodegradability of tannin and lignin (high colour), high nutrients contents (P and N), biochemical oxygen demand, chemical oxygen demand, total organic carbon and suspended solids.

The characteristics and strengths of wastewater may vary depending on the type of pulping processing. Various toxic chemicals such as resin acids, unsaturated fatty acids, diterpene alcohols, juvaniones, chlorinated resin acids, and others are generated in the pulp and paper making process. The characteristic of wastewater at various pulp and paper mill industry process is state in Figure 2.1. It is clear that an individual pulping stage produce different quantities, qualities and types of pollutants. At wood preparation stage, the effluent contain suspended solids because the soils, dirt's and barks removed from the wood and chips are separated from the barks and water is utilized to clean the wood. Then, the wastewater from digester house is called "black liquor" contains the cooking and chemicals as well as lignin and other extractives from the wood. Therefore, resins, fatty acid, colour, BOD, COD, AOX, VOCs will produce in wastewater. The effluent will change colour to dark brown at stage pulp washing. Then, the wastewater generate from bleaching where chlorine based compounds are used and wastewater contain contains dissolved lignin, carbohydrate, colour, COD, AOX, and inorganic chlorine. Particulate waste, organic compounds, inorganic dyes, and COD contain in wastewater at paper making stage.

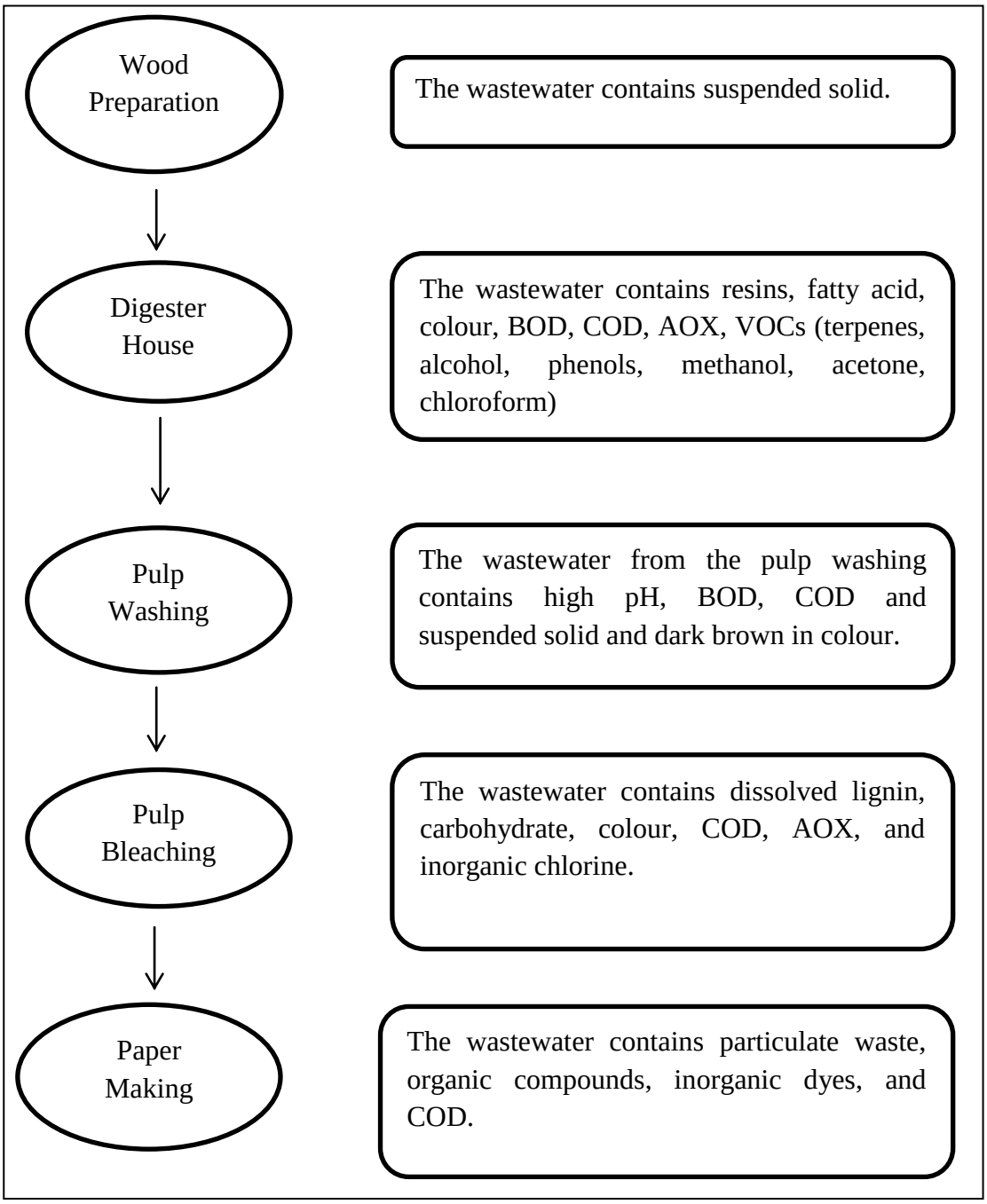

Figure 2.1: Pollutants from various sources of pulping and paper making (Sridhar *et al.,* 2011)

The characteristics of the wastewater are affected by the characteristics of raw material and degree of contamination, percentage of virgin pulp used in paper making, the chemicals used for pulp preparation, degree of water conservation and percentage of wastewater recycling (Monte *et al.,* 2009).

Pulp and paper mill effluent produced from various stages such as wood preparation, digester, pulp washing, pulp bleaching and paper making process (Sridhar *et al.*, 2011). There are 4 general types of processes designed to break down the wood to separate cellulose from hemicelluloses and lignin in pulp and paper mill industry:

1) Mechanical pulping

Mechanical pulping uses mechanical energy to separate and weaken fibers from wood by a grinding action. The advantage of mechanical pulping is the yield of the pulp for this process is high which is 90–95% (Smook, 1992). However, the quality of the pulp is low grade because this process does not dissolve lignin and mechanical grinding produces shorter fibers. Mechanical pulping requires more raw materials to remove contaminants such as dirt and knots than chemical pulping process.

2) Chemical pulping

The wood chips are cooked with chemicals in an aqueous solution at an elevated temperature and pressure to break chips into a fibrous mass. The yield of the pulp by this process is 40–50% of the original wood material (Smook, 1992). The chemical pulping is carried out in two media which are alkaline and acidic.

(a) Kraft process: The wood chips are cooked in a solution of sodium hydroxide (NaOH) and sodium sulfide (NaS_2).

(b) Sulfite process: The wood chips are cooked in a mixture of sulfurous acid (H_2SO_3) and bisulfide ions (HSO_3^-) to dissolve lignin.

3) Chemi-mechanical pulping (CMP)

Chemical mechanical pulping technology is a process where wood raw material is converted into pulp for paper making by using both chemical and mechanical means. The raw material is treated chemically and subjected to drastic mechanical treatment to separate the fibers also. The efficiency of pulp obtained from 85–90% and the strength of the pulp is better than the pulp from the mechanical pulping alone. For hardwood, the earliest CMP technology used in the industry was cold caustic soda process (CCS) which cold caustic chemicals were used to pre-treat wood chips before the chips were refined.

4) Thermo-mechanical pulping (TMP)

In TMP wood chips are first steamed to soften them before being ground same as Refiner Mechanical Pulping (RMP) process which is in RPM wood feedstock is ground between two grooved discs. The TMP process generate highest grade mechanical pulp and it also a high energy intensity process due to its steam use. This process produced a darker pulp that is more costly to bleach. TMP is the common mechanical process use today. The thermo-mechanical process is further modified using chemicals during the steaming stage, and the process is called chemi-thermomechanical pulping (CTMP). The chemical pre-treatment of wood chips allows for less destructive separation of fibers from the feedstock, resulting in longer fibers, higher fiber content and far fewer shives. This process also produces more flexible fibers which provide higher sheet density, burst strength and tensile strength and higher pulp brightness more than the TMP process. The primary drawback is high energy intensity process.