

Treatment of Waste Water
from Coke Production
Feasibility Study of Huaxi Jiohua Ltd,
Wuhai, Inner Mongolia, PRC

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Master of Science Thesis
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TREATMENT OF WASTE WATER FROM COKE PRODUCTION

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INNER MONGOLIA, PRC



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Abstract

China is the most populous country in the world and has an increasing economy. A growing economy enhances the electricity requirement, product demands and so on, which affects both the surrounding environment but also the global environment.

Wuhai is an industrial city and the most polluted city in Inner Mongolia, China. Numerous amounts of the industries are lacking in the emission treatment and the PM10 is more than 10 times the allowed amount of European Union.

This master thesis is a part of a bigger project, a corporation between IVL Swedish Environmental Research Institute Ltd and Environmental Protection Bureau in Wuhai.

The Coke Company Huaxi Jiohua Ltd. was founded 1992, and has a producing capability of 300.000 tons coke per year. The treatment station is a model of an ASP, without a sludge recycling and a sludge thickener instead of sedimentation basin. The treatment efficiency is failing in phenol removal.

The aim of this thesis is to perform a feasible study of the wastewater treatment methods for an improvement of the separation of pollutions in coke wastewater and to give a proposal for improvement of energy efficiency from wastewater treatment.

Treatment efficiency of methods such as A^2/O , A/O, SBR, and ASP was taken in consideration.

Due to the lack of basic treatment, a first suggestion is to optimize the biological parameters, and introduce sludge recycling to the system together with either a following sedimentation pool or a MBBR as a pre-treatment step.

To gain energy from the wastewater treatment station, a replacing of the current aerator system in the aeration unit to fine bubble diffusers and introduce a heat exchanger in the cooling of gas step could be done.

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Abbreviation list:

A ² /O	Anaerobic-Anoxic-Aerobic System
A/O	Anaerobic-Aerobic System
AOP	Advanced Oxidation Processes
ASP	Activated Sludge Process
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
F/M	Food-To-Microorganisms ratio
GDP	Gross Domestic Product
HRT	Hydraulic Retention Time
LC ₅₀	Lethal concentration 50 %
MBBR	Moving Bed Biofilm Reactor
MLSS	Mixed Liquor amount
PAH	Poly Aromatic Hydrocarbons
SBR	Sequential Batch Reactor
SLR	Solids Loading Rate
SS	Suspended Solids

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1. Introduction

“If China sneezes, the whole world gets a cold”. China, the most populous country in world, is a developing country with an increasing economy. What China does, leaves marks. Therefore it is highly important that China has a good environmental status. A growing economy enhances the electricity requirement, product demands and so on.

Steel production is one of China’s mainly industries, and when producing steel, coke is needed as a fuel. Emissions from the coke process, steel production include; greenhouse-gases, acidification substances, ammonia, organic material such as PAHs and more. These emissions occur both to air and water. Therefore, it is highly important to have a functional treatment station for removal of these substances.

Wuhai, an industry city in Inner Mongolia, China, is highly polluted and is the most polluted city in Inner Mongolia. Swedish government is helping Wuhai to become a green city by helping them to improve their present treatment methods, and implement environmental thinking. Wuhai has several coke factories that all together produce 4-5 million tones coke/year, with capacity of 6-7 million tones coke/year. The treated coke wastewaters go directly into the Yellow River and with this high amount of coke production, it is of great significance to have a well functional treatment station to decrease the amount tones of pollutants that go out in the river every year. One coke factory that does not have a good treatment station is the coke factory Huaxi Jiaohua Ltd that produces 300 000 tones/year.

The government of China has decided that small coke factories that produce less than 900 000 tones of coke per year should close by the end of year 2007 if their wastewater treatment is not satisfactory. An appropriate wastewater treatment will delay the closing date to the end of 2009.

The company Huaxi Jiaohua Ltd produces 300 000 tones coke per year and delivers energy to Wuhai community. Due to insufficient wastewater treatment the factory needs to close down by the end of 2007, if no improvements take place. To be able to use the energy produced from coke process as long as possible, Wuhai community has asked IVL Swedish Environmental Research Institute Ltd for help with the improvements. However, the information about closing is new for IVL and was not known when the project was initiated and therefore is not going to be discussed any further.

This master thesis is a part of a bigger project, a corporation between IVL Swedish Environmental Research Institute Ltd and Environmental Protection Bureau in Wuhai.

2. Aim and Objectives

The aim of this thesis is to perform a feasible study of the wastewater treatment methods for an improvement of the separation of pollutions in coke wastewater and to give a proposal for improvement of energy efficiency from wastewater treatment.

A general idea of where the factory is on the environmental scale can be established and analyzed based on gathering the information on coke wastewater treatment, western coke factories and energy efficiency in general. With those data as background info, the following objectives have been settled:

- To compare different wastewater treatment stations, both with regard to efficiency of reduction of phenol and PAHs, as well as economic aspects.

- To suggest an improvement in wastewater recycling
- To suggest improvement in energy efficiency of the wastewater station

3. Methodology

This work was conducted through information retrieval, field trip and contacts with different factories, wastewater treatment technique suppliers and researchers. The work was supposed to be based on facts provided by the coke factory. Unfortunately most of the requested information was not provided and the one provided was misleading and did not bring any useful meaning to the whole picture. The received data was difficult to use, see appendix 1. Hence, the results and the discussion are therefore based on assumptions.

4. Background

4.1 Environmental Situation in China

China is the most populous developing country in the world. In just 30 years, China has succeeded with economic growth that took Western countries more than 100 years to accomplish. As a result, China has been facing environmental problems all at once that Western countries suffered from during different phases of their 100-year-long industrialization process [1].

Environmental pollution and ecology deteriorations have caused huge economic losses and endangered people's lives and health [3]. The environmental damage is due to the country's key industries; iron and steel, chemicals, mining, textiles, petrochemicals and building materials, all consuming large amounts of energy and create a great deal of pollution. Therefore, the Chinese economy remains dominated by the resource-hungry and inefficient polluters [2].

It is estimated that one-third of country's urbanites breathe seriously polluted air while one-quarter of the Chinese people drink substandard water. Rivers flowing through cities are polluted in section of the downtown area; one fifth of Chinese cities suffer from serious air pollution. One water pollution accident per day takes place in China today, resulting in severe damage to public health [2,3].

Protecting the environment is in line with the long-term development of Chinese nation, and so far China has signed the Kyoto Protocol and other 50 international environmental accords [3].

Historically, the developed nations started solving their environmental problems when their annual GDP per capita reached levels 8,000-10,000 USD. Year 2003, GDP per capita in China was 900 USD (a) and it is predicted that when China's GDP per capita reaches 3,000USD, the environmental crisis will accelerate. Therefore, it is needed to resolve the environmental problems as soon as possible [2].

4.2 Description of Wuhai city

Wuhai is an industrial city with more than 450000 inhabitants. It is located in the Western part of EerDuoSi highland, Inner Mongolia, surrounded by three different deserts. The HuangHe (Yellow) River flows from south to north through Wuhai City, length 105 km.

Wuhai started to grow in the beginning of the sixties when coal and calcium carbonate were found in the area [4]. The city is rich in mining resources and after 40 years of growth, the GDP for Wuhai has increased 40 times since the fifties. The main industries in Wuhai are coal, chemistry, construction material and metallurgy [5].

An average annual temperature of 10.0 C in Wuhai provides a typical continental arid seasonal wind climate. The highest temperature appears in July, 40.2 C and the lowest in January, -28.8C. See table 1 for annual average climate data. [4].

Table 1- Climate factors

<i>Climate factors</i>	<i>The Annual average</i>	<i>Spring/ Summer</i>	<i>Winter</i>
Temperature *C	10.0	40.2 (july)	-28.8
Air pressure hpa	893.0		
Moisture %	42%	28% (april)	50%
Precipitation mm	163.3	139.3	24
Evaporation mm	3185.1		

Wuhai is the most polluted city in Inner Mongolia and its air pollution is severe. The location in the transition belt of pasture and desert makes the environment of Wuhai very exposed [6]. The main pollution sources are fly dust, coal smoke and dusty particles. PM10 is a measure of hazardous air particles that can enter the human body through the breathing system and cause diseases. Wuhai is severely polluted with PM10. 2004, PM10 pollution exceeded 3.4 times the national NO₂ level. European Union has specified the limit values for PM10 to 50 µg/m³ for the 24-hour average and 40 µg/m³ for the annual average [b]. Wuhai's PM10 concentration level between 0.112-1.008 mg/m³ is in range of 10 times more than allowed limit of the European Union [5].

The main pollutants over the limit values in HuangHe River are oil and ammonia nitrogen related due to coke industry discharge. Pollutants exceeding limit levels in drinking water are Total Hardness, Cl⁻, F-NO₃-N, and Escherhia Coli. The NO₃-N pollution is due to the discharge from Coke industry and municipal wastewater [4].

There are 6 to 10 companies in the region, each producing 300.000 to 1.000.000 tons of coke. The production of 100 000 tons generates an average of 300.000 m³ wastewater derived from the coke manufacturing process itself and the cooling of the coke [4,5]. The present coke production capacity per year in Wuhai is 4-5 million but should be 6-7 million [7].

The inhabitants are totally dependent of the industry sector and therefore it is extremely important to minimize the environmental impact from those industries in such a way that they

still can generate enough electricity and products in an environmentally friendly way. For the moment, the industrial sector recycles 60 % but due to limited water supply in the region these figures must be higher in the future to minimize the environmental impacts.

The Short term goals are to improve Air Quality focuses on coal burning industries; improve water quality by controlling the discharge from all the pollution sources and creating a green city. The Long term goal is to be able to control the urban pollution and also make sure that the water quality reaches national standards for drinking water [4,5].

4.3 Energy

Since the beginning of the industrialization, the energy demand has significantly increased worldwide. Over the last 100 years the global energy needs has increased 16 times, while the global economy 14 times, approximately proportionally. This energy need is linearly growing in time. It is estimated by *The Energy Information Administration (EIA)* of the *US Department of Energy (DOE)* that between 1999 and 2020, the total world energy use will increase from 403 EJ* to 645 EJ, a 60-65%* growth. Two-thirds of the increased energy demand and the energy-related CO₂ emissions over this period relate to China and other developing countries. Factors such as population growth, getting higher standards of living, and further industrialization are likely to have a great level of energy consumption in developing countries. Energy-related emissions are expected to grow most rapidly in China, due to the highest rate of income growth per capita and fossil fuel use.

Energy technologies which rely on combustion of carbon-based fuels stand for a large proportion of our current pollution problems, including emissions of greenhouse gases, acid rain precursors (SO_x , NO_x), carbon monoxide and photochemical oxidants.

Coal, oil and natural gas are today main global energy sources. Coal dominates energy markets and stands for app. 44 % of fossil energy consumption while oil for 32 % and natural gas for 24 %. Coal is the most copious fossil fuel worldwide, with current reserves expected to last more than 200 years. It is fossilized plant material preserved by burial in sediments. The environmental effects of burning all the lasting coal could be catastrophic, due to its CO₂ per unit of energy generated. Among the fossil fuels, coal generates most CO₂. It is expected that coal use worldwide will increase at a rate of 1.7 % per year between 1999 and 2020. China and India are projected to stand for 85 % of the coal use increase.

Currently, the use of coal as energy source in the industrialized countries is between 20-30%, while in China is nearly 75 %. The high coal energy consumption in China forces actions to prevent more green-house emissions.

Global warming brings the hazards of a global environmental impact that is irreparable after centuries of exposure. It is predicted that over the very long term, two to three centuries, the temperatures can rise by as much as 10 to 18°C if the energy consumption linearly increases in time.

Therefore, one of the most important means for preventing of global pollution is the right strategy to reduce the energy consumption derived from combustion of carbon-based fuels. The right strategies are decreased fossil fuel consumption, increases in energy efficiency, energy conservation in transportation and choosing replacements for fossils fuels on both on a man-to-man level and governmental level. If factories worldwide would maximize their

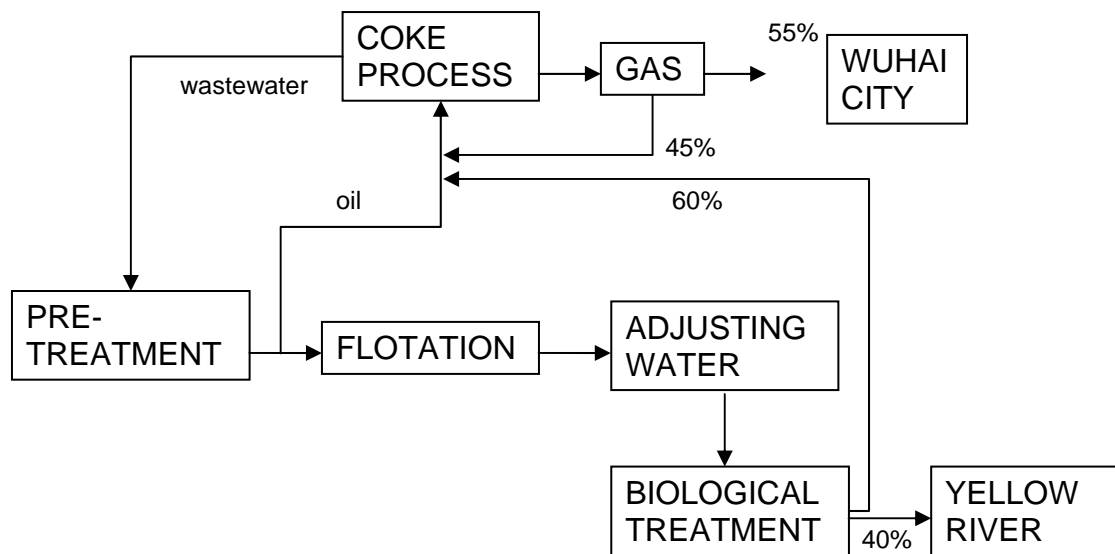
energy efficiency, the consumption of fossil fuel and cost would significantly decrease. One way to maximize the energy efficiency is heat recovery of the produced heat [1,2].

4.4 Description of the Company

The company Huaxi Jiohua Ltd. was founded 1992, and today has producing capability of 300.000 tons coke per year. Since the very beginning the company planed to build wastewater treatment station to utilize the water resources in most efficient and economical way and to decrease the pollution. Due to different reasons the wastewater treatment station could not meet the nation primary emission standard requirements in the initial stage of operation. To improve the situation, the company asked *Qinghua Tongfang water engineering company* to do a technological transformation. After one year's work, the wastewater treatment station was improved; see Table 2 for the current functional status of the wastewater treatment station [8].

Table 2- Current functional status of the wastewater treatment station. * The lowest level is for first class (most restricted) and the highest level is for second class.

Measure	Wastewater before treatment [mg/L]	Wastewater after treatment [mg/L]	Nat. emission standards [mg/L]*	World Bank limit values [mg/L]
NH ₃ -N	2900	74	15-50	--
COD	4500	196	60-120	150
Volatile phenol	5000	158	20-100	0.5



The flow diagram shows the processes of the company.

The present treatment methods do not enough reduce the amount of phenol. 40 % of the treated wastewater goes directly into the Yellow River with a too high amount of phenols. In a near future this amount needs to be reduced. The company recycles 60 % of the wastewater and 45 % of the produced energy, with plans to improve this percentage.

55 % of the company's produced energy is delivered to Wuhai City. Hence the interest of keeping this company running as long as possible [9].

The Environment Protection Bureau (EPB) has asked IVL for help with the improvement of environment around coke factory. The company has already asked Beijing Sande technology Ltd to do the feasibility study of the wastewater treatment station to achieve the national primary emission standards as soon as possible, and to fulfill the target of zero discharge gradually, see Economic calculus for more details [8].

Even though the latest measurement of EPB shows that the wastewater treatment is not efficient enough, the company claims that the treatment is not as bad as the latest numbers show. On question what has the highest priority on the improvement list; the answer was an extra anoxic tank as a complement to the existing aerobic one. At the same time they didn't know what improvements could be achieved by such a step. The improvement of each treatment step was not considered to be of highest importance. [9].

4.5 The coke factory and its process

Coke is needed as a reduction mean, while extracting iron from iron ore. The carbon and calorific power required for iron smelting is obtained from the destructive distillation of coking coals at temperatures of between 900 and 1100°C (6). When coal is heated in the absence of air, it becomes buoyant and all the volatile matter break down to yield gases, liquid and solid organic compounds of lower molecular weight and the non volatile carbonaceous residue known as coke (1,4,6). Then, the coke is cooled by water. The resulting wastewater is a complex industrial wastewater present in steel production facilities that originates from the process of making coke [13]. The resulting wastewater contains sizable amount of ammonia salts and toxic compounds such as phenols, PAHs, SCN^- and CN^- . Much of the chemical oxygen demand (COD) occurs from phenols, which is a carbon source for acclimatized microorganisms, but also a toxic inhibitory substrate for microorganisms [d,10,11,13].

4.5.1 Chemical Water Quality

4.5.1.1 Phenol

Phenol compounds make up 60-80 % of COD in wastewater and are degraded by microbial activity to carbon dioxide, methane and other compounds. It is toxic for higher freshwater organisms; with the lowest LC_{50} values on 3 and 7 mg/L for crustaceans and fish. A toxicity threshold of 64 mg/L was found for bacteria. Phenol is absorbed from any media and is rapidly distributed to all tissues. Exposure of phenol to the general population mainly occurs by inhalation. Minor oral exposure may arise through the consumption of drinking-water and/or smoked food [20].

4.5.1.2 Poly Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a division of a broad category of chemicals. PAHs are found in fossil fuels, oil, coal, wood, and natural gas and is a complex mixture containing thousands of organic compounds. It is also found as suspended particulate matter in the urban atmosphere, from a partial combustion/pyrolysis of fuels (coal, oil, natural gas, and wood).

PAHs are characterized by three or more aromatic (e.g., benzene) rings, typically fused together, where each pair of fused rings shares two carbons, and often other substances than hydrocarbons, i.e. nitrogen, fluorine. PAHs include compounds such as xylene, toluene, benzene, anthracene, phenanthrene, dibenzacridine, benzophenanthrene and more. Several of PAHs are carcinogenic and degraded under aerobic conditions to CO_2 , H_2O and new cell materia. Carcinogens are capable of inducing cancer in humans or animals after short-or long-term exposure.

The biodegradation of PAHs is highly dependent on the number of aromatic rings they consist of, meaning its hydrophobicity. The more hydrophobic a compound is the higher

bioaccumulation. PAHs are metabolised by the same enzyme as oestrogen and is classified as an endocrine disrupter. Endocrine disrupting compounds can affect the hormone system in organisms and are the subject of environmental and human health concerns.

4.5.1.3 Over-fertilization

The coke wastewater contains high amount of nitrogen compounds. Nitrogen is a nutrient that is needed for growth. The microorganisms need both nitrogen and phosphor as nutrients. The coke wastewater does not contain phosphor, and phosphor is needed to be added.

The main factors causing the over-fertilization in seas and lakes are the contribution of nutrients such as nitrogen and phosphor- containing substances. With an excessively amount of nutrients, the water quality will be deteriorated which in turn will lead to changes in the surroundings. Increased nutrients amount leads to overproduction, reduced visibility in deep, lack of oxygen, metabolism problems and finally, hydrogen sulphide on the ground.

4.5.1.4 Chemical oxygen demand, COD

COD is a measure of existence of organic material in water. Organic materials in water squander the oxygen, which leads to low levels of oxygen in the lakes and seas. Therefore, it is important not to release too much organic compounds into the water. Circa 80% of the COD consists of phenol [Jan stigsäter].

4.5.1.5 Biochemical Oxygen Demand, BOD

BOD is a measure of the amount of food for bacteria that can be oxidized, i.e. the existence of organisms (bacteria and dead organic matter).

4.5.1.6 Other compounds and parameters

Cyanide (CN^-) in water will form hydrogen cyanide (HCN) and evaporate. However, HCN is a very toxic substance for aquatic organisms and can cause long term effects on the aquatic environment. Free cyanide is known to be the most toxic pollutant to nitrifiers, and must be removed below 0.1 mg/L, before inflowing into nitrification step. Thiocyanate (SCN^-) is a nitrification inhibitor, and if high amount (>100 mg/L) be able to inhibit the nitrification.

Total Organic Carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality or cleanliness. Low TOC can also confirm the absence of potentially harmful organic chemicals in wastewater.

Dissolved Oxygen (DO) Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress; the lower the concentration, the greater the stress. Oxygen levels that remain below 1-2 mg/l for a few hours will result in high fish mortality [g].

4.5.2 Wastewater treatment

In a typical treatment plant, the wastewater is directed through a series of treatment steps with specific waste load reduction tasks, such as:

- Pre-treatment Physical and/or chemical
- Primary treatment Physical
- Secondary treatment Biological
- Advanced treatment Physical and/or chemical and/or biological

4.5.2.1 Pre-treatment

Pre-treatment is a first step in wastewater treatment prior to the next conventional secondary treatment biological process. Physical pre-treatment methods include flow balancing, screenings and grit removal. Besides the physical pre-treatment, industrial wastewater often need to combine the pre-treatment with chemical methods, such as air flotation (oil removal) and air stripping (ammonia removal).

4.5.2.2 Primary treatment

The primary treatment allows the wastewater to settle for a period of ~2 hours in a settling tank. Consequently it produces a more clarified liquid effluent in one stream and a liquid-solid sludge in a second stream. A sedimentation tank is used for this purpose. This step is often called clarification, sedimentation or settling. Primary treatment requires liquid retention time to complete solids separation from the water to be treated; otherwise, solids may be carried over into the subsequent processes, reducing the overall effectiveness of the treatment process [16,e].

4.5.2.3 Secondary treatment

Biodegradation is the dominant mechanism of organics removal for wastewater, i.e. municipal and industrial. The microorganisms convert biodegradable organic substances and some inorganic fractions into new biomass and by-products such as water and carbon dioxide. There are three types of secondary treatment systems:

1. Suspended growth
2. Attached growth
3. Dual biological suspended and attached growth

Suspended growth achieves a high microorganism concentration through the recycle of biological solids. Types of suspended growth systems include activated sludge systems, aerated lagoons, constructed wetlands, containment ponds and stabilization ponds.

Attached growth systems or fixed film reactors allocate a microbial layer to grow on the surface of the media (plastic, stone) while it draws its oxygen from the exposed atmosphere. A *Dual biological suspended and attached growth system* utilize two stage arrangements of suspended growth and fixed film process with the ambition to achieve a very high quality effluent standard [16].

4.5.2.4 Advanced treatment

If the composition of the wastewater is not satisfactory, an advanced treatment is often used, for example Ion exchanger, sand filter and more.

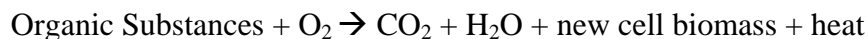
5. Biological Treatment

There are several treatment methods for reduction of ammonia, phenols and cyanides. Even though one of the main problems dealing with toxic compounds is the limited impact of biological process for the treatment of such effluents [15], the most widely used form of wastewater treatment for industrial wastewater is the biological treatment method; activated sludge process [10].

Aeration serves two purposes;

1. To provide oxygen to the aerobic microorganisms
2. To keep the activated sludge flocks in constant agitation to provide a sufficient contact between the flocks and the incoming wastewater

An adequate dissolved oxygen (DO) concentration is also important for the activity of the microorganisms, especially nitrifying bacteria. The DO level must be in the 0.5-0.7 mg/L range. Nitrification ceases when DO is below 0.2 mg/L [20].

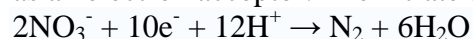


Nitrification is the conversion of nitrogen matter (NH_3) into nitrates by autotrophic bacteria in an aerobic environment.



The autotrophic bacteria using carbon source (e.g. phenol) for growth to convert the nitrogen matter.

Denitrification is the conversion of nitrate to nitrogen gas by heterotrophic bacteria in anoxic environment. The heterotrophic bacteria need an electron acceptor for respiration of organic matter. When the oxygen is depleted, anoxic environment, the bacteria turns to nitrate to use as an electron acceptor. The nitrate then converts to nitrogen gas [h].



Consequently, a good nitrification is needed for good removal efficiency for COD and $\text{NH}_3\text{-N}$.

The hydraulic retention time is very important in this step. If the water is not in the aeration process for a sufficient length of time, the effluent discharged may have an unsatisfactory high level of BOD and ammonia [e].

The metabolism of phenols and cyanides can easily be accomplished with biological treatment, such as active sludge process with a surplus of oxygen, a pH of 7-9, adequate amount of nitrogen and phosphorus. If the amount of phenol is high, i.e. > 2000 mg/L it requires to be diluted, to gain a non-volatile working metabolization (Anox).

The environmental impact of industrial wastewaters containing ammonia unfolds at three different levels: toxicity toward water-born organisms; overmanuring of surface water and consumption of oxygen through nitrification [14]. Reduction of ammonia can easily be done by nitrification followed by denitrification step. However, an active sludge process (only the aerobic treatment) often seems to reduce enough of ammonia due to assimilation while it reduces phenol.

The activated sludge process is the most widely used form of wastewater treatment for industrial wastewater [10]. However, research has indicated that the technique *Sequential Batch Reactor (SBR)* is more efficient reducing ammonia, phenol, COD, SS and BOD_5 concentration than an active sludge process. This is probably a result of that the SBR activated sludge microorganism proved to be more resistant to the variation of influent phenol content than the corresponding activated sludge process, i.e. having a higher survival ratio [15].

5.1 Conventional Activated Sludge System

A conventional activated sludge system is a suspended-growth process and includes an aeration tank and a sedimentation tank. In the aeration tank, the aerobic oxidation of organic matter occurs to CO_2 , H_2O , NH_4 and new cell biomass, while the sedimentation tank is used for sedimentation of microbial flocks (sludge) produced while oxidations phase in the aeration tank. The recycling of a large portion of the biomass is an important characteristic of this process.

The primary effluent is introduced and mixed together with return activated sludge to form the *mixed liquor (MLSS)*. The MLSS is the total amount of organic and mineral suspended solids, including microorganisms [1]. Then, the MLSS is transferred to the settling tank where the sludge separates from the treated effluent. A fraction of the sludge is recycled back to the aeration tank, while the rest is further treated in an aerobic or anaerobic digestion.

The Activated Sludge flocks contain mostly bacterial cells as well as other microorganisms, inorganic and organic compounds. Microbial cells occur as aggregates or flocks, as a response of low nutrient conditions, i.e. low F/M ratio (see chapter 5.1.1). Sludge settling depends on the F/M ratio and sludge age. Good settling occurs when carbon and energy sources are limited and when the microbial specific growth rate is low. The optimum F/M ratio is 0.2-0.5 and a mean cell residence time of 3-4 days is necessary for effective settling. Poor settling can also be caused by physical parameters (e.g. pH, temperature), presence of toxicants (heavy metals) which can cause a partial deflocculation of the activated sludge [1].

Activated sludge is particularly suitable for high organic industrial wastewater. The effluent quality is the same as the wastewater quality in the basin. A slow food substrate to microbe ratio has the ability to withstand shock loads.

The popularity of using this method depends mainly of both an efficient reduction of organic substances and the non-to-hard maintenance.

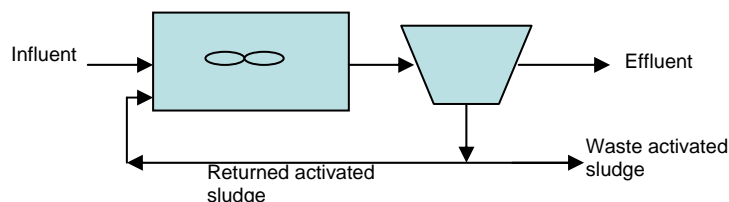


Figure 1- Activated Sludge Process.

5.1.1 Biological Parameters

Factors that affect the efficiency of the biological treatment includes *Food-To-Microorganism Ratio (F/M)*, *Hydraulic Retention Time (HRT)*, *Sludge Age*, *pH* and *Temperature*.

5.1.1.1 F/M ratio

F/M ratio indicates the organic load into the activated sludge system and is expressed in kg BOD or COD per kg MLSS per day:

$$F / M = \frac{Q \times BOD}{MLSS \times V}$$

where:

Q= flow rate of sewage in million gallons (3,78541 L) per day (MGD)

BOD= five-day biochemical oxygen demand (mg/L)

COD= Chemical oxygen demand (mg/L)

MLSS= mixed liquor suspended solids (mg/L)

V= volume of aeration tank (gallons)

The F/M ratio is controlled of the rate of activated sludge wasting. The F/M ratio for a conventional aeration tanks is between 0.2-0.5 lb BOD₅/day*lb MLSS. A low F/M ratio signifies starving microorganisms which generally leads to a more efficient wastewater treatment [1]. 1 lb

5.1.1.2 HRT

HRT is the average time spent by the influent liquid in the aeration tank of the ASP, and interacts with the dilution rate D:

$$HRT = \frac{V}{Q} = \frac{1}{D}$$

HRT is expressed in order of hours.

5.1.1.3 Sludge Age

Sludge age is the mean residence time of microorganisms in the system and intermingles with the microbial growth rate. Sludge Age is expressed as:

$$Sludgeage(days) = \frac{MLSS \times V}{SS_e \times V + SS_w \times Q_w}$$

where:

MLSS= mixed liquor suspended solids (mg/L)

V= volume of aeration tank (L)

SS_e= suspended solids in wastewater effluent (mg/L)

Q_e= quantity of wastewater effluent (m³/day)

SS_w= suspended solids in wasted sludge (mg/L)

Q_w= quantity of wasted sludge (m³/day).

Sludge age possibly will vary from 5 to 15 days depending on the seasons. It is higher during winter [20].

5.1.1.4 Recycling ratio (R)

The recycling ratio is the sludge being recycled to the reaction after settling tank.

$$R = \frac{Q_R}{Q}$$

where Q_R is the flow of the sludge being recycled and Q the influent flow.

5.1.1.5 Temperature and pH

Temperature affects the biomass directly and indirectly. Every organism has an optimal range of temperatures. The optimal temperature for growth will not necessarily be the same as the

optimal temperature for substrate oxidation/reduction. The optimal temperature is affected of factors such as electron donor, or acceptor availability, the chemical formation of the substrate at given temperatures and pHs, sensitivities to inhibitors at different concentrations, and the involved enzymes efficiency. Drastic temperature changes strain the bacteria which can lead to severe efficiency of the metabolism [21].

The success of the nitrification process is dependent on both temperature and pH.

As figure 2 shows, temperature and pH works co-dependent. At lower pH, nitrification is less dependent on temperature, but its initial rate is very slow. At higher temperature, nitrification is strongly dependent on pH, and its initial rate is very fast at pH7. The present optimum condition for nitrification by activated sludge seems to be 38°C and pH 8.0, with the initial nitrification rate of 8.2 mg/g*h [25].

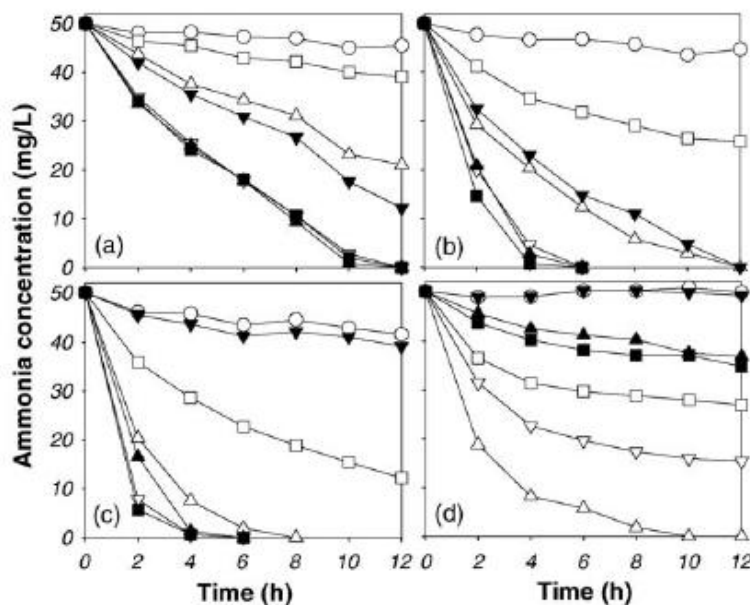


Figure 2- Effects of pH on nitrification at: (a) 20 °C; (b) 29 °C; (c) 38 °C; (d) 45 °C. This study was a batch experiment. Concentration of activated sludge was 3350–3360 mg/L and ash content 19–21%.

Symbols: (○) pH 6.0; (□) pH 6.5; (Δ) pH 7.0; (▽) pH 7.5; (■) pH 8.0; (▲) pH 8.5; (▼) pH 9.0 [25].

5.2 Sequencing Batch Reactors (SBR)

A SBR is a complete mix activated sludge system, with suspended growth and without a secondary clarifier. Aeration and clarification are carried out in one tank and within the single aeration basin, there are five different sequences; Fill, React, Settle, Draw and Sludge waste, see figure 2 for flow diagram.

Figure 3- Flow diagram for a SBR.

Sequence One: Fill

Add Substrate

Aeration: Cycled On-Off

Percent of Cycle Time: Approximately 25%

Sequence Two: React

Biochemical Oxidation of Organic

Aeration: On-Off to promote Denitrification

Percent of Cycle Time: Approximately 35%

Sequence Three: Settle

Clarification of Suspended Solids & Biomass

Aeration: Off

Percent of Cycle Time: Approximately 20%

Sequence Four: Draw

Remove Clarified Effluent

Aeration: Off

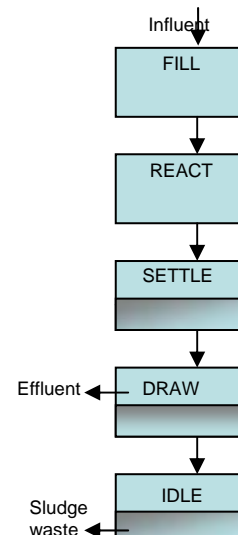
Percent of Cycle Time: Approximately 15%

Sequence Five: Idle

Waste Sludge

Aeration: Cycled On-Off

Percent of Cycle Time: Approximately 5%



The basin is filled with influent (Fill), then an aeration occurs when 100 % full (React), followed by a sedimentation and clarification (Settle). After settle, the effluent is withdrawn from the top of the tank (Draw) and the sludge is wasted from bottom of the tank (sludge waste).

An important element in the SBR process is that a tank is never completely emptied; rather, a portion of settled solids are left to seed the next cycle. This allows the establishment of a population of organisms uniquely suited to treating the wastewater [29].

5.3 MBBR

Bio filter

Moving Bed Biofilm Reactor (MBBR) is based on the process of fixed films. The advantages of MBBR are a continuous process without any risks for clogs and needs for backflash, with low pressure and high accessible specific surface. This is achieved by letting biofilm grow on a numerous small plastic carrier that moves along with the water in the reactor. It also belongs suspended through aeration.

The carriers vary in size and forms, they normally look like small cylinders and are made by polyethylene or polypropylene with a density close to water, see figure 1.

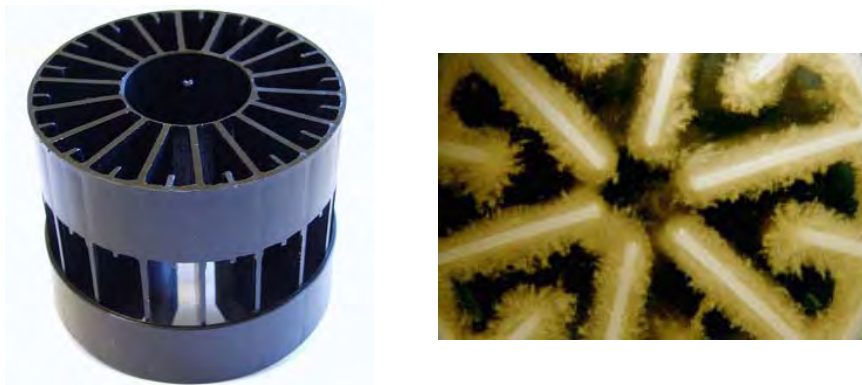


Figure 4. Left picture shows a typical MBBR carrier. Right picture shows the fixed film layer on the carrier [11].

The microorganisms are well protected which make the process strong towards variations, disturbance and extreme strains. The process is easy-manageable and the amount of active biomass is self-regulated and depends on the income strains. The carrier is continuous in movement due to oxygen from a bottom air system, which makes the process insensitive towards suspended material in the influent water. The effluent leaves the reactor through grating or strainers, which keeps the carrier behind in the process. The surplus sludge that continuously repeals from the carrier in a natural process, is transports with the effluent through the grating next to a post treatment step [17].

5.4 Nanofiltration

Nanofiltration can be used as an advanced treatment. NF is a membrane technology and is used for removal of dissolved particles ($>0.001\ \mu\text{m}$) from wastewater and can be used as a disinfected method before storage for reclaimed water. NF removes everything over the pore limits, including both organic and inorganic substances, bacteria and viruses. However, this method is not going to be discussed any further.

5.5 Ozonation

Ozone is a cost-effective chemical treatment method for many types of industrial wastewaters. Ozone can increase the *biodegradability* of wastewater, to be precise, increase the ratio BOD/COD before the activated sludge process with a factor of 10, if used as a pre-treatment step.

Ozone has a complex impact on wastewater parameters; it improves taste and odour, reduces colour, kills bacteria and virus and also, due to a combination of reactions with molecular ozone and organic species; oxidation of example phenol, iron, cyanide and other pollutants occurs.

Ozone dissolves in water better than oxygen. Dissolved ozone decomposes in water solutions faster the higher the pH. It is a very strong oxidant; it's only fluorine and $\cdot\text{OH}$ radicals that have higher oxidation potential. In reaction with unsaturated hydrocarbons, ozone forms very instable intermediates, *ozonides*, which decompose very quickly resulting in formation of polymers or aldehydes, ketones and organic acids. Ozonation of phenol advances through the steps of resorcinol's formation and decyclisation to muconic acid, muconic aldehydes and fumaric and maleic acids.

In *alkaline* conditions, ozone decomposition leads to the formation of $\cdot\text{OH}$ -radicals and to *indirect* and *non-selective* oxidation reactions (AOPs). The rate of attack by $\cdot\text{OH}$ -radicals is in general 10^6 to 10^9 times faster than the corresponding rate for molecular ozone [1,2].

Advance Oxidation Processes (AOPs)

The AOPs are called the *water treatment processes of the 21st century*. When applied in the right place, it can reduce the contaminants concentration from several hundreds ppm to less than 5 ppm. AOPs are defined as near ambient temperature and pressure water treatment processes which initiate complete oxidative destruction of organics based on the generation of hydroxyl radical $\cdot\text{OH}$. AOPs used for wastewater treatment includes, among others:

- Ozone at elevated pH (8.5)
 $3\text{O}_3 + \text{OH}^- + \text{H}^+ \rightarrow 2 \cdot\text{OH} + 4\text{O}_2$
- Ozone + hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$)
 $2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH} + 3\text{O}_2$
- Fenton system ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$)
 $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$
- Ozone + hydrogen peroxide + UV-radiation ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$)
 $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$
 $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH}$

The more advanced the more costly. For phenol and PAHs treatment, the best alternative is to generate hydroxyl radicals by the use of ozone and hydrogen peroxide, see figure 5. However, ozone treatment fulfils a good reduction for a much lower price.

AOPs are often used as either a primary treatment step or as post-treatment step [30,31].

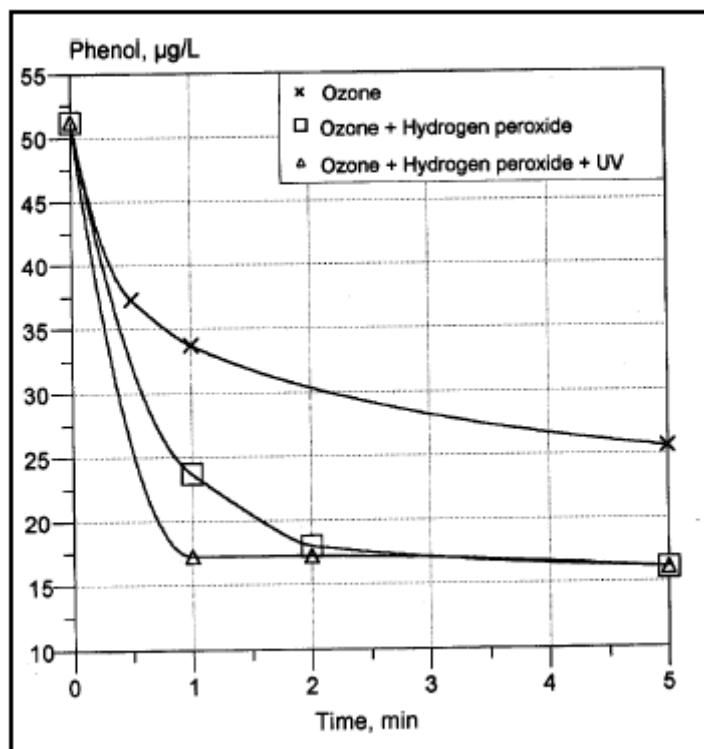


Figure 5. Phenol concentration reduction versus time [Preis et al., 1995]

5.6 Anaerobic-Anoxic-Aerobic system (A^2/O)

Many persistent organic compounds, such as PAHs have been found to degrade more rapidly under anaerobic conditions than under aerobic conditions. The critical steps in anaerobic degradation of these compounds include partial scission of polycyclic or heterocyclic rings and degradation of organics through anaerobic fermentation. Yet, the anaerobic degradation of organic compounds is generally slow and therefore less attractive for full-scale applications. As an alternative, use of the first phase of the anaerobic process as a pre-treatment process to partially convert persistent organics to intermediates that are more willingly degradable in aeration basin may be attractive for a good removal efficiency [36].

The system includes an anaerobic tank followed by anoxic and aerobic tank. The anaerobic unit mainly uses three biochemical reactions as a pre-treatment step [e]:

- Hydrolysis- Enzyme mediated transformation of complex organic compounds into more simple ones.
- Acidogenesis- Bacterial conversion of simple compounds into substrates for methanogenesis (acetate, formate, hydrogen, carbon dioxide).
- Methanogenesis- Bacterial conversion of methanogenic substrates into methane and carbon dioxide.

In the anoxic unit, organic compounds are oxidised by nitrate and phenol, while nitrate is also reduced to nitrogen gas and excess from the system. Organisms in anoxic system use the nitrite or nitrate as an electron acceptor and release nitrogen in the form of nitrogen gas. The heterotrophic denitrifiers using phenols as a carbon source, thus most of phenols are removed in this step. Additionally, very toxic free cyanide can be removed to some degree by anaerobes. In the aerobic unit, autotrophic nitrifiers convert ammonia into nitrite or nitrate into nitrite or nitrate. Meanwhile, autotrophic thiocyanate-oxidizing bacteria convert thiocyanate into ammonia and sulphate. These following microbial reactions can remove most

of pollutants within the cokes wastewater. The efficiency of A²/O system is significantly influenced by the chemical nature of wastewater, pH, and temperature, hydraulic retention time (HRT) and so on [16, 25, e].

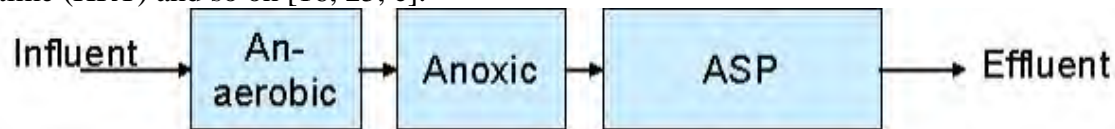


Figure 6- A²/O system

A single-sludge process with recycle of nitrified effluent, i.e. pre-denitrification process, has been preferred in Korea and seems to be popular in China, due to its simplicity and economic benefits [25]. This process consists of an anoxic tank followed by an aerobic one, i.e. an A²/O without the first anaerobic step.

5.7 Ammonia Steam-Stripper

The high ammonia content in the wastewater generated from coke industry renders the efficient of the activated sludge process in dire straights. A normal treatment method for these wastewaters is steam stripping as a pre-treatment method. Steam stripping or hot gas, such as air, can remove most of the ammonia, hydrogen sulphide, carbon dioxide and substances such as phenol, cyanides and light organics [18].

6. Huaxi Jiaohua Ltd.

The company uses 720 m³ water/day and claims that their treatment methods are unique and on a pilot scale. The unique methods include changing the wastewater time of duration in the biological treatment step and also adding oxygen after the active sludge process to reduce the sludge amount. With a high amount of oxygen, a conversion of sludge to CO₂ and H₂O will occur. However, they also admit that these methods are lacking some in efficiency. See flow diagram of the company's treatment methods.

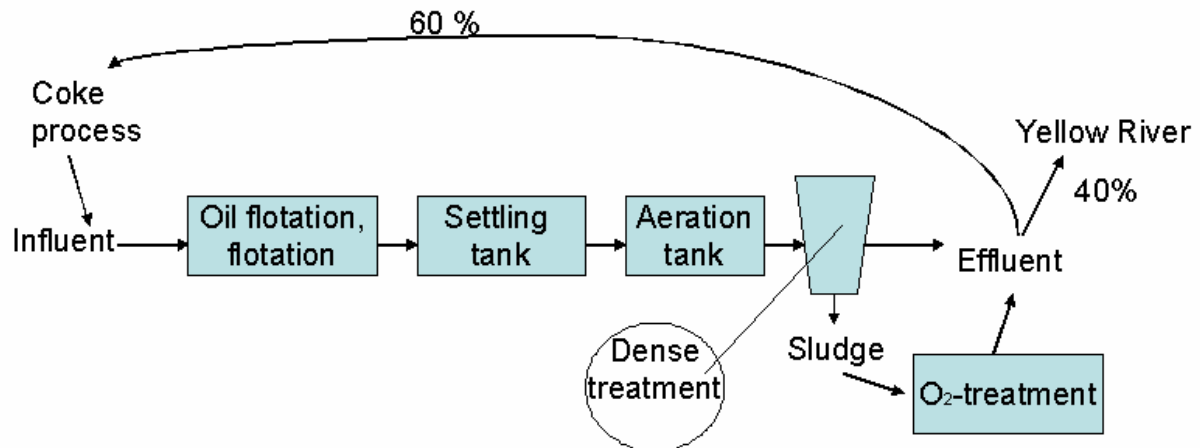


Figure 7- Flow diagram of the treatment station

6.1 Pre-treatment

After the coke cooling, the wastewater is treated with coal adsorbent. In this pretreatment station, oil is removed from the wastewater. This station concentrates the oil by creating flotation. The easy weight molecules go up to surface while the heavy weight molecules sink to the bottom. With this method a separation of oil can easily be done. However, it is very energetic costly. The coal together with the remaining oil is reused in the coke process, both as fuel and as coal.

This station is followed by a flotation step to separate oil and other organic compounds. The company would like to skip the latter flotation step, to be able to save energy costs.



Figure 8- the pre-treatment station containing coal flotation

6.2 Primary Treatment

Before the biological treatment step the company adjust the water quality, i.e. keep the wastewater stored in tanks.



Figure 9- the settling tank

6.3 Secondary treatment

The biological treatment step consists of a modified active sludge process. This step is under constantly changes. To reach the maximal reduction of phenols, and ammonia the company investigate which time of duration is best for the treatment. Therefore, according to the company, the time of duration of wastewater in the biological treatment step is somewhere between 15 to 36 hours from day to day.



Figure 10- The ASP

The bacteria are collected from communal wastewater treatment plant with a sludge age of 7-10 days. The aeration tank is followed by a thickener and not a clarifier. The primary propose of thickening is to increase the concentration of the sludge, whereas that of clarifier is to remove a small quantity of it.

6.4 Advanced treatment

The final step of treatment deals with the small amount of the produced sludge in the active sludge process. In this step, oxygen is added and the sludge transforms into CO_2 and H_2O . According to the company, this is a new treatment method, and no further information of the amount of oxygen or of the method could be announced due to patent policy.

After oxygen treatment 60 % of the treated water is recycled to the coke process, and the rest 40 % goes directly into the Yellow River, i.e. every day they discharge 220 m³ water. The company wants to be able to recycle more of the water.

6.5 Biological Parameters

When water comes directly from the cooling step in the coke process it has a pH between 7-8 and the water temperature is around 60-70°C. After oil removing and flotation the water temperature are 45-46°C. When the wastewater enters the biological treatment step it has a temperature of 39-40°C and a pH of 6,5-7. According to the company it is not a problem to run the wastewater treatment during winter times. They claim that during winter the temperature is 15°C less in every step and still high enough to make the treatment efficient, i.e. 45-55°C, 30-31°C and 24-25°C.

The Hydraulic Retention Time (HRT) is 15 hours and there is no information available for the other biological parameter such as F/M ratio or MLSS.

6.6 Levels of emissions

On the word of the company they measure the COD and NH₃-N one time per day, Dissolve Oxygen every second hour and phenols measurement take place from time to time. For concentration values before, and after treatment, see table 3.

Table 3- Concentration values before/after treatment that the company asserts to have.

<i>Measure</i>	<i>Before treatment [mg/L]</i>	<i>After treatment [mg/L]</i>
NH ₃ -N	4500	<100
COD	5000	220-230
Phenols	3000	<1.0
CN ⁻	> 50	No information
S	3000	<1.0

These values should not be taken seriously, according to EPB. The company claims that the current values are going to improve and by the end of September they will be reached: COD less than 150 mg/L; Phenols, S and CN⁻ <0.5 mg/L and NH₃-N less than 100 mg/L. These values should also not be taken seriously. See table 4 for the latest documented values from EPB, stated 2006-06-14.

Table 4- latest documented values from EPB.

<i>Measure</i>	<i>Before treatment [mg/L]</i>	<i>After treatment [mg/L]</i>
NH ₃ -N	2900	74
COD	4500	196
phenols	5000	158

The values in table 4 are more trustworthy and should be taken seriously. However, it is possible to reduce the amount from 158 mg/L to 1.0 mg/L by changing parameters. But, it is more likely that 1.0 mg/L refer to the effluent of the oxygen treated sludge. Therefore, the values stated by EPB are going to be put on focus, treated and discussed for improvement.

The data about the influent flow is contradicted, see table for values. Therefore, all three flow values are going to be discussed further.

Table 1- The influent flow of the company. The flow capacity and flow 2 were provided by mail, while the flow 1 was given on field trip.

	<i>Flow Capacity</i>	<i>Flow 1</i>	<i>Flow 2</i>
[m³/h]	30	550	720

Based on the amount of produced coke per year and a comparison with SSAB Tunnplåt AB, the most probable flow is 30 m³/h and is going to be further used, see appendix 2 for calculations.

7. SSAB Tunnsplåt AB as a comparison model

SSAB Tunnsplåt AB is the largest steel sheet manufacturer in Scandinavia and one of Europe's leaders in the development and manufacture of high-strength steel grades. It was formed in 1988 by the joining of the steelworks in Borlänge and Luleå. The company has a coking plant, blast furnaces and steelworks in Luleå, and steel sheet manufacturing in Borlänge. The production of Luleå factories supplies the factories in Borlänge.

Coke production	741 000 tonnes (2005)
Turnover	10 billion (2002)
Employees	4400 (Sweden)
Production capacity	2.8 million tonnes annually

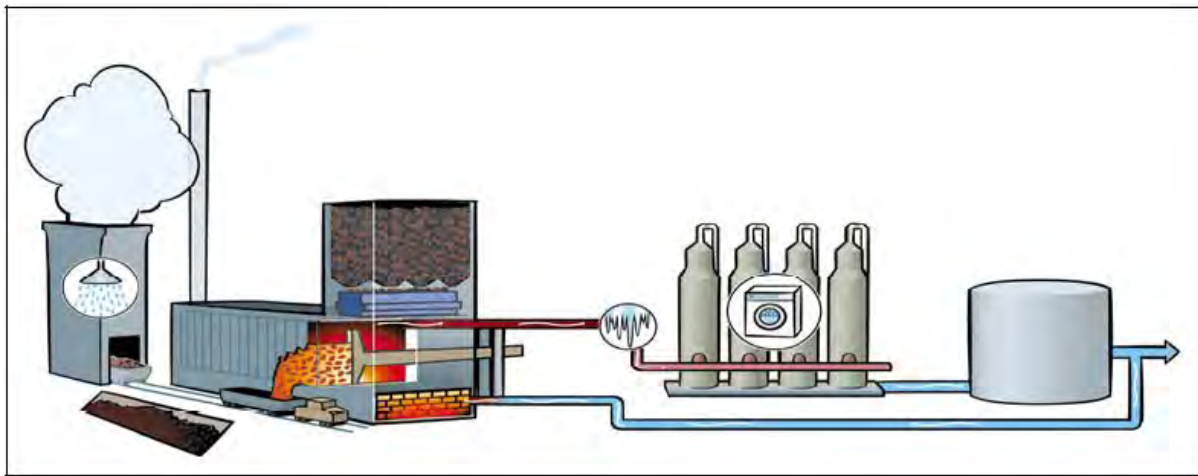


Figure 11- Coke factory with gas treatment [SSAB Tunnsplåt Luleå Environmental Rapport 2005].

7.1 Environmental Influence

The environmental influence that is caused by the SSAB Tunnsplåt activity is mainly connected to the consumption of reduction means in form of coal and cokes. The activity primarily causes air emission of dust and combustion (CO_2 , NO_x , SO_2).

7.1.1 Environmental picture of the coke factory

Energy and raw materials: The coke production delivers an energy-rich coke gas that in 40-45 % is reused to heat up the battery. The rest is consumed for other purposes.

Waste and rest products: Bi-products from the production; tar, raw benzene and sulphur, are sold. The remaining wastes are reused together with the coal.

The air emission occurs among others, from pressing, battery and cooling tower. The gas treatment consists of two dust filter; one is used for coal management, and the other is used for air treatment from the pressing. In the cooling tower the dust treatment takes place through screens. Emissions of CO_2 , NO_x and SO_2 arise from combustion of coke gas in battery and steam furnace. Water emissions occur after biological treatment to cooling water outlet and contain less amount of ammonium, organic and suspended substances.

The wastewater treatment is fairly good, and therefore, SSAB Tunnsplåt is taken as a reference for further considerations and comparisons.

7.2 The waste water treatment station

As a treatment method SSAB have chosen an active sludge process with a following flotation step to reduce the sludge escape, see figure 14. Active sludge process provides a good reduction of phenols and cyanides and PAHs that are stored in the sludge. The disadvantage with this process is the cost of operation of air fans; ~100 kWh with the processwater flow at 25 m³/h, HRT of 48 hours and MLSS of 10 kg/h. For further reduction of sludge escape, ironchlorid is added into the sedimentation pool (1).

Table 5- Average concentration of substances before and after treatment, yr 2005.

<i>Substance</i>	<i>Influent [mg/L]</i>	<i>Effluent [mg/L]</i>
N-NH ₃	50	16
Phenol	700-1000	0.05
COD	4500	240
Cyanide free	100-200	
SS	10000-15000	8.9
PAHs	--	0.5

The biggest problem for SSAB Tunnpå AB is the varied thiocyanate concentrations. Thiocyanate converts to ammonia and sulphur compounds. They are also very toxic towards the nitrifiers.

A suggestion by SSAB Tunnpå AB for improving the reduction of thiocyanate, is to introduce a primary anaerobic settling tank of 2000 m³, and a bigger clarifier. A greater clarifier reduces the needs of precipitate chemicals and the strain of the followed flotation step. A flotation step is needed to reduce the suspended sludge of 10-15 g/L to 20 mg/L. The temperature and pH in the aeration tank are 30° respective 7.1, the pH is adjusted with lye. See appendix 3 for level of emissions during 2002-2005.

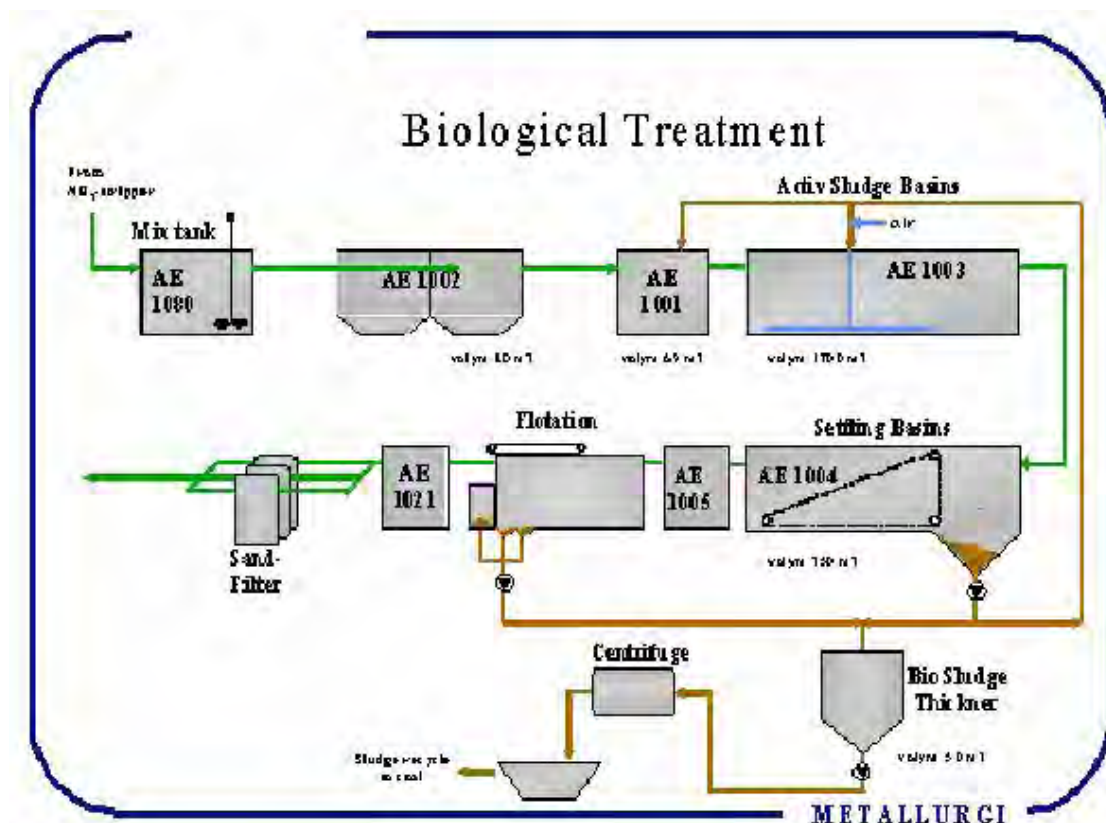


Figure 12-Biological treatment of coke-oven wastewater at SSAB Tunnsplåt.

SSAB Tunnsplåt AB has chosen a NH_3 -stripper as a pre-treatment step followed by a settling secondary one. The NH_3 -stripper reduces the ammonia by heating up NH_3 with the steam. A NH_3 -stripper is necessary to have low ammonia concentrations in the influent. After the ASP the water pass a flotation step and a sand filter to be able to reduce the suspended sludge. The suspended sludge produced in the ASP is after advanced treatment such as; flotation, bio-sludge thickener and centrifuge burned together with the coal, see table 6 for comparison of the treatment step between Huaxi Jiaohua Ltd and SSAB Tunnsplåt AB.

Table 6- Comparison of different treatment methods between Huaxi Jiaohua and SSAB Tunnsplåt AB

Type of treatment	Huaxi Jiaohua Ltd.	SSAB Tunnsplåt AB
Pre-treatment	Oil flotation, flotation	NH_3 -steam stripper
Primary treatment	Settling pool	Settling pool
Secondary treatment	ASP	ASP
Advanced treatment	Oxygen treatment	Flotation, sandfilter

Table 2- comparison of concentration between the two factories.

	Huaxi Jiaohua Ltd (june 2006)		SSAB (2005)	Tunnplåt AB
Substance	<i>Influent</i> [mg/L]	<i>Effluent</i> [mg/L]	<i>Influent</i> [mg/L]	<i>Effluent</i> [mg/L]
N-NH ₃	2900	74	50	16
Phenol	5000	158	700-1000	0.1
COD	4500	196	4500	
Cyanide free				0.06
SS	--	--	10000-15000	20
SCN ⁻			100-200	
PAHs	--	--		0.5

8. Possible Improvements

The ideal treatment plant is associated with minimal pollution discharge, minimum treatment cost and maximum social-cultural benefits. When optimizing the present treatment station, factors such as multiple economic, technical and administrative performance criteria, land area, discharge and more, needs to be considered.

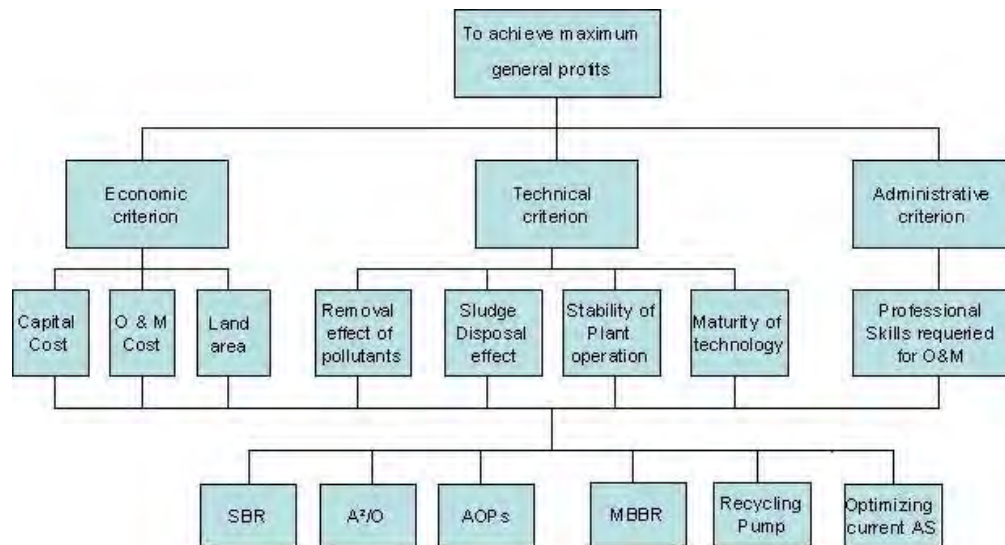


Figure 13- A hierarchy decision model for optimizing the wastewater treatment plant alternative selection.

8.1 Improvements on treatment steps

The Environmental Protection Bureau claims that the amount of emission that the company Huaxi Jiaohua Ltd state to have, is wrong. In reality, it is not impossible to achieve the reduction of phenol from 158 mg/L to 1.0 mg/L in two months by changing parameters such as flow rate. Yet, this thesis are only going to considering improvements for how to reduce 158 mg/L phenol to 0.5 mg/L. The improvements can be made either by optimizing secondary treatment step, or by add treatment methods as a pre- or advanced treatment step.

Five different modifications are recommended for reducing the amount of phenol from 158 mg/L to 0.5 mg/L:

1. Modify the pre-treatment step
2. Optimize secondary treatment step
3. Add an advanced treatment step
4. Replace the current station with SBR
5. Final clarifier and sludge treatment

8.1.1 Add a pre-treatment step

The current treatment station includes a flotation as an oil flotation followed by a flotation step as a pre-treatment. The company would like to exclude the flotation step, due to cost savings. A modification could be done, either by adding an AOP to the station or by replacing the flotation, alternative put in on hold, see figure 14. The chosen AOP would include either ozonation, O_3/H_2O_2 or $H_2O_2/Fe(II)$.

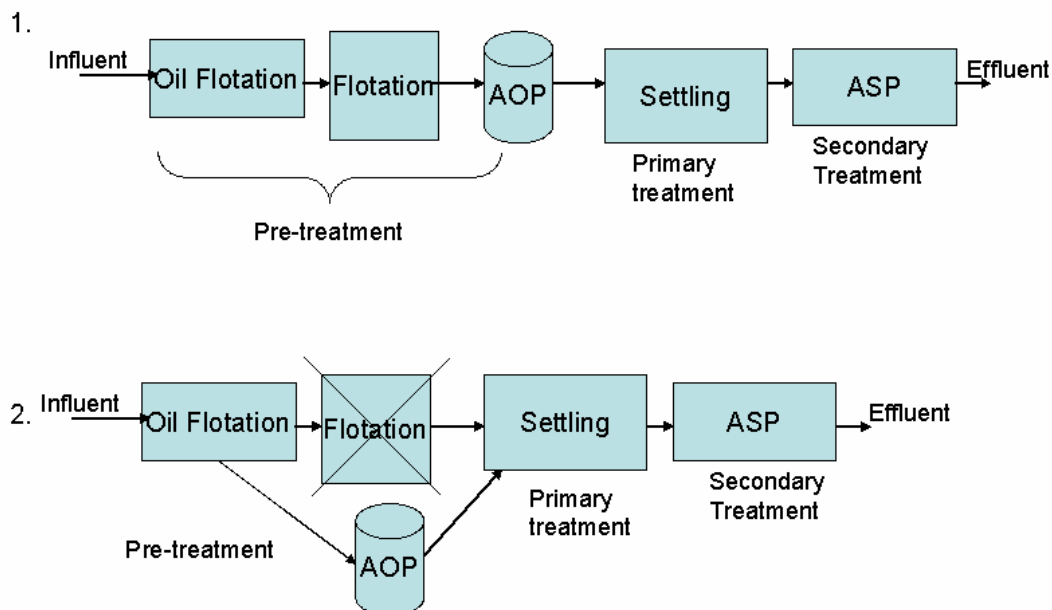


Figure 14- Modification of the pre-treatment step. Figure 1 shows the adding of AOP into the system, while the figure 2 shows the replacement of flotation of AOP.

8.1.2 Optimize the current secondary step

The secondary step can be optimized by either modification of the biological parameters in the current activated sludge system, or by adding anaerobic-anoxic tanks to it.

8.1.2.1 Modification of the biological parameters

Optimizing the biological parameters can improve the nitrification process and the removal of pollutants. During the winter time, the coke wastewater in the aeration tank will decrease with 15 degrees assumed that the pH is the same as in summer time. It is shown that temperature and pH are related to each other and the nitrification process is dependent of both parameters. An improvement of nitrification would be if the pH in the aeration tank reaches 8.0 during all the seasons.

Table 3- The temperature and pH in the aeration tank during summer and winter

<i>Aeration tank</i>	<i>Summer</i>	<i>Winter</i>
Temperature °C	39-40	24-25
pH	6.5-7	6.5-7

The F/M ratio for a conventional ASP should be between 0.2-0.5 lb BOD₅/day/lb MLSS. There is no current value of the company's F/M ratio available, but if it's more than 0.4 BOD₅/day/lb MLSS a decrease to 0.2 would improve the nitrification. A decrease in F/M ratio can be made by either enhancing the flow/BOD, and/or reducing the volume/MLSS. However, this is not subjected to further considerations due to lack of information on F/M or MLSS values from the company.

The sludge age for a conventional activated sludge varies from 5 to 15 days. The present sludge age of the coke factory is 7-10 days; an increased sludge age to 12 days would probably acclimatize the nitrifiers (especially when no recycling of the sludge occurs), which will improve the removal efficiency.

With enlarged tanks, a longer hydraulic retention time (HRT) is possible. With a longer break time and lower flow, the sludge would have more time to metabolise more phenol.

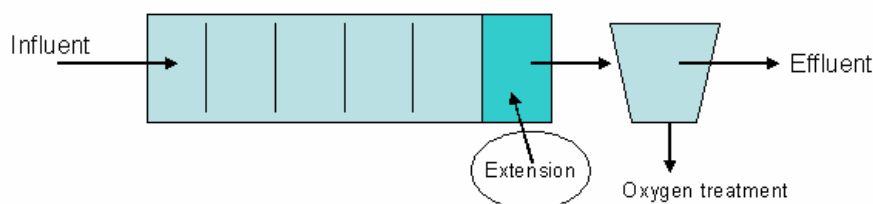


Figure 15-An extension of the aeration tank would enhance the HRT

HRT of at least 12.6 hours is required for a functional nitrification. A longer HRT requires a bigger volume of the aeration tank; see RESULT for conceivable volume and costs.

8.1.2.2 Modification of the present Activated Sludge System

When optimizing the biological parameters such as F/M ratio, pH, sludge age, stabilizing the temperature does not result in enough reduction of COD then modifications on the ASP should be performed. There are two possible modifications for the activated sludge system;

1. Introducing a recycle pump
2. Enlarge the volume and introduce a recycle pump

The present system does not recycle the sludge. This is a waste, not only do they need to introduce new bacteria from urban wastewater treatment, but also, the bacteria are not very selective towards phenol. If a recycling of sludge would be introduced to the system, the sludge would be more selective, which would improve the phenol reduction. With a recycling, the current last step (the oxidation step) is not necessary, and also the amount of imported new sludge from urban wastewater treatment would decrease. A combination of an extra tank and recycling of the sludge would improve the reduction of phenol and other substances a number of times.

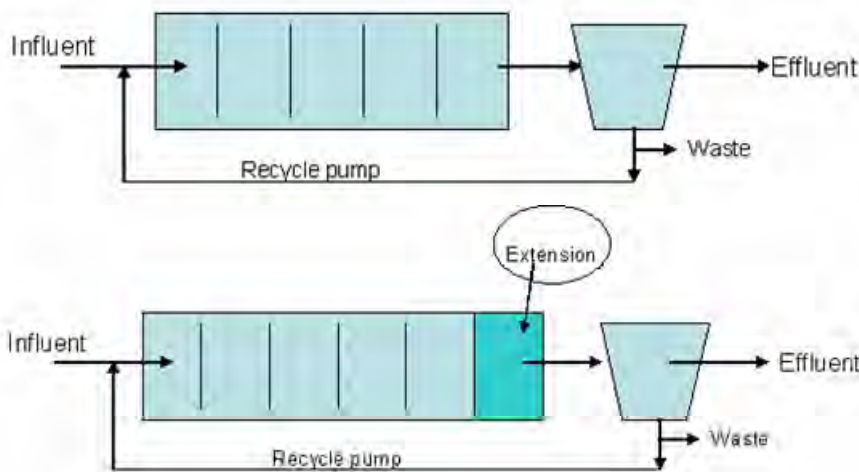


Figure 16- A schematic picture of an introduction of a recycle pump and volume extension

8.1.2.3 Modification to A²/O

The management of the company wanted to introduce anaerobic and anoxic tanks in the present system to yield a better reduction of the COD. This would modify the present ASP to an A²/O system.

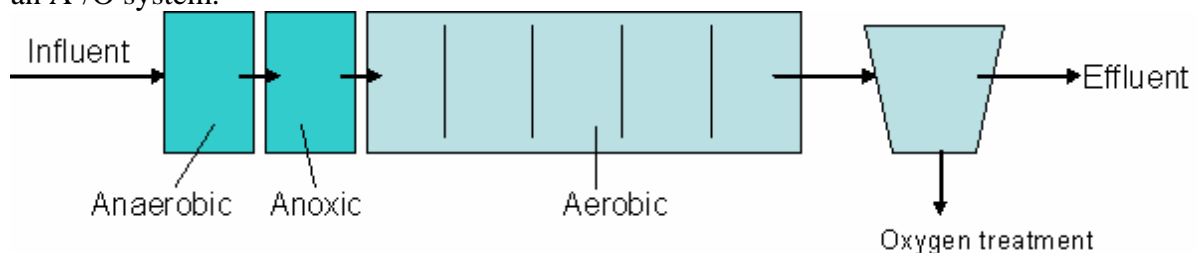


Figure 17- Modification of ASP to an A²/O system

Alternative, instead of introducing both anaerobic and anoxic tank, an anoxic tank could be established. The primary treatment step contains an anaerobic settling pool, and to save money and land area only an anoxic tank needs to be set up.

8.1.3 Addition of an advanced step

8.1.3.1 Biofilm as a post-treatment step

It is not necessary to replace the existing Active Sludge system into a biofilm system, but an introduction of a MBBR as a post-treatment step would reduce the amount of phenol to the levels of emission standards. This post-treatment would be put directly after the biological step. With this extra step, the surplus sludge that continuously repeats from the carrier in a natural process and follow the effluent through the grating can possibly be reused and improve the status of the active sludge system. Also, with this step, the sludge amount would decrease and an oxidation-treatment step is not necessary.

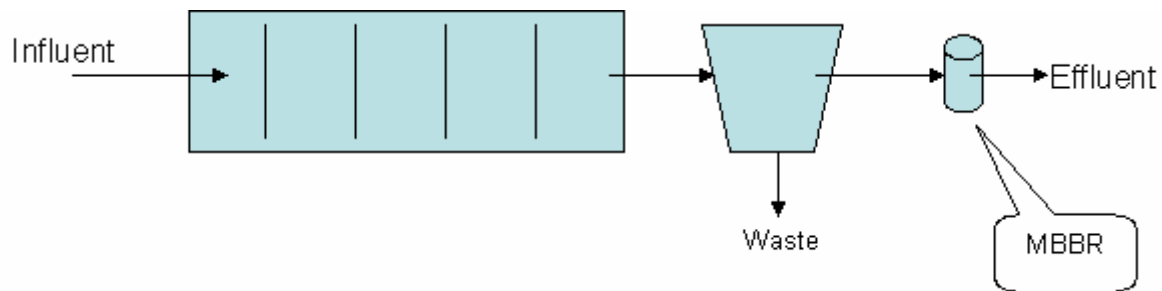


Figure 18. MBBR as a post treatment step

8.1.3.2 AOPs as a post-treatment step

It has been shown in several studies that AOPs to be very effective for the destruction of different organic pollutants, including phenol and PAHs. AOPs as a post-treatment step after the clarifier, see figure 21, would include a reactor with one of the following ozone treatment; O_3 , H_2O_2 , UV, O_3/H_2O_2 , O_3/UV or $O_3/H_2O_2/UV$. AOPs as an advanced step would also act as a disinfection step.

8.1.4 Replacement of the current station with SBR

The fourth alternative includes a replacement of the present system with a Sequential Batch Reactor. SBR is known to be very effective towards substances such as phenol. The sludge is very tolerant towards toxic shocks, strains and so on. A replacement would include either a parallel treatment station next to the present active sludge system, if plenty of space, or a demolishing of the present system. The latter would force the production of coke on rest while constructing the SBR, which would put the coke battery on strains. This would consecutively, generate a huge economic loss for the company and have an effect on the battery's status.

8.1.5 Secondary Clarifier and sludge treatment

The final alternative includes introduction of a final clarifier and sludge reuse. Currently, the sludge is not recycle back to the aeration tank but is treated with high amount of oxygen. The oxygen treatment is not as efficient as wanted, and consumes much electricity and oxygen. As an alternative to oxygen treatment is to recycle the sludge back to the aeration tank and introduce a final clarifier directly between the aeration tank and the thickener. The sludge that is not going to be recycled back is pumping to the thickener, and then centrifuged as a dehydration method. The remaining sludge is then collected and used as a fuel together with coal.

9. Results

9.1 Removal Effect on Pollutants

9.1.1 Modification of pre-treatment step

Ozonation of some phenols has shown to produce ozone-resistant toxic by-products. Among them are phenol, 2- and 4- cresols and more. Therefore, it is important that the ozonation not only improves the biodegradability but also reduces the toxicity.

These findings are based on experiments on semicoke from an oil shale [23]. Semicoke contains 5-10 % of organics, 65-75 % of ash and 1.5 % of total sulphur [24]. The waste heaps forms toxic leachate while exposed to rainwater and snow. The leachate contains high amount of phenols (up to 500 mg/L).

The experiments show that ozonation as a pre-treatment step removed from 40 to 63 % of organics in a three-hour period (pH 9.36-10.37). However, it did not detoxify but instead enhanced the phenol toxicity. An enhanced toxicity would be devastating for the nitrifiers. Therefore, it is not recommended to use ozonation as a pre-treatment. Nevertheless, when adding a catalyst (Fe^{2+}) to the Fenton Reaction, a COD reduction of 72-86 % was achieved during 24 hours period, with an increase in the biodegradability and a 2.3-fold reduction in toxicity (pH 9.36-10.37). Hence, the Fenton treatment may be applied as a pre-treatment step [23]. Normally a Fenton reaction occurs in low pH (~ 3), but the experiments showed that the COD removal was even greater without a pH adjustment (i.e. pH 9-10). The COD removal was strongly dependent on the $\text{H}_2\text{O}_2/\text{COD}$ ratio when the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was keep constant at 10:1, see appendix 4. The commonly used ratios of $\text{Fe}^{2+}/\text{COD}$ are 0.5, 0.1 and 0.05, whereas the $\text{H}_2\text{O}_2/\text{COD}$ ratio is 1 [26].

The pH of the influent before the settling pool is 7-8 and after 6.5-7, which means that no pH adjustment is needed for treatment of AOP, Fenton reaction.

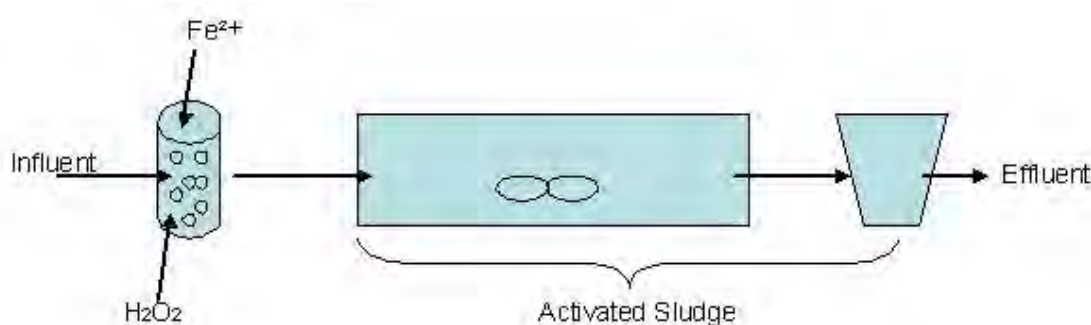


Figure 19- Fenton process as a pre-treatment step

Around 80 % of the COD is phenol, and a reduction of 72-86 % of the COD would give the phenol concentration between 504-1000 mg/L, see table 1. The following nitrification would be able to reduce the phenol concentration under 60 mg/L, see table 2.

Table 4- The concentration of COD and phenol at a HRT of 24 hours.

	72 %	86 %
COD [mg/L]	1260	630
Phenol [mg/L]	1008	504

9.1.2 Optimizing the biological parameters

9.1.2.1 HRT

These findings are based on biodegradation of coke wastewater on a laboratory-scale of activated sludge plant composed of a 20 L volume aerobic reactor followed by a 12 L volume settling tank [12]. The influent fed into the reactor was coke wastewater that had been subjected to a stripping pre-treatment. See figure 20 for the relation between removal efficiency and HRT.

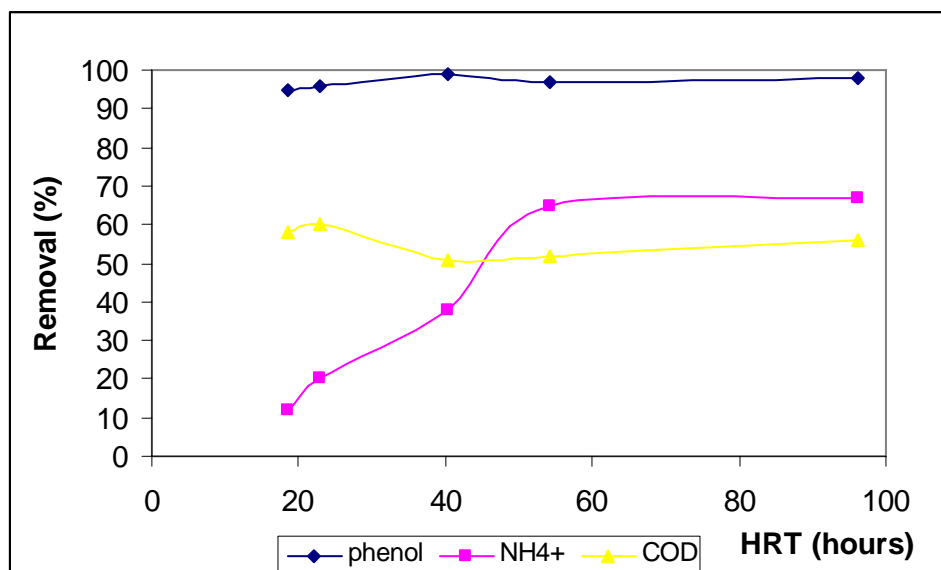


Figure 20- The removal efficiency proportional to HRT [values from reference 12].

As can be noted in the figure 20, the phenol removal is not dependent on the HRT. However, the NH_4^+ removal depends on the HRT. The optimal HRT for NH_4^+ removal in this study is 54.3 hours and nitrification does not take place using HRT below 12.6 h (the current HRT is 15 h). Yet, the NH_4^+ removal in the current treatment station are working fine and therefore, no greater consideration of the HRT needs to be taken.

Nonetheless, an extension would indeed dilute the mixed liquid, and the thiocyanate amount would decrease.

9.1.2.2 Temperature and pH

To be able to have good removal efficiency during winter time an enhancement of pH to 8.0 would improve the nitrification with circa 80%. A study of nitrification efficiency in condition to different pH and temperature demonstrated that temperature of wastewater of 20-38 °C is best nitrified at a pH 8.0, but at temperature 45°C best nitrified at pH 7.0, see figure 3 [25].

9.1.3 Modification of the activated sludge process

The present secondary treatment step of the coke factory is a modified activated sludge process.

A rebuilding of the present ASP to a conventional ASP, i.e. with recycling of the sludge and a following settling tank, would improve the nitrification.

These values are gathered from the study of efficiency of removal of coke wastewater, see reference [15]. An influent with a phenol content of 700-1200 mg/L results in operation problems for the ASP, such as:

- Decrease in the removal capacity of the organic load (BOD, COD)
- Decrease in nitrification efficiency
- Limited phenol degradation → effluent phenol content ranged from 10-60 mg/L
- Decrease in sedimentation capacity

The high phenol and cyanide concentration greatly affected the ASP, due to toxic effects on the microfauna generating in high COD values. The removal efficiency of a conventional ASP is shown in table 5.

Table 5- removal efficiency of a conventional ASP compared to the present ASP, b.t – before treatment, a.t- after treatment.

<i>Pollutants</i>	<i>Before treatment [mg/L]</i>	<i>After Treatment [mg/L]</i>	<i>Removal Efficiency [%]</i>	<i>Huaxi Jiaohua Ltd [mg/L]</i>	<i>Huaxi Jiaohua b.t. Ltd a.t. [mg/L]</i>	<i>Removal Efficiency [%]</i>
NH ₄ ⁺ -N	200-328	25-91	83-95	2900	74	97
Phenol	700-1200	10-60	91-95	5000	158	97
CN ⁻	70-270	1.1-2.8	97-99	--	--	--
COD	4000-7000	295-1500	67-93	4500	196	96
BOD ₅	3040-6000	150-500	82.5-95	--	--	--

The MLSS varied from 2100 to 5300 mg/L showing the toxic response of phenol and cyanide. The MLSS in the current treatment station would most likely differ even more. With a recycling of the sludge, the microfauna would be more stabilized, more selective towards phenol, and the MLSS would not differ as much. See figure 21 for the relation between COD removal and recycling ratio (R) [13].

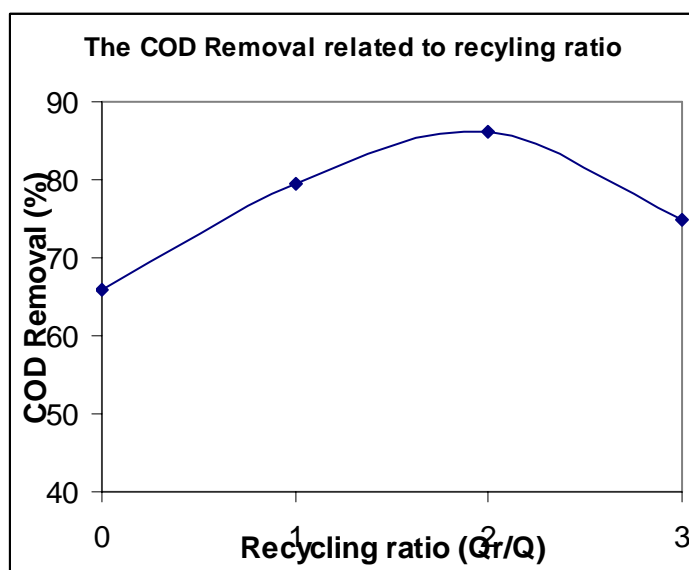


Figure 21- The COD Removal relative the recycling ratio, HRT= 98 h.

According to Figure 20, the best recycling ratio is achieved at level 2.0.

Table 6- Average COD and $\text{NH}_4^+\text{-N}$ removals under different working conditions

HRT	R	kgCOD/ m^3d	VSS (g/L)	kgCOD/kgVSS/day	COD removal (%)
27.8	0	1.33	3.0	0.41	45.5
42.4	0	0.82	2.6	0.31	68.6
61	0	0.48	2.0	0.26	77.6
98	0	0.29	2.1	0.13	65.9
98	1	0.35	2.5	0.13	79.6
98	2	0.42	2.8	0.13	86.2
98	3	0.78	2.6	0.15	74.9

The removal efficiency of some pollution in the current ASP is in some extent better than the ones in the study. Even so, a dilution of the 5 times would improve the phenol reduction.

9.1.4 Modification to an A^2/O or A/O system

These results are gathered from a comparison study between A^2/O and A/O of coke wastewaters [36]. At a total HRT of 37.9 h for $\text{A}_1\text{-A}_2\text{-O}$ *biofilm system*, more than 85% COD, 97% BOD and 98% NH_3 were removed from a coke wastewater with COD 600-900 mg/L and NH_3 200-300 mg/L, see table 7. It should be noted that after acidogenic stage, the COD concentration decreased but the BOD concentration to some extent increased, probably due to that some refractory compounds were converted into more readily biodegradable compounds. With a decrease in total HRT, the COD, BOD and NH_3 removal remained the stable while organic-N declined from 89 % to 80 % and 76 % for a total HRT of 29.8 h respectively 26.0 h. Meaning, a decline of HRT results in a reduced NO_3 concentration, but a significant accumulation of $\text{NO}_2\text{-N}$ concentration. Hence, to avoid the accumulation of NO_2 a high HRT should be maintained. This is important due to the presence of NO_2 contributes around half of the COD in the final effluent.

Table 7- Performance of A₁-A₂-O biofilm system at HRT_{A1}=7.6, HRT_{A2}= 10.6, and HRT_O=19.7h, inf=influent, eff=effluent [36].

Analytical items	Acidogenic unit			Anoxic unit			Aerobic unit		Overall removal (%)
	Inf	Eff	Removal (%)	Inf	Eff	Removal (%)	Eff	Removal (%)	
COD, mg/l	860	768	11	258	158	39	131	17	85
BOD, mg/l	294	313	+	70	20	72	9	52	97
NH ₃ , mg/l	232	244	+	52	66	+	4	94	98
Organic-N, mg/l	107	102	5	30	27	10	12	57	89
NO ₂ ⁻ , mg/l	0	2	+	5.91	11	+	7	/	/
NO ₃ ⁻ , mg/l	42	32	23	133	95	29	158	/	/

Note: Symbol “+” means the item increased.

At same or similar level of HRT, the A/O system had almost same levels of COD, BOD, and NH₃ removals, but with a declining organic-N removal. See table 8 for performance of A/O system.

Table 8- Performance of A/O biofilm system at HRT_A= 18.2 h and HRT_O=19.7 [36]

Analytical items	Raw wastewater	Anoxic unit			Aerobic unit		Overall removal (%)
		Inf	Eff	Removal (%)	Eff	Removal (%)	
COD, mg/l	800	262	168	36	127	24	84
BOD, mg/l	230	51	11	79	7	39	97
NH ₃ , mg/l	218	45	51	+	1	97	99
Organic-N, mg/l	118	38	19	51	18	5	85
NO ₂ ⁻ , mg/l	0	2	7	+	3	/	/
NO ₃ ⁻ , mg/l	43	128	95	26	149	/	/

Note: Values in the brackets were COD excluding the part of COD attributed by nitrite.

In both systems, a short HRT do not result in any particular effects on the COD, BOD and NH₃ removal efficiencies, but it does influence the organic-N removal and distribution of oxidized nitrogen in the final effluent. Meaning, for total nitrogen removal an A²/O system is more efficient, but otherwise, the both system works more or less the same. However, these results are based on biofilm process and not suspended growth; yet, it indicates the differences in removal efficiency between the both systems and can be used as a guide.

Another study made by S. Chakraborty [37] shows that in an anoxic-aerobic suspended growth process the removal of an influent containing; phenol, NH₄⁺-N, SCN⁻ and CN⁻, a good removal was achieved, see table 9.

Table 9- Removal efficiency of an A/O suspended growth process.

Substances	Influent [mg/L]	Effluent [mg/L]	Removal [%]
Phenol	185	1.85	99
NH ₄ ⁺ -N	100	22	78
SCN ⁻	100	4	96
CN ⁻	60	0.6	99

Yet, the present station is currently dealing with an influent of more than 10 times concentrations of phenol and NH₄⁺-N. If the same removal efficiency would be applied on this influent, a reduction from 5000 to 50 mg/L phenol and 2900 to 638 mg/L NH₄⁺-N would be achieved, i.e. a decline in reduction of NH₄⁺-N.

9.1.4 Add an advanced treatment step

9.1.4.1 MBBR

MBBR process is easy to maintain and stable towards treatment of difficult industry wastewater. It can manage strains, and removes COD well from the system.

According to the manufacture of MBBR, AnoxKaldnes, the phenol concentration of 158 mg/L is going to reduce to a level under 10 mg/L with a HRT of 3.33 h. 60-80 % of COD is phenol, which is easy degradable. PAHs is not very biodegradable and a MBBR process would indeed

Denna process är lättskött och stabil och lämpar sig därför mycket väl till behandling av knepiga industrivatten.

9.1.4.2 AOPs

These facts are based on experiments on different AOPs treatment on phenol and PAH [27, 28].

Among the treatment methods using ozone, O_3 , O_3/H_2O_2 and $O_3/H_2O_2/UV$, the two latter ones achieved best results. O_3/UV enhanced the ozone requirements when compared with simple ozonation and therefore will not be considered as an alternative for AOP. Phenol concentration was correspondingly reduced after 60 s of treatment by 58%, 67 % and 67 %. The efficiency of the different oxidation methods is summarized in table 10.

Table 10- The efficiency of Oxidation Methods. d_{O_3} - dose O_3 , [D]C- removal of total phenols. The changes in the concentration of total phenols are given as percentages.

	d_{O_3} [mg/L]	T (min)	[D]C
O_3	3	1	58
O_3/H_2O_2	3	1	67
$O_3/H_2O_2/UV$	3	1	67

A 58 % reduction of phenol would give a value of effluent of 66 mg/L phenol for a 1 minute ozone treatment.

Ozone was shown to be very efficient for degradation of PAH, several of PAH can be removed completely in a few minutes of ozonation. The behaviour of PAH in ozonation and AOP treatment is compound-specific and the reaction rate of ozonation is always higher in acidic and neutral media than in basic one, see appendix 5.

Yet, ozonation do not reduce the toxicity of effluents. What toxic ozonation by-products are formed and in what extent, is still unknown. Higher ozone doses would likely reduce the toxicity due to destruction of the preliminary by-products, but it requires the laboratory tests for the certain effluent to determine the exact required ozone dose. Thus, the toxicity problem is complicated and needs more systematic studies, before treatment application [33].

The chemistry of the wastewater matrix is different for each wastewater, pilot testing is recommended every time a deeper study is initiated. The objectives of pilot testing are to test the technical achievability, to obtain usable design data and information and to obtain operating experience with a specific AOP. Factors such as high concentrations of carbonate and bicarbonate, suspended material, pH and contents of COD can reduce the efficiency of AOP [32].

The current station does not have any clarifier after the aeration tank, but a thickener. The thickener increases the solids content from 3 to 6 per cent. This does not have any good effect on the AOPs. On the contrary, it will react with the OH^* which requires a longer ozonation time for an efficient treatment.

9.1.5 Replace the current station with SBR

These values are taken from a comparison study between a conventional ASP and a SBR treating coke wastewater. The study shows that introduction of high phenol influent concentration (700-1200 mg/L) did not especially affect the operation of the SBR, resulting in effluents of high quality [15], see table 1 for removal efficiency.

The SBR system showed almost complete phenol degradation for influent concentrations up to 1200 mg/L. The coke wastewater in this factory has an influent value of 5000 mg/L which is needed to be diluted to a concentration of 1000 mg/L to generate a good reduction of both phenol and other pollutions. The addition of phenol and cyanide slightly affected the microorganism's concentration, but did not decrease its degradation efficiency. The MLSS content varied between 4600 and 600 mg/L. The removal of organic matter, COD, BOD₅, and of ammonia nitrogen was done by 87-99 % and was not affected neither by the high phenol amount nor the cyanide amount.

Table 11- Removal Efficiency of SBR compared to the current treatment station.

<i>Pollutants</i>	<i>Before treatment</i> <i>[mg/L]</i>	<i>After Treatment</i> <i>[mg/L]</i>	<i>Removal Efficiency</i> <i>[%]</i>	<i>Huaxi Jiaohua Ltd b.f</i> <i>[mg/L]</i>	<i>Huaxi Jiaohua Ltd a.f</i> <i>[mg/L]</i>	<i>Removal Efficiency</i> <i>[%]</i>
NH ₄ ⁺ -N	200-328	2-23	93-99	2900	74	97
Phenol	700-1200	1.0-4.6	>99	5000	158	96,7
CN ⁻	70-270	1.1-2.8	97-99	--	--	--
COD	4000-7000	270-550	87-95	4500	196	95,6
BOD ₅	3040-6000	60-152	95-99	--	--	--

Sequential Batch Reactor is a good treatment alternative with regard to pollution removal efficiency. A pre-treatment step of a 5-10 times dilution for a good removal of NH₄-N and phenol is recommended, with reference to the values in Table 11. Alternative let the current primary settling pool act as a pre-treatment step, if the volume of the pool is adequate for a dilution or introduce a NH₃ steam stripper.

9.2 Land Requirements

9.2.1 AOPs of pre-treatment step

Fenton Process with a HRT of 24 hours would decrease the COD reduction of 72-86 %. The inside volume required for this are 720 m³ (Q= 30 m³/h).

9.2.2 Optimizing the biological parameters/ modify the present ASP

The volume required for an extension of the Aeration tank depends on the requested HRT. See figure 19 for more details. At the present time, changes up to HRT= 36 hours can occur, meaning, preference to a greater HRT than 36 h would require an extension of the volume. For a HRT of 50 h, the required volume is 1500 m³, i.e. an extension volume of 420 m³. No extra land area is required for other modifications of the biological parameters.

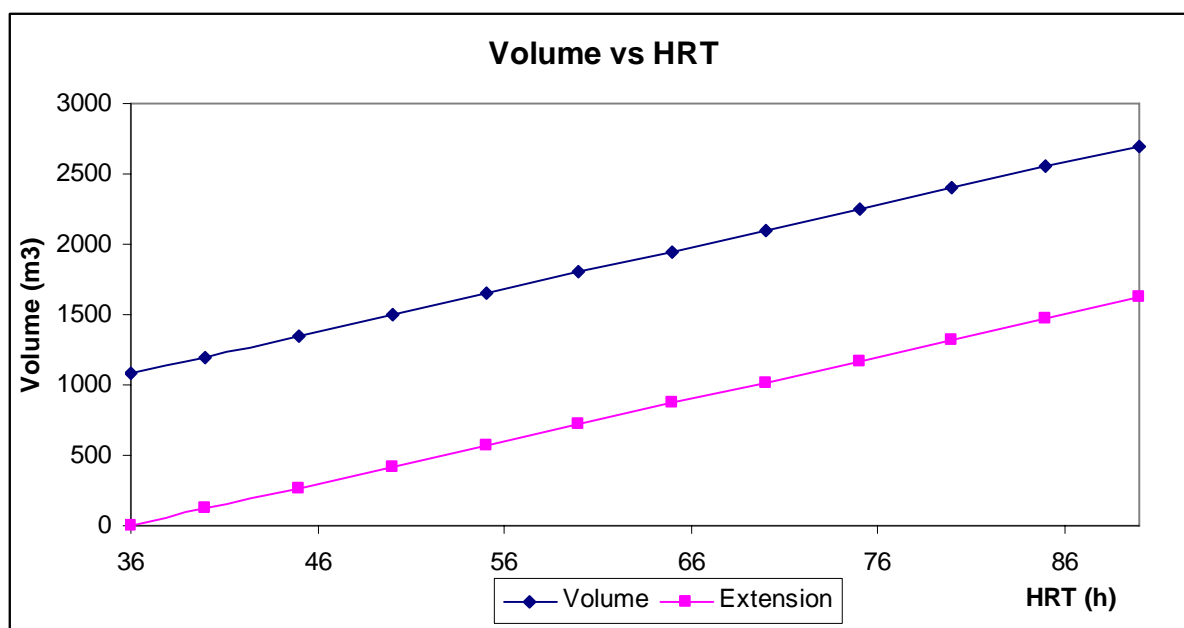


Figure 22- The volume needed for a specific HRT and the extension volume, $Q = 30 \text{ m}^3/\text{h}$.

The HRT differs from time to time, between 15-36 hours. This means that a volume required for an ASP with a flow of $30 \text{ m}^3/\text{h}$ is 1080 m^3 (if $\text{HRT} = 36 \text{ h}$). There are no available data of the existing ASP dimensions. However, if the ASP has similar dimensions as SSAB Tunnpå AB, the current dimensions would be in range of 290 m^2 for area and 4 m for depth. An extra tank for 5 times dilution would require an extra volume of 5400 m^3 and a land area of 1452 m^2 if the depth is 4 m .

9.2.3 Modification to an A^2/O or A/O system

The volume required for an anoxic tank in an A/O is $260\text{-}900 \text{ m}^3$ with a detention time of 30-12 h with F/M ratio of $0.2\text{-}0.5 \text{ lb BOD}_5/\text{lb} \cdot \text{day}$, see appendix 6.

According to the study [36], the relationship between the anaerobic-anoxic-aerobic tanks is: 5:7:13. For an aerobic tank of 1080 m^3 , a correspondingly volume of 582 m^3 for an anoxic tank with detention time of 19.4 h and 415 m^3 for an anaerobic tank are needed.

9.2.4 Add an advanced treatment step

9.2.4.1 MBBR

9.2.4.2 AOPs

The land Area required for an AOP is depended on the time of ozonation. For 1 minute ozonation, a volume of 0.5 m^3 is needed, see figure 23. Good removal of both phenol and PAH requires an ozonation time of app. 5 minutes. The volume of the reactor would be 2.5 m^3 .

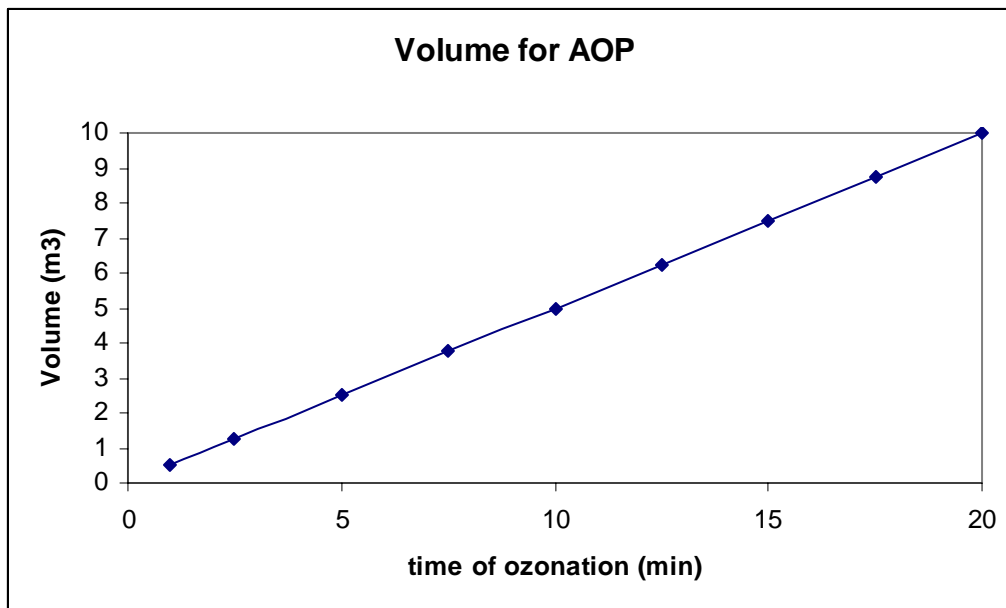


Figure 23- Volume of reaction vs. time of ozonation, $Q = 30 \text{ m}^3/\text{h}$

9.2.5 Replace the current station with SBR

The land requirements represent the total area required for the system plus peripherals (pumps, controls, access areas, etc.), see figure 24. Besides the SBR a clarifier tank is needed for dilution of the high phenol amount. A clarifier for 5 times dilution requires a volume of 5400 m^3 .

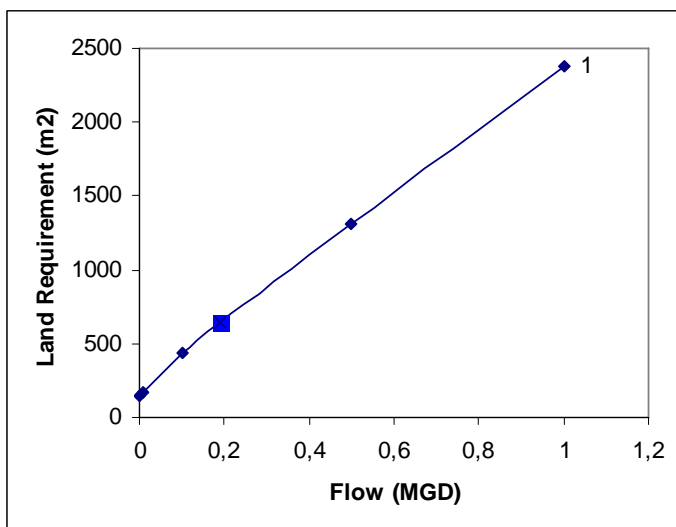


Figure 24-Land Requirement for SBR is 645 m^2 for a flow at $720 \text{ m}^3/\text{day}$

9.3 Economics

The selection and design of wastewater treatment facilities is greatly dependent on the costs associated with treatment processes. These costs include; capital costs, Operation and maintenance (O&M), land requirements, sludge handling and disposal and monitoring costs. The capital cost includes a one time cost of total equipment costs (equipment, installation, piping, instrumentation and controls) and total indirect costs (engineering and contingency).

The annual O&M costs include the costs of maintenance, taxes and insurance, labour, energy, treatment chemicals (if used) and residuals management (if needed) [16] .

9.3.1 AOPs of pre-treatment step

With a H_2O_2 /COD ratio of 1, the amount of H_2O_2 required is 4500 mg/L.

The cost of equipment, reactor etc.

For costs of ozone, O_3 / H_2O_2 treatment, see 9.3.5.2

9.3.2 Optimizing biological parameters/Modify ASP

Extension:

The capital costs include costs for an extension of 5 times requires a basin of volume 5400 m³ (1.07 million US\$) and installed cost of aeration equipment:

- Mechanical: ~US\$ 20-53/lb O_2 / d capacity, \$1900/hp for 25 hp aerator
- Diffused aeration systems: US\$ 7.70-11-30/lb O_2 / d capacity, blower \$250-\$550 / hp for 500-1000 hp aerator, 14-20 \$/lb O_2 /hp-hr

The O&M costs for aeration:

- **power for aeration:** O_2 for carbon removal, lb/d = Q, MGD * S_o , mg/L * 8.34
 O_2 for nitrogen removal, lb/d = Q * 4.57 * N_o * 8.34
- **typical oxygen transfer efficiency** 2 lb O_2 /hr/hp, motor efficiency ~90% hp for O_2 trans * 0.746 kw/hp * 24 * 365 / 0.9 = kwh/yr
- **power cost approx.** \$0.07 / kwh

Alkalinity:

The costs include the mass of chemical $CaCO_3$ to obtain the pH at 8.0.

Nitrification consumes 7.2 lb / lb N. The wastewater treats 2900 mg/L, i.e. an everyday amount of 4.61 lb/d.

9.3.3 Modification to an A²/O or A/O system

The capital and O&M costs for an anaerobic-anoxic-aerobic system are assumed to be 30 % higher than for a conventional ASP [34]. Meaning, the total cost of a new A²/O would be around 46.8 million US\$. However, a rebuilding of the present system would require the construction costs of the septic tanks, pumps and electricity.

Capital costs:

Anoxic Basin: 115171 US\$ (1991)

Anoxic Baffle walls (8"thick reinforced concrete):8564 US\$ (1991)

Anaerobic Basin: 82123 US\$ (1991)

Anaerobic baffle walls: 5713 US\$ (1991)

Mixers in anoxic and anaerobic zones: 824531 US\$ (1991)

C.C. A²/O= 1036102 US\$ (1991)

C.C. A/O= 948266 US\$ (1991)

O&M costs for anoxic unit

Mixing time for anoxic tank: 19.4 h

Reactor size: 582 m³

Energy: 10 kW/10³m³

Power= 582*10/10³= 5.82 kW total for mixing time 19.4 h

Power US\$/Yr= 5.82 * 24*365 *0.07 \$/kWh= 9700 US\$/year (1991)

9.3.4.1 MBBR

9.3.4.2 AOPs

Table 12- Power Requirements per 1 Mole of Total Phenols, US\$ yr 1995.

<i>Method</i>	<i>X (mole O₃/mole phenol)</i>	<i>E (W/mole)</i>	<i>Energy costs (US\$/mole)</i>	<i>Total expenses (US\$/mole)</i>
O ₃	3.6	10.900	0.18	0.14
O ₃ / H ₂ O ₂	3.1	9.300	0.15	0.50
O ₃ / H ₂ O ₂ /UV	3.1	9.300	0.15	-

Even though an ozone treatment in combination with H₂O₂ has better removal efficiency, the total expenses are almost 3 times higher.

The total expenses include capital costs and O&M costs. The total expenses would be 546784 US\$ for O₃ and 1952798 US\$ for O₃/ H₂O₂ (1995). The yearly energy costs is 79460 US\$ for O₃ and 66217 US\$ for O₃/ H₂O₂ (1995). The energy required for O₃ is 4.81 MWh/yr

9.3.5 Replace the current station with SBR

According to US Environmental Protection Agency (EPA) the total capital cost for a SBR can be calculated, see appendix 7. The Operation and Maintenance (O&M) costs for the SBR system include electricity, maintenance, labour, taxes and insurance. No chemicals are utilized in the SBR system. EPA assumed the labour requirements to be four hours per day, and based the electricity costs on horsepower requirements.

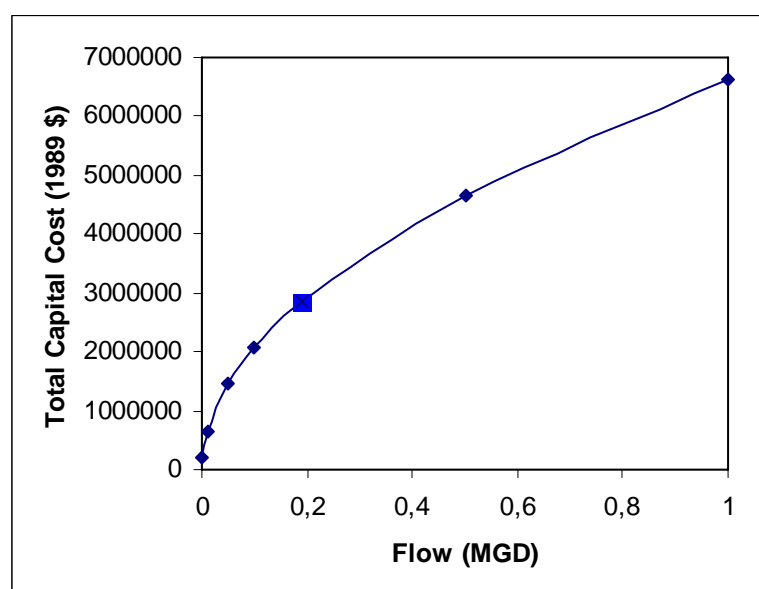


Figure 25- Total Capital Cost Curve for SBR Systems, the capital cost is 2851384 US\$ at the flow 720 m³/day.

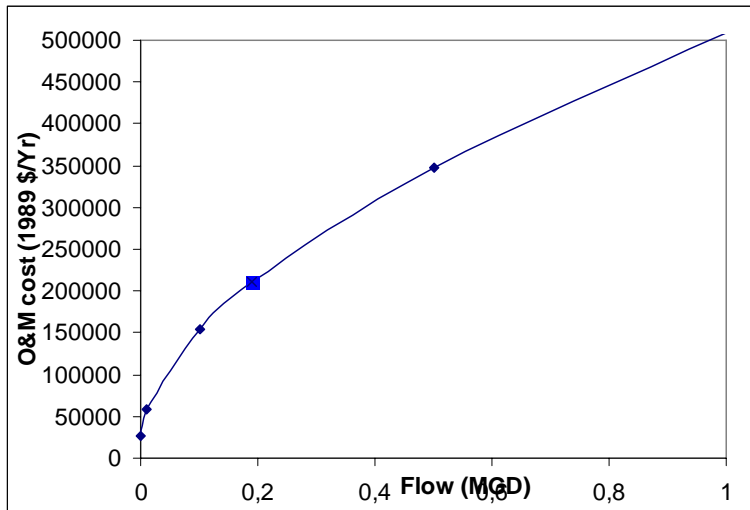


Figure 26- O&M costs for SBR for a flow of 720 m³/day is 211369.

EPA estimated electricity requirements at 0.5 kWh per 3.79 litre of wastewater treated, i.e. 34.7 GWh/year for a treatment plant with flow at 720 m³ [19], which corresponds to a cost of 2.4 Million US\$/year.

9.4 Secondary Clarifier, pumps and sludge treatment

The present sludge treatment happens with oxidation of the sludge from the thickener. If a second clarifier would be introduced, so must sludge treatment be too.

There are several different types of thickener (gravity, flotation, centrifugation etc); an assumption is that the present thickener at the treatment station is a gravity thickener, which is similar to a conventional circular sedimentation basin. The thickened sludge is pumped to oxidation treatment while the supernatant leaves to the Yellow River.

Currently, there is no recycle pump from the thickener to the AS. The capital cost of sludge recycling, from the thickener, for a flow of 720 m³/day is 5158 US\$ and the O&M costs are 6295 US\$ (1996). The costs are based on sludge mass of 0.227 kg/m³ at 4 % solid concentration [35].

Instead of pumping the sludge to the oxidation treatment, a sludge recycling to the aeration tank would be much more efficient. However, if a secondary clarifier is introduced before the thickener, the remaining sludge that is not recycled back to the ASP is pumped to the thickener, which is going to dense it up before it leaves to a sludge method for dehydration. A modest increase in solids content (from 3 to 6 per cent), by the thickener, can decrease the total sludge volume by 50 %.

There are several approaches used in the design of secondary clarifier. The most common one is to base the design on a consideration for the surface overflow rate and the solids loading rate (SLR).

$$\text{SLR} = (Q + Q_R) * \text{MLSS} / A \quad [\text{kg/m}^2 * \text{h}]$$

A = clarifier cross-sectional area, m².

Overflow rates are based on wastewater flowrates instead of the mixed liquor flowrates due to that the overflow rate is equivalent to an upward flow velocity. The return sludge flow is drawn off the bottom of the tank and does not contribute to the upward flow velocity. For a settling following air-activated sludge an average overflow rate of 16-28 m³/m²*d, with a solids loading of 4-6 kg/m²*h and depth of 3.5-6 meter are typically used [32].

The selection of the appropriate sludge-dehydration technique depends on the characteristics of the sludge to be dewatered, available space, and moisture content requirements of the sludge cake for ultimate disposal. When land is available and sludge quantity is small, natural dewatering systems such as drying beds is most attractive. Mechanical dewatering methods include vacuum filter, centrifuge, filter press and belt filter press systems [35].

The O&M of the gravity thickener is 4155 US\$ (1996).

The capital cost for a final clarifier with aeration basin is 51141 US\$, and the O&M costs are 364 US\$ (1996). The clarifier is a flocculator type with a design overflow rate of 24.5 m³/m²*d. The capital cost includes sludge return and waste sludge pumps. And is applied for circular clarifiers with area > 46.56 m² and diameter < 61 m, and for rectangular clarifiers with area < 46.56 m².

The capital cost of sludge drying beds is 4852 US\$ and the O&M costs of 8280 US\$ (1996). The capital cost include sand beds, sludge inlets, underdrains, cell dividers, sludge piping, underdrain return and other structural elements. The sludge solids and solids loading on the beds are 0.108 kg/m³ and 97.6 kg/m²/year. The O&M cost are 1.7 times more than the capital cost.

Table 13- Summary of costs for the different treatment methods. * Cost and Producer Index [j].

<i>Method (Year of price)</i>	<i>Total cost [US\$]</i>		<i>Capital costs [US\$]</i>		<i>O&M costs [US\$]</i>		<i>Energy [MWh/yr]</i>
	Cost yr X	Costs 2006 *	Cost yr X	Costs 2006	Cost yr X	Costs 2006*	
Fenton	----	----	----	----	----	----	----
Extension (1991)	> 1070000	>1583789	----	----	----	----	----
A ² /O (1991)	1036102	1533614	----	----	----	----	----
A/O (1991)	948266	1403601	938566	1389243	9700	14358	50.98
MBBR (2006)	----	101054	----	----	----	----	----
O ₃ (1995)	546784	723305	----	----	----	----	4.81
SBR (1989)	3062753	4979444	2851384	4635799	211369	343645	34670
Final clarifier (1996)	51505	66179	51141	65711	364	468	----
Sludge recycling(1996)	11453	14716	5158	6627	6295	8088	----
Sludge drying beds (1996)	13132	16873	4852	6234	8280	10639	----

10. Water Recycling

The amount of water that is recycled back into the coke process is highly dependent on the effluent quality and the storage of the reclaimed water. Historically, the water quality discharge requirements were monitored directly at the discharges to the environment, but nowadays it is more common to meet discharge requirements set at the treatment plant. Yet, when the water is redrawn, the applicable requirements should be met for reuse, but it would normally require disinfection; both before and after storage. If the effluent was not disinfected before being stored, the quantity of microorganisms would be reduced by sedimentation and natural decay, depending on the storage conditions. Also, disinfection limits the growth of micro-organisms on the walls of the transmission pipelines and other places.

The storage reservoirs can be either open or enclosed. Open ones are most common. The issues involved in water recycling include;

- What is the storage need?
- Does it meet the water quality discharge requirements?
- Problems involved with open and enclosed storage reservoirs

In the current stage, only 60 % of the treated wastewater is recycled, with an aspiration for a higher percentage level. At the present, the effluent does not meet the discharge requirements and is in urgent need for an improvement of treatment efficiency. The problems include:

1. Physical aspects
 - Colour change of the wastewater, often caused by the presence of humic materia
 - Odours, primarily of H₂S, is the most common problem encountered with storage
2. Chemical aspects

- Low DO can cause bad odour
- 3. Biological aspects
 - Including microorganisms regrowth, clogging and bad odours

The present flow is 720 m³/day. Meaning, everyday, an amount of 288 m³/d wastewater goes directly into the Yellow River and 432 m³ water/d is recycled back. It requires 0.6 ton water for every ton of produced coke. With a production of 300 000 tones coke/year, the daily requested water is 493 m³/day. Consequently, together with the reclaimed water, an every day amount of 61 m³/d is needed to be put into the coke process. A recycling of 70% of the treated water would give an amount of 504 m³/d. This would reduce the penalty fees for discharges and save purchase of water. The emission would decrease from 288 m³/day to 210 m³/day that corresponds to 28470 m³/year and results in reduction of phenol emission at 4.5 ton.

Disinfection or a storage reservoir of the current reuse effluent does not exist. An introduction of a storage reservoir or a final clarifier of a volume of 3600 m³ would allow the wastewater to settle for 5 days and separate more organic materia from the effluent.

11. Strategies for reducing energy consumption at a coke factory

Improving energy efficiency can be done by either reducing the energy consumption or the energy recycling. Energy reuse can occur either by reducing the energy required for the processes, or by introducing a heat exchanger.

Generally, the electricity needed for the treatment step is 88 kWh/h (633600 kWh) representing 14 % of the energy use. The energy usage in a typical wastewater treatment plant employing the activated-sludge process is distributed between the AS aeration, clarifiers, influent pumps, flotation and more. To be able to improve the energy efficiency, the information on the various elements of the treatment process is required. This is not the case here. The largest consumer of energy in the treatment station is the aeration tank. Aeration is a leading nominee for considering alternative energy-management measures which can result in reduced cost and power use. Small things such as optimize physical operations (such as pumping, settling, blowers' control) could generate a big impact on energy reuse, see table 14. The recommendations based on audits of existing wastewater treatment plants include [Burton, 1996];

- Installation of DO monitoring and control in aeration tanks
- Installation of adjustable-speed drives on pumps and blowers for variable flow operations
- Repair or replacement of inefficient pumps
- Change or reduction of pumping operations
- Installation of electric load monitoring devices
- Operation of emergency generators during peak periods to reduce power demand

Table 14- Energy impacts on technologies on wastewater treatment. Adapted in part from Burton (1998) [wastewater engineering]

<i>Technology</i>	<i>Energy impact MJ/1000 m³</i>
Fine pore diffusers (for aeration)	-120 to -140
Ultrafine pore diffusers	-170 to -210
DO control systems (compared to manual control)	-48 to -95
Energy-efficient blower control system (adjustable-speed drives)	-48 to -140
Energy-efficient aeration blowers	-95 to -140

Heat Recovery

Industrial processes use large quantities of electricity and fuel that in the end produce heat. Heat recovery is the process of capturing heat that normally would be wasted and delivering it to a device or process where it can be used. It may save up to approximately 20 % of a facility's annual fuel bill [3]. Recovered heat made for effective use replaces purchased energy and reducing fuel consumption and cost, as well as emissions of harmful air or thermal pollutants [4].

The waste heat's usefulness is proportional to its temperature; the higher the temperature, the higher the quality or value. The waste-heat-recovery devices are heat exchangers, which transfer heat from a high-temperature effluent stream to a lower-temperature input stream, or change the input stream from a liquid to a vapour. Waste heat can as well be used by passing hot gases or steam through a turbine, to generate electricity or to drive pumps, fans or other mechanical equipment.

It is critical that the waste heat is enough hotter than the input requirements, that the energy savings makes up for capital and operational cost of the heat-recovery device [3].

There are several types of heat exchanger. Conventional shell and tube exchangers are normally used. The amount of energy that can be recovered will depend on the temperature, flow, heat capacity, and temperature changes. Before the determination of the heat transfer area required for the process, an estimation of the temperature difference ΔT_m must be made. The practical minimum temperature difference in a heat exchanger will usually be between 10 and 20 °C [35].

The temperature of the wastewater right after the cooling of the coke is around 60-70 °C, while 40 °C in the biological step. A temperature decrease of 20-30 degrees is lost during the treatment station which corresponds to energy recovery losses. An introduction of heat exchanger after the cooling step of the coke process could recover the lost energy. Yet, it is only worth considering power recovery from high-pressure liquid streams (>15 bar) and no information considering the wastewater pressure is available [35].

12. Discussion

12.1 Wastewater station

This thesis was supposed to be based on data received from the coke factory. Yet, the data collected was poor in facts and also contradicts from earlier values. Therefore, making suggestions of improvements without having all the facts makes these suggestions more theoretical than practical.

When none or failing information of land area, dimensions, discharges and costs, were given, assumptions such as plenty of land to use, similar dimensions as SSAB Tunnplåt AB had to be done. Important biological factors such as F/M ratio, MLSS, HRT in the adjusting unit were not received and an assumption that these factors was in the range of levels of performing an efficient treatment also had to be done when calculating dimensions for the anaerobic and anoxic units.

With an ambition of comparing the present coke factory with several other western coke factories, I quickly realized that I had to concentrate my time on only one or few of them. I found SSAB Tunnplåt AB to be a good comparison model, due to good emission levels and easy available data.

The wastewater treatment station fails in removal of phenol. The PAH levels are unknown, but probably proportional to the removal of phenol due to that PAH is less biodegradable than phenol. An improvement is needed and an improvement could occur in every treatment step. There is no special step that is not considered as a prime candidate for improvement.

Compared to SSAB Tunnplåt AB, this coke factory neither has a NH_3 -steam stripper, do not sludge reuse nor have a sludge treatment and do not have any disturbance problems, but still has a somewhat efficient pollutant removal, which is rather surprising. According to SSAB Tunnplåt AB, there treatment station fails somewhat of cyanide disturbance, and they would like to extend the aeration tank and sedimentation pool to dilute and improve the sludge separation.

The pre-treatment step could be improved by introduction of AOP. SSAB Tunnplåt is using a NH_3 Steam-stripper as a pre-treatment step. Huaxi Jiaohua Ltd does not seem to have enough problems with the ammonia removal. Also, ammonia steam stripper requires to be followed by either condensation or a gas furnace (producing air emissions). Therefore, it does not have a high priority concerning economic aspects, but using AOP as a pre-treatment should be put in focus. After collecting the information concerning different treatment methods, AOPs seemed to be both a cost-effective and an effective removal treatment method. It later became noticed that the by-products of Ozonation of phenol was more toxic than the phenol compound itself. However, using a modify Fenton process would give a good removal and decrease the toxicity. Normally, Fenton processes are carried out in acidic environment (pH 3), but this would require both a decrease of pH before the Fenton process and a pH increase before entering the biological step. This would result in extra costs for chemicals. However, studies indicate that the processes work fine in pH up to 8. The management of the coke factory wanted to skip the flotation step. The flotation step is needed to reduce the sludge escape, which contain PAHs. If the flotation step would be on hold, a longer Fenton treatment is required, correspondingly to a bigger reactor volume and higher costs of chemicals and electricity.

Good removal efficiency can be reach by changing parameters such as F/M, HRT and pH. However, it would probably not be too effective. Without sludge recycling, new sludge must be added. This makes the sludge new and non-selective. A better alternative is to reuse the sludge, which makes the microorganisms more selective towards phenol and PAHs, hence better removal efficiency.

Introducing an A²/O or A/O tank before the aerobic step would improve the COD removal. The COD removal is actually greater in an A/O system than in the A²/O system, this because the acidogenesis makes more persistent substances more biodegradable. However, if consideration is taken for total N-removal, an introduction of A²/O is in favor, but the present total N-removal is sufficiently enough and therefore is only an A/O system recommended. The anoxic unit removes COD 1.5 -2.3 times better than the aerobic unit. Phenol is rather biodegradable compared to PAHs. It is rather known that removal of persistent pollutants occur more rapidly under anaerobic conditions than aerobic ones. Thus, an anoxic unit would be a good supplement to the present aerobic unit. Yet, to be able to gain a removal efficiency corresponding to the national emissions standards, an A/O requires further treatment as an advanced treatment step, alternative, use a good pre-treatment step.

The MBBR process is build after the request of emission standards plus it is very efficient and would decrease the emission of phenol to less than 10 mg/L. The nitrogen level is going to reduce to due to assimilation. Phenol is an easy degradable substance and COD contain between 60-80 % of it. It is uncertain what the latter 20-40 % of COD material is, but PAHs are probably one of them. PAHs are not easy biodegradable but a treatment with MBBR would probably remove great amount of them. MBBR is both easy maintain and also good to withstand strains. Therefore, it is highly recommended to use MBBR as a post-treatment method.

If this coke factory did not have any form of treatment for wastewater, the best alternative, both considering removal efficiency, land requirement and economy would be to use a SBR. Still, a functional treatment station does exist at this coke factory, and therefore, rebuilding the present station and adding pre/post-treatment steps would probably achieve the same removal results but for less money and land area. Plus, there is no information received concerning the present dimensions of the station. If there is no available land area to build a new SBR, the present station is needed to be on hold, for reconstruction to a SBR. There are two possible outcomes if the treatment station have to be on hold; either the coke wastewater goes directly out from cooling step to the Yellow River, without any treatment, or the coke battery is on hold too. The first one is bad for environment, including higher sewage fees for the company; the latter one includes production losses, strains on the battery which results in bad quality of coke and higher risks for faults of battery. Therefore, a SBR process is not to recommend to this coke factory due to lacking of information of the current status.

According to the management of the coke factory, there is less to none amount of sludge for sludge handling. This is quite hard to believe, because SSAB Tunnpå AB working with much sludge; adding ironchlorid to reduce sludge escape followed by two advanced treatment step (flotation and sand filter) to reach a good emission level. The sludge contains much organic materia, which makes it important to control the sludge emissions. It is possible that the coke factory believes that the wastewater contains only small amount of sludge; due to that 99 % of the sludge contains water. The coke factory does not have any sludge waste, and an introduction of a final clarifier, demands sludge handling in form of sludge collection tank, and a dehydration method before it is reuse together with coal as a fuel. If the thickener works as it should, a sludge volume reduction of 50 % can be achieved. The present unit for oxygen treatment can be used as a collection tank of the sludge. There are several types of dehydration methods to choose between. With an assumption that there are enough of land requirements, sludge drying beds, typically sand beds seems as a good option, when the sludge is not of great amount.

12.2 Wastewater Recycling

Wastewater reuse would decrease the emissions of phenol and COD to the Yellow River. An improvement of 70 % recycling would spare 4.5 ton phenol per year. There is no data given of a current storage reservoir, and therefore an assumption of no one is made. For storage during long time (weeks or more) disinfection before storage is required to maintain good quality of the effluent. A possibility is to use AOP as an advanced treatment step for disinfection. However, with the current station, 60 % of the effluent is recycled, with assumption that it would be more if there was enough of space. If the effluent is not going to be stored for a longer time, an alternative to a storage reservoir is to introduce a final sedimentation pool after the thickener. This would not only improve the effluent quality (PAH is stored in sludge, plus more selective microorganisms) but also give opportunity to reuse more wastewater. The sludge is then gathered in a sludge collecting tank, for dehydration, followed by mixing with coke for coking.

12.3 Energy Recovery

Liquids contain less energy to recover than gas and are therefore important that the liquid has a high pressure, flow to be considerable to recover. A heat exchanger after the cooling step can be applied, but the temperature differences is around 20-30 °C and is quite close to the minimum temperature difference for a heat recovery at 10-20 °C. Therefore, energy savings program can be more energy efficient than the energy extracted from a heat exchanger.

However, the coke process yield gases when the battery has temperatures above 700 °C. A cooling of gas occurs while it transfers from the battery to the gas clock. At SSAB Tunnsplåt AB, the temperature of gases decreases from 700°C to 80°C. A temperature difference of 630°C would generate more energy. There is no information available if it already exist a heat exchanger. If not, a heat exchanger there would recover much energy and is highly recommended.

Thus, the best alternative to gain energy from wastewater treatment is by energy efficiency. By making small changes, example make sure that the pumps are whole, digital controlling instead of manually, take help from gravity by monitoring pumps on different heights, can save much energy.

A good example is to change the mechanical aerators to fine bubble diffusers, see figure of cumulative annual cost differences. In 10 years time, a gaining of 250 000 US\$ in annual cost is achieved. Annual costs include debt repayment on capital expenses and operating costs for electricity, membrane replacement, and maintenance [g]. Changing the present aeration to fine bubble diffusers can save energy demand with up to 50 % (depending of what type the present aeration is, 50% if the present method is mechanical aeration), requires less maintenance and improve the capability of nitrification [h].

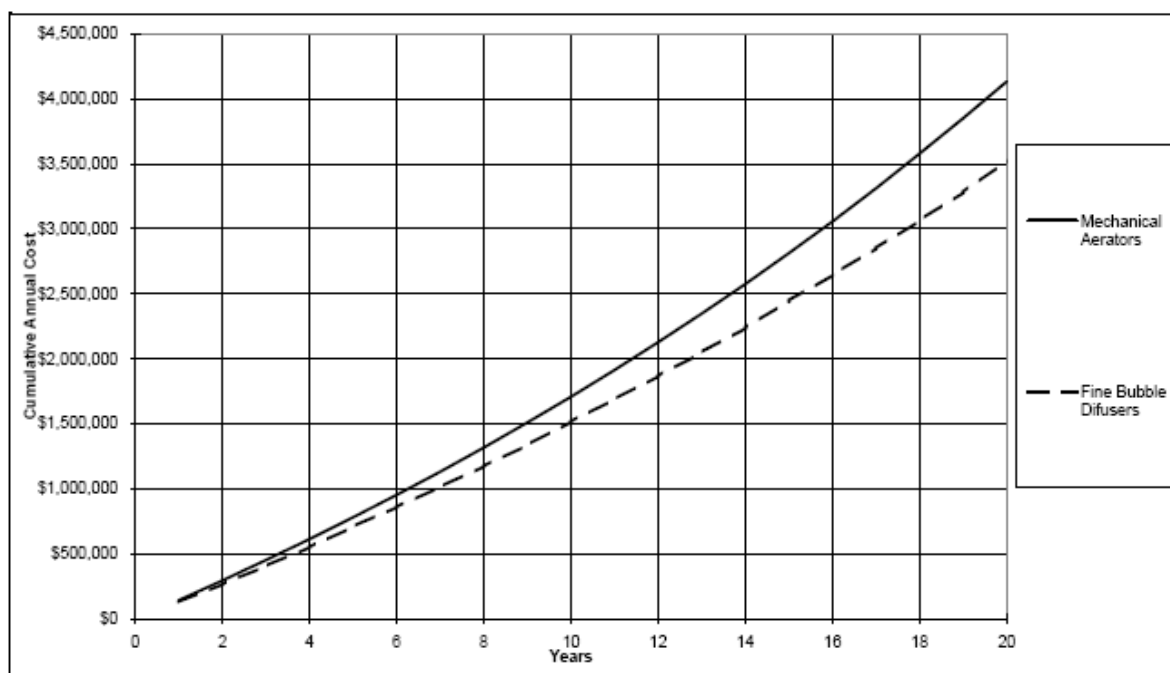


Figure 27- Comparison of Cumulative Annual Cost between mechanical aerators and fine bubble diffusers in US\$ (1996) [g].

12.4 Recommendations

I first suggest optimizing all the biological parameters, such as F/M ratio, HRT, MLSS and sludge age. A low F/M ratio, a long HRT and enough of MLSS and good sludge age are essence for a good functional nitrification.

The flotation pre-treatment step is necessary to have to reduce the amount of sludge. Much PAHs are stored in the sludge and if the flotation would be on hold, the microorganisms would be more on stress. Therefore, flotation is recommended to not be on hold.

If the optimization of the biological parameters is not efficient enough, I recommend either to introduce a sludge recycling together with a MBBR, or a sedimentation unit together with sludge drying beds and MBBR. A sludge recycling is basic in a treatment station, and should be implemented here.

<i>Methods</i>	<i>Total Cost</i>	<i>Capital Costs</i>	<i>O&M Costs</i>
MBBR	101054	----	----
Final clarifier	66179	65711	468
Sludge recycling	14716	6627	8088
Sludge drying beds	16873	6234	10639

The total costs of MBBR, Final clarifier and sludge drying beds are 184106 US\$. The total costs of MBBR and sludge recycling are 115770 US\$.

An introduction of sedimentation unit will make it possible to store the effluent in a few days time, meaning making it possible to reuse more wastewater into the coke process.

Energy efficiency

To gain energy from the wastewater treatment station, I suggest replacing the current aerator system in the aeration unit to fine bubble diffusers and introduce a heat exchanger in the cooling of gas step.

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14. Appendices

Appendix 1- received data

Appendix 2- Calculation: flow 30 m³/h

Appendix 3- Emission levels during 2002-2005 of SSAB Tunnplåt AB

Appendix 4- Proportion between COD removal and the H₂O₂/COD ratio

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Appendix 1

received data from the company

These facts were provided upon request.

Cost to produce gas: 0.2 RMB/m³

Sell gas to houses: 0.8 RMB/m³

Sell gas to companies: 1.0 RMB/m³

Cost to transport to Gas Company: 1.0 RMB/m³

Cost for producing 1 ton coke and 350 m³ gas: 500 RMB

Produce coke: 200 RMB/ton + price of coal

1.4 tones coal produce 1.0 ton coke

Electricity is 58% of total cost of wastewater treatment

Using water: 20-30% of total cost of wastewater

60% water treatment
20% chemicals
20% administration } total cost of company

1 ton coke → 35 tones water, including both gas cooling and wastewater

Tonnes of water per ton of produced coke: 0.6 tonnes

Cost of wastewater treatment: 6 RMB/ton

Energy

Electricity: 15 kWh/ ton coke

Wastewater: 88kWh/h → 7200 h/year → 633600 kWh

Total cost of company: no information available (n.i.a.)

Total gain of company: n.i.a.

Cost of production: n.i.a.

Gain of production: n.i.a.

Energy cost: n.i.a.

Production of gas m³: n.i.a.

Amount of produced gas: n.i.a.

Appendix 2

- Calculation: flow 30 m³/h

	<i>Flow Capacity</i>	<i>Flow 1</i>	<i>Flow 2</i>
[m ³ /h]	30	550	720

The HRT is between 15 to 36h, and therefore the basin volume is at least 36 times the flow.

<i>flow</i>	<i>hours</i>	<i>volume</i> (<i>flow*hours</i>)	<i>area m2</i>	<i>m</i>
30	36	1080	270	16.43168
550	36	19800	4950	70.35624
720	36	25920	6480	80.49845

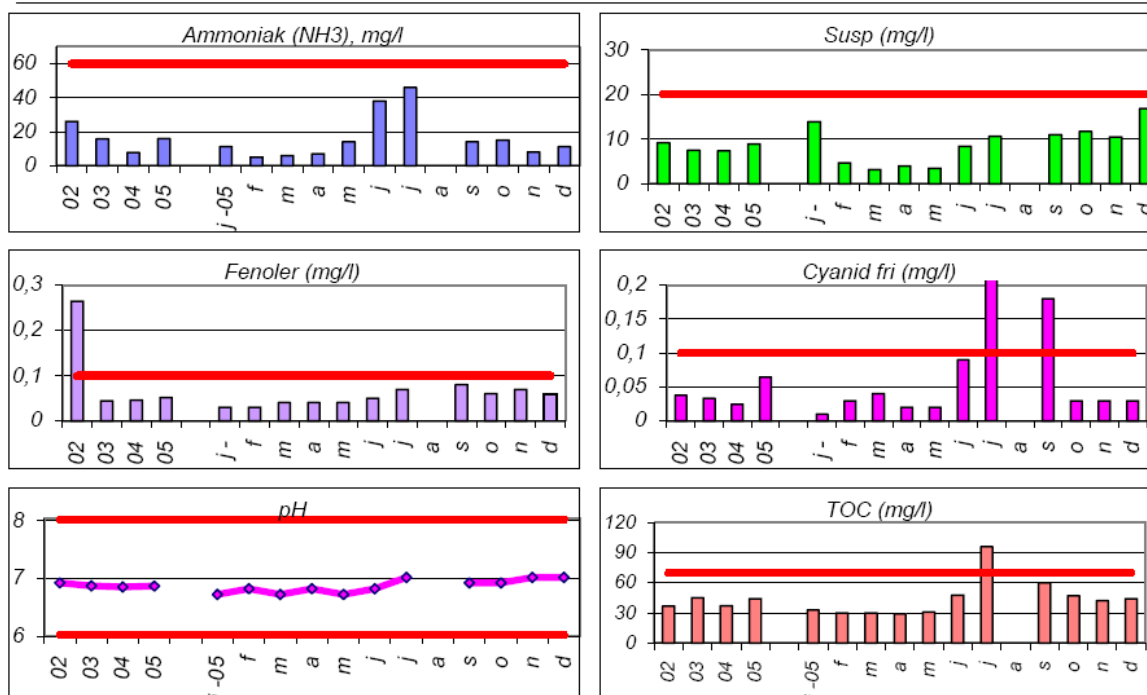
If the deep of the tank is around 4m, an area of 270 m² is needed. The secondary treatment step was not big enough for a flow at 550 m³.

Appendix 3

Level of emissions of SSAB Tunnpå AB

Tabell 15. Sammanfattning analyser från biologin.

	NH3 mg/l	Fenol mg/l	CNfri mg/l	Olja mg/l	susp mg/l	PH pH	TOC mg/l	Flöde m3/h
2002	26	0,26	0,04	<0,14	9,2	6,9	37	39
2003	16	0,04	0,03	<0,05	7,5	6,9	45	37
2004	8	0,05	0,02	<0,06	7,4	6,8	37	38
2005	16	0,05	0,06	<0,05	8,9	6,8	45	37
jan	11	0,03	<0,01	<0,05	14	6,7	33	38
feb	5	0,03	0,03	<0,05	5	6,8	30	39
mar	6	0,04	0,04	<0,05	3	6,7	30	40
apr	7	0,04	0,02	-	4	6,8	29	38
maj	14	0,04	0,02	<0,05	4	6,7	31	37
jun	38	0,05	0,09	<0,05	8	6,8	48	35
jul	46	0,07	0,23	<0,05	11	7,0	96	35
aug	-	-	-	-	-	-	-	-
sep	14	0,08	0,18	-	11	6,9	60	36
okt	15	0,06	0,03	<0,05	12	6,9	47	38
nov	8	0,07	0,03	<0,05	11	7	42	37
dec	11	0,06	0,03	<0,05	17	7	44	40
Riktvärde	60	0,1	0,1	<0,5	20	6-8	70	
min	5	0,03	<0,01	<0,05	3,2	6,7	29	35
max	46	0,08	0,23	<0,05	17	7,0	96	40



Riktvärde; condition of emissions

Appendix 4

Proportion between COD removal and the $\text{H}_2\text{O}_2/\text{COD}$ ratio

The COD removal was strongly dependent on the $\text{H}_2\text{O}_2/\text{COD}$ ratio when the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was keep constant at 10:1, The commonly used ratios of $\text{Fe}^{2+}/\text{COD}$ are 0.5, 0.1 and 0.05, whereas the $\text{H}_2\text{O}_2/\text{COD}$ ratio is [26].

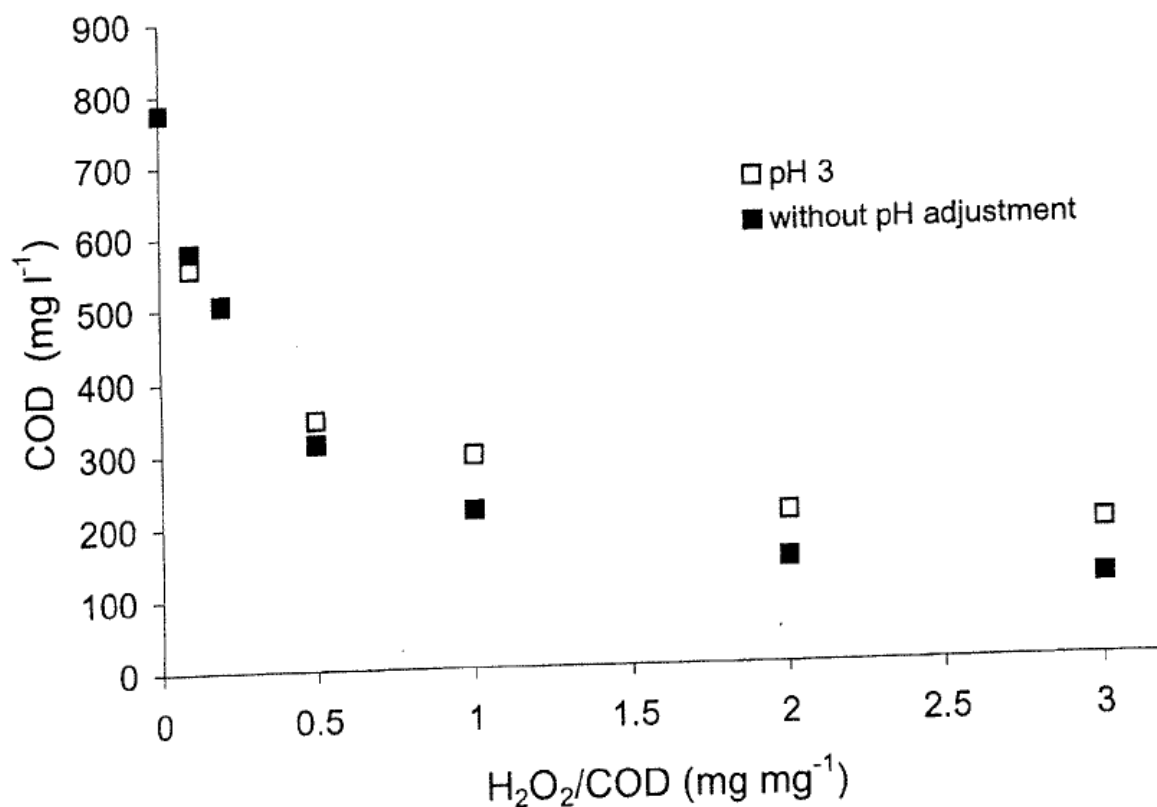
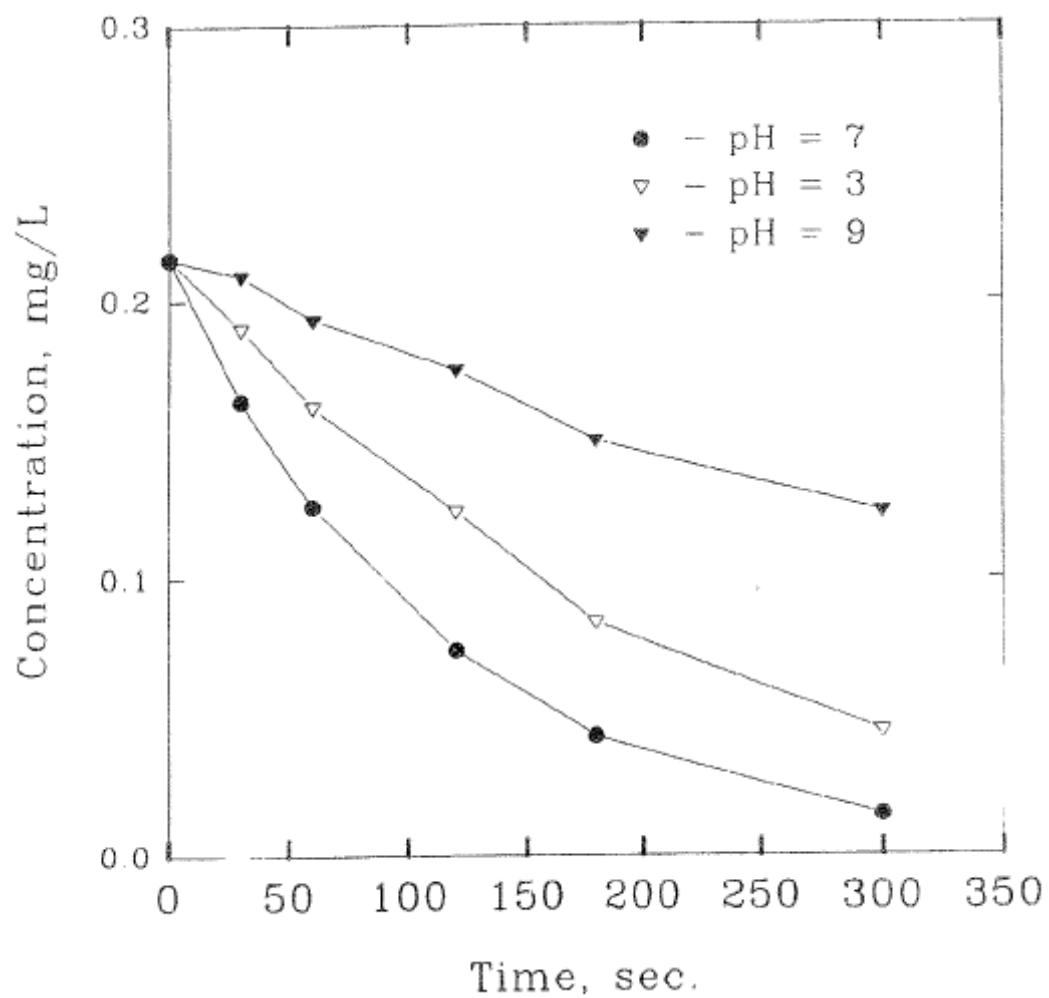


Figure 4. COD after the Fenton oxidation versus $\text{H}_2\text{O}_2/\text{COD}$ ratio for Leachate 1.

Appendix 5

The Ozonation rate in acidic and basic media

Kinetic curves of flouranthene Ozonation.



Appendix 6

Calculation: Volume of anoxic tank

Wastewater characteristics:

Constituent	Concentration [g/m ³]
BOD	3600
bCOD	3717
rbCOD	899
NO _x	28.3*
TP	6*

Circa 80% of COD is BOD → 3600 g/m³

0.826 of TCOD is bCOD [k]

0.424 of bCOD is rbCOD [k]

Design conditions:

Parameter	Unit	Value
Influent flowrate	m ³ /d	720
Temperature	°C	39.5
MLSS	g/m ³	3000*
MLVSS	g/m ³	2370*
Aerobic SRT	g/ m ³	12.5*
Aeration basin volume	m ³	1080
RAS ratio	Unitless	0.6*
k _d	g/g·d	0.088*
Y	g VSS/g COD	0.40*

*No given values, therefore using the values in the book [32] (p762-765).

Assumptions:

1. The values given in the book (*) works on this system
2. The HRT 36h is the maximal HRT that gives the basin volume 1080 m³.
3. Nitrate concentration in RAS=6 g/m³.

Solution

1. Determine the active biomass concentration using Eq.(7-43) and substitute V/Q for τ.

$$X_b = \left[\frac{Q(SRT)}{V} \right] \left[\frac{Y(S_0 - S)}{1 + (k_d)SRT} \right]$$

Where $S_0 - S \approx S_0$

$$X_b = \left[\frac{(720 \text{ m}^3 / \text{d})(12.5 \text{ d})}{1080} \right] \left[\frac{(0.40 \text{ g VSS})(3717 \text{ g} \cdot \text{bCOD} / \text{m}^3)}{1 + (0.088 \text{ g} / \text{g} \cdot \text{d})(12.5 \text{ d})} \right] = 5900 \text{ g} / \text{m}^3$$

2. Determine the IR ration using Eq. (8-45)

Aerobic tank NO₃ concentration = N_e = 6.0 g/ m³

$$IR = \frac{NO_x}{N_e} - 1.0 - R = \frac{(28.3 \text{ g} / \text{m}^3)}{6 \text{ g} / \text{m}^3} - 1.0 - 0.60 = 3.1$$

3. Determine the amount of NO₃-N fed to the anoxic tank

Flowrate to anoxic tank = IR Q = RQ

$$= 3.1(720 \text{ m}^3/\text{d}) + 0.60(720 \text{ m}^3/\text{d})$$

$$= 506.4 \text{ m}^3/\text{d}$$

$$\text{NO}_x \text{ feed} = (506.4 \text{ m}^3/\text{d})(6.0 \text{ g/m}^3) = 3038.4 \text{ g/d}$$

4. Determine the anoxic volume.

As a first approximation, use a detention time = 2.5h

$$\tau = \frac{2.5 \text{ h}}{(24 \text{ h/d})} = 1.04 \text{ d}$$

$$V_{\text{nox}} = \tau \times Q = 1.04 \text{ d} \times (720 \text{ m}^3/\text{d}) = 74.88 \text{ m}^3$$

5. Determine F/M_b using Eq. (8-43).

$$F/M_b = \frac{QS_0}{V_{\text{nox}}(X_b)} = \frac{(720 \text{ m}^3/\text{d})(3717 \text{ g BOD/m}^3)}{(74.88 \text{ m}^3)(5900 \text{ g/m}^3)} = 6.057692 \text{ g BOD/g} \cdot \text{d}$$

6. Determine the SDNR using the curve with an F/M_b range of 0 to 2 given on Fig. 8-23.

$$\text{Fraction of rbCOD} = \text{rbCOD/bCOD} = (899 \text{ g/m}^3) / (3717 \text{ g/m}^3) = 0.241861716 = 24\%$$

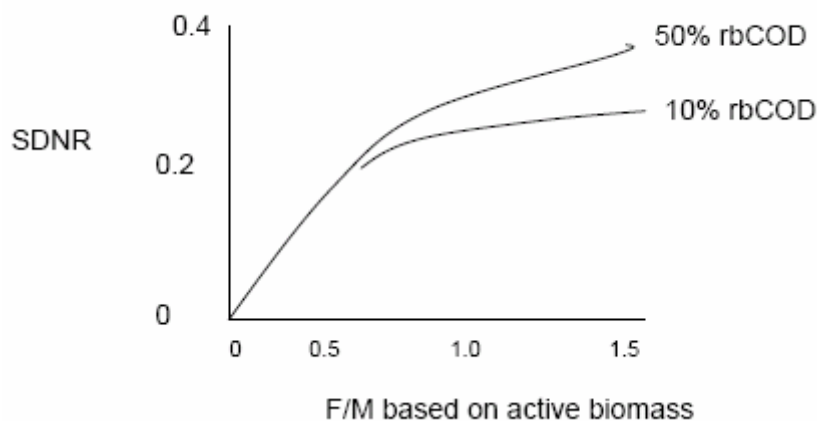
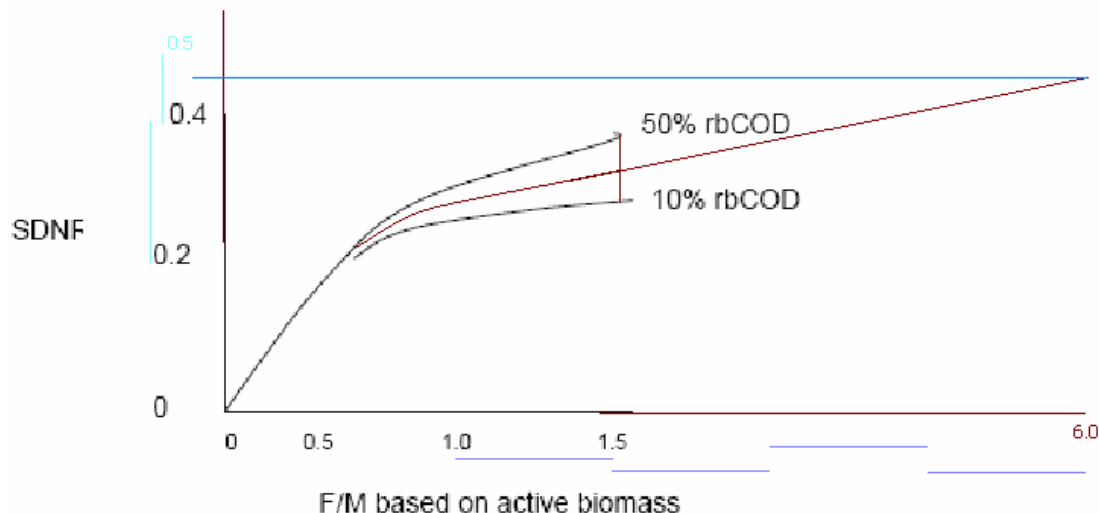


Fig.8-23

As notice in the figure a value of F/M_b at 6.06 is not shown. A very uncertain appreciation of value 6.06 would give a SDNR of 0.47 at 20°C.



Apply temperature correction using Eq. (8-44):

$$SDNR_{39.5} = 0.47(1.026)^{39.5-20} = 0.775302872 \text{ g/g} \cdot \text{d}$$

7. Determine the amount of $\text{NO}_3\text{-N}$ that can be reduced using Eq. 98-41.

a. Check NO_r based on $\tau = 2.5$ h.

$$\begin{aligned} NO_r &= (V_{nox})(SDNR)(X_b) \\ &= (74.88 \text{ m}^3)(0.775302872 \text{ g / g} \cdot \text{d})(5900 \text{ g / m}^3) = 342522.6 \text{ g/d} \end{aligned}$$

Comparing 342522.6 g/d versus 3038.4 g/d, there is about 100 times greater excess nitrate-removal capacity. Thus, $\tau = 2.5$ h is not acceptable; a lower detention time is needed.

b. Evaluate new value for τ .

Select new τ . If the same SDNR is used, $\tau = 2.5 \text{ h} / 112.7$

Appendix 7

Calculations: Total cost, O&M cost, land requirement of SBR

Table 11-18. Cost Equations for *Sequencing Batch Reactors*

Description	Equation	Recommended Flow Rate Range(MGD)
Capital cost for sequencing batch reactors	$\ln(Y1) = 15.707 + 0.512\ln(X) + 0.0022(\ln(X))^2$	1.0 E -7 to 1.0
O&M cost for sequencing batch reactors	$\ln(Y2) = 14.1015 + 0.81567\ln(X) + 0.03932(\ln(X))^2$	3.4 E -7 to 1.0
Land requirements	$\ln(Y3) = -0.531 + 0.906\ln(X) + 0.072(\ln(X))^2$	1.9 E -3 to 1.0

Y1 = Capital Costs (1989 \$)

Y2 = Operation and Maintenance Costs (1989 \$ /year)

Y3 = Land Requirement (Acres)

X = Flow Rate (million gallons per day)

Figur 28- EPAs cost Equations [19]

X= 0,1902 MGD (720 m³)

Y1=2851383 \$

Y2=383108 \$/yr

Y3= 645.07 m³ (0,1594 acres)

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