# Bachelor thesis Chemical Engineering

## Coal as aid for the removal of hormones from the effluent of a WWTP and an insight in the micro-plastics problem

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**Preface**
This research is the final part of the bachelor program of Chemical Engineering at the Rijksuniversiteit Groningen (RUG). The project started 22 april 2013 and took 3 months to complete. The given assignment has been a reflection of the skills and knowledge acquired in the bachelor program.
I would like to thank M.W.M. Boesten for his guidance and criticism, A. Haijer from Water and Energy Solutions for extra assistance, A.C. Meinema for giving access to hormones and last but not least I would like to thank J.H. Marsman for help with the analysis and the experimental overall,

Jasper Kabel

**Abbreviations**
WWTP – Waste Water Treatment Plant
PE – Polyethylene
PP – Polypropylene
STOWA – Stichting Toegepast Onderzoek Waterbeheer
LOES – Landelijk onderzoek Oestrogene stoffen
DSC – Dry Solid Content
OBD – Overall Block Diagram
PFD – Process Flow Diagram

**Commonly used terms**
Influent - Wastewater flowing into a treatment plant
Effluent -Treated wastewater
Estrogen – female hormone

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# 1. Introduction

## 1.1 Introduction WWTP Garmerwolde

The Waste Water Treatment Plant (WWTP) situated in Garmerwolde is part of the 'Waterschap Noorderzijlvest'. The plant cleans the sewage water from Groningen and surroundings with mechanical, biological and chemical treatments. The result is clean water, which is released in the Eemskanaal, and sludge. The sludge is processed in the WWTP to remove as much water and hazardous chemicals as possible. The processed sludge is then transported to Swiss Combi for further drying. Swiss Combi is separate company located on site. They sell sludge granulates to ENCI in Maastricht. ENCI burns these granulates to produce energy.

The Rijksuniversiteit Groningen (RUG) has been collaborating with 'Waterschap Noorderzijlvest' for a few years now. This collaboration provided the Waterschap with possible solutions and improvements, while students had the possibility to their thesis on a subject related to the Waterschap. The first students were Gijsbert Haaksman (2009) and Martin meelker and Olivier Burgering (2010), who did their master thesis about various subjects related to the WWTP Garmerwolde. These thesis's were quite successful, resulting in more opportunities for students in both the master and bachelor trajectory. This year (2013) Marc Meijerink, Marthe Sveistrup, Henrieke Heideman, Machiel van Essen and I are doing our bachelor thesis in collaboration with Garmerwolde. Although my assignment is not directly related to the WWTP in Garmerwolde it can give insights for the future.

## 1.2 Objective research and scope

The objective of this research is to look at the possibility of coal to decrease the concentration of certain hormones and to look in to the micro-plastic (micro PE, micro PP etcetera) problem.

The choice to use coal comes from earlier research which shows that coal improves the dewatering and can be used for flocculation (Meelker, 2010) and because the EDCAT project in Great-Britain showed that active coal improved the effluent on hormonal level (STOWA Lahr & de Lange, 2009), thus coal could be interesting as well. It will not be a research based on the circumstances at a WWTP, because it is not sure if coal can decrease the concentration of hormones. This means other parameters need to be ruled out. The coal used is not activated and thus if adsorption is proved with the experimental, the adsorption will be expected not to be that great. Even with low adsorption rates, the coal will still be viable thanks to the large amounts of coal that are available as well as the relative low costs of it.

The micro-plastic problem is looked at from the Garmerwolde WWTP with the assumption that the micro beads go through the system fairly unhindered. The problem will be looked at purely theoretical and the possibility to combine the solution to the micro PE problem and the concentration decrease of hormones will be sought.

## 1.3 Assignment

To address this objective, an assignment was formulated:
*At laboratorial scale the effectiveness of coal as filter aid for the removal of the hormone Bèta-estradiol is tested and the micro-plastic problem is addressed by looking at the Garmerwolde  WWTP. After these two goals the possibility of combining the solution to the micro-plastic problem and the coal as filter aid will be sought. A literature study is done on the micro-plastic problem, the hormone problem and on coal adsorption in general.*
The practical work should be reproducible.

## 1.4 Problem definition

In the literature study part the problems given by the hormones, medicine and micro-plastics will addressed.

The definition of the removal of Bèta-estradiol will be:
In this case removal means that the material exists in the influent and will exist less in the effluent. This means the material is not removed from the environment, but just from the waste stream. The removal will be a result of either filtration or adsorption. Because the WWTP sludge is burned in the Netherlands, the hormones (in this case just Bèta-estradiol) will not be available for the environment.

Many parties are involved, they are called stakeholders.

Stakeholders

*Society*: Both one of the reasons of the hormone, medicine and micro-plastic pollution and a victim. The victim role can be seen in several ways. First of all the hormones and medicine could be harmful for people, secondly a lot of people are not aware of what kind of pollution certain products give. This asks for campaigns to raise awareness, so people know what kind of pollution they bring in the environment themselves.

*WWTP's*: The Waste Water Treatment Plants should be the ones cleaning the water. Important is that innovation should be sought all the time to keep the risks of pollution coming in the surface water as low as possible. The WWTP's should be involved with the awareness campaigns, because the WWTP's measure the concentrations of their outlets, knowing what still pollutes the environment.

*Green organizations*: For example Noordzee and the Plastic Soup Foundations. These organizations try to raise awareness for the environment, in some cases with success. The Plastic Soup Foundation addressed several cosmetic companies about micro-plastics, resulting in some positive responds by banning micro-plastics from products by Colgate, Palmolive, Loreal and Beiersdorf (Noordzee, 2013).

*Health care industry*: The companies that produce medicine, hormones and use micro-plastics. These companies primary goal is to make profit, which can result in violation of legislation about the concentrations medicine and hormone in waste water. These companies most likely clash with the green organizations.  But they do care about their image (bad image means less profit most of the time), resulting in some cooperation with the green organizations and government.

*Government*: The government uses legislation to keep pollutions at decent levels. The legislation is designed in cooperation with researches and science institutes to adjust the parameters and decent levels for both the industry and the environment. The government also uses campaigns to raise awareness so that society will realize what harm certain products can do.

*Institutes*: Institutes like STOWA research and measure valuable parameters to enhance the knowledge about waste water and their treatment plants. The institutes mostly provide knowledge and lack real power to enforce changes at the WWTP's and companies.

## 1.5 Research schedule

<u>Literature study</u>
Before the practical work, a literature study will be done. The study will focus on:

*Coal*
The overall coal filtration and adsorption process will be studied, along with the differences between normal coal and active coal. The information will be gathered from scientific researches and STOWA reports.

*Micro PE*
The problem the micro PE gives will be looked, along with a look at the reasons why micro PE was implemented in products in the first place. The sources will be STOWA reports and reports from Green Organizations.

*Hormones/medicines*
The problems and uncertainties the hormones and medicines give will be studied. The basis of the research will be reports from STOWA, which provide information from the branch.

<u>Experimental</u>
The experimental work is focused on decreasing the concentration of a hormone in a solution with the help of coal.

The experimental work will not be a small scale replica from the actual WWTP. No sludge and such will be used, because the focus lays at the study if lowering of the concentration of the hormone is possible, no other factors should have a chance to play a role.

The influent will be a solution of a hormone.
First the smallest particle size coal is used, because it is expected to have the best adsorption possibilities. If interaction has been proven, a random sample of the coal will be used with an expected lower decrease of the concentration of the hormone. Also the time and the amount of coal will be varied, with for both parameters an expected larger decrease of the concentration if their amount is increased.
Taking a sample of the smallest particle size will affect the PSD of the batch coal used. Therefor a new batch of the coal will be taken for the experimental with a random sample of coal.

# 2. Theory

## 2.1 Hormones

The last 15 years there have been more attention to the influences of hormones on the environment. Hormones can disrupt an organism in several ways (STOWA Lahr & de Lange, 2009):
● The hormones induces an error in the genitalia, also known as intersex
● Changes in the sex distribution of an organism
● Unwanted production of the female protein vitellogenin in the male

These three disruption ways will in principle lead to a disrupted reproduction, which will result in a lower population growth.

The hormones can disrupt the organism via four different effects, shown in table 1.

| Effect | Mechanism | Result |
|---|---|---|
| Estrogen effect | Stimulated estrogen receptor | Feminization |
| Anti-estrogen effect | Blocked estrogen receptor | Defeminization |
| Androgenic effect | Stimulated androgenic receptor | Masculinization |
| Anti-androgenic effect | Blocked androgenic receptor | Demasculinization |

**Table 1 *Hormone disruptions***

The most attention in studies goes to the female hormone group of estrogens. The estrogens can be divided in four groups (STOWA Lahr & de Lange, 2009):
●Natural estrogen hormones: These are produced by vertebrate animals
●Synthetic estrogen hormones: Hormones produced for anti-conception or to enhance the feminine fertility
●Xeno-estrogen hormones: Foreign chemical substance that exhibit a certain degree of estrogen behavior
●Fyto-estrogen hormones: Substances from botanical origin that exhibit estrogen behavior

A big study in the Netherlands called 'Landelijk onderzoek Oestrogene stoffen' (LOES) proved that certain hormones exist in surface waters. The results from LOES are shown in appendix A.
So it is established that hormones do exist in waters in concentration in the order of ng/l to μg/l. The question now is, are these hormones harmful and if so in what concentrations.

The first suggestions that a change in hormones could be harmful comes from a Danish study from the early '90. The study showed that the sperm quality of men was dropping. This study was followed up by the book 'our stolen future' (colbern, 1996) in which alarm was raised because of the drop of fertility of both men and animals due to hormone disrupting substances.
A nuance to the alarm came from the 'Gezondheidsraad' (a Dutch instance), which concluded that exposure to hormones/hormone disrupting substances are not a direct threat for the public health. The different opinions are logic, because the direct effect of exposure to a hormone or hormone disrupting substance is hard to determine. Overall there is no hard proof that the exposure to hormones is indeed harmful for humans, for example even the highest measured concentration of ethinyl estradiol is approximately 3500 times below the normal doses in the anti-conception pil (STOWA Derksen & Lahr, 2003).
This does not mean we can dump the hormones and hormone disrupting substances anywhere we want, because damage to several organisms has been proven (STOWA Hekster & Mons, 2004) (STOWA Lahr & de Lange, 2009).

*Snails*
Lab research to several fresh water snails proved feminization due to hormones including ethinyl estradiol and Bisphenol A. The concentrations that were needed to see an effect were in the ng/l range. The concentrations found with LOES were in the same range.
No field research has been done (yet), because the research is labor-intensive because the snails must be picked out of their shell.

*mussels*
For mussels the fresh water mussel (*Elliptio complanata*) has been studied well in Montreal, Canada. The fresh water mussel was studied at a WWTP were they compared the percentage female mussels before and after the WWTP. The difference between before and after was found to be quite significant. Before the WWTP 41% of the mussels was female, but after the WWTP 66% was female.

*Rainbow trout*
In the nineties a study in Britain with rainbow trout was done. The trouts were put in cages and these cages were let in mobile flow-through systems. In these systems the trouts were exposed to different dilutions of effluents. After three weeks the trouts were examined. A heighted concentration of vitellogenine (VTG) was found in the blood of the males. VTG is a yolk protein that is normally produced in the liver of the females. VTG will accumulate in the males, because in contrary to the females the males do not have a natural way of losing it. The females lose the hormone when they lay eggs.
Another interesting thing found, was that female ovules where found in the tissue of the male genitalia.

*Fathead minnow*
A study in Canada for three years showed the effect of 17-alfa-ethinylestradiol (one of the components in the anti-conception pil) on the fathead minnow (Pimephales promelas). This fish was almost extinct at the test area after maintaining a constant concentration of 5-6 ng/l. Before becoming extinct the males had the same symptoms as the rainbow trout (VTG and female ovules). The females had impaired genitals and a slowed egg production. This study was unique in a sense that it was the first study showing that estrogens had effect on a population level of organisms.
A side note worth mentioning is that a few years after stopping the exposure to 17-alfa-ethinylestradiol the survivors of the fathead minnow population were able to create a new population.


Conclusion
Although there are no studies that show direct harm to humans, harm to several organisms has been proven. Harming organisms will disrupt the balance in nature, which can backfire to the humans in a later stadium. And for a future perspective, if hormones are kept being let in the surface waters the concentrations will increase which could give a harmful situation for humans in the future.

## 2.2 Medicines

Hormones are not the only materials that might cause problems for organisms. A broad spectrum of medicine has been found in the surface waters as well. Most medicine have to properties that they are soluble in water, mobile and that they work at low concentrations. These three properties give problems in the environment, because the medicine problem will spread out quickly and will still give problems due to fact that the hormones will work at low concentrations.

The first time attention was paid to medicine in the environment was in the early eighties. A few studies (de Roij & de Vries, 1982; van der Heide & Hueck-van der Plas, 1982; Watts, 1983: Richardson & Bowron, 1985) looked in to the matter. But it was not till 1992 when it the attention became serious. In Germany an unknown substance was found while screening ground water for herbicides and pesticides. The unknown substance was a breakdown product from fibrates (see table 2). Further research showed that these breakdown products were provable in a lot of waters. These results resulted in new studies in Denmark, Germany, Switzerland and the Netherlands measuring concentrations in influents, effluents, several rivers, the North sea and drinking water (STOWA Derksen & Lahr, 2003) (STOWA Derksen & ter Laak, 2013).

One of the organizations in the Netherlands is the RIZA/RIWA.
According to the RIZA/RIWA approximately 12000 human medicine and 2500 animal medicine are allowed. For the environment the active medicine are the most interesting, resulting in a shortlist of 850 humane medicine and 250 animal medicine. From the humane medicine around the 200 are monitored. Table 2 shows the important groups of humane medicines, table 3 show the important animal medicine (STOWA Hekster & Mons, 2004) (KWR STOWA Derksen & ter Laak, 2006).

| Group Medicine | Application | Example of active compound |
|---|---|---|
| Analgetica | Painkillers | Aspirin, ibuprofen |
| Antibiotica | Treatment of infections | Amoxicillin, erythromycin |
| Anti-epileptica | Treatment of epilepsy | Carbamazepine |
| Béta-blocker | Treatment high blood pressure and heartproblems | Metoprolol, sotalol |
| Cytostatica | Treatment of cancer | Cyclofosfamide |
| Fibrates | Fatregulating | Bezafibrate, fenofibrate |
| Psychofarmaca | Treatment of depression | Diazepam |
| X-ray contrast material | X-ray diagnostics | Amidotrizoineacid, iopamidol |

**Table 2** *human medicine*

| Group Medicine | Compound groups | Example of active compound |
|---|---|---|
| Antibiotics | Aminoglycosiden<br>Bèta lactam derivatives<br>Diaminopyrimides<br>Macroliden<br>Quinolen<br>Sulfonamiden<br>Tetracyclinen | Neomycine, Spectinomycine<br>Amoxycilline<br>Trimethoprim<br>Erythromycine, Tylosine,<br>Enrofloxacin, Flumequin<br>Sulfachloorpyridazine<br>Doxycycline, Oxytetracycline |
| Antiparasitica | - | Flubendazol, Ivermectine |
| Coccidiostatica | - | Monensin, Nicarbazine,<br>Salinomycine |

**Table 3 *Animal medicine***

On the next page (figure 1) a few monitored medicine are shown. In the figure the removal percentage from the waste water stream is given. The percentage is an average of eight WWTP's. The n value is on how many measurements the average is based. The standard deviation is shown as well. For some medicine the removal percentage is quite high, but not one medicine is removed completely, this means the stream leaving the WWTP will always contain medicine.

In appendix A. the results of LOES are three tables with maximum measured concentration of several medicine. Both figure 1 and these results show that medicine will come in the environment. Same as with the hormones, the question is do the medicine harm and if so in what concentration.

The knowledge about the effects is increasing, but a lot is still unknown. A problem with the studies is that the concentrations in the surface waters are a lot lower than the concentrations used in the lab. Another problem is that in the lab mostly the short term effects are measured, while in the environment organisms are exposed to the medicine for a long time to a mixture of a lot of medicine. To judge the risks it is important to look at the long term effects and the combination of several medicine. A third problem is that the effects of the medicine are not always measurable with standard biological measure methods.

For humans the expectation is that the low concentrations of medicine will not have a harmful effect on humans, mainly because the concentrations are around a factor $10^6$ lower than the doses prescribed. The only small effect some medicine can have is an allergic reaction, because really small amounts can evoke a reaction. Most of the time these reactions disappear when exposure to the medicine is stopped. Most of the medicines that evoke an allergic reaction are antibiotics.
These antibiotics have another problem. They are used against bacteria's, but bacteria's have to tendency to become resistant if exposed to the antibiotics, because the bacteria's with the highest resistance to the antibiotics will survive. If this happens in nature all the time, none of the antibiotics will be working well. This can give major health issues on global scale in the future (STOWA Derksen & Lahr, 2003) (KWR STOWA Derksen & ter Laak, 2006).

For other organisms the medicine can give problems at this stage and the concentrations that are now measured. The medicine are labeled with an $EC_{50}$ concentration. The $EC_{50}$ concentration is the *half maximal effective concentration*, which is the concentration of a drug, antibody or toxicant which produces 50% of the maximal possible response for that drug, antibody or toxicant. The lower this $EC_{50}$ concentration, the more toxic the compound is. In graph the results of a study from Derksen (2001) are shown. The study was a collection of Eco toxicological data of about 120 of the most used humane medicines. The result is a distribution of the number of medicine per $EC_{50}$ concentration, which is shown in graph 1. When the $EC_{50}$ concentration is larger than 100 mg/l the compound is considered not toxic, between 10 – 100 mg/l the compound is considered harmful and an $EC_{50}$ concentration smaller than 10 mg/l means a compound is toxic. As can be seen in graph 1 several

medicine can be considered at least harmful. But because the concentrations measured are in the order of ng/l or µg/l no direct harm is expected, although chronic negative effects have to be considered as possible outcome (STOWA Derksen & Lahr, 2003).
And on a longer term the medicine can accumulate in different kinds of tissue of organisms. This does not give direct problems for these organisms themselves, but when they are consumed they can poison their predator or when they die they can release a relative high dose of medicine in a local area. The precise damage this causes is unknown and it is hard to be studied precisely.

For some organisms some specific effects are studied and proven (STOWA Derksen & Lahr, 2003) (STOWA Hekster & Mons, 2004):
●Extra sensitivity for algae and cyanobacteria for antibiotics
●Extra sensitivity for algae for beta blockers
●Kidney damage caused by diclofenac for humans
●Mass come out of ovums and spermatozoons by mussels caused by fluoxetine
●Disruption of the skinning of lobster-like animals
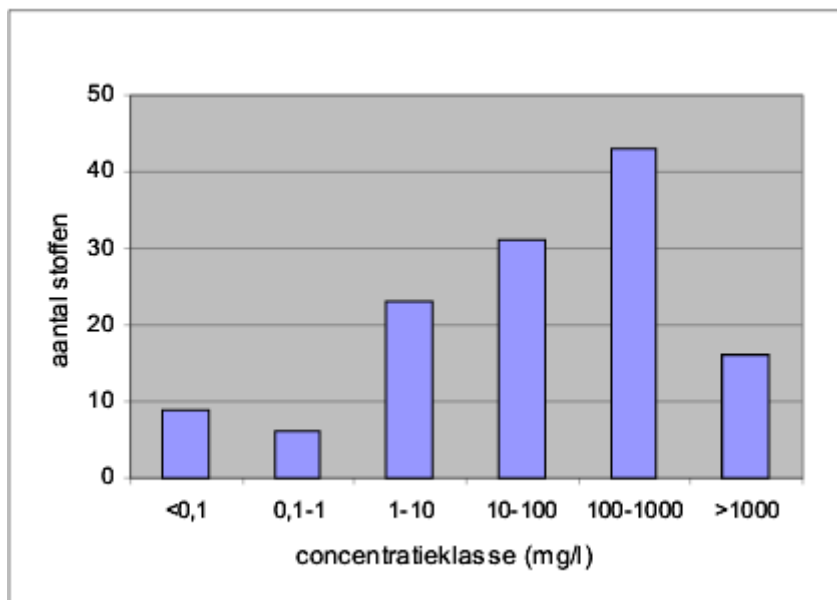


**Graph 1**

Conclusion
It is expected that humans will not have direct negative effects from the medicines found in surface waters at the concentrations at which they are measured. However some effects for other organisms are suggested and proven which means action should be taken to at least prevent an increasing concentration of the medicines. In a future perspective, preventing an increase of the concentrations is essential to prevent the concentrations from getting in the concentrations ranges in which they might have effect on humans.
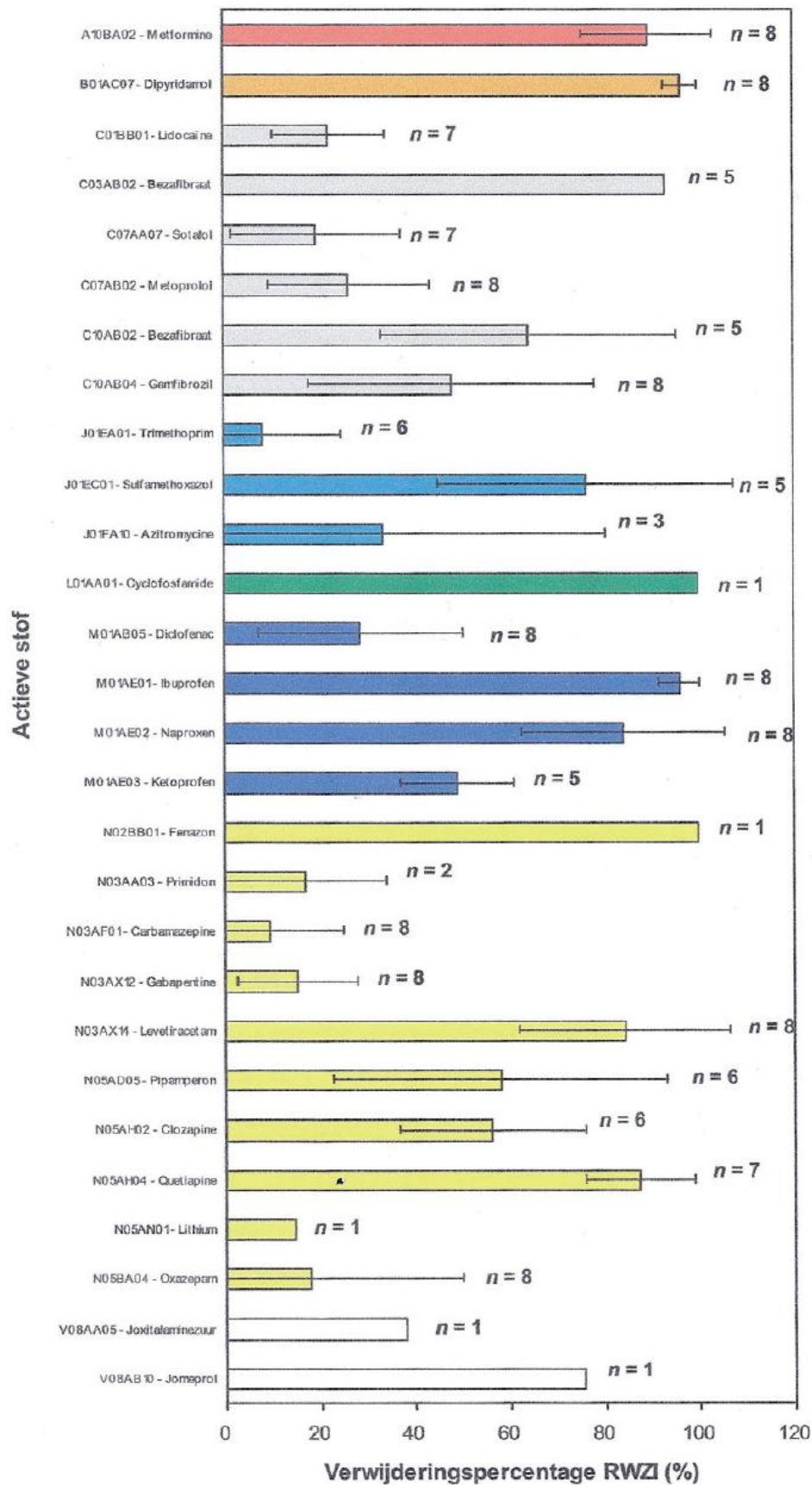
**Graph 2** *Removal percentages of medicine*

## 2.3 Coal

In principle coal as filter aid will work via adsorption. Adsorption is a heterogeneous reaction where a particle in gas or liquid phase(the adsorbate) is bound to a solid or liquid called the adsorbent. In this way the particle is removed from the gas or liquid phase. This process creates a layer of the adsorbate on the adsorbent. The limit of adsorption lays in the adsorbent, because of this layer forming. When in theory all the surface of the adsorbent is covert, no more adsorption can take place. After adsorbing, the adsorbent has to be destroyed or regenerated. Active coal is the most used form for coal filtration (Glossary, 2009) ((wordnet), 2011) (Anon., 2009).

Adsorption is described via isotherms. Isotherms are the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid). By normalizing with the mass of the adsorbent comparison between different materials is possible.
There are different ways to describe the isotherms:
●Linear adsorption isotherm
●The Freundlich adsorption equation
●Langmuir isotherm
●BET Theory
●Kisliuk model

*Linear adsorption isotherm*
The simplest way to describe the isotherm is the linear adsorption isotherm or Henry adsorption constant.

For gasses: $\qquad\qquad X = K_H \times P$

For liquids: $\qquad\qquad X = K_H \times C$

Where: X = The fraction of surface covered by the adsorbate (-)
$\qquad$ $K_H$ = Henry's adsorption constant (1/atm or l/mol)
$\qquad$ P = Partial pressure adsorbate (atm)
$\qquad$ C = Concentration adsorbate (mol/l)

The linear adsorption isotherm can be used to describe the initial part of many practical isotherms. It is typically taken as valid for low surface coverages, and the adsorption energy being independent of the coverage (Yildirim, 2006).

*The Freundlich adsorption equation*
This equation is a curve relating concentration of a solved material on the surface of an adsorvent to the concentration of the solved material in the liquid.

For gasses: $\qquad\qquad \dfrac{X}{m} = K\, p^{1\ n}$

$\qquad\qquad$ Or $\qquad \log\dfrac{X}{m} = \log K + \dfrac{1}{n}\log p$

For liquids: $\qquad\qquad \dfrac{X}{m} = K\, c^{1\ n}$

$\qquad\qquad$ Or $\qquad \log\dfrac{X}{m} = \log K + \dfrac{1}{n}\log c$

Where: X = Mass of adsorbate (gr)
m = Mass of adsorbent (gr)
p = Equilibrium pressure of adsorbate (atm)
c = Equilibrium concentration of adsorbate in solution (mol/l)
K and n = Constants for a given adsorbate and adsorbent at a certain temperature (1/atm or l/mol)

The adsorption will become independent of the pressure at high temperature, because $\frac{1}{n} = 0$ for high pressures.
The Freundlich adsorption equation is used when the actual identity of the solved material is unknown (Anon., 2008).

*Langmuir isotherm*
Irving Langmuir created this model that relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration above the solid surface at a fixed temperature. It is the most common used isotherm equation thanks to its simplicity and its ability to fit a variety of adsorption data. This model is based on four assumptions:
●All of the adsorption sites are the same and can only fit one molecule
●The surface is energetically homogeneous and there is no interaction between adsorbed molecules
●The are no phase transitions
●At the maximum adsorption point, only a monolayer is formed. The adsorption only occurs on localized sites on the surface, not on other adsorbates.

When these four assumptions are met, there is an ideally situation. Unfortunately there are always imperfections on the surface, adsorbed molecules are not per se inert and the adsorption mechanics will differ for the first molecule compared to the last. The fourth assumption gives the most trouble, as always more molecules will be adsorbed than just the amount to form a monolayer.
This isotherm is most used in applications in surface kinetics and thermodynamics.

The model suggests that adsorption takes place via the following mechanism:
$$A + S \leftrightarrow AS$$
Where: A = A molecule
S = An adsorption site

The kinetic rate constants are k and $k^{-1}$. The surface coverage as the fraction of the adsorption sites occupied at equilibrium will be defined as θ. This gives:
$$K = \frac{k}{k^{-1}} = \frac{\theta}{1 - \theta} \frac{}{P}$$
Or $\quad \theta = \frac{K \times P}{1 + K \times P}$

Where: P = The partial pressure of the gas or the molar concentration of the solution  (atm)

This model gives at low pressures $\theta = K P$, and at high pressures $\theta \approx 1$.
θ is hard to measure experimentally, thus it is replaced by $\frac{v}{vmon}$. This is the quantity in moles or grams adsorbed at standard temperature and pressure per gram of adsorbent (v) divided by the volume of material that's getting adsorbed to form a monolayer on the adsorbent at standard temperature and pressure (vmon).
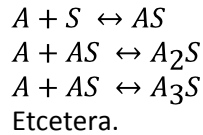
This gives the expression:

$$\frac{1}{v} = \frac{1}{K \times vmon \times P} + \frac{1}{vmon}$$

(Anon., sd)

*BET Theory*
The BET theory is a modification of the Langmuir isotherm taking multilayer adsorption into account. The mechanism becomes:

$$A + S \leftrightarrow AS$$
$$A + AS \leftrightarrow A_2S$$
$$A + AS \leftrightarrow A_3S$$
Etcetera.

The derivation of the formula is more difficult than with the Langmuir isotherm, but for gasses one finally obtains:

$$\frac{x}{v(1-x)} = \frac{1}{vmon \times c} + \frac{x(c-1)}{vmon \times c}$$

Where: x = Pressure divided by the vapor pressure for the adsorbate (-)
v = volume of adsorbed adsorbate at standard temperature and pressure (cm$^3$)
vmon = amount of adsorbate required to form a monolayer at standard temperature and pressure (cm$^3$)
c = The equilibrium constant K used in Langmuir isotherm multiplied by the vapor pressure of the adsorbate (-)
(Brunauer, et al., 1938)

*Kisliuk model*
This model is an alteration of the Langmuir isotherm. The basis from the alteration comes from the observation that adsorption is more likely to occur around already adsorbed molecules on the surface of the adsorbent. This renders Langmuir's isotherm ineffective for the purpose of modeling. Paul Kisliuk thought of a precursor state theory to compensate for the increasing probability of adsorption around molecules present on the adsorbent surface. This theory states that molecules enter a precursor state at the interface between the solid adsorbent and the adsorbate. From this state the adsorbate either adsorbs to the adsorbent or desorb back in the gas or liquid.

Implementing the precursor state theory the following formula is obtained:

$$\theta \ t \ = \frac{1 - e^{R' \ 1+kE \ t}}{1 + kE \times e^{R' \ 1+kE \ t}}$$

Where: θ = The fractional coverage of the adsorbent with adsorbate (-)
R' = Rate constant, represents the impact of diffusion on the monolayer formation and is proportional to the square rot of the system's diffusion coefficient (s$^{-1}$)
t = The immersion time (s)
kE = This is the sticking coefficient, which is $kE = \frac{SE}{kES \times SD}$, with SD is the adsorption rate constant, kES is the rate at which the adsorbate desorbs and SE is the desorption rate constant (-)
(Sivaraman, et al., 2009)

For this bachelor thesis not active coal, but normal coal is used. Normal coal is likely to be significant less active as an adsorbent. This comes because of the one big difference between 'normal' coal and active coal. The big difference lies in the structure, the structure of active coal creates an internal surface in the order of 500 – 2000 $m^2$ /gram coal. The internal surface of normal coal is in the order of 50 $m^2$ / gram coal. (Thomas & Damberger, 1976)

Commercially there are two version of active coal, powder and granulate version.
(Dąbrowski, et al., 2005)

## 2.4 Micro-Plastics

### 2.4.1 Problem
Micro-Plastics are microbeads of plastics (for example polyethylene or PE, polypropylene or PP and polyethylene terephthalate or PET) which are smaller than 5 mm (see image 1 for an example). Microbeads are uniform polymer particles which are used in a wide area of applications. The micro-plastics are popular because of their polishing and emulsifying ability and the ease at which the properties can be adjusted to fulfill the desirable function. The three properties that are adjusted the most are density, color and roughness.



**Image 1** *Microbeads*

For several decades the micro-plastics are used, but the possible problems where first addressed in 2004 by Richard Thompson. In his article in Science he was wrote about the presence of micro-plastics on beaches and in water columns of the North Sea. In 2011 the first recap of the scientific work addressing the micro-plastics was made by Leslie. The conclusion was that still little is known about the amount of micro-plastics used and how much micro-plastics end up in the surface waters via WWTP's. The first estimate of how much micro-plastics people use came not long after the recap by Gouin (2011). This estimate was about polyethylene alone and was only about polyethylene from liquid soaps. Gouin came at an average of 2.4 mg per person per day.
(Roex, et al., sd)

In 2012 a study in the Netherlands measured the concentration of micro-plastics at the WWTP in Heenvliet. The influent had an average of 200 micro-plastic particles per liter, the effluent contained round 20 particles per liter. This means 90% of the micro-plastic particles do get filtered out.

This seems a rather small number, but with estimated 2 milliard cubic meters purified every year in the Netherlands, the amount of micro-plastics that end up in the surface waters is:

$$2 \times 1000 \times 10^9 \times 20 = 4 \times 10^{13} \text{ particles / year}$$

Or: $\frac{4 \times 10^{13}}{365} = 109{,}6 \times 10^9$ particles / day

The question is what harms can and will these plastics do. These plastics are stable, because it can be assumed that the most unstable variants are part of the 90% of the micro-plastics that get filtered out. This means the plastics will remain in the environment for at least decades, because the degradability lies in that order or even higher. This means there will be an accumulation of plastics in the environment in the years that are coming. This still would not have been a big problem if the plastic were completely harmful, but the opposite is true. Several studies show different types of ways the micro-plastics can exert certain damage or be a threat for organisms (Roex, et al., sd).

For instance a literature study by Deltares and IVM shows that humans and animals are able to absorb micro-plastics in their tissue and bodily fluid. After being absorbed, the particles can be taken in the digestive system. Via the digestive system the particles are able to reach the cardiovascular system and the lymphatic system. There the micro-plastics could cause local infections and changes in gene expression. Wick (2010) proved that polystyrene particles with a maximum size of 240 nm can be carried from mother to child via the placenta (Roex, et al., sd) (Appie, 2012).

This in combination with the ability of the micro-plastics to absorb certain other materials gives a broad spectrum of problems the plastics can give. The plastics can have these materials absorbed by choice of design or by absorbing them later. This means the plastics can introduce chemical contaminations and pathogens in organisms that were in initially in the plastic by design, but it is also possible that chemical contaminations that exist in for example surface waters like pesticides are absorbed and then introduced in an organism (Appie, 2012).

An example of a specific effect on an organism comes from a study from the United States by Bhattacharya in 2011. This study proved that the micro-plastics have a negative effect on the photosynthetic capability of green algae (Leslie, et al., 2012).

A system that can be used to take small particles out of a solution is a DAF. DAF stands for Dissolved Air Flotation. The removal is done by dissolving air in the water under pressure. This air is released at atmospheric pressure in a flotation tank or basin. The air will form tiny bubbles which will adhere to the small particles. The small particles will float to the surface where the can be removed. A baffle will prevent the floating material to continue in the system (Kiuru & Vahala, 2000).
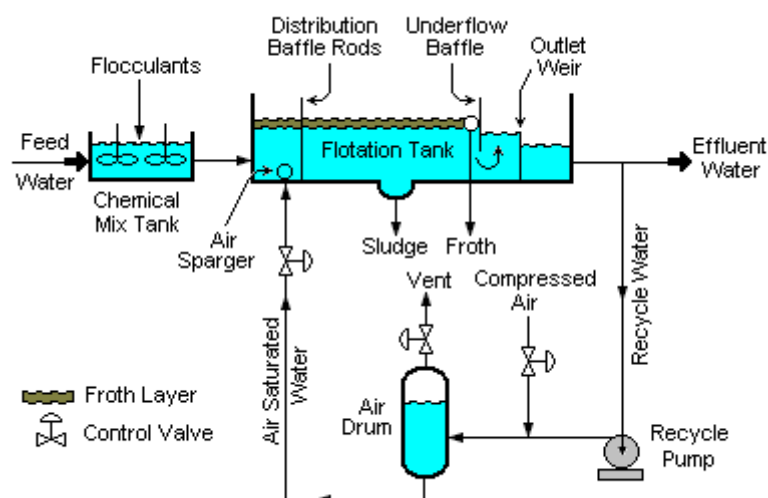


**Image 2 *DAF***

The DAF is not used for micro-plastics mainly because the concentration of the micro-plastics is fairly low. Considering the DAF will be installed at the end of the WWTP system the concentration will be around 20 particles per liter. The DAF will be very inefficient with such low amount of particles (Kiuru & Vahala, 2000).

Conclusion

The attention that micro-plastics and the possible problem is getting is significantly increased the last decade. The first reports about the effects and possible effects of the micro-plastics justify this. Although a lot of studies are still running, the few studies that show result all point in the same direction.

Because the micro-plastics are stable, the only chance to keep the thread away is by taking the micro-plastics out of the water. This brings the WWTP's in an important role. Although, if most WWTP's do not differ to much in effectiveness, the WWTP's have an effectiveness of ~90%, everything that can improve this number should be considered. A special deeper look can be done on DAF systems, although they do not seem viable for the relatively low concentration of micro-plastics the DAF still could be interesting if it is combined with the removal of other problematic particles as well (Leslie, et al., 2012).

### 2.4.2 Micro-plastics and Garmerwolde

The WWTP Garmerwolde has to filter as much micro-plastics out as possible, like any other WWTP. The area Garmerwolde manages is 144000 hectares big, this covers approximately 375000 people. If the earlier mentioned average of Gouin (2.4 mg per person per day (Roex, et al., sd)) is used, a total mass of $2{,}4 \times 10^{-3} \times 375000 = 900$ gr micro-PE has to be removed from the influent every day. Of course this is only micro-PE and only from liquid soaps. If considered that the three most used micro-plastics (PE, PP and PET) are the majority of the micro-plastics and if PP and PET are used at a same amount as PE, the total mass micro-plastics per day will be 2700 gr. This is still only from liquid soaps. Other sources are toothpaste, skin care products, paint etc. The amount of micro-plastics these other sources produce will be considered roughly the same as for liquid soap. This gives a total mass of 5400 gr. micro-plastics per day that have to be removed from the influent.

The total amount of water that is processed at Garmerwolde is 29000000 cubic meters per year (STOWA, sd). This means 79000 cubic meters per day. This gives a concentration of micro-plastics of $\frac{5400}{79000000} = 68$ µg per liter in the influent. Considering the ~90% removal effectiveness, the effluent will have a micro-plastic concentration of 6.8 µg per liter. The removed micro-plastics will be in the slib, which will be burned in a later stage. This means this plastic has no chance to come back in the environment.

## 2.4.2.1 Overall schematic

Image 3 is the OBD (overall block diagram) of the WWTP focusing on the hormones and micro PE.



FeCl3
-130 kg/h
-40 wt% FeCl3 in water
-10 °C
-1.01325 bar

Poly-electrolyte
-15 kg/h
-1 wt% Poly-electrolyte in water
-10 °C
-1.01325 bar

Extern sludge
-22831 kg/h
-3.2% DSC
-10 °C
-1.01325 bar
-sludge(L)

H&Aa sludge
-13575 kg/h
-3.7% DSC
-10 °C
-1.01325 bar
-sludge(L)

Influent
-2916667 kg/h
-12.9 °C
-1.01325 bar
-Water (L)
-7.5 pH
-Contains:
  -Micro-plastics 0.20 kg/h
  -Hormones 0.050-0.44 g/h

WWTP Garmerwolde

Effluent
-2947481 kg/h
-12.9 °C
-1.01325 bar
-Water (L)
-7.1 pH
Contains:
  -Micro-plastics 0.020 kg/h
  -Hormones 0.002-0.029 g/h

Sludge cake
-5736 kg/h
-25.87% DSC
-10 °C
-10.01325 bar
-Sludge (S)
-Contains:
  -Micro-plastics 0.18 kg/h
  -Hormones 0.048-0.41 g/h

Biogas
-251 m3/h
-30 °C
-1.01325 bar
-Gas (G)

**Image 3** *overall schematic of Garmerwolde*

The percentage of the micro-plastics is based on the calculations earlier. It is assumed that the smallest micro-plastics will leave the WWTP with the water, because the smaller particles will be more likely to float instead of sediment.

The percentage of hormone is based on the concentrations from β-estradiol from the LOES (STOWA Derksen & Lahr, 2003). The raw waste water concentrations vary from 17-150 ng/l, while in the effluent the concentration is between 0.8-10 ng/l.

## 2.4.2.2 Detaillistic schematic

Image 3 shows a PFD (process flow diagram) of the Garmerwolde WWTP. As earlier assumed the smallest/lightest micro-plastics will float. A ton is equivalent to 1000 kg.



**Image 4** *Detaillistic schematic of Garmerwolde* **(Stoffelsma, 2012)**

●The influent has 68 µg per liter micro-plastics, this is considered 100%. Following the trail of the influent the micro-plastics will first pass the mechanical filter. Only the b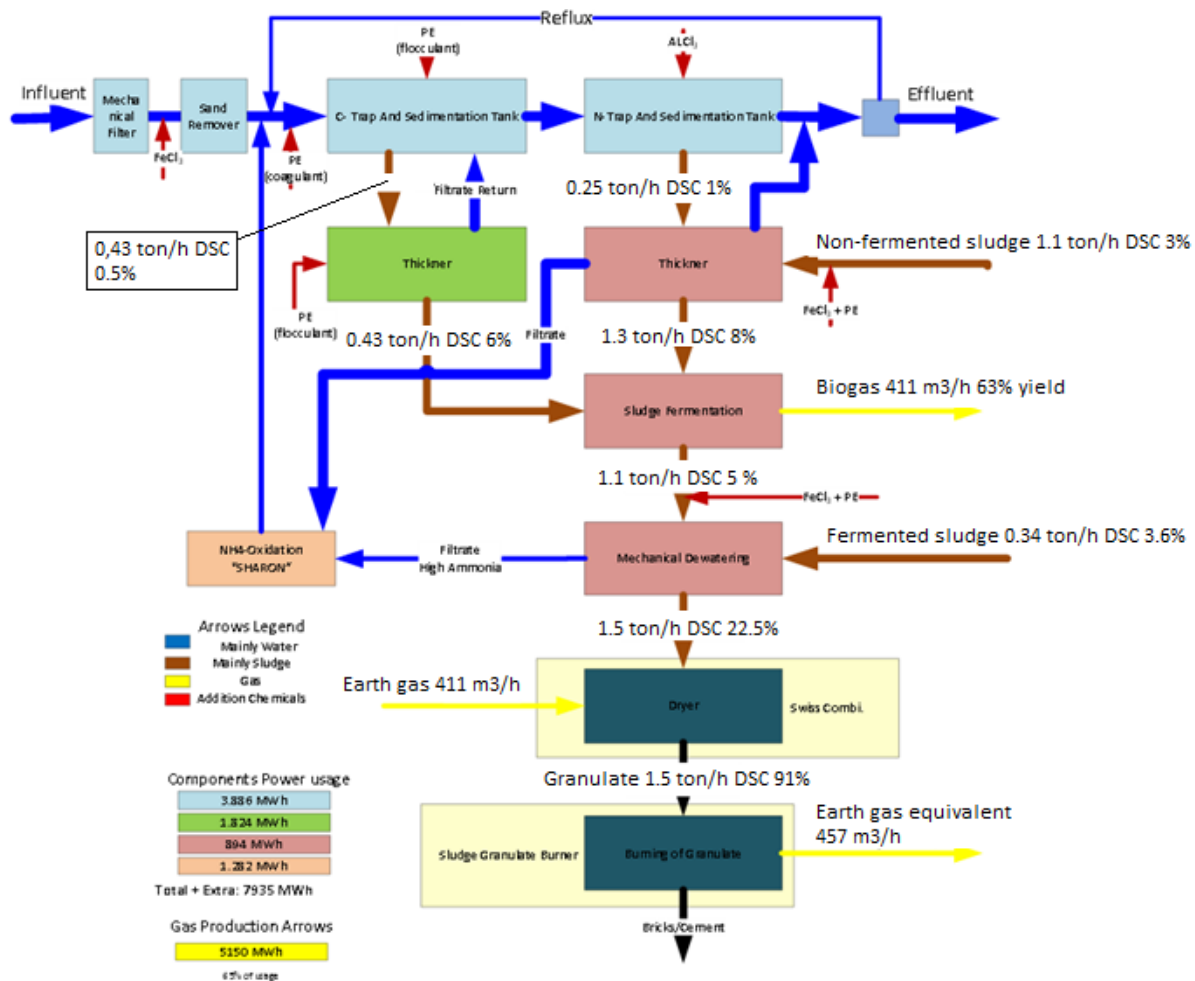iggest micro-plastics might be filtered out here. Assumed is that 60% of the micro-plastics will continue, this leaves a concentration of 40.8 µg per liter in the stream.

●The sand remover will not remove micro-plastics. The sand remover is based on density and the density of the micro-plastics is significantly lower, meaning that the micro-plastics will not sediment. This means the concentration of 40.8 µg per liter still remains in the stream.

●The reflux stream will increase the micro-plastic concentration, because of the way it is added. The adding can be compared with pouring, which means the floating particles will be poured out. The amount added is the same as will be mentioned at the reflux part later.

●Next the plastics will pass the two sedimentations tanks. Only the heavier micro-plastics might sediment here, but most of the bigger/heavier micro-plastics have already been removed from the stream. Still there is assumed roughly 20% of the initial concentration will be lost here because some micro-plastics will be captured in the sludge.

●Next the reflux will decrease the concentration by 75%. This value will be added to the stream earlier (see point 3). This drops the concentration to about 7.3 µg per liter in the initial situation. This stream leaves the WWTP, meaning the effluent also has a concentration of about 7.3 µg per liter.

This process has a big flaw on the micro-plastics area. In the initial situation the outcome will be 10% of the ingoing concentration, but because of the reflux stream there will be an accumulation of micro-plastics. This comes because the reflux stream takes 75% of the concentration of the stream just before the reflux. Even if the ingoing concentration of the system remains the same, the concentration of the stream just before the reflux will keep increasing. This means the absolute value of micro-plastics in the effluent will increase as well and thus the system needs adjustments.

# 3. Experimental

## 3.1 Setup

The first problem was how to test the adsorption of hormones. After discussing with my supervisor Boesten the choice became a delta measurement. This means that not the direct adsorption to coal is measured, but the differences in the concentration of hormones before and after exposure to the coal.

This gave the general outline for the practical, but some things had to be specified, like what hormone(s) is/are used and how the concentration of hormones will be measured. In discussion with Jan-Henk Marsman from the analytic department of the RUG, the hormone choice became Beta-estradiol (also known as 17-β-oestradiol), simply because as seen in the LOES results (STOWA Derksen & Lahr, 2003) it is one of the hormones measured in surface waters and because it was in stock at the biochemical department of the RUG.

Jan-Henk also helped thinking of a way of measuring the concentration of beta-estradiol, which resulted in UV-spectrometrics. This is a fairly easy measurement method, which works because beta-estradiol has two absorption peaks, at 225 nm and 281 nm (Anon., sd).

## 3.2 Chemicals & Equipment

Chemicals: demi-water, ethanol (99%), beta-estradiol, coal (87% DSC)
Equipment: Heater, magnetic stirrer, measuring cylinder, beakers, spatulas, Buchner funnel

## 3.3 Method

*Preparation*
Put an amount of the coal in an oven overnight at approximately 100 °C to dry it. Weight before and after to control the DSC.

*Method*
First the PSD (particle size distribution) is determined of the coal. Pour an amount of the dried coal on a stack of sieves with each a different pore size (see image 2). The stack consisted of four sieves with pore sizes 0.025 mm, 0.050 mm, 0.100 mm and 0.200 m. Under the sieves a tray is placed to catch the smallest fraction (< 0.025 mm).But the stack in shake machine for ~30 min.
Now the particle size distribution of coal can be determined from the different fractions.



**Image 5** *Stack of sieves*



**Image 6** *Stirring setup*

Next different hormone solutions are made. This is done in water and ethanol in the concentrations:
● 1 microgram/l
● 100 microgram/l
● 10 mg/l
● 100 mg/l
These concentrations are tested in the UV-spectrometric to see if they have a high enough absorption to get clear results. The concentration with good results is taken as basis for the rest of the practical.

After choosing a suitable concentration, the following tests are run:

| Test number | Volume solution | Amount of coal | Type of coal | Stirring time |
|---|---|---|---|---|
| 1 | 200 ml | 0.044 gram | PS < 0.025 mm | 1 hour |
| 2 | 200 ml | 0.063 gram | PS <0.025 mm | 24 hours |
| 3 | 200 ml | 0.402 gram | PS < 0.025 mm | 24 hours |
| 4 | 200 ml | 0.406 gram | Mixture | 24 hours |

**Table 4** *Different tests for experimental*

Every test had a blanco without hormone running with the same concentration of coal and same stirring time. This blanco is needed for the UV-spectrometric measurements.

After the stirring time every test had to be filtered thoroughly to make sure there is no coal left in the solution. This is done over a Büchner funnel. The same is done for the blanco solutions.



**Image 7** *Filter setup*          **Image 8** *UV-spectrometric*

After this the UV-measurements can be done. Essentially two UV-measurements are done for every test.
1. This first measurement is done with a baseline of pure ethanol, and a measurement of the ethanol and hormone solution before adding the coal
2. The second measurement is with the filtered blanco as baseline and the filtered ethanol, coal and hormone solution as actual measurement

By comparing these two UV-measurements one can determine if hormone adsorption had taken place or not.

Two other smaller things have been looked at. The first one is the behavior of coal in water, this is simply done by putting 0,205 gram coal in 200 ml water. This is stirred for a few minutes and then the behavior is looked at.
Also the coal of test three has been looked at. By washing 0,203 gram coal that has been taken of the filter with 100 ml ethanol for several times (re-using the ethanol). This 100 ml ethanol will also be UV tested against a blanco of 100 ml ethanol. This is done to test the adsorption strength.

# 4. Results and discussion

## 4.1 Results

### 4.1.1 Overall
Although the literature stated that beta-estradiol solves reasonable well in water, there were some problems solving it in water. For the two lowest concentrations it worked after stirring for approximately one hour while heating at 50 °C. These concentrations were not sufficient enough to get a nice peak at the UV-spectrometric. Because higher concentrations could not be achieved in water, the solvent was switched to ethanol. At 100 mg/l the absorption of light at the 225 nm peak was exceeding the 1.0 A, but for 281 nm it was around 0.75 A. This peak was used as reference for the delta measurement.

For the first three adsorption tests the fraction of the coal with the lowest particle size (< 0.025 nm) was used. For the fourth test the coal before sieving it was used, because that is the coal mixture that actually will be used at the WWTP. This means the concentration of the smallest fraction will be lower compared to the first three adsorption tests.
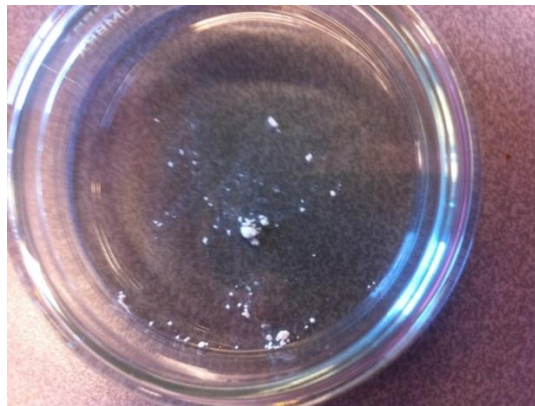

**Image 9** *Unsuccessful solving in water…*

More tests could have been done, but the supply of hormone was not unlimited. This means choices had to be made.

-The first test was the amount of coal expected to be added according to Meelker´s report. He added the amount of coal to get a concentration of around the 0.2 gram coal per liter (Meelker, 2010). In this first test this concentration is achieved as well.

-Because the first test resulted in no adsorption noticeable, the amount of coal was slightly increased and the stirring time was significantly increased.

-The second test showed adsorption. This third test was to check if in the same amount of stirring time more adsorption can take place.

-The fourth test was about comparing the coal mixtures adsorption ability to the smallest fractions adsorption ability.

## 4.1.2 Coal

First the dry solid content (DSC) of the delivered coal was checked. The lid of the container of the coal stated a DSC of 87% and that it had to be determined again. For determining the DSC the assumption that after drying for 24 hours at 105 °C the DSC will be 100% has been made. This means that the weight difference before and after the drying is the weight of the water.
The DSC results are in table 4.

| Mass before drying | 6.65 gram |
| Mass After drying | 5.87 gram |
| Difference(mass water) | 0.79 gram |
| Dry solid content | 88.2% |

**Table 5 *Dry solid content***

After drying and determining the DSC, the Particle Size Distribution was determined. See table 5, graph 3 and 4 and images 6,7,8,9 and 10 for the results. Particles larger than 0,100 mm make up for the majority (more than 60%) of the particles.

| Particle size | Mass (grams) | Fraction of total | Cumulative |
|---|---|---|---|
| < 0,025 mm | 0.93 | 0.16 | 0.16 |
| 0,025 mm < PS < 0,050 mm | 0.47 | 0.08 | 0.24 |
| 0,050 mm < PS < 0,100 mm | 0.74 | 0.13 | 0.37 |
| 0,100 mm < PS < 0,200 mm | 1.38 | 0.23 | 0.60 |
| > 0,200 mm | 2.35 | 0.40 | 1 |

**Table 6 *Particle Size Distribution***
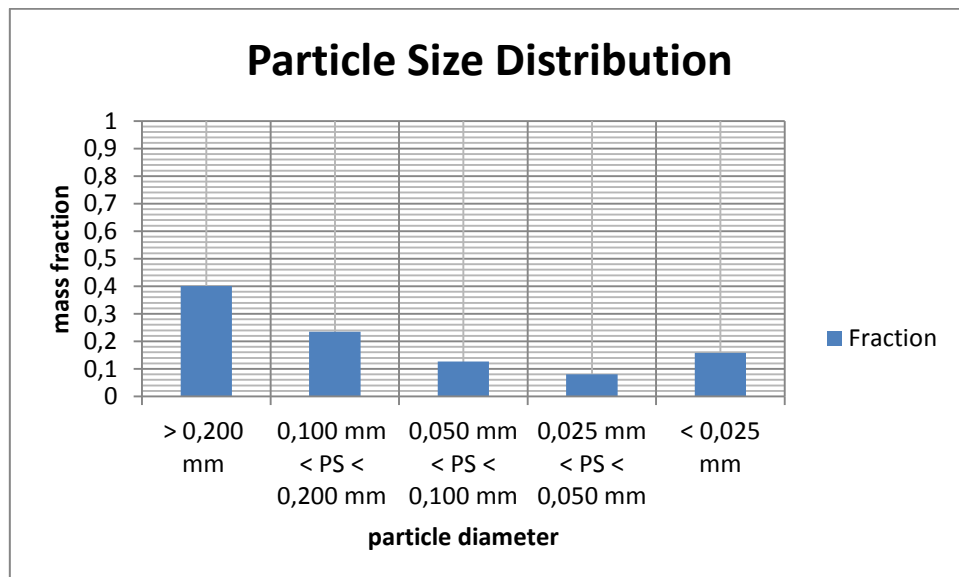


**Graph 3 *Particle Size Distribution 1***

**Particle Size Distribution Coal**
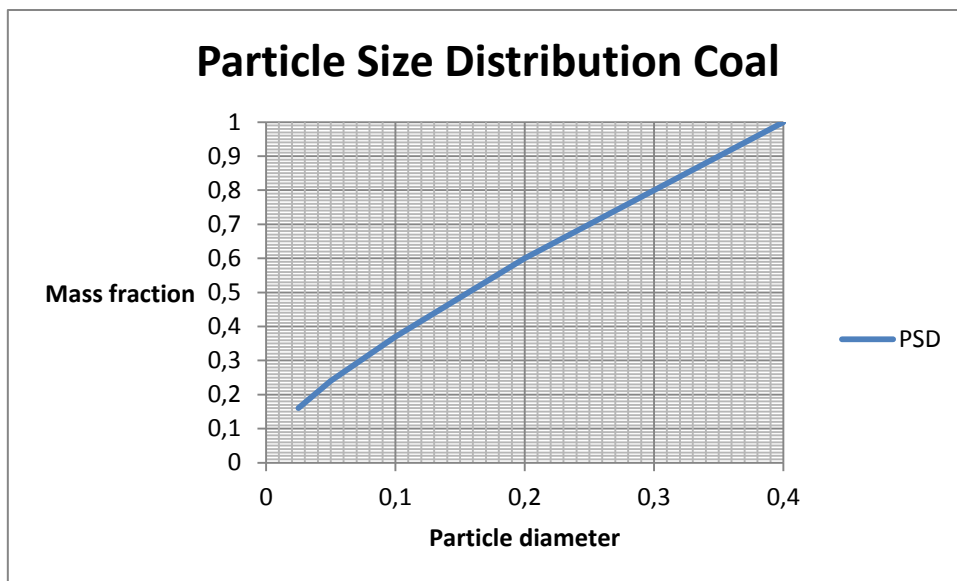
Graph 4 *Particle Size Distribution 2*



**Image 10** *PS > 0.200 mm*
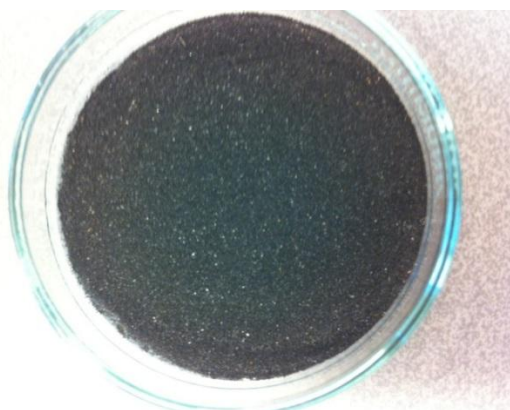


**Image 11** *0.100 mm < PS < 0.200 mm*
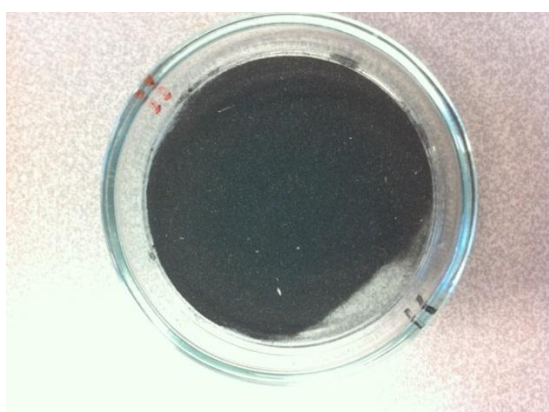


**Image 12** *0.050 mm < PS < 0.100 mm*



**Image 13** *0.025 mm < PS < 0.050 mm*

**Image 14** *PS < 0.025 mm*

The behavior of coal in water gave the insight that most of the coal is settled after 40 minutes. Only a few small particles were floating around. These were probably the particles from the smallest fraction.

### 4.1.3 β-estradiol

The results from the different tests (see experimental) are displayed and discussed in this section. But first the graphs of the UV-measurements to find an optimum concentration to work with are shown.

The first three concentrations that were tried are:

● 1 μg β-estradiol/l water
● 100 μg β-estradiol/l water
● 10 mg β-estradiol/l water

The graphs of the UV-spectra are graphs 4,5 and 6.


**Graph 5** *UV-spectrum concentration test 1 μg/l*
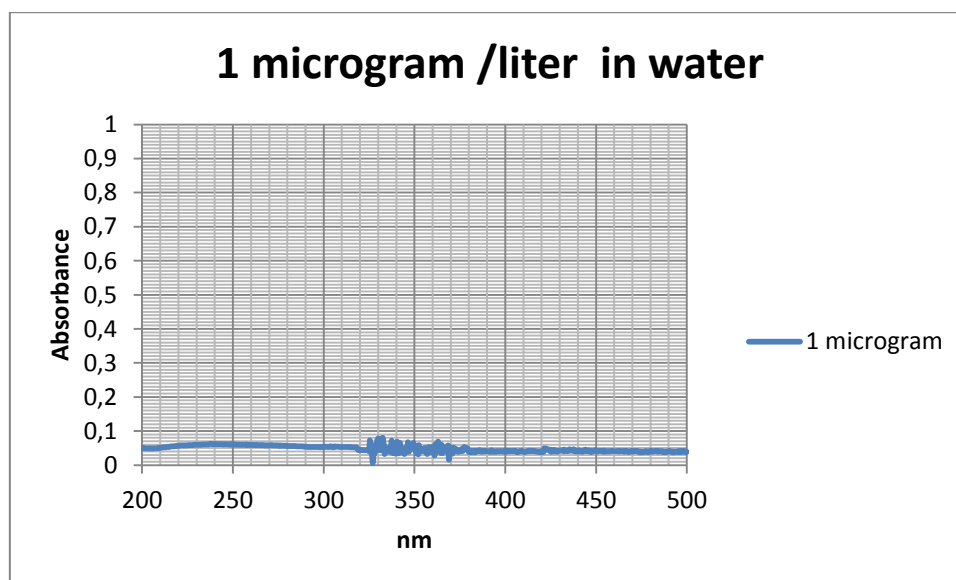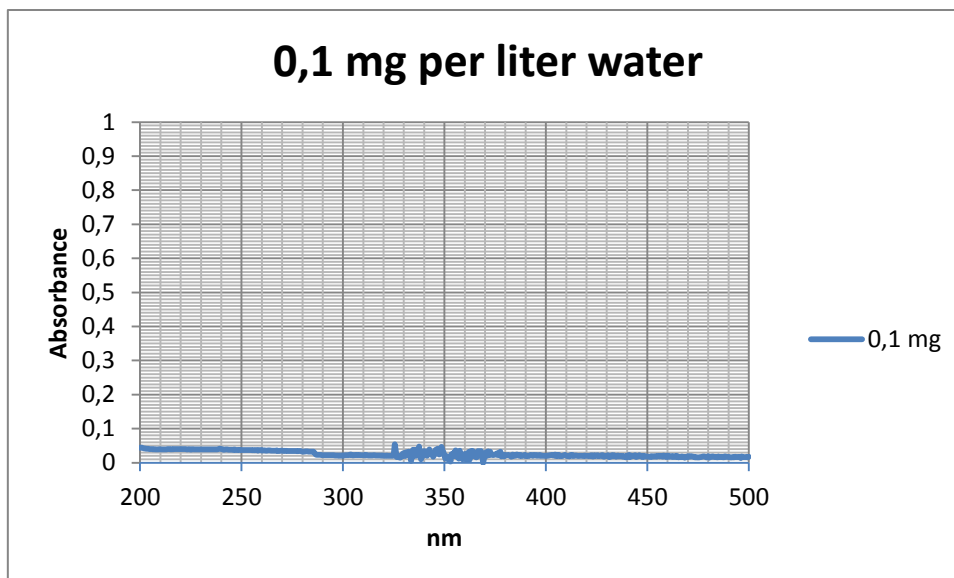
**Graph 6** *UV-spectrum concentration test 100 µg/l*
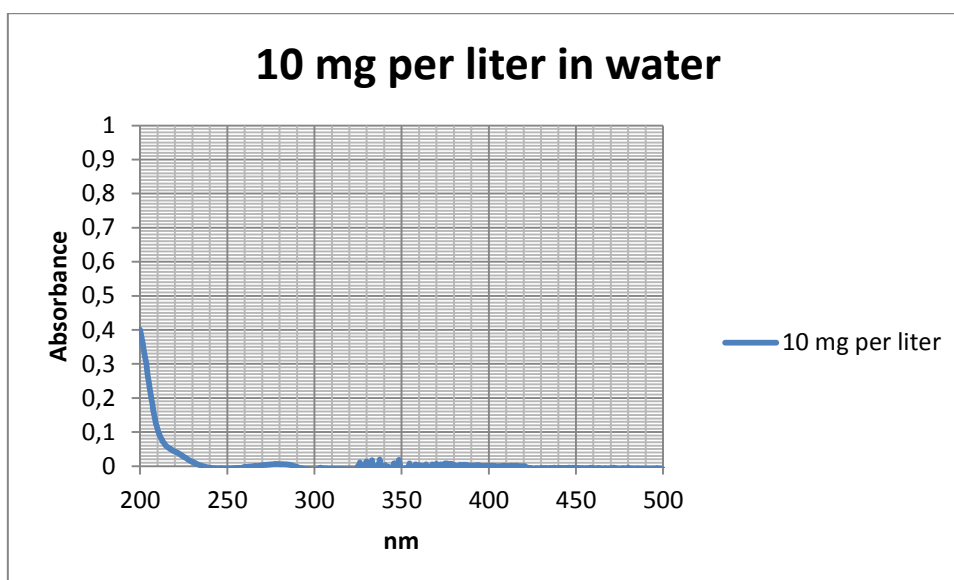


**Graph 7** *UV-spectrum concentration test 10 mg/l*

As can be seen on the graphs, these concentrations were too low to see a clear light absorption peak. This means the concentration had to be increased. As mentioned earlier, this was not accomplished in water. This resulted in trying the following two concentrations:

● 50 mg β-estradiol/l ethanol
● 100 mg β-estradiol/l ethanol

Graph 7 and 8 show the UV-spectra from these concentrations.
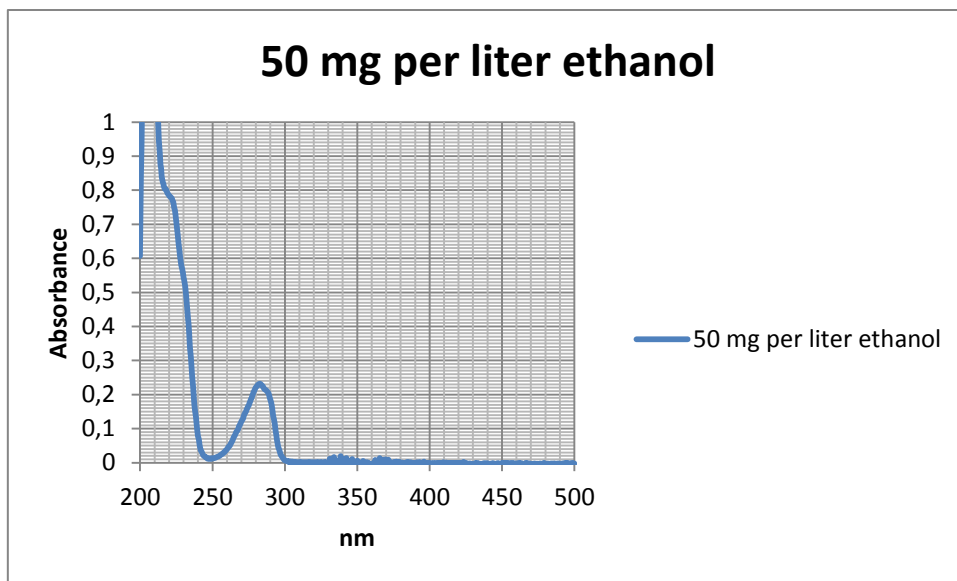
**Graph 8** *UV-spectrum concentration test 50 mg/l*
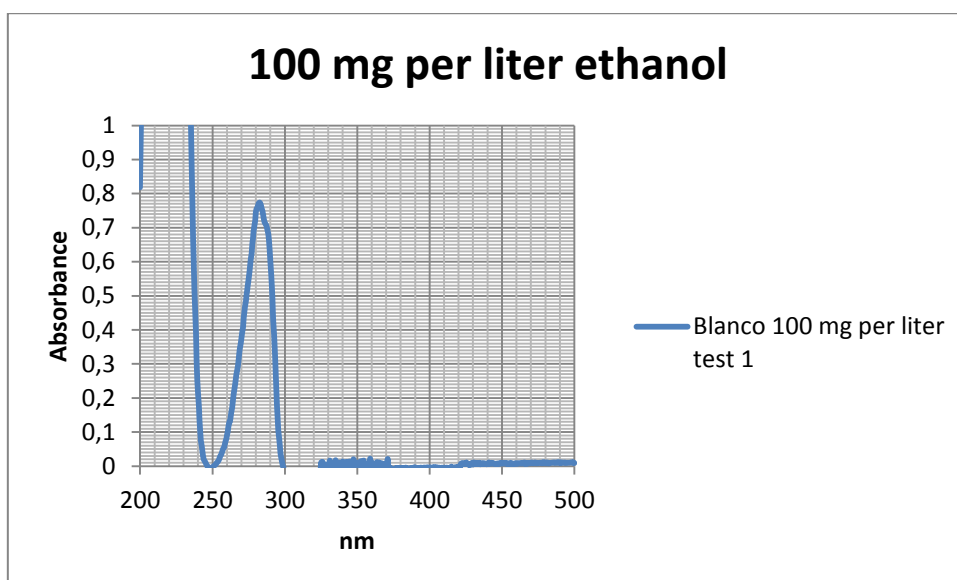


**Graph 9** *UV-spectrum concentration test 100 mg/l*

For the measurements of the tests the 100 mg β-estradiol / l ethanol concentration is used.

*Test 1*
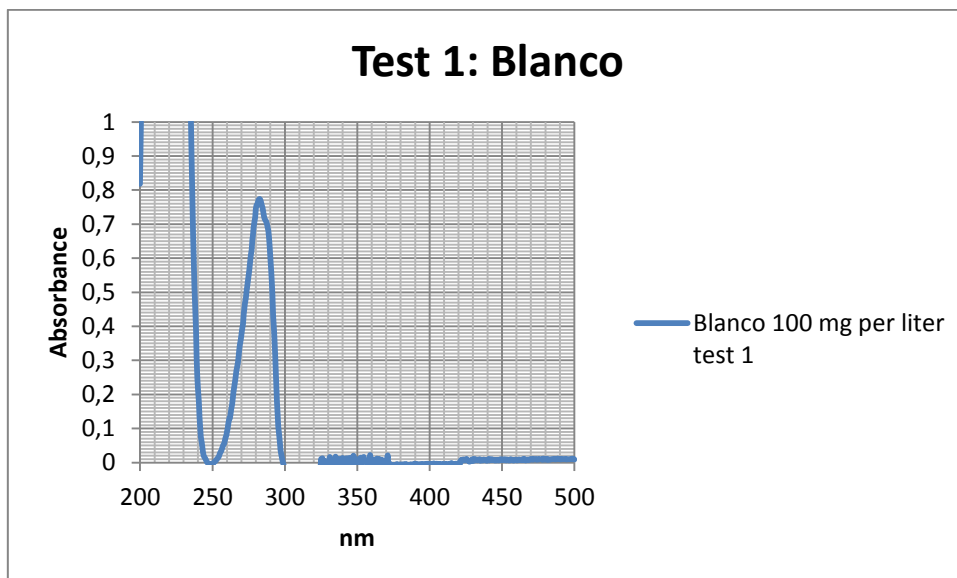


**Graph 10** *Test 1 blanco*
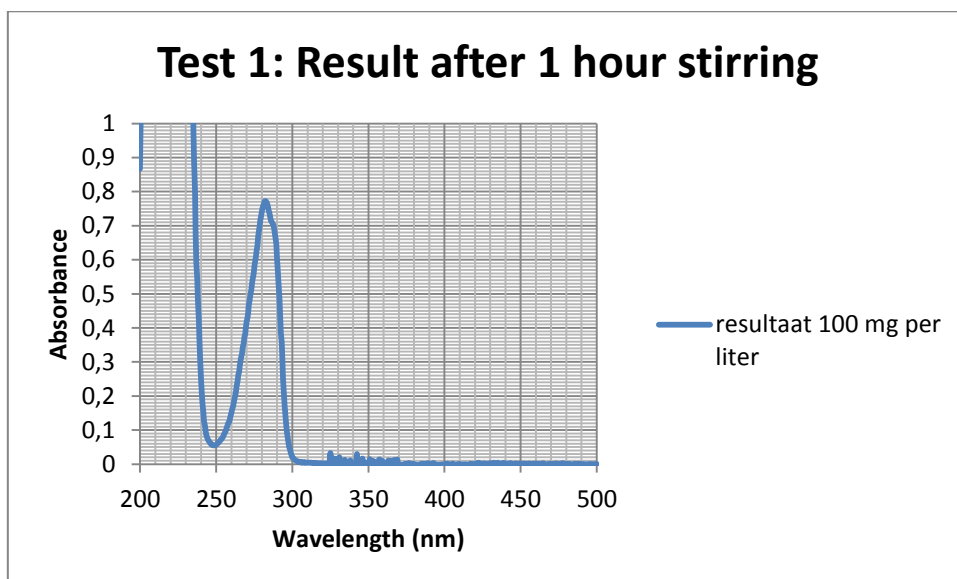


**Graph 11** *Test 1 result*

*Test 2*
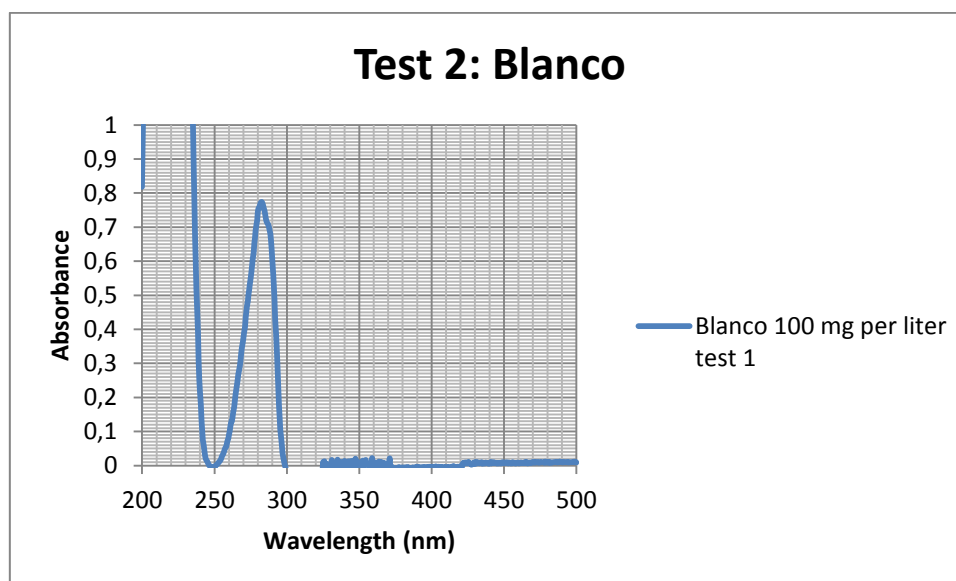


**Graph 12** *Test 2 blanco*
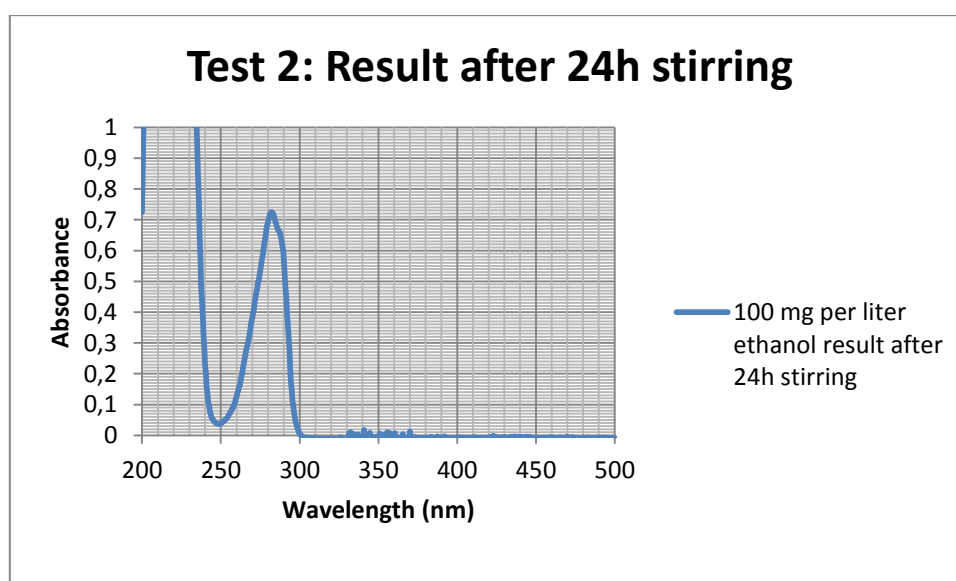


**Graph 13** *Test 2 result*

*Test 3*
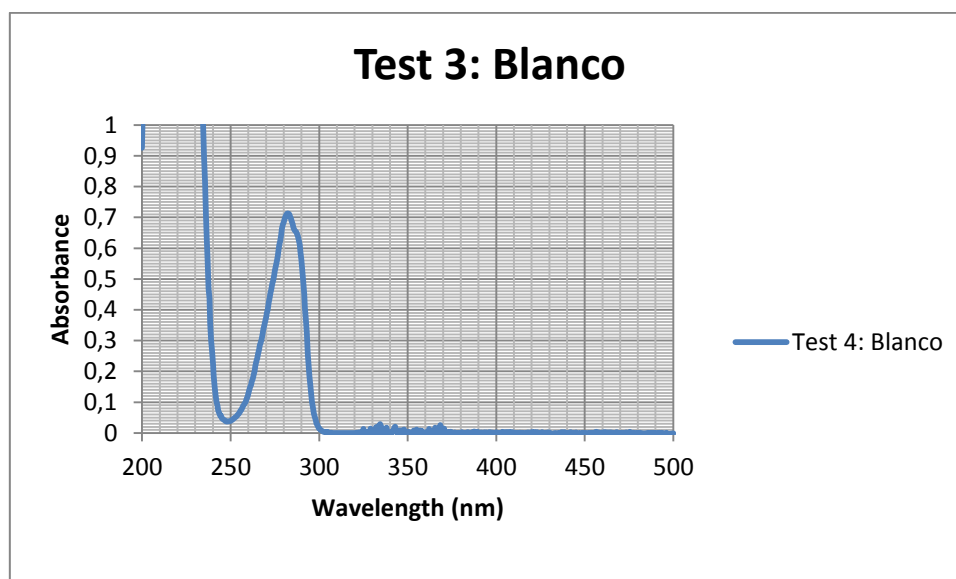


**Test 3: Blanco**

**Graph 14 *Test 3 blanco***



**Test 3: Result after 24h stirring**
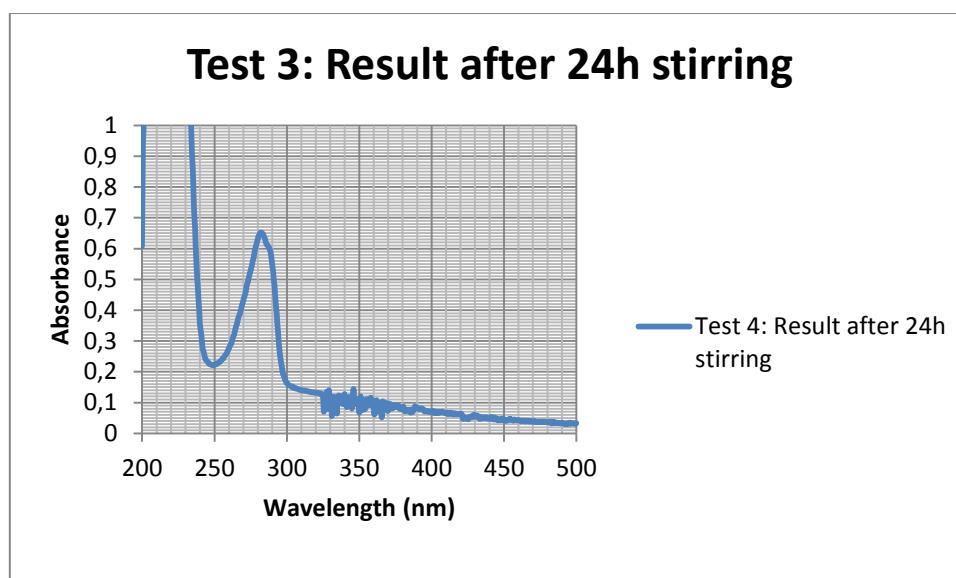
**Graph 15 *Test 3 result***

*Test 4*

## Test 4: Blanco



**Graph 16** *Test 4 blanco*

## Test 4: Result after 24h stirring
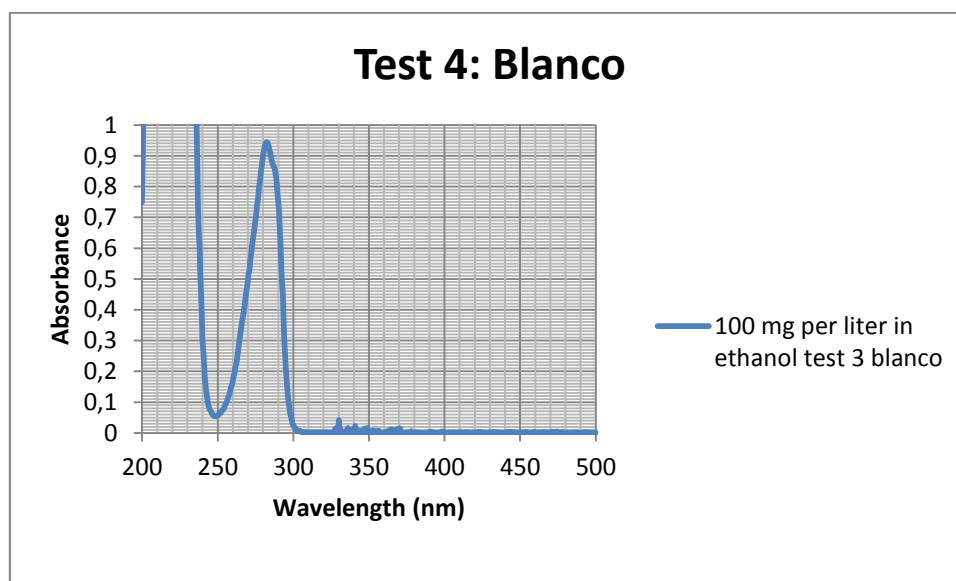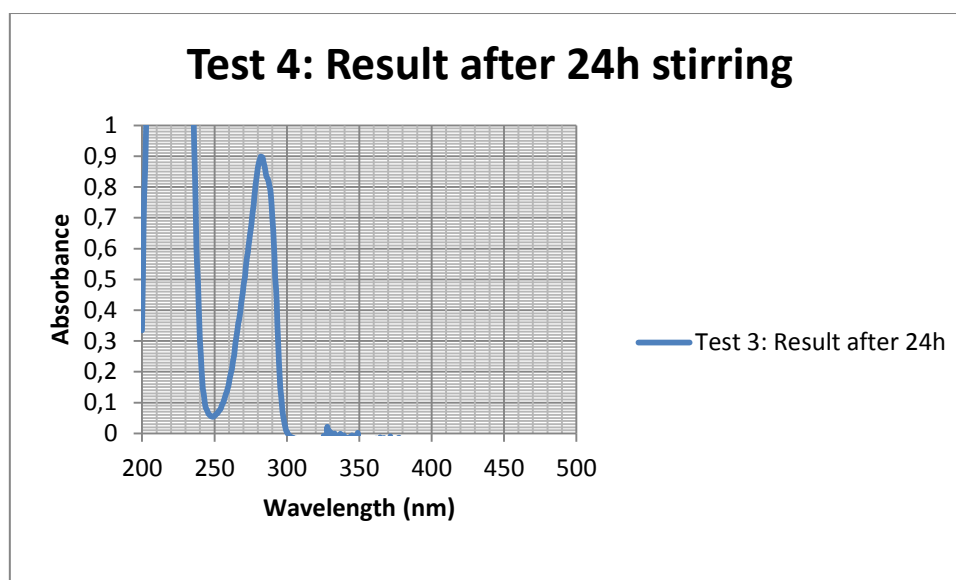


**Graph 17** *Test 4 result*

The important thing to take out these graphs is the light absorption value at 281 nm. The differences in these values between the blanco and the result can be calculated in to concentrations. These concentration differences resemble the adsorption of β-estradiol to the coal.
In table 7 the values of the peaks are shown.

| Test number | Peak value blanco | Peak value result |
|---|---|---|
| 1 | 0.7589 | 0.7562 |
| 2 | 0.7589 | 0.7150 |
| 3 | 0.7019 | 0.6451 |
| 4 | 0.9279 | 0.8860 |

**Table 7** *Peak values*

These peak values can be calculated to concentrations via the Beer-Lambert law. This law relates the absorption of light to the properties of the material through which the light is traveling.

To express this relation, the law states that a logarithmic dependence between transmission of light through a substance and the material, the distance the light travels through the material and the absorption coefficient of the material. The absorption coefficient is the product of the molar concentration and the extinction coefficient of the material.

For liquids this relation can be written as (Ingle & Crouch, 1988):

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\varepsilon l c}$$

Where: T = Transmission, this is the fraction of the incoming light that comes through the material (-)
  I = The intensity of light measured after passing through the material (-)
  $I_0$ = The intensity of the incoming light (-)
  α = Absorption coefficient (1/cm)
  l = Distance the light travels through the material (pathway) (cm)
  ε = Molar extinction coefficient (l /mol.cm)
  c = molar concentration (mol/l)

This relation uses transmission; however the equipment used at this practical used absorbance (A). The relation between absorbance and transmission is defined as (Ingle & Crouch, 1988):

$$A = -\log_{10}\left(\frac{I}{I_0}\right)$$

With this relation the Beer-Lambert law can be written as:

$$A = \varepsilon \times l \times c$$

Where:  l = Distance the light travels through the material (pathway) (cm)
  ε = Molar extinction coefficient ($\frac{l}{mol \times cm}$)
  c = molar concentration ($\frac{mol}{l}$)
  A = Absorbance

The used cuvettes all had a pathway of 1 cm. The molar extinction coefficient ε has a value of $2040\frac{l}{mol \times cm}$. This means a concentration 100 mg per liter (must be in moles per liter, thus the concentration is divided by the molar mass: 272,38 gram per mole) will result in absorbance of:

$$A = 2040 \times 1 \times \frac{100 \times 10^{-3}}{272,38} = 0.749$$

Comparing this to the concentrations made at the tests, test 1 and 2 (which are from the same reservoir of solution) are quite accurate and around the 100 mg per liter. Test 3 and 4 are a little of set.

For every test the concentrations will be calculated from the absorbance, see table 8 for the data.

| Test number | Concentration blanco (g/l) | Concentration result (g/l) | Difference (g/l) |
|---|---|---|---|
| 1 | 0.1013 | 0.1010 | 0.0003 |
| 2 | 0.1013 | 0.0955 | 0.0058 |
| 3 | 0.0937 | 0.0861 | 0.0076 |
| 4 | 0.1239 | 0.1183 | 0.0056 |

Table 8 *calculated concentrations*

Out of these concentrations the percentage adsorbed β-estradiol and the adsorption per gram coal can be calculated. See table 9 for the percentage adsorbed β-estradiol per test. These percentages are calculated by dividing the concentration differences from table 8 by the blanco concentration.

| Test number | adsorbed β-estradiol (%) |
|---|---|
| 1 | 0.296 |
| 2 | 5.726 |
| 3 | 8.111 |
| 4 | 4.520 |

**Table 9** *Percentage adsorbed β-estradiol*

To calculate the adsorption per gram coal, the concentration of coal is needed. Then the concentration difference (see table 8) is divided by the concentration of coal. In table 10 the concentrations coal and the adsorption per gram coal are shown.

| Test number | Volume solution | Amount of coal | Concentration coal (g/l) | Adsorption per gram coal (g/g) |
|---|---|---|---|---|
| 1 | 200 ml | 0.044 gram | 0.220 | 0.0014 |
| 2 | 200 ml | 0.063 gram | 0.315 | 0.0184 |
| 3 | 200 ml | 0.402 gram | 2.010 | 0.0038 |
| 4 | 200 ml | 0.406 gram | 2.030 | 0.0028 |

**Table 10** *Adsorption per gram coal*

Also the strength of the adsorption was tested. This resulted in the UV-spectrum in graph 17.
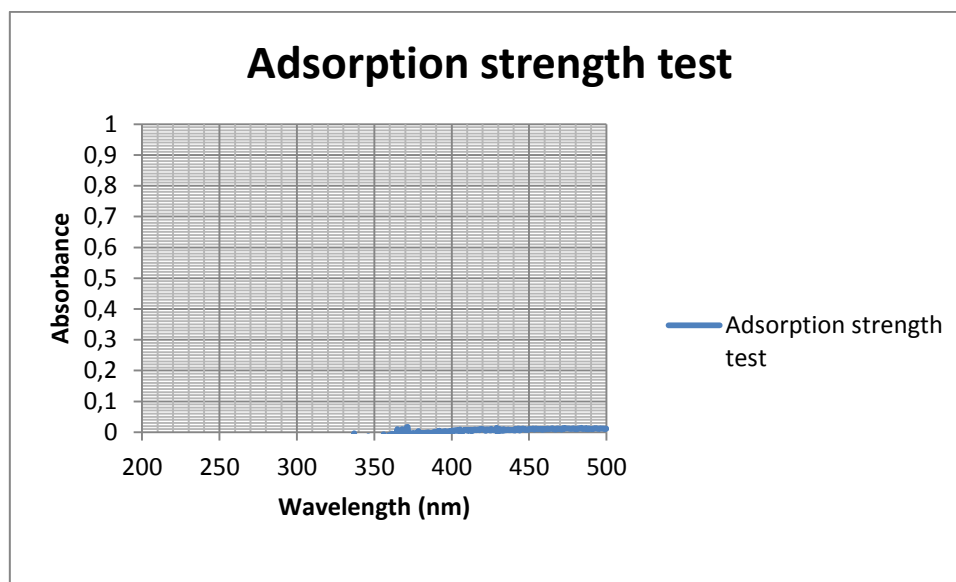


**Graph 18** *Adsorption strength test*

## 4.2 Discussion

The results will be discussed here.

### 4.2.1 Coal

The choice to use the smallest fraction after the PSD determination came from the comparison with active coal. Active coal are very defined small coal particles. The reasoning was that the smallest fraction will have also be relatively defined giving it a bigger internal surface compared to the bigger fractions, which would lead to a higher adsorption and therefor clearer results. This does mean that these results are less useable if wanted to apply on a WWTP, because there the whole coal mix will be used.
A settle time of roughly 40 minutes opens opportunities, because this means the coal can settle along with the sludge at the WWTP. This gives the adsorbed hormones no chance of getting in the environment, because the coal is combined with the sludge and the sludge will be burned.

### 4.2.2 β-estradiol

Overall the experiments went well. One thing that is clearly noticeable is the difference in adsorptions, although the concentrations were supposed to be 100 mg/l. This is to blame to the two different mass balances each giving slightly different masses as answer. The problem was that some of the time one of the mass balances was taken by a PHD student (he owned the mass balance). These differences in concentration do not matter for the calculations and results, because the experiments were about a delta measurement, meaning the difference was looked at.

Another observation that can be made is that at most of the UV-spectra a static can be seen from 300 nm and higher. These small adsorptions cannot be blamed on bad filtering because they are noticeable at the blanco measurements as well. Except for test 3, at which the result has an extremely higher adsorption above 300 nm compared to every other UV-measurement.
The cause could be that the UV-spectrometer is not calibrated perfectly.

If the results of test 3 and 4 are compared, is it seen that the test 3 has the higher adsorption, both percentage and per gram coal. This comes from the usage of the smallest coal particle fraction compared to a random sample of the coal. This means test 3 uses more defined coal and because the particles are smaller it will most likely have a greater internal surface per gram compared to the mix. This greater internal surface should result in a higher adsorption, which is supported by the results.

The stirring time is not looked at intensify, but comparing test 1 and 2 suggest that a longer contact time will result in a higher adsorption. This could be explained by the use of normal coal. This coal, even the smallest fraction, will be less defined than active coal. This could mean that the hormone and coal will have a harder time to 'find' each other to make the adsorption happen. The time needed to get a decent adsorption is not examined.

Comparing test 2 and 3 at the adsorptions per gram coal it is quite interesting that when significantly more coal is added the adsorption per gram coal will be a lot lower. The coal concentration was increased with a factor of 6.38, but the adsorption per gram coal dropped with a factor 4.84.
The cause of this could be 'overfill'. There is too much coal in the solution, making the coal sit close to each other making adsorption harder. Although this does not seem very likely, considering the fairly low concentration, the results do point in that direction. A longer stirring time might increase the adsorption per gram coal.

The concentrations used here are in no way directly comparable with the concentrations in the WWTP. The hormone concentrations used (100 mg/l) is a factor $10^6$ higher than the highest concentration measured in the environment (STOWA Derksen & Lahr, 2003). The concentration coal was initially in the same order as in which it would be used (Meelker, 2010), and was even increased

by a factor 10 for test 3 and 4. This means the ratio hormone:coal differs a factor of $10^6$ or $10^5$ compared to the WWTP conditions.
If these conditions were met, the coal concentration would have to be 20 kg/l or 2 kg/l. Both those concentrations are a bit inconvenient to work with.


## 4.3 Conclusions

The conclusion that can be taken from the coal experiments are the PSD, which can be seen in graph 3 and table 6, and that essentially all the coal settles in roughly 40 minutes.

The β-estradiol experiments result in the following conclusions:
1. Coal can be used for adsorption of β-estradiol. The other estrogens are very alike suggesting that adsorption will work for the other estrogens as well.

2. The smaller the coal particles are, the higher the adsorption will be. This suggests the smaller coal particles are more defined and have a higher internal surface. This does mean that if the coal mixture is used, the adsorption will be less effective.

3. The use of more coal results in a higher hormone adsorption. But the adsorption effectiveness of the coal will drop, resulting in a lower adsorption per gram coal.

4. The adsorption to the coal is good. Washing the coal did not lead to the hormone letting go of the coal and going back in solution.

# 5. Conclusions and recommendations

## 5.1 Conclusions experimental

The experimental proved that the coal delivered has the ability to adsorb hormones. The adsorption showed to be irreversible making the coal an interesting choice for WWTP's. However a lot is still uncertain. The optimal conditions for the adsorption has to be found, including the amount of coal and the stirring or contact time. Because the experimental was not done at WWTP conditions, it is not proved it will work at that scale and the much lower concentrations compared to this experimental. Overall the experimental do show promising results, but much work and study has to be done before implementing it in a WWTP.

## 5.2 Combining coal and micro-plastics

If the hormone adsorption with coal was implemented in the WWTP of Garmerwolde, the coal will be added along with the first sedimentation tank to assure a relative long contact time. The removal of the coal from the system is done with filters. These are implemented after the sedimentation tanks and will be an adjustment to the reflux stream. The choice for more than one filter is a choice made to keep the system continuous. After a certain time amount the stream has to be reversed at the filters to clear them. While clearing filters, the main stream will be lead over other filters.
The reversed stream with the coal that is cleared from the filters will be lead to the thickener belonging to the c-trap sedimentation tank. Leading it to this sedimentation tank will assure that the amount of water that is refluxed will come back in the system at almost a similar place as in the old situation. The coal with adsorbed hormones will remain in the thickener and are now essentially part of the sludge.  After dewatering with improved effect thanks to the coal and fermenting the sludge, the sludge will be dried more by Swiss Combi and eventually been sold and burned. In this way the hormones are removed from the water stream with no chance of returning to surface waters.

This new reflux route would clear the system of certain amount of micro-plastics as well, because the micro-plastics have an overlap in its PSD with the coal that is used. This means if the filters are able to filter out the coal, the filters should be able to filter out micro-plastics as well. Image 15 shows the overall block diagram (OBD) of the new system and image 16 shows the process flow diagram (PFD). In image 15 the amount of coal that is added is assumed as the 0.2 g/l from Martin Meelkers report (Meelker, 2010). Also there is assumed that the weight of one liter from the influent and effluent weights roughly one kilogram, giving a density of 1 kg/l.
Image 16 shows only two filters, this is only to show the principle of the reverse stream idea, in the piping and instrumental diagram (P&ID) (image 18) the basis will be three filters.

The P&ID of the system for adding the coal is shown in image 17. It is a fairly simple system using the measured DSC to adjust the valve that controls the coal addition. At I-1 a sample of the stream is taken and the DSC is determined. The DSC has to be in the order of 4%. If the DSC is too high or too low the valve is either closed or opened a bit more to get the correct addition of coal.
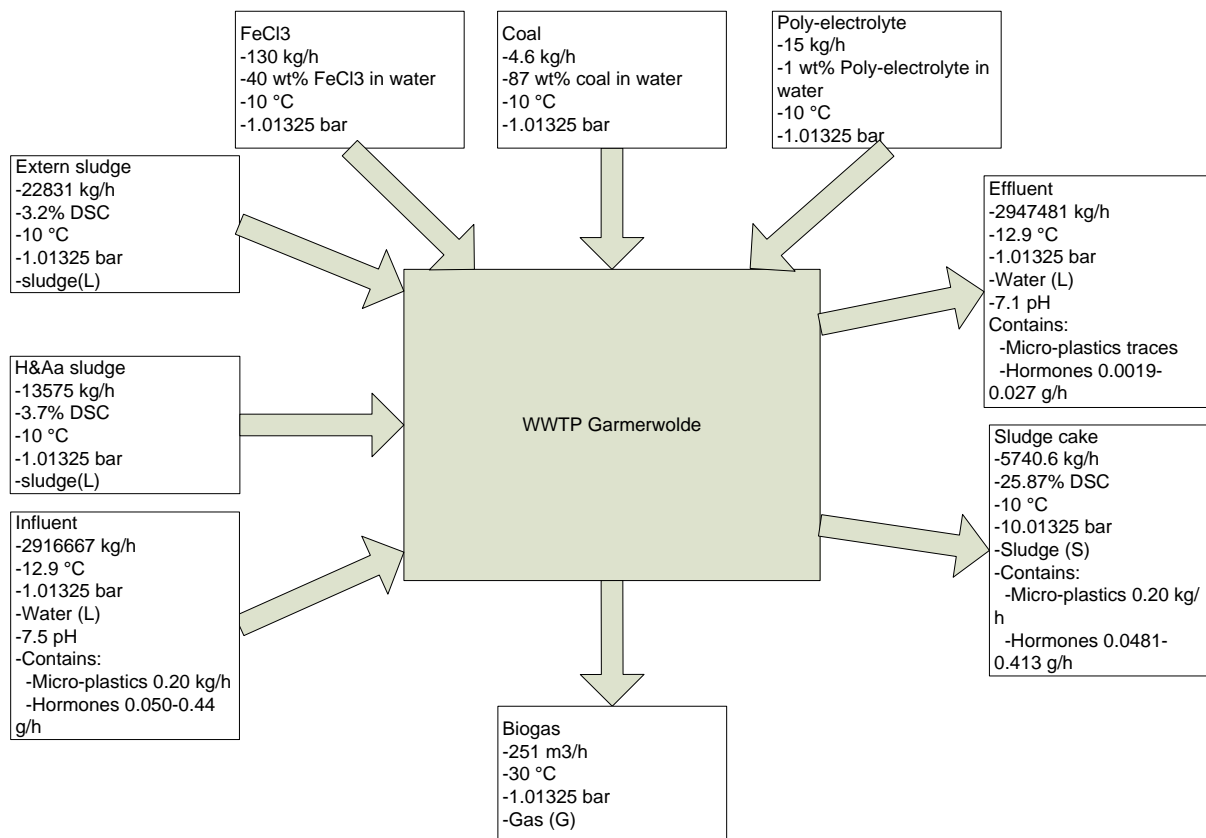
**Image 15** *Overall Block Diagram new situation*

The block diagram shows the WWTP Garmerwolde process with the following streams:

**Inputs:**

FeCl3
-130 kg/h
-40 wt% FeCl3 in water
-10 °C
-1.01325 bar

Coal
-4.6 kg/h
-87 wt% coal in water
-10 °C
-1.01325 bar

Poly-electrolyte
-15 kg/h
-1 wt% Poly-electrolyte in water
-10 °C
-1.01325 bar

Extern sludge
-22831 kg/h
-3.2% DSC
-10 °C
-1.01325 bar
-sludge(L)

H&Aa sludge
-13575 kg/h
-3.7% DSC
-10 °C
-1.01325 bar
-sludge(L)

Influent
-2916667 kg/h
-12.9 °C
-1.01325 bar
-Water (L)
-7.5 pH
-Contains:
  -Micro-plastics 0.20 kg/h
  -Hormones 0.050-0.44 g/h

**Center:** WWTP Garmerwolde

**Outputs:**

Effluent
-2947481 kg/h
-12.9 °C
-1.01325 bar
-Water (L)
-7.1 pH
Contains:
  -Micro-plastics traces
  -Hormones 0.0019-0.027 g/h

Sludge cake
-5740.6 kg/h
-25.87% DSC
-10 °C
-10.01325 bar
-Sludge (S)
-Contains:
  -Micro-plastics 0.20 kg/h
  -Hormones 0.0481-0.413 g/h

Biogas
-251 m3/h
-30 °C
-1.01325 bar
-Gas (G)



**Image 16** *Process Flow Diagram new situation*
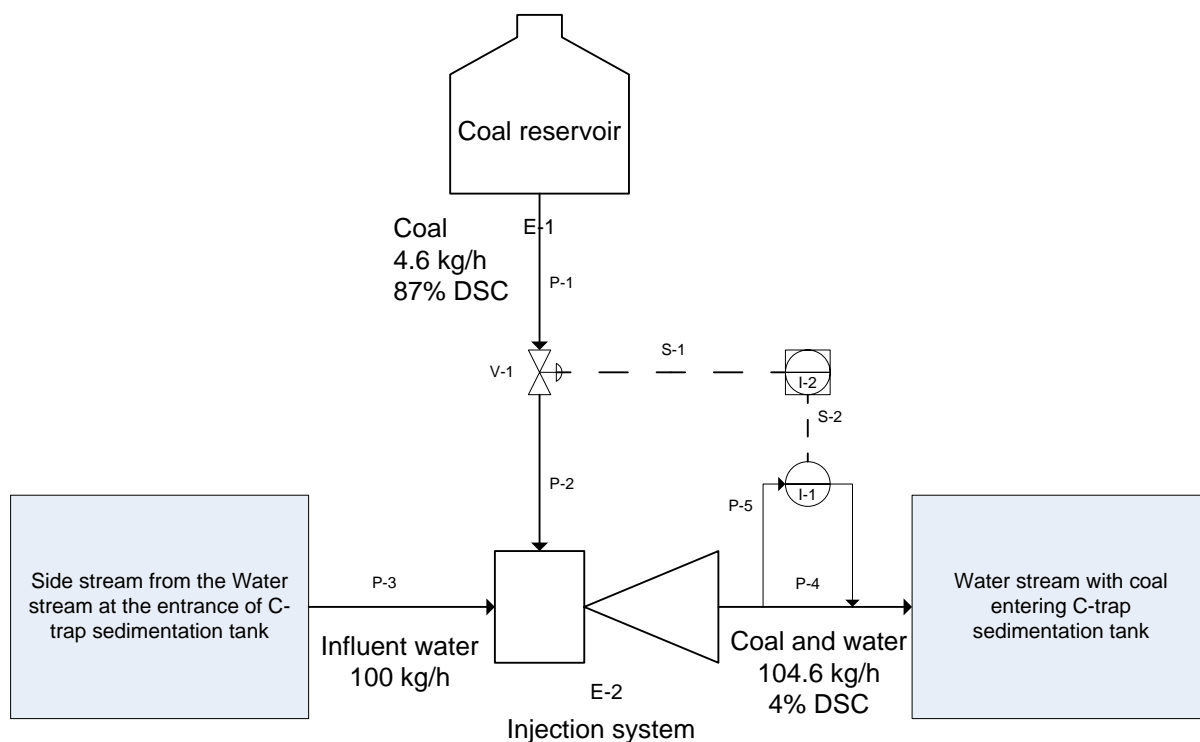
**Image 17** *Piping and instrumental diagram (P&ID) of the coal part*

| Code | Description |
|---|---|
| I-1 | Indicator where a sample is taken to determine the DSC |
| I-2 | Controller, if the sample shows more or less coal has to be added the valve has can be adjusted by this controller |
| S-1 | Connection between the valve and the controller |
| S-2 | Connection between the controller and the indicator |
| V-1 | Valve |
| E-1 | Coal reservoir |
| E-2 | Injection system for safety issues (see appendix C) |
| P-1 | Pipe between the reservoir and the valve |
| P-2 | Pipe between the valve and the injection system |
| P-3 | Pipe between just before C-trap sedimentation tank to the injection system |
| P-4 | Pipe between injection system and the C-trap sedimentation tank |
| P-5 | Bypass pipe between injection system and the C-trap sedimentation tank going through the indicator |

**Table 11** *Code description P&ID of the coal part*

Image 18 shows the P&ID of the filter part. Three filters form the basis of this part. At start or valves are closed except valves V-1 and V-7. This assures a stream through filter E-1 to the water reservoir E-4 and eventually out of the WWTP. When flow meter I-1 measures a lower flow because the filter is getting full, it will give a signal to the control room. The control room will close V-1 and open V-2 and V-4. Now the stream goes through filter E-2 instead of filter 1. The reflux stream coming from the water reservoir is not stopped anymore after valve-7, because it can flow through V-4. This stream will enter filter E-1 through the other side than the main stream from left to right would do, meaning it will clean the filter. This stream continues through P-12 to the thickener belonging to the C-trap sedimentation tank.

The same principle holds up when flow meter I-2 measures a lower flow, the system will then switch to filter E-3.

Assumed is that per hour every filter is used one time, meaning each filter will have to deal with 1.53 kg coal and 972222 kg water in 20 minutes (810 m$^3$/s). This means the filter surface has to be 81 m$^2$ at a flow speed of 10 m/s. This does not mean one big filter has to be used in every unit, several smaller units parallel of each other can achieve the same filter surface.

The filter has several requirements to comply:
-Pore size
-Cleanable
-Durable
-Easy replaceable

*Pore size*
The most important requirement for the filter. The filter has to have pore size smaller than the coal particles. This means the PSD of coal is very important to be determined precisely. According to the PSD determined at the experimental the pore sizes have to smaller than 0.025 mm, because the smallest coal fraction determined was smaller than this. An estimate pore size to capture most of the coal is set at 0.010 mm.

*Cleanable*
The filter must be cleanable by a water stream, thus the coal (and maybe a bit sludge that comes along) must not be able to attach to the filter. Also the filter must be cleaned easily by machine or man in a short amount of time (40 minutes max) if maybe some coal and sludge happen to stay attached.

*Durable*
The filters must wear well, because the system at the WWTP runs every day of every week. This means the system cannot be delayed all the time to replace the filters.

*Easy replaceable*
At some point even the most durable materials wear off, meaning the filters will have to be replaced at some point. The ideal situation would be that the system does not have to be shutdown to replace the filter. This means the filters need to be replaced fairly easy and in a short amount of time.
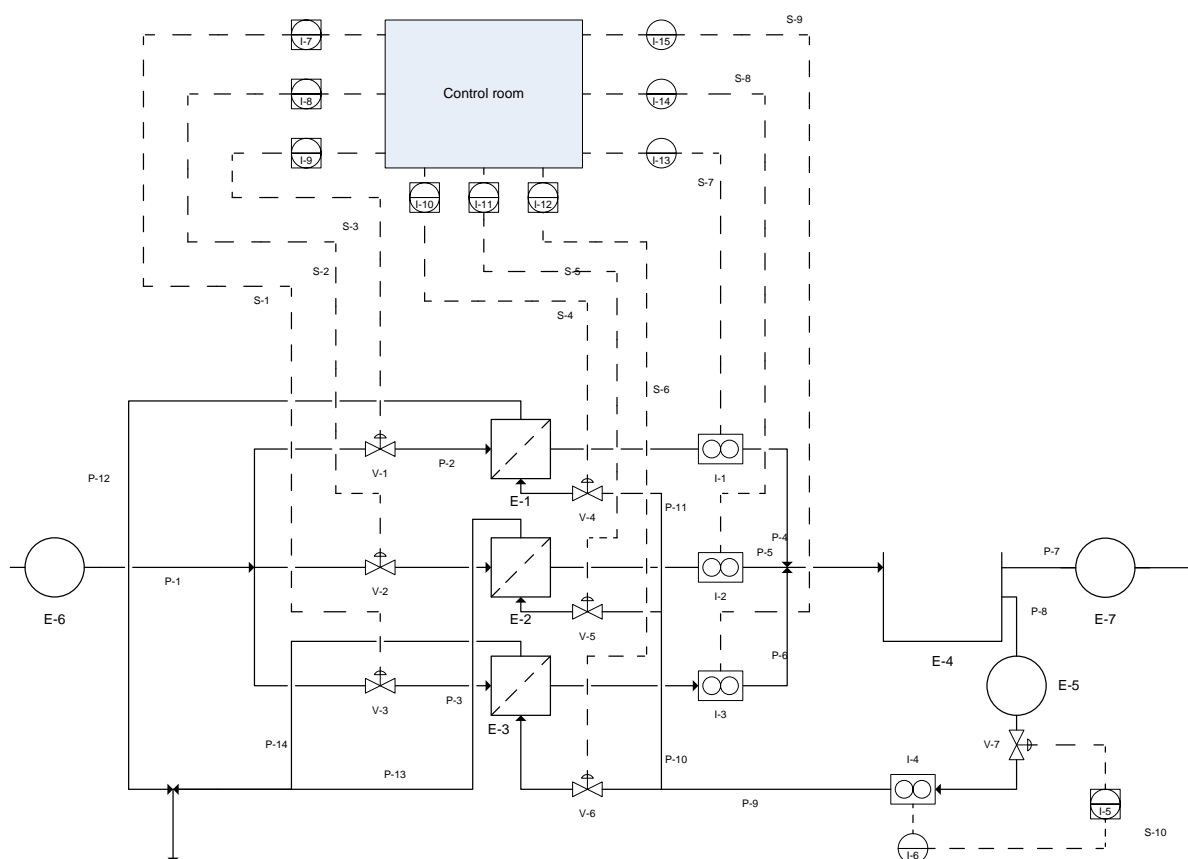
**Image 18** *Piping and instrumental diagram (P&ID) of the filter part*

| Code | description |
|---|---|
| P-1 | Pipe from the N-trap sedimentation tank through E-6 and V-2 to E-2 |
| P-2 | Pipe from P-1 through V-1 to E-1 |
| P-3 | Pipe from P-1 through V-3 to E-3 |
| P-4 | Pipe from E1 through I-1 to P-5 |
| P-5 | Pipe from E-2 through I-2 to E-4 |
| P-6 | Pipe from E-3 through I-3 to P-5 |
| P-7 | Pipe from E-4 through E-7 to the exit of the WWTP |
| P-8 | Pipe from E-4 through E-5 |
| P-9 | Pipe from E-5 through V-7 , I-4 and V-6 to E-3 |
| P-10 | Pipe from P-9 through V-5 to E-2 |
| P-11 | Pipe from P-10 trough V-4 to E-1 |
| P-12 | Pipe from E-1 to the thickener |
| P-13 | Pipe from E-2 joining P-12 to the thickener |
| P-14 | Pipe from E-3 joining P-12 and P-13 to the thickener |
| E-1 | Filter 1 |
| E-2 | Filter 2 |
| E-3 | Filter 3 |
| E-4 | Water reservoir |
| E-5 | Pump |
| E-6 | Pump |
| E-7 | Pump |
| V-1 | Valve to open or close the water flow from the C-trap sedimentation tank to filter 1 |
| V-2 | Valve to open or close the water flow from the C-trap sedimentation tank to filter 2 |

| | |
|---|---|
| V-3 | Valve to open or close the water flow from the C-trap sedimentation tank to filter 3 |
| V-4 | Valve to open or close the water flow from the water reservoir to filter 1 |
| V-5 | Valve to open or close the water flow from the water reservoir to filter 2 |
| V-6 | Valve to open or close the water flow from the water reservoir to filter 3 |
| V-7 | Valve to regulate the amount of water that is refluxed |
| I-1 | Flowmeter 1 |
| I-2 | Flowmeter 2 |
| I-3 | Flowmeter 3 |
| I-4 | Flowmeter 4 |
| I-5 | Controller for the amount of water that is refluxed, uses flowmeter 4 and indicator 1 |
| I-6 | Indicator 1 |
| I-7 | Controller for V-1 |
| I-8 | Controller for V-2 |
| I-9 | Controller for V-3 |
| I-10 | Controller for V-4 |
| I-11 | Controller for V-5 |
| I-12 | Controller for V-6 |
| I-13 | Indicator 2, gives signal about the flow in P-4 to the control room |
| I-14 | Indicator 3, gives signal about the flow in P-5 to the control room |
| I-15 | Indicator 4, gives signal about the flow in P-6 to the control room |
| S-1 | Wire for signal between V-3 and I-7 |
| S-2 | Wire for signal between V-2 and I-8 |
| S-3 | Wire for signal between V-1 and I-9 |
| S-4 | Wire for signal between V-4 and I-10 |
| S-5 | Wire for signal between V-5 and I-11 |
| S-6 | Wire for signal between V-6 and I-12 |
| S-7 | Wire for signal between I-13 and I-1 |
| S-8 | Wire for signal between I-14 and I-2 |
| S-9 | Wire for signal between I-15 and I-3 |

**Table 12 *Code description P&ID filter part***

## 5.3 Overall conclusions and recommendations

The literature studies showed that the hormones and micro-plastics are already a small threat to some organisms, but it is expected that this threat will grow in the future giving possibly problems for humans.

The usage of coal to lower the concentrations of hormones is proved and because the experimental work showed the adsorption is irreversible it might be interesting for WWTP's as a help to prevent a bigger threat in the future. A possible combining with a better removal of micro-plastics is a possibility because the PSD's of the coal and the micro-plastics are partially in the same range. However the question if coal is the solution is not answered. This report was about showing adsorption takes place, it does not show if it is a viable choice. The coal adsorbed about 5-8% of the hormone, but the regular system removes already in the order of 90% (although it depends a bit on what hormone is looked at). To determine if the coal adsorption will be a viable choice in the future a lot will have to be looked at in future studies.

Some recommendations for further study are given below.

The results show that coal adsorbs β-estradiol, but it is unclear where the optima are. A study focusing at finding the ideal adsorption scenario would be a great step forward. The parameters stirring time and the amount of coal have to be varied to find this optimum. Also a look can be taken at the adsorption of other hormones. The ideal situation would be that coal is an effective adsorbent for most of the hormones available in waste water.

A second possible study for the future is a look on the adsorption per gram coal related to the amount of coal. This study will focus on the effectiveness and why it is influenced greatly by the amount of coal used.

Another possible research topic is looking at the coal adsorption at lower concentration by using analyze techniques that go in more detail. This brings the research closer the WWTP conditions, which is the final goal. This means with better analyze techniques the conditions at a WWTP can be simulated better, to give the final answer if coal will be a significant aid in reducing the hormone concentrations.

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# Lists of the graphs, image, figures and table

## Graphs

## Tables

# Images

# Appendices

# Appendix A. LOES Results

Hormones
*Natural estrogen hormones*
The natural estrogen hormones alfatradiol (17alfa-oestradiol), estradiol (17beta-oestradiol) and estrone (oestron) where most encountered during the LOES. See figure 1, table A.

*Synthetic estrogen hormones*
The most encountered synthetic estrogen hormone is  ethinyl estradiol (17 alfa-ethinyl-estradiol). See figure 1, table A for the concentrations.

*Xeno-estrogen hormones*
There are three type of xeno-estrogens that are encountered: Bisphenol-A, Alkylfenolethoxylates and ftalates. The concentrations of the hormones that belong to each type are shown in figure 1, table B,C and D respectively.

A. *Hormonen*

| Emissiebron | $17_\alpha$-oestradiol | $17_\beta$-oestradiol | oestron | $17_\alpha$-ethinyl-oestradiol |
|---|---|---|---|---|
| Regenwater (ng/l) | < 0,3 | < 1,5 | < 0,6 | < 0,3 |
| ruw stedelijk afvalwater (ng/l) | < 0,7 – 15 | 17 – 150 | 20 - 130 | < 0,3 - 5,9 |
| effluenten rwzi's (ng/l) | < 0,4 | < 0,8 | < 0,3 - 11 | < 0,3 - 2,6 |
| industrieel afvalwater (ng/l) | < 0,3 - 7,1 | < 0,8 – 54 | 13 - 120 | < 0,3 - 3,9 |
| mest (ng/g droge stof) | 120 – 190 | 46 – 50 | 28 -72 | < 1 |
| **Watermilieu** | | | | |
| Oppervlaktewater (ng/l) | < 0,3 - 0,4 | < 0,8 – 1,0 | < 0,3 – 7,2 | < 0,3 – 0,4 |

B. *Bisfenol-A*

| Emissiebron | bisfenol-A |
|---|---|
| regenwater (ng/l) | < 15 – 57 |
| ruw stedelijk afvalwater (ng/l) | 250 – 5620 |
| effluenten rwzi's (ng/l) | < 43 - 4090 |
| industrieel afvalwater (ng/l) | < 13 – 800 |
| mest (ng/g droge stof) | 23 – 24 |
| **Watermilieu** | |
| Oppervlaktewater (ng/l) | < 8,8 – 1000 |
| zwevende stof (ng/g droge stof) | 5,6 – 56 |
| sediment (ng/g droge stof) | < 1,1 – 43 |
| **Waterdieren** | |
| vis, spierweefsel (ng/g natgewicht) | 0,18 – 2,6 |
| mossel, totaal ( ng/g natgewicht) | 0,22 – 1,8 |

C. *Alkylfenolen & alkylfenolethoxylaten*

| Emissiebron | octylfenolen | octylfenol-ethoxylaten | nonylfenolen | nonylfenol-ethoxylaten |
|---|---|---|---|---|
| regenwater (µg/l) | < 0,08 – 0,28 | < 0,48 | < 0,41 | < 0,36 – 0,99 |
| ruw stedelijk afvalwater (µg/l) | < 0,3 – 13 | < 1,1 - 24 | < 0,2 - 19 | < 0,8 - 125 |
| effluenten rwzi's (µg/l) | < 0,5 - 1,3 | < 0,7 | < 0,6 - 1,5 | < 1,9 – 2,2 |
| industrieel afvalwater (µg/l) | < 0,2 – 0,5 | < 0,4 - 12 | < 0,4 - 39 | 50 - 22500 |
| **Watermilieu** | | | | |
| Oppervlaktewater (µg/l) | < 0,05 – 6,3* | < 0,16 – 17* | < 0,11 – 4,1* | < 0,18 – 87* |
| zwevende stof (µg/g droge stof) | < 0,001 – 0,40 | < 0,002 – 1,7 | < 0,003 – 4,1 | < 0,005 - 22 |
| sediment (µg/g droge stof) | < 0,002 - 0,026 | < 0,034 | < 0,01 - 3,8 | < 0,01 - 2,8 |
| **Waterdieren** | | | | |
| vis, spierweefsel (µg/g natgewicht) | < 0,01 – 0,08 | < 0,01 – 0,01 | < 0,01 – 0,16 | < 0,01 – 0,52 |
| mossel, totaal (µg/g natgewicht) | < 0,01 – 0,05 | < 0,06 | < 0,03 – 0,45 | < 0,05 – 0,23 |

\* de hoogste waarden zijn hoger dan normaliter

D. *Meest voorkomende ftalaten*

| Emissiebron | DEP diethylftalaat | DMPP dimethylpropyl-ftalaat | DBP di-*n*-butylftalaat | BBP butylbenzyl-ftalaat | DEHP di(2-ethylhexyl)-ftalaat |
|---|---|---|---|---|---|
| regenwater (µg/l) | < 0,24 - 0,43 | 0,38 - 0,53 | 0,28 – 0,88 | 0,14 - 0,26 | 0,69 – 1,7 |
| ruw stedelijk afvalwater (µg/l) | < 4,1 - 44 | 1,9 - 15 | < 0,4 - 51 | 0,6 - 4,9 | < 13 - 101 |
| effluenten rwzi's (µg/l) | < 0,3 – 0,9 | < 1,0 - 20 | < 0,4 - 0,8 | < 0,1 - 0,3 | < 0,5 – 2,4 |
| industrieel afvalwater (µg/l) | < 0,2 – 5,2 | < 0,7 - 405 | < 0,7 - 21 | < 0,2 - 1,3 | 1,0 - 1498 |
| **Watermilieu** | | | | | |
| Oppervlaktewater (µg/l) | < 0,07 – 2,3 | < 0.05 – 2,4 | < 0,066 – 3,1 | < 0,010 – 1,8 | < 0,90 – 5,0 |
| zwevende stof (ng/g droge stof) | < 46 – 2692 | 87 – 920 | < 51 – 4100 | < 4,5 – 3000 | < 92 – 19000 |
| sediment (ng/g droge stof) | < 65 – 1200 | < 400 – 1700 | 34 – 1000 | < 4,5 – 60 | < 123 – 7600 |
| **Waterdieren** | | | | | |
| vis, spierweefsel (ng/g natgewicht) | < 6,7 – 320 | niet gemeten | < 0,71 - 150 | < 0,22 – 9,1 | < 2,2 – 1500 |
| mossel, totaal (ng/g natgewicht) | 11 -92 | iet gemeten | 30 - 1900 | <0,07 - 56 | < 2,2 – 400 |

**Table 13 *Hormone concentrations***

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Medicine

The next 3 tables contain the maximum concentration in which several medicine have been measured.

| matrix type geneesmiddel | maximum > 10000 ng/l | Maximum > 1000 ng/l | maximum > 100 ng/l | maximum > 10 ng/l | maximum > detectielimiet | niet aangetoond < detectielimiet |
|---|---|---|---|---|---|---|
| **rioolwater** | | | | | | |
| fibraten/β-blokkers | | Bezafibraat<br>Clofibrinezuur<br>Fenofibrinezuur<br>Gemfibrozil | Pentoxifylline | | | |
| anti-epileptica | | Carbamazepine | Primidon | | | |
| analgetica | Ibuprofen<br>Paracetamol<br>Salicylzuur | Acetylsalicylzuur<br>Diclofenac<br>Dihydrocodeïne<br>Gentisinezuur | Indometacine<br>Ketoprofen<br>Naproxen<br>Propyfenazon | | | |
| cytostatica | | Methotrexaat | Cyclofosfamide | Ifosfamide | | |
| overige middelen | | Hydrocodon | Crotamiton<br>Fenoprofen | | | |
| **effluent rwzi** | | | | | | |
| fibraten/β-blokkers | | Bezafibraat<br>Clofibrinezuur<br>Fenofibrinezuur<br>Gemfibrozil<br>Metoprolol | | | | |
| anti-epileptica | | Carbamazepine | | | | |
| analgetica | | Acetylsalicylzuur<br>Diclofenac<br>Dihydrocodeïne<br>Ibuprofen<br>Ibuprofen-OH | Fenazon<br>Gentisinezuur<br>Ibuprofen-COOH<br>Indometacine<br>Ketoprofen<br>Naproxen<br>Salicylzuur | | | |
| cytostatica | | | | Bleomycine<br>Cyclofosfamide<br>Ifosfamide | | |
| antibiotica | | Erythromycine<br>Roxithromycine<br>Sulfamethoxazol | Chloramphenol<br>Clarithomycine<br>Erythromycine<br>Terbutalin<br>Trimethoprim | | | |
| antidepressiva | | | | | | Diazepam |
| röntgencontrast-middelen | Iopromide | Diatrizoaat<br>Iopamidol | | Iothalamisch zuur | Ioxithalamisch zuur | |
| overige middelen | | Acetominofen<br>Hydrocodon | Clenbuterol<br>Sulbatamol | Fenoterol | | Fenoprofen<br>Tolfenamine |

**Table 14 *Medicine concentrations (1)***

| matrix type geneesmiddel | maximum > 10000 ng/l | maximum > 1000 ng/l | maximum > 100 ng/l | maximum > 10 ng/l | maximum > detectielimiet | niet aangetoond < detectielimiet |
|---|---|---|---|---|---|---|
| **Oppervlaktewater** | | | | | | |
| fibraten/β-blokkers | | Bezafibraat Bisoprolol *Clofibrinezuur* Metoprolol | Carazolol Fenofibraat *Fenofibrinezuur* Gemfibrozil Pentoxyfilline Propanolol | Betaxolol Timolol | Clofibraat Nadolol | Etofibraat |
| anti-epileptica | | Carbamazepine | | | | |
| analgetica | | Detroproxyfeen Diclofenac *Gentisine zuur* *Ibuprofen-OH* *Propyfenazon* *Salicylzuur* | Acetylsalicylzuur Fenazon Ibuprofen Indometacine Naproxen | *Ibuprofen-COOH* | | Paracetamol |
| cytostatica | | | | Bleomycine | | Cyclofosamide Ifosfamide Methotrexaat |
| antibiotica | | Erythromycine | Clarithrymycine Roxithromycine Sulfamethoxazol Trimethoprim | Chloramfenicol | | Cloxacilline Dicloxacilline Doxycycline Methicilline Nafcilline Oxacilline Oxytetracycline Penicilline G Penicilline V Tetracycline |
| antidepressiva | | | | | Medazepam | Diazepam |
| röntgencontrast-middelen | Iopamidol | | Diatrizoaat Iopromide | Iomeprol Iothalamisch zuur Ioxithalamisch zuur | | |
| overige middelen | | | | Clenbuterol Fenoterol Salbutamol | Terbutalin | Tolfenamisch zuur |
| **Grondwater** | | | | | | |
| fibraten/β-blokkers | | Clofibrinezuur | | Fenofibraat | | Clofibraat |
| analgetica | | Fenazon | Ibuprofen Propyfenazon Diclofenac | | | |
| röntgencontrast middelen | | diverse middelen | | | | |

**Table 15** *Medicine concentrations (2)*

| matrix<br>type geneesmiddel | maximum<br>> 10000 ng/l | maximum<br>> 1000 ng/l | maximum<br>> 100 ng/l | maximum<br>> 10 ng/l | maximum<br>> detectielimiet | niet aangetoond<br>< detectielimiet |
|---|---|---|---|---|---|---|
| **Drinkwater** | | | | | | |
| fibraten/β-blokkers | | | Clofibrinezuur | | | Betaxolol |
| | | | Fenofibraat | | | Bezafibraat |
| | | | | | | Bisoprolol |
| | | | | | | Carazolol |
| | | | | | | Clofibraat |
| | | | | | | Metoprolol |
| | | | | | | Nadolol |
| | | | | | | Propranolol |
| | | | | | | Timolol |
| anti-eleptica | | | | | | Carbamezepine |
| analgetica | | | | | | Diclofenac |
| | | | | | | Ibuprofen |
| | | | | | | Paracetamol |
| | | | | | | Salicylzuur |
| cytostatica | | | | Bleomycine | | Ifosfamide |
| | | | | | | Methotrexaat |
| | | | | | | Erythromycine |
| | | | | | | Sulfamethoxazol |
| antidepressiva | | | | Diazepam | | |
| röntgencontrast-<br>middelen | | | | Diatrizoaat | | Ioxithalamisch zuur |
| | | | | Iopamidol | | |
| | | | | Iopromide | | |
| | | | | Iothalamisch<br>zuur | | |
| overige middelen | | | | | | Clenbuterol |
| | | | | | | Terbutalin |
| | | | | | | Salbutamol |

**Table 16 *Medicine concentrations (1)***

## Appendix B. Experimental

For every test two UV-spectra.
● Ethanol with β-estradiol in a certain concentration with baseline ethanol
● Same ethanol with β-estradiol as the first UV-spectra, but after adding coal and stirring it for a certain time and filtering it. The baseline is made with a filtered ethanol + coal mixture (same concentration coal as with the solution with hormone) that was stirred for the same time as the hormone solution

Test 1

| Type | Volume solution | Amount of coal | Type of coal | Stirring time |
|------|----------------|----------------|--------------|---------------|
| Baseline | 100 ml | 0.021 gram | PS < 0.025 mm | 1 hour |
| Measurement | 200 ml | 0.044 gram | PS < 0.025 mm | 1 hour |

**Table 17** *test 1 appendix*

Test 2

| Type | Volume solution | Amount of coal | Type of coal | Stirring time |
|------|----------------|----------------|--------------|---------------|
| Baseline | 100 ml | 0.032 gram | PS < 0.025 mm | 1 hour |
| Measurement | 200 ml | 0.063 gram | PS <0.025 mm | 24 hours |

**Table 18** *test 2 appendix*

Test 3

| Type | Volume solution | Amount of coal | Type of coal | Stirring time |
|------|----------------|----------------|--------------|---------------|
| Baseline | 100 ml | 0.202 gram | PS < 0.025 mm | 24 hour |
| Measurement | 200 ml | 0.402 gram | PS < 0.025 mm | 24 hours |

**Table 19** *test 3 appendix*

Test 4

| Type | Volume solution | Amount of coal | Type of coal | Stirring time |
|------|----------------|----------------|--------------|---------------|
| Baseline | 100 ml | 0.212 gram | Mixture | 24 hours |
| Measurement | 200 ml | 0.406 gram | Mixture | 24 hours |

**Table 20** *test 4 appendix*

For the adsorption strength 0,205 gram coal from test 3 was taken. This was washed with 100 ml ethanol for several times (re-using the same ethanol).

For the behavior of coal a solution of 0.205 gram coal in 200 ml ethanol was used. This was less coal than test 3 so that the solution would be less dark, making it more visible how the coal behaves.

## Appendix C. Chemical Safety

*Ethanol*
Ethanol is a liquid that can be harmful when inhaled and/or swallowed. Possible effects are nausea, headache, dizziness, unconsciousness and coma, nervous system depression and respiratory tract irritation. Contact with skin and eyes must be avoided, because ethanol can cause severe skin and eye irritation. On the skin it may cause cyanosis of the extremities. The eye may become painful sensitive to light and the corneal can be damaged (Anon., sd).


*Bèta-Estradiol*
Bèta-estradiol is a solid that is harmful when inhaled and/or swallowed. Contact with the skin must be avoided.  If inhaled bring the victim to fresh air and keep the victim at rest in a comfortable breathing position. When the victim gets unwell contact a doctor or poison centre. When swallowed rinse the mouth and always contact a doctor or poison centre.
If Bèta-estradiol has been contacted with the skin wash with plenty of soap and water.
In case of eye-contact, hold eyelids apart and flush eyes with plenty of water for at least 20 minutes. Have the eyes examined and tested by medical personnel (Company, sd).


*Coal*
The used coal is a solid powder of different particle sizes. Ingestion, contact with eyes and skin may cause irritation. On the long term inhalation can cause chronic bronchitis and emphysema. Chronic bronchitis and emphysema cause lung inflammation, coughing attacks and difficulties with breathing. The environment worked in has to be ventilated and safety glasses, gloves and lab coat are recommended. See appendix D for more detail.


*Safety study*
The biggest danger with dry coal is dust explosion. A dust explosion is an explosive detonation of dust with oxygen in the air. The essentials needed are a dust, air, detonation source and that the dust and air are available in a certain ratio, see image 16 for an graph with the limits. All not-oxidized dusts can be a source for a dust explosion.
Dust explosion are similar to gas explosions, but are more powerful and have a chance on secondary explosions. The first explosion (primary explosion) brings new dust in motion which can result in a new explosive dust air mixture. This can result in a chain reaction in which every explosion will cause a new explosion. (Company, 2005)

**Explosion pressure/explosion limits**
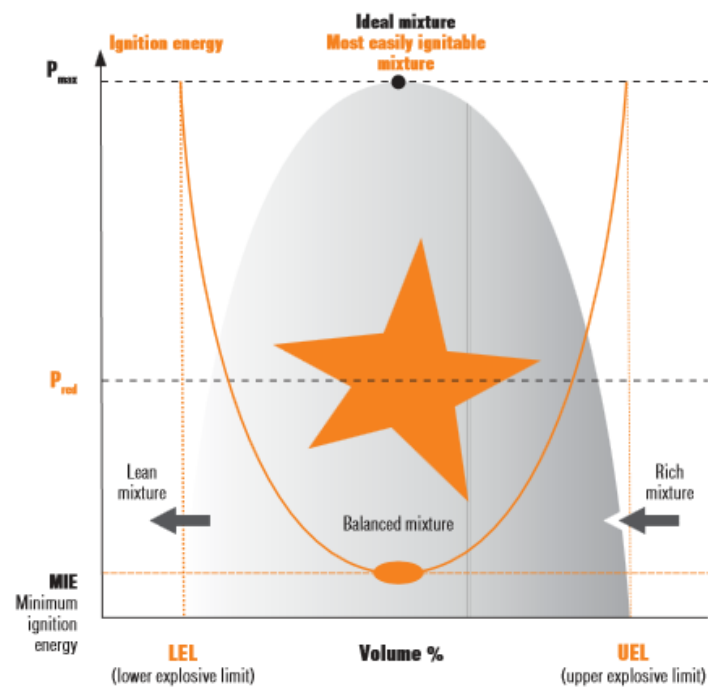
**Image 19** *Explosive mixtures*

With the continue need for coal if it will be implemented in a WWTP, dust explosions can be a problem. The large amounts that need to be at storage as well as the constant motion of some coal to the water tank can give situations in which dust explosions can occur.

To prevent dust explosion some procedures must be followed at all cost. First of all, all the electrical equipment must follow the following points:

●They must not create static electricity

●They must not have hot surfaces

●They must no create sparks

●Combustible dust must not have a chance to enter an enclosure with an internal source of ignition

Following those points takes most of the chance of an ignition source away. Since the dust (coal) and the air cannot be taken away everywhere, taking the chance on an ignition source away is the most important step in preventing dust explosions. But still some actions can be taken to prevent the formation of a dangerous dust/air mixture. One of these actions is implementing an injection system. The injection system gives the coal dust little chance to get in an explosive mixture with air.
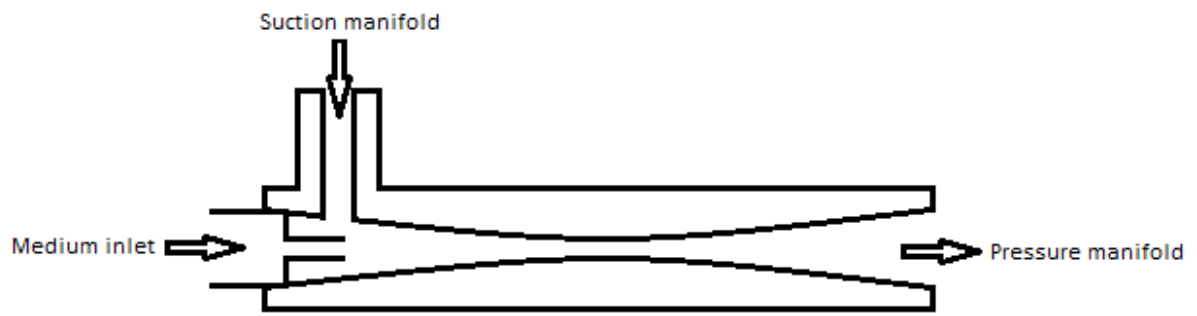
**Image 20** *Injection system*

Image 17 shows a schematic of an injection system. The medium (in this case water) will enter at the left and leave at the right side. The suction manifold is connected with the silo and will suck the coal powder in. The coal will immediately come in the water stream, giving it no chance to become an explosive mixture with air (Anon., sd).

**Appendix D. MSDS COAL**

## 1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

| | | |
|---|---|---|
| Commercial Product Name | : | Columbian COAL |
| Specific use(s) | : | Fuel |
| Company | : | Enerco BV<br>Keerweg 2<br>6122 CL Buchten, NL<br>Tel.: 0031 46 4819900<br>E-mail: j.herben@enerco.nl |
| Emergency telephone number | : | 0031 46 4819900 (9h - 17h) |

## 2. HAZARDS IDENTIFICATION

| | | |
|---|---|---|
| Classification | : | Not a hazardous substance or mixture according to EC-directives 67/548/EEC or 1999/45/EC. |
| Most important hazards | : | not hazardous |
| Specific hazards | : | Risk of dust explosion. |
| Main symptoms | | |
| Inhalation | : | May cause irritation of respiratory tract.<br>Cough |
| Skin contact | : | No adverse effects are expected. |
| Eye contact | : | May cause eye irritation. |
| Ingestion | : | No adverse effects are expected. |
| Environmental properties | : | not hazardous |

## 3. COMPOSITION/INFORMATION ON INGREDIENTS

| Substance name | Values (%) | CAS no | EC No | EC Index | Symbol(s): | R-phrase(s) |
|---|---|---|---|---|---|---|
| Coke (coal) | <= 100 | 65996-77-2 | 266-010-4 | - | - | - |
| Sulfur | 0,5 - 1 | 7704-34-9 | 231-722-6 | 7704-34-9 | Xi | R38 |

## 4. FIRST AID MEASURES

| | | |
|---|---|---|
| First aid measures | | |
| Inhalation | : | *May cause irritation of respiratory tract.- Cough*<br>Move to fresh air.<br>Keep at rest. |
| Skin contact | : | *No adverse effects are expected.*<br>Wash off immediately with soap and plenty of water. |
| Eye contact | : | *May cause eye irritation.*<br>In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. |

| Ingestion | : | No adverse effects are expected. Clean mouth with water and drink afterwards plenty of water. |
| Additional advice | : | If you feel unwell, seek medical advice. Never give anything by mouth to an unconscious person. Treat symptomatically. |

## 5. FIRE-FIGHTING MEASURES

| Suitable extinguishing media | : | Use dry chemical, $CO_2$, water spray or alcohol resistant foam. |
| Extinguishing media which shall not be used for safety reasons | : | High volume water jet |
| Specific hazards | : | Dust may form explosive mixture in air. In case of fire hazardous decomposition products may be produced such as: Carbon oxides SOx Fire residues and contaminated fire extinguishing water must be disposed of in accordance with local regulations. |
| Special protective equipment for fire-fighters | : | Wear personal protective equipment. In the event of fire, wear self-contained breathing apparatus. |

## 6. ACCIDENTAL RELEASE MEASURES

| Personal precautions | : | See also section 8. Wear personal protective equipment. Evacuate personnel to safe areas. Avoid dust formation. Do not breathe dust. Keep away from open flames, hot surfaces and sources of ignition. |
| Environmental precautions | : | Do not flush into surface water or sanitary sewer system. |
| Methods for cleaning up | : | Avoid dust formation. Remove all sources of ignition. Hose down gases, fumes and/or dust with water. Sweep up and shovel into suitable containers for disposal. After cleaning, flush away traces with water. Dispose of in accordance with local regulations. |

## 7. HANDLING AND STORAGE

| Storage | : | Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from open flames, hot surfaces and sources of ignition. Do not store near or with any of the incompatible materials listed in section 10. |
| Handling | : | See also section 8. Wear personal protective equipment. Avoid dust formation. Do not breathe dust. Use only in well-ventilated areas. Do not smoke. Handle in accordance with good industrial hygiene and safety practice. Keep away from open flames, hot surfaces and sources of ignition. |
| Specific use(s) | : | Fuel |

## 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protective equipment

Respiratory protection : When workers are facing concentrations above the exposure limit they must use appropriate certified respirators.
Respirator with a particle filter (EN 143)
type P1

Hand protection : Protective gloves
EN374

Eye protection : Safety glasses
EN166

Skin and body protection : Overalls, apron and boots recommended.

Hygiene measures : Handle in accordance with good industrial hygiene and safety practice.
Remove and wash contaminated clothing before re-use.
Wash hands before breaks and immediately after handling the product.
When using, do not eat, drink or smoke.

Engineering measures : Use only in area provided with appropriate exhaust ventilation.

Environmental exposure controls : Do not flush into surface water or sanitary sewer system.

Exposure limit(s)

Component : Coke (coal) (65996-77-2)

TLV-TWA (mg/m³) : 10 (Inhable dust, graphite); 4 (Respirable, graphite); 6 (Inhalable dust, silica, amorphous); 4 (Respirable, silica, amorphous)

Component : Sulfur (7704-34-9)

TLV-TWA (mg/m³) : 6 (RU, LV)

## 9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance : granular
Colour : black
Odour : odourless

pH : 12 (10%)
Boiling point/boiling range : no data available
Melting point/range : no data available
Flash point : ca. 350°C
Autoignition temperature : 470 - 850 °C
Explosive properties : no data available
Oxidizing properties : No data available
Evaporation rate : No data available
Vapour pressure : no data available
Vapour density : no data available

| | | |
| --- | --- | --- |
| Water solubility | : | 3 g/100 ml (25°C) slightly soluble |
| Viscosity | : | No data available |
| Density | : | 500 - 800 kg/m³ (15°C) |
| Partition coefficient: n-octanol/water | : | no data available |

## 10. STABILITY AND REACTIVITY

| | | |
| --- | --- | --- |
| Stability | : | Stable under normal conditions. |
| Hazardous decomposition products | : | Sulphur oxides<br>Carbon oxides |
| Materials to avoid | : | Incompatible with oxidizing agents. |
| Conditions to avoid | : | Avoid dust formation.<br>Keep away from open flames, hot surfaces and sources of ignition. |

## 11. TOXICOLOGICAL INFORMATION

General Information

Acute toxicity

| | | |
| --- | --- | --- |
| Component | : | Sulfur(7704-34-9) |
| LD50/oral/rat | : | > 3000 mg/kg |
| LD50/dermal/rabbit | : | > 2000 mg/kg |
| LC50/inhalation/4h/rat | : | > 0.047 mg/l/4h |
| Inhalation | : | May cause irritation of respiratory tract.<br>Cough |
| Skin contact | : | No adverse effects are expected. |
| Eye contact | : | May cause eye irritation. |
| Ingestion | : | No adverse effects are expected. |

Chronic toxicity

| | | |
| --- | --- | --- |
| Chronic toxicity | : | No adverse effects are expected. |

## 12. ECOLOGICAL INFORMATION

| | | |
| --- | --- | --- |
| Ecotoxicity effects | : | not hazardous |
| Component | : | Sulfur(7704-34-9) |
| LC50/96h/fish | : | 866 mg/l (Brachydanio Rerio); > 10.000mg/l (Gambusia affinis) |
| Mobility | : | moderately soluble |
| Persistence and degradability | : | Readily biodegradable. |
| Bioaccumulation | : | Does not bioaccumulate. |
| Partition coefficient: n-octanol/water | : | no data available |

## 13. DISPOSAL CONSIDERATIONS

| | | |
|---|---|---|
| Waste from residues / unused products | : | Keep product and empty container away from heat and sources of ignition. Dispose of in accordance with local regulations. Where possible recycling is preferred to disposal or incineration. |
| Additional ecological information | : | Do not flush into surface water or sanitary sewer system. |
| Codes of waste (2001/573/EC, 75/442/EEC, 91/689/EEC) | : | The following Waste Codes are only suggestions: 05 06 99 - wastes not otherwise specified Waste codes should be assigned by the user based on the application for which the product was used. |

## 14. TRANSPORT INFORMATION

ADR/RID

| | | |
|---|---|---|
| ADR/RID | : | Not classified as dangerous for conveyance in the meaning of the Carriage of Dangerous Goods by Road and Rail. |

IMDG

| | | |
|---|---|---|
| IMDG | : | Not classified as dangerous in the meaning of transport regulations. |

ICAO/IATA

| | | |
|---|---|---|
| ICAO/IATA | : | Not classified as dangerous in the meaning of transport regulations. |

## 15. REGULATORY INFORMATION

| | | |
|---|---|---|
| Classification | : | Not a hazardous substance or mixture according to EC-directives 67/548/EEC or 1999/45/EC. |
| Commercial Product Name | : | Columbian COAL |
| | | - |
| R-phrase(s) | : | - |
| S-phrases | : | - |
| WGK | : | nwg |

## 16. OTHER INFORMATION

| | | |
|---|---|---|
| Text of R phrases mentioned in Section 3 | : | R38 -Irritating to skin. |
| Sources of key data used to compile the datasheet | : | http://ecb.jrc.it |

The contents and format of this SDS are in accordance with EEC Commission Directive 1999/45/EC, 67/548/EC, 1272/2008/EC and EEC Commission Regulation 1907/2006/EC (REACH) Annex II.

# Appendix E. Machines

The machines used:
- ●Vacuum pump
- ●Oven
- ●Stirring plates
- ●Shake machine
- ●UV-spectrometer


*Vacuum pump*


**Image 21** *vacuum pump*


*Oven*
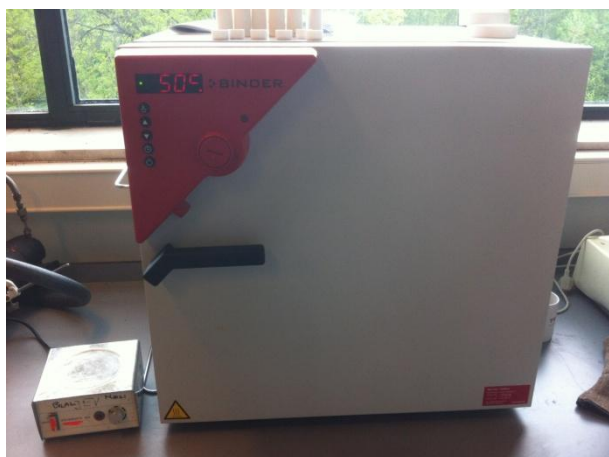

**Image 22** *Oven*

*Stirring plates*



**Image 23 *Stirring plates***


*Shaking machine*



**Image 24 *stack sieves needed for shake machine***



**Image 25 *Shake machine***

| **Image 26** *Shake machines case 1* | **Image 27** *Shake machines case 2* |

## UV-spectrometer



**Image 28** *UV-spectrometer*

**Appendix F. Basis of Design (BoD)**

| DESIGN BASIS FOR | INFORMATION **DESIGN BASIS** |
|---|---|
| **Filter system** | Bachelor thesis |
| PROJECT: **Bachelorproject s2036908** | |
| Approved: Process Eng. Dept. | Date of issue:05-07-2013 |
| Client        : | Page 69 of 109 |

## DRAFT

Confidential

# WWTP Garmerwolde - PLANT *(name of the plant)*

*Garmerwolde WWTP* project no. s2036908

By: ***Jasper A. Kabel***

Rev: 0, dated   XXXXXX

## TABLE OF CONTENT OF DESIGN BASIS (this is the standard design basis)

0.    INTRODUCTION


1.    SCOPE

1.1.   Function of the facilities

1.2.   Description of the facilities

1.3.   Plant site information

1.4.   Plant capacity and flexibility

1.5.   Product specifications

1.6.   Feedstock specifications at battery limit

1.7.   Waste stream specifications

1.8.   Utility specifications at battery limits

1.9.   Existing ISBL utility data


2.    DESIGN CRITERIA AND POLICIES

2.1.   Design consideration

2.2.   Total quality management aspects

2.3.   Design standards and codes

2.4.   Plant availability and sparing policy

2.5.   Legal requirements and company requirements

2.6.   Safety, health and environmental considerations

2.7.   Process control philosophy

2.8.   Overdesign factors

2.9.   Fouling resistance's for design

2.10.  Corrosion allowance

2.11.  Economic criteria for optimisation of sub-systems

2.12.  Temperatures and pressures for mechanical design

3.    GENERAL DESIGN DATA

3.1.    Units of measurement

3.2.    Meteorological data (Limburg)


4.    ATTACHMENTS (part of the Conceptual Process Design Package)

Appendix 1: Process Flow Diagrams (PFD's)

Appendix 2: Equipment list

Appendix 3: Heat and Material Balances

Appendix 4: Process Description

Appendix 5: Preliminary lay-out and Plot plan

Appendix 6: Duty Specs/datasheets special equipment

Appendix 7: Batch time sequence (if applicable)

Appendix 8: Process Safety Analysis (if applicable)


Note:   In general there will be no attachments available at the start of the conceptual

engineering

## 0. INTRODUCTION

The purpose of this document it to give general guidelines during the conceptual/basic engineering of the so-called Filtersystem at WWTP Garmerwolde. All numbers and values as well as descriptions have been agreed upon between the client and Engineering-company. Therefore this document will form the solid basis for the conceptual/basic engineering to be started. It is the intention of *the WWTP Garmerwolde and the RUG* to investigate with a xx % accuracy the feasibility of xxxxxx plant and to prepare all required documents to support the feasibility study. *ETC*

## 1. SCOPE

### 1.1. Function of the facilities

1.1.1.   The function of the facilities designated as the WWTP Garmerwolde plant is to produce 5740.6 kg/h  of Sludge from sludge, influent and coal as a feedstock.

1.1.2.   The WWTP Garmerwolde plant will be close to the existing WWTP Garmerwolde plant in Garmerwolde. Feed will be made available from XXXXX. Products will be send to Swiss Combi. Byproducts will be dumped in the Eemskanaal.

1.1.3.   A warehouse will be constructed for the storage of the products. The capacity of this warehouse will be for 10 weeks production.

1.1.4.   Waste water will be send to the process sewer system and from there to the biological pond waste water treatment plant (wwtp). All waste streams (gas, liquid or solid) should be dealt with in agreement with governmental laws, permit requirement, and corporate requirements and guidelines.

Vent gasses will be routed through a vent gas scrubber. A stack will be installed from which the gasses are sent to atmosphere.

1.1.5.   The utilities will be available at battery limits, see also stream summary 1.1.9.

1.1.6. On stream time basis 7800 hours/year. This leads to a sludge production of 5.7406 t/h.

1.1.7. **All pressures referred to in this design basis are absolute pressures**.

1.1.8. The facilities of the Garmerwolde WWTP plant will be designed with a life time expectancy of 20 years, where possible.

## 1.1.9  Stream Summary

This will show a sketch (block flow diagram) of all in and outgoing streams). An example of such a sketch is given below.

FeCl3
-130 kg/h
-40 wt% FeCl3 in water
-10 °C
-1.01325 bar

Coal
-4.6 kg/h
-87 wt% coal in water
-10 °C
-1.01325 bar

Poly-electrolyte
-15 kg/h
-1 wt% Poly-electrolyte in water
-10 °C
-1.01325 bar

Extern sludge
-22831 kg/h
-3.2% DSC
-10 °C
-1.01325 bar
-sludge(L)

Effluent
-2947481 kg/h
-12.9 °C
-1.01325 bar
-Water (L)
-7.1 pH
Contains:
 -Micro-plastics traces
 -Hormones 0.0019-0.027 g/h

H&Aa sludge
-13575 kg/h
-3.7% DSC
-10 °C
-1.01325 bar
-sludge(L)

WWTP Garmerwolde

Sludge cake
-5740.6 kg/h
-25.87% DSC
-10 °C
-10.01325 bar
-Sludge (S)
-Contains:
 -Micro-plastics 0.20 kg/h
 -Hormones 0.0481-0.413 g/h

Influent
-2916667 kg/h
-12.9 °C
-1.01325 bar
-Water (L)
-7.5 pH
-Contains:
 -Micro-plastics 0.20 kg/h
 -Hormones 0.050-0.44 g/h

Biogas
-251 m3/h
-30 °C
-1.01325 bar
-Gas (G)

## 1.2. Description of the facilities

The plant includes the following sections:

(see also PFD's in Attachment 4.1 and Process Description in Attachment 4.4. if applicable)

### 1.2.1. Tag coding of equipment

Equipment will be tag coded as laid down in memo XXXXXX

### 1.2.2. Production and Utility Facilities

The plant will include the following production sections, this section numbering will form the basis of the PFD's:

Section XXX                    Utilities

Section XXX                    Reactors

Section XXX                    XXXXX section

Section XXX                    Distillation

The utilities available at battery limit are specified in Chapter 1.8.

A detailed survey of the utility tie-ins is indicated in the project specifications of the mechanical department.

### 1.2.3. General facilities

### 1.2.3.1. Water treating and sewerage

Surface water which can reasonably be expected not to be contaminated shall be collected in a clean water sewer system, which has to be connected to the existing main sewer.

(Domestic sewage shall first be treated in a biological pond prior to drainage into the clean water sewer system.) Process water and contaminated surface water shall drain to a process sewer system. And then (via an API-separator) to the biological pond (*if applicable*). The maximum allowable temperature of waste water in sewage systems is 30 °C.

### 1.2.3.2. Bleed, relief and disposal systems

- The relief system has to protect equipment and piping against overpressure, and shall be designed in such a way that the maximum credible relief quantity can be handled, regardless of mode of operation. The system shall be designed in such a way that a release cannot upset the operation of other sections in the plant or adjacent installations.

- Gases containing combustible components which are blown off by safety valves shall be relieved to a flare system or to 'safe location'. Dispersion calculations might be required to determine 'safe location'. A risk assessment study and evaluation will have to be made before the start of the basic engineering. Gases containing non-combustible, non-poisonous or non-odorous components, may be relieved to local vents. The design of these vents must prevent dangerous ground level concentrations of suffocating components ($N_2$, $NH_3$, $CO_2$ etc.) and liquid entrainment. Venting should always be to a safe location.

-

Waste gases produced continuously during normal operation and containing significant amounts of combustible, poisonous or odorous components shall be incinerated, or sent to not applicable.

- For draining of liquids containing combustable, poisonous or odorous components a closed piping system and/or a slop tank shall be installed. Organic liquids not miscible with water are separated and recovered.

### 1.2.3.3. Control room, social rooms, offices, workshop

The existing facilities of the WWTP Garmerwolde plant will be used as much as possible. It is assumed that the plant will have a mixed crew of operators. For the main facilities reference is made to WWTP Garmerwolde OR

The erection or expansion of operator- and social rooms, an office, workshop and additive storage is excluded from the project scope of work. This project will only cover the control room.

### 1.2.4. Outside battery limit (OSBL)

OSBL connections are detailed in the stream summary 1.1.9.

## 1.2.5. Safety measures and facilities

All *the WWTP Garmerwolde and the RUG* and government standards are to be adhered to, see also 2.6.

## 1.3. Plant site information

The plant will be located in Garmerwolde (The Netherlands) on the WWTP Garmerwolde location.

The plant will be as indicated in the preliminary lay-out, see Attachment 5. (start basic engineering).

The following details are shown:

- battery limits of the plant

- access and internal roads

- areas designated for construction facilities

A preliminary plot plan is shown in Attachment 5. ( start basic engineering)

The site will be flat and free of obstacles and underground cables.

With regard to earthquakes is referred to Government Building Regulations.

A preliminary report of geotechnical survey will be included in the Project specification of the civil department. (start basic engineering)

It will be assumed that the soil at the site is not polluted, and that a so called 'Clean soil statement' will be given ('schone grond verklaring') *(or write something different)*.

## 1.4. Plant capacity and flexibility

The WWTP Garmerwolde will have a production capacity of 5740.6 kg/h sludge with a composition as given in Paragraph 1.5. See also 1.1.1.

The production of 1000 kg of sludge will not require more than 0.8 kg coal feedstock, based on the normal feedstock specification as per Section 1.6. and not more than XXXX steam. etc etc

When operating at 70 % of design capacity (turn down ratio), the plant shall still be able to produce products which meet their specification as given in Section 1.5 and consumption figures of feedstock and/or utilities as agreed upon and listed above.

## 1.5. Product specifications

### 1.5.1. Product Sludge

Composition: variety of materials, not consistent

Battery limits conditions

pressure bar: atmosphere, atmosphere, atmosphere

temperature °C: environment temperature

Physical data:

### 1.5.2. Co-product effluent

Water, solved minerals, traces of hormone and micro plastics

## 1.6. Feedstock specifications at battery limit

### 1.6.1.  Feed Coal

Composition: 99% coke, 1% sulphur

Battery limits conditions

pressure bar:               1bar, 1.2 bar 1.5 bar.

temperature °C:             environment temperature

Physical data:


### 1.6.2.  Feed xxx

same as above


## 1.7. Waste stream specifications


### 1.7.1.  Air pollution

The maximum allowable emissions figures are: .....

The maximum allowable concentrations are: ........

The expected emissions are: ......................


Remark: The maximum allowable emissions figures and concentrations mentioned here are
        the figures mentioned in the 'Wet Milieubeheer'.


The emissions include the total of:

- normal and continuous vent and purge losses

- normal leakage from flanges, pumps, valves

- the losses during cleaning and/or repair of equipment

Not included are:

- the expected losses due to blow-off of relief valves

- other losses which are not normal but can be expected (start-up and shut-down losses)

### 1.7.2.  Water pollution

The water flow to the process sewer should be as minimal as feasible. The quantity of organic and inorganic components in the water should be known for normal operating conditions as well as special cases e.g. start-up, shut-down, blow-down and grade change. The temperature is typically 25 °C and shall not exceed 30 °C, see memo XXXXXXX for details.

### 1.7.3.      Soil pollution

The soil should be protected to prevent possible pollution.  *(Or write a complete story which may include something about existing pollution).*

## 1.8. Utility specifications at battery limits

The utility data as well as the statement that the total capacity will be available at Battery Limits will be confirmed and approved by *company x* Utility department *(or other utility supplier)*. All utility figures mentioned in this chapter shall be verified and adapted if necessary and have to be approved by the Utility Supplier and the client.

### 1.8.1.  Electric power

Reference to be made to Project Specification PS 3.5-(project number) (see PEM 40.20.20

page 4). For preliminary Conceptual engineering, the following information can be used.

STANDARDIZED VOLTAGE

Alternating current: 50 Hz

### 1.8.1.1. 10,000 VOLT - 3 PHASE - 50 CYCLES

Derived from the utilities system outside battery limits. The system is or shall be neutral grounded by an 8 Ohm resistance. The maximum short circuit level may be 250 up to 500 MVA. For motors above 400 kW.

### 1.8.1.2. 690/400 VOLT  - 3 PHASE + NEUTRAL - 50 CYCLES

This system shall be derived from the 10 kV system with delta-star (DYn) connected transformers. The secondary starpoint of the feeding transformers shall be solidly grounded in the low voltage main switchboard.

690 V main switchboard:

motors from 55 kW with a maximum power (in kW) equal to 17 % of the rated power of one transformer feeder (in kVA).

690 V MCC:

motors from 15 kW up to and including 90 kW.

### 1.8.1.3.  400/230 VOLT  - 3 PH + NEUTRAL - 50 CYCLES

This system shall be derived from the 10 kV or 690 V system with DYn-connected transformers. The secondary starpoint of the feeding transformers shall be solidly grounded in the low voltage main switchboard.

400 V main switchboard:

motors from 55 kW with a maximum power (in kW) equal to 17 % of the rated power of one transformer feeder (in kVA).

To a combined main switchboard/MCC all motors up to the above mentioned maximum power may be connected.

400 V MCC:

motors up to and including 55 kW.

In case of variable speed drives, different power ratings can apply for the connection to the switchboards. Proposals have to be discussed with owner.

The motor of a drive and the motor of the spare-drive, e.g. the A and B drive, shall be connected to different sides of the buscoupler or to different MCC's fed from different sides of the buscoupler. All motors which belong to a specific unit, for instance motors and the auxiliary motors of a compressor, shall be connected to one and the same side of the HV and/or LV buscoupler(s) and/or to one and the same MCC.

### 1.8.1.4.  230 VOLT - 2 WIRE - SINGLE PHASE - 50 CYCLES

This system is derived from a 400 Volt - 3 phase - 4 wire system having the neutral
grounded.

### 1.8.1.5.  42 VOLT  - 2  WIRE - SINGLE PHASE - 50 CYCLES

This system is normally derived from local installed 230/42 Volt  100 VA transformers.

### 1.8.2. Electric Power - Direct Current

### 1.8.2.1.    110 VOLT DC - non earthed system

This system shall be derived from the 400/230 V system by rectifier(s) and shall have a battery back-up.

### 1.8.2.2.    110 VOLT DC - earthed system

This system shall be derived from the 400/230 V system by rectifier(s) and shall have a battery back-up. The +pole of the system shall be earthed in the first 110 V DC switchboard.

### 1.8.2.3.    24 VOLT DC - non-earthed system

This system shall be derived from the 400/230 V system by rectifier(s) and shall have a battery back-up.

### 1.8.2.4.  24 VOLT DC - earthed system

This system shall be derived from the 400/230 V system by rectifier(s) and shall have a battery back-up. The -pole of the system shall be earthed in the first 24 V DC switchboard

### 1.8.2.5. Other voltage systems and networks

Other voltage systems and networks can be used for special instruments (e.g. computer systems). This will be subject to owners approval. These voltages shall always be derived from the 400/230 V system by means of transformers or -in case of DC- rectifier(s) with suitable battery back-up.

Equipment other than motors shall be connected to the different voltage systems as mentioned here-under:

- heater                                                          : 400V or 690V 3 phases

- packaged units                                          : 400V or 690V 3 phases

- welding socket outlets                              : 400V 3 pH

- heat tracing                                              : 230V

- lighting                                                      : 230V

- socket outlets                                            : 230V

- computer systems                                      : 230V

- socket outlets or handlamps and portable

  tools in enclosed spaces                           : 42V

- control of HV switchgear                           : 110V DC non-earthed

- control of LV switchgear                           : 110V DC earthed

- emergency lighting in control room and switch room        : 110V DC earthed

- network annunciator systems in switch room     : 110V DC earthed

- telephone system                                      : 60V DC

- process control equipment                         : according to EP 5.6-2.1

### 1.8.3. Steam

The situation of the used and/or generated steam should be **checked** carefully because there are many types of steam (check for specific site).

The following steam conditions apply at the battery limit: *DISCUSS*

For technological design the temperature of the saturated steam will be used at the normal operating pressure minus the pressure drop over the inlet lines and valves.

**Import**

|  |  | AVERAGE | MIN. | MAX. |
|---|---|---|---|---|

**1.8.3.1.** 31 bar

| | | AVERAGE | MIN. | MAX. |
|---|---|---|---|---|
| pressure | : bar | 25 | 23.5 | 31 (setpoint PSV) |
| temperature | : °C | 285 | 250 | 300 |
| design | : 300 °C and 0-31 bar (steam condensate: 300 °C) | | | |
| | fouling coeff. : 10,000 W/m$^2$ K | | | |

**1.8.3.2.** 13 bar

| | | AVERAGE | MIN. | MAX. |
|---|---|---|---|---|
| pressure | : bar | 11.5 | 10.5 | 13 (setpoint PSV) |
| temperature | : °C | 250 | 210 | 300 |
| design | : 300 °C and 0-13 bar (steam condensate: 250 °C) | | | |
| | fouling coeff. : 10,000 W/m$^2$ K | | | |

**1.8.3.3.** 4 bar

| | | AVERAGE | MIN. | MAX. |
|---|---|---|---|---|
| pressure | : bar | 3.5 | 3 | 4 (setpoint PSV) |
| temperature | : °C | 200 | 175 | 250 |
| design | : 250 °C and 0-4 bar (steam condensate: 200 °C) | | | |
| | fouling coeff. : 10,000 W/m$^2$ K | | | |

**1.8.3.4. Steam condensate return (at B.L.)**

- conductivity        max. 50 µS/cm

- iron content      max. 0.5 mg/l

- temperature     100-130 °C

- pressure        xxx bar

The steam condensate return will be free of oil, poisonous components and volatile combustible components.


### 1.8.4. Water


### 1.8.4.1. Canal water

The cooling tower make - up water is flocculated water from the *Canal* .

| pressure (at ground level) | average | : 7.5 | bar |
|---|---|---|---|
| | max. and design | : 16 | bar |
| | minimum | : 6 | bar |
| temperature | average | : 14 | °C |
| | max. and design | : 25 | °C |
| | minimum | : 4 | °C |

Quality of flocculated canal water:

| Component | Unit | average value | maximum value | minimum value |
|---|---|---|---|---|
| chloride (as $Cl^-$) | mg/l | 60 | 130 | 20 |
| Sulphate | mg/l | 60 | 90 | 35 |
| Nitrate | mg/l | 10 | 15 | 3 |
| Bicarbonate | mg/l | 180 | 245 | 120 |
| Active $SiO_2$ (silicagel) | mg/l | 6 | 15 | 2 |

| | | | | |
|---|---|---|---|---|
| Inactive $SiO_2$ (silicagel) | mg/l | 0.3 | 0.8 | 0.1 |
| Calcium | mg/l | 75 | 105 | 45 |
| Magnesium | mg/l | 7 | 12 | 3 |
| Sodium | mg/l | 35 | 90 | 13 |
| Potassium | mg/l | 5 | 7 | 3 |
| Ammonium | mg/l | 2 | 4 | <1 |
| Total iron | mg/l | $\leq 0.2$ | 0.2 | <0.2 |
| $KMnO_4$-number | mg/l | 7 | 10 | 5 |
| pH | - | 7.7 | 8.0 | 7.4 |
| suspension of $SiO_2$ | mg/l | 1 | 2 | 0.6 |
| suspended components | mg/l | 1.2 | 3 | 0.7 |
| conductivity | :S/cm | 500 | 850 | 300 |
| total hardness | mg eq/l | 4.3 | 5.8 | 2.8 |

Maximum values are based on a dry summer with low water levels in the river Maas and adjacent Julianakanaal. The above shown figures for maximum and minimum values do not necessarily occur simultaneously.


## 1.8.4.2. Cooling water


Cooling water is a factor 3 concentrated from the make-up water for this plant   CHECK

pressure　　　　　　　pump discharge　　　　　　　　　　　　　　　　　　　　: 5 bar

　　　　design　　　　　　　　　　　　　　　　　: 7 bar

temperature　　　　　minimum　　　　　　　　　　　　　　　　　　　　　　　: 5 °C

　　　　design　　　　　　　　　　　: 80 °C   *CHECK*

Maximum allowable temperature increase  of the total return　　　　　: 10 °C

for individual pieces of equipment   *(to be determined)*　　　　　　: 17 °C

Maximum allowable pressure drop for individual equipment　　　　　　: 0.7 bar

Maximum allowable pressure drop for equipment in series　　　　　　: 1.0 bar

The cooling water system will be designed for a cooling water system inlet temperature of 35 °C, outlet temperature 25 °C at a wet bulb temperature of 18 °C. This situation will be exceeded on average 2 % per year.

For cooling water based on concentrated and fully conditioned canal water, the design film temperature of the water film in coolers shall not exceed 60 °C for new equipment. The maximum outlet temperature for a new individual cooler must not exceed 42 °C.

For fouling factors to be used in the design reference is made to section xxxx of this document.

### 1.8.4.3. Inhibitor and conditioning system

The same conditioning system as used for the WWTP Garmerwolde plant will be used, *(DISCUSS  dearborn 5472. This is a 5-10 % solution of acetodiphosphone acid, CAS-number 2809-21-4. DISCUSS AND CHECK)*

### 1.8.4.4. Demineralised water at battery limits

| Quality | | average | max. | min. |
|---|---|---|---|---|
| active $SiO_2$ | mg/l | 0.03 | 0.05 | 0.02 |
| inactive $SiO_2$ | mg/l | 0.04 | 0.08 | 0.01 |
| total $SiO_2$ | mg/l | 0.07 | 0.10 | 0.03 |
| Total Fe | mg/l | 0.02 | 0.05 | 0.01 |
| conductivity | µS/cm | 0.2 | 0.5 | 0.1 |
| pH | - | 7 | 7.5 | 6.5 |
| oxygen | mg/l | 10 | 12 | 8 |
| total hardness | mg eq/l | 0.001 | 0.001 | 0.001 |
| temperature | °C | 15 | 30 | 4 |
| pressure | bar | 4.5 | 7.5 | 3.0 |

For fouling factors to be used see section xxxxxxxx

### 1.8.4.5.    Potable water at battery limits

Pressure               minimum                   : 3 bar

normal             : 4.5 bar

max. and design   : 6 bar (set pressure for safety valve)

Temperature      minimum            : 10 °C

maximum: 14 °C

### 1.8.4.6.    Fire fighting water

See canal water. In case of fire the pressure will be boosted up to 16 bar, which is the design pressure of the system.

### 1.8.5.  Air

### 1.8.5.1.    Instrument air

Pressure              min.                       : 4.5 bar  *(to be determined)*

max. and design   : 8 bar  (setpoint PSV)

norm.             : 5.8 bar

Temperature      norm.                 : ambient

design             : 50  °C

dew point : -30 °C   OR  -40 °C *(to be determined)*

quality            : free of oil and dust

A filter shall be installed ISBL. *(to be determined)*

### 1.8.5.2. Plant & Breathing air

Pressure              min.                       : 5.5 bar for plant air

: 4.5 bar for breathing air

max. and design   : 8 bar (setpoint PSV)

norm.             : 5.5 bar

Temperature      norm.                 : ambient

design : 50 °C

dew point : ambient

An ISBL filter for breathing air will be installed. *(to be determined)*

### 1.8.6. Nitrogen (oxygen free)

Pressure         min.                        : 4.0  bar

        max. and design   : 7.0 bar (setpoint PSV)

        norm.              : 5.0 bar

Temperature      min.                        : 10 °C

        max. and design   : 50 °C

        dew point : -60 °C

composition

nitrogen         min.                        : 99.9 % (vol.)

hydrogen         max.                        : 3 ppm

oxygen          max.                        : 5 ppm

carbon dioxide   max.                        : 5 ppm

### 1.8.7. Natural gas     *(CHECK    CHECK)*

### 1.8.7.1. Low caloric

type                              : Low calorific without odorant

temperature                       : 15 °C

pressure          typical          : 17 bar (reduced ISBL to approx. 2 bar)

Composition                       : typical

saturated hydrocarbons             : vol. %      85

$N_2$                 : vol. %           14

$CO_2$                               : vol. %      0.9

| | | |
|---|---|---|
| UHV | : MJ/Nm$^3$ | 35 |
| LHV | : MJ/Nm$^3$ | 32 |
| Wobbe no. | : MJ/Nm$^3$ | 45 |
| Wobbe no. | : MJ/kg | 31 |
| Total sulphur content | : mg/Nm$^3$ | 0.4 |
| density at T=273 K | : kg/Nm$^3$ | 0.83 |

## 1.8.7.2. High caloric

type                              : High calorific without odorant

temperature                       : 15 °C

pressure        max.              : .... bar

    min.              : .... bar

Composition

| | | |
|---|---|---|
| Hydrocarbons (CH$_4$) | : vol. % | 95 |
| CO$_2$ | : vol. % | 1.5 |
| N$_2$ | : vol. % | 3 |
| Total S | : mg/Nm$^3$ | 0.4 |
| UHV | : MJ/Nm$^3$ | 41 |
| LHV | : MJ/Nm$^3$ | 37 |
| density at T=273 K | : kg/Nm$^3$ | 0.8 |
| Wobbe no. | : MJ/Nm$^3$ | 52 |
| Wobbe no. | : MJ/Nm$^3$ | 36 |

Explosion limits        (at 0 °C and 1.013 bar)        5.8 - 15 vol.%

Stoichiometric air (m$^3$/m$^3$)                        9.75 in dry air at 0 °C and 1.013 bar

    9.87 in wet air at 0 °C and 1.013 bar

### 1.9. Existing ISBL utility data

*In case of a revamp or debottlenecking all relevant data of existing utilities to be given here.*
*TO BE DISCUSSED AND AGREED UPON*

## 2. DESIGN CRITERIA AND POLICIES

### 2.1. Design consideration

- The plant shall be designed as a commercial unit for the performance as listed in 1.1.1.

- Where possible inherently safe design shall be applied.

- Where possible the design shall have a minimum impact on the environment and shall be as

  energy efficient as possible.

- Establish project key criteria and objectives.

- Establish design life time of the total installations and/or individual pieces of equipment.

- Determine which process parameters should be defined, taken into account the limitations of the technologies selected.

- Asses the significance of the process parameters.

- Identify the basic design parameters (key process parameters).

- Assure that the requirements of all key parties (operation, maintenance, marketing, finance, management, safety, quality) are recognised and presented so as to facilitate priorisation and resolution of conflicts.

- Mention the design criteria references and assumptions (test results, R & D reports, licence package etc.).

- All relevant design criteria of each piece of equipment have to be motivated in a separate document (e.g. Design Condition Analysis).

### 2.1.1. State of the art of the technologies and process

- The plant and equipment design shall, where possible, incorporate only those modern (state of the art), available and proven technologies that are consistent with highly reliable, low SHE (safety, health, environmental) risk plant design and with the Corporate Requirements and Guidelines.

- The technologies shall be evaluated with 'state of the art' knowledge from inside and outside *WWTP Garmerwolde and RUG*. The benchmarking position shall be indicated with an approximate technical/economical evaluation of the considered process.

- Any contractor is expected to consider recent developments of the technologies during design and consult Engineering-Stamicarbon before these are incorporated or rejected.

- The implications of the technologies on equipment design and selection shall be assessed.

### 2.1.2. Operational requirements

- During process engineering the operating procedures are translated into process design. Operating philosophy must be defined before basic engineering to assure that the designed plant can be operated according to these instructions.

- The degree of atomisation and controlling of the plant is determined by the operating philosophy. Atomisation and control system choice should lead to minimum manning.

- Main and by-product logistics (storage, transport etc.), interference with other plants; off-spec routing shall be indicated.

- Indicate the auxiliary requirements (catalyst, inhibitors, etc.) including handling aspects.

- Operational flexibility shall be assessed in accordance with ideas of the client.

- The installation has to meet the highest performance criteria during transitions: for instance feed composition changes, throughput variations, start up and shut down.

- The design shall be based on maximum and minimum operating conditions including, start up, shut down and cleaning or maintenance procedures, unless otherwise is specified.

- Specify required regeneration equipment (catalyst, adsorbent regeneration etc).

### 2.1.3. Maintenance requirements

- The specific maintenance philosophy shall be determined by client and Engineering-Stamicarbon.

- The plant equipment and materials of construction shall be consistent with a high service factor and low maintenance cost.

- Preventive, predictive maintenance and regular revision and maintenance intervals should be taken into account.

- The plant design shall allow carrying out as much routine maintenance as possible during operation or during downtime inherently necessary for process reasons.

### 2.1.4. Allowances for future extension and/or product upgrading

- Allowances for future extension and installation of equipment for product upgrading and off spec routing have to be determined in consultance with client.

- In case of constructing an additional line, the plot-plan of the first line must be designed in such a way that operation of the lines gives synergistic effects.

- In production plants with expected future expansion the capacity of special equipment may be over-designed. This shall be mentioned in the Design Basis and determined by the client.

### 2.1.5. Project and Technological risks

- The following major technological and project risks and uncertainties are present during the conceptual engineering phase of this project: (kinetics, powder characteristics and thermodynamics partly unknown etc etc.) (*CHECK CHECK*)

- The investigation of risk reduction options and remedial actions are part of this project.

- Indicate with sensivity analysis the economics of the considered risk options.

- After approval of the owner, the contractor is allowed to use other technologies than mentioned in the design.

- Experiences of *WWTP Garmerwolde and RUG* with vendors are reflected in the preferred vendor-list.

- Appreciation's of client can also determine the choice between several alternatives.

- The choice between a commercially proven, pilot plant proven, and a recently developed technology is complex and shall be assessed and agreed by Engineering-Stamicarbon and client.

### 2.1.6. Equipment including package units

Package units are equipment and/or process systems, which are purchased from specialised vendors in order to obtain the necessary performance integrity.

Package units include:

- Pumps, compressors, blowers, centrifuges, mixers, extruders, granulators and other rotating equipment

- Cooling towers, refrigeration equipment, cooling belts

- All fired equipment, incinerators and flares, hot oil furnaces

- Solid handling equipment including storage, filters, sieves, pneumatic transport, dosing units

- Hoisting equipment, bagging, debagging and packing equipment

Design, manufacturing and erection of package units shall comply with:

- Dutch national and local codes

- International design standards and specifications

- Additional requirements as mentioned in owners dedicated project specifications

- Additional requirements according to owners standard specifications as mentioned in the dedicated project specifications

- The *WWTP Garmerwolde and RUG* Corporate Requirements and Guidelines and Operational Requirements.

Equipment, lines, valves etc. shall be designed according to ANSI/DIN specifications where possible.

The scope of supply shall at least include the design, manufacturing, delivery and, when applicable, erection of equipment and or parts, necessary to achieve the required duty and safe operations.

The contractor remains fully responsible for a good design and the fitness for successful operation of the equipment and package units. The contractor remains also fully responsible for delivery in time of documents, services and materials.

In principle, only equipment, components and constructions, which have been proven during at least two years successful operation in similar process conditions, are acceptable.

The contractor makes sure, that at least the following guarantees (by Vendor) are incorporated in the agreements with Vendors:

- The compliance of the units, the components and the performance of the installation with the applicable technical specifications.

- That the installation and its individual parts function properly in all respects and that they are free from defects and sound in terms of design, workmanship and fabrication.

- Specific performance guarantees with regard to consumptions, capacities and quality of products; these specific performance guarantees shall be described as detailed as possible in figures which are easily measurable in the installation while operating.

In principle the Owner will provide a 'Vendor list'. The contractor is allowed to add other vendors to the list, resulting in the 'proposed Vendor list'. The Owner has the right to make modifications to this list. After Owner's approval, the modified/approved Vendor list will be appointed as the 'project Vendor list'. In case no Vendor list is provided by the Owner, the contractor shall compose and provide a 'project Vendor list'. The Owner has the right to make modifications to this list.

## 2.2. Total Quality Management Aspects

The contractor shall demonstrate that its organisation is supported by a Quality System, which preferably meets the requirements mentioned in ISO9001, in order to achieve quality of engineering. The organisation and procedures of the contractor can be assessed by means of a quality audit. This audit gives information about the deviations between ISO9001 and the contractor's activities. The contractor shall prepare a project quality plan to demonstrate that engineering is executed according to ISO9001. This plan is to be regarded as the translation of the quality system in working procedures during the project. The same applies in rough outlines for the construction phase.

The contractor shall demonstrate a SHE project plan according to *WWTP Garmerwolde and RUG* and government standards and requirements.

## 2.3. Design standards and codes

The facility shall be designed in accordance with:

- *WWTP Garmerwolde and RUG* -design specifications and Process Design Guides (if applicable) as defined in the Project specification have to be used.

- Recommended practices as laid down in API reports and bulletins shall be adhered to.

- For the design or rating of shell and tube heat exchangers, the design methods of HTRI, or on contractors request HTFS, are strongly recommended.

- For heat exchanger types different from shell and tube, the design methods of HTFS are recommended or the design methods of approved vendors.

- For the design of fractionators the design methods of FRI are strongly recommended or for specific types of packing or tray types, the design methods of approved vendors.

- For the earthing of equipment the LP3 or LP4 safety measures shall be taken, in compliance with NEN1014.

## 2.4. Plant availability and sparing policies

### 2.4.1. Availability

The plant shall be designed for an annual availability of 7800 hours (5.74 tons per h) on-stream time. Availability should be read as availability for starting, stopping, production and regular cleaning procedures (e.g. Cleaning in Place). While the planned shut-down of the whole plant for maintenance and 'Stoomwezen' inspection might take place every X years for Y-Z weeks, the unexpected plant outages may add up to approximately 20 days per year. Regular maintenance or inspection shall not entail the total shut-down of the plant. It should be noted that the plant gets its feed directly from plant XXXXX, a shutdown of the latter will generate a shutdown of the subject plant. This effect has been taken into account in the annual availability.

### 2.4.2. Sparing policy

#### 2.4.2.1. Vital services

Vital services are those which in the event of failure could cause an unsafe condition of the installation, jeopardising life and/or equipment. Running equipment in vital service shall be 100 % spared with one of the power sources being electric drive whilst the other motive source should be steam, diesel or gas turbine. The spare equipment shall always be available for operation and therefore a third facility should be available to allow essential maintenance to be carried out while the plant remains onstream. Vital services will include:

- Safeguarding devices (XPV's) for S1 situations

- Pressure relief systems (two PSV's when must be cleaned after use)

- Instrument air supply (ring line)

- Firewater supply (ring line)

- Electrical supply to control room

- Electrical supply to instruments being part of S1 safety loop

Note:   In general there will not be installed two pressure relieving devices, the second being a back-up for the first. However this is required when it is expected that the relief valve will not re-open easily after closure, this may be caused by a sticky product. A second relieving device may be dictated by risk analysis.

### 2.4.2.2. Essential services

The essential services are those which, in the event of their failure, would result in the plant not being available to operate at 100% capacity and make it impossible to obtain the required availability between planned shut-downs.

Normal running equipment in essential service shall be 100 % spared. The spare unit driver does not require an alternative power source. If more than one piece of equipment, say n units, are required to obtain 100% design capacity, n+1 units shall be installed.

- It may be agreed upon not to install a second pump, but have a complete spare pump and spare motor in stock. This can be done when it is guaranteed that the change can be made in a couple of hours.

Other equipment in essential service shall have adequate provision to ensure operation in accordance with the above definition.

- In some cases, however, i.e. sparing of expensive equipment, the economics may be overriding in sparing policy decisions. (e.g. extruders, compressors)

Essential services include:

- Boiler feed water treating and steam generation facilities

- Seal oil/Lube oil systems of major equipment

- Effluent treatment facilities   *(to be determined)*

- All process unit feed, reflux and product pumps

- Fuelgas supply

- Cooling water supply

### 2.4.2.3. Non-essential services :

Non-essential services are those which, in the event of failure for a limited time, would not impair production. Rotating equipment in non-essential service need not be spared. Non-essential equipment shall not have provisions for performing essential services.

### 2.5. Legal requirements and company requirements

The complete list of legal requirements applicable to this project will be defined in the Project specification. It will include requirements derived from the following laws:

- 'Wet Milieubeheer' (Environmental Protection Law)

- 'Stoomwet' (Rules for Pressure Vessels)

- 'Arbeidsomstandighedenwet' (Occupation Safety and Hazard Act)

- 'Wet verontreiniging oppervlaktewateren' (Water pollution Act)

- 'Bouwvergunning' (Building Permit)


Policies of *the WWTP Garmerwolde and RUG* management:

- Corporate Requirements and Guidelines and Operational Requirements

- 'Beleidsverklaring' (*WWTP Garmerwolde and RUG* Policy Statement)


## 2.6. Safety, health and environmental considerations


Careful consideration must be given to operability and safety under normal operation, turn down, start up, shutdown and emergency conditions.


### 2.6.1. Corporate Standards


Translate the Corporate Safety and Environmental policies into key design features. Anticipation of the likely Safety, Health and Environment (SHE) restrictions of the permit and *WWTP Garmerwolde and RUG* corporate standards is made in the process design. *WWTP Garmerwolde and RUG* requirements are among others the Corporate Requirements and Guidelines.


The major potential hazards will be identified using the following methods:

- Systematic process safety analysis (PSA: 'Process Safety Analysis') (Proces Veiligheids Analyse)).

- MCA analyses (Max. Credible Accident) to be based on plot plan, lay out and site.

- Risk analyses, effect calculations and damage calculations.

- Standard for dust prevention in the plastics industry NFPA 654-1975, NFPA-68.

- VDI directive for dust explosion.

- DOW F&E Index

The following design standards are to be met:

- Process Design Guide 3.1 "Pressure relieving devices" latest revision.

- For venting requirements, fire protection, evaporation losses, protection against ignitions (several sources), personal protection and design see relevant API-recommendations.

Designing for external fire condition shall be determined by mutual agreement between Engineering-Stamicarbon and owner. According to Corporate Requirements and Guidelines and API-reports all equipment shall be protected against overpressure i.e. also caused by external fire. However indiscriminately designing for external fire conditions has to be avoided by:

Thorough analysis of the cause and the source of the fire. Calculations must be made if the maximum pressure increase, due to external fire, may exceed the design pressure regarding the amount of burning component present.

The contractor shall establish the scope and standard in co-operation with *WWTP Garmerwolde and RUG* for:

* drain systems

* fire protection

* fire proofing, insulation and/or coating

* emergency showers, eye showers

### 2.6.2. Asbestos

Asbestos or composites containing asbestos will not be used in this plant.

### 2.6.3. Noise

The maximum allowable noise level of individual pieces of equipment shall be according to DIN 80 dB(A) at 1 meter distance, under all circumstances. However a noise level of less than 75 dB(A) at 1 meter is strongly preferred. The total noise level shall not exceed the so called site noise 'Contours'. For the noise 'Contours' reference is made to drawing XXXXX.

### 2.6.4. Energy conservation

- Energy and thermal integration aspects should be considered in relation with corporate philosophy and client standpoint or view.

- Pinch Analysis and Exergy Analysis might be applied to check the energy efficiency.

## 2.7. Process control philosophy

- For the key process parameters (only 5 to 10) 'Statistical Process Control' (SPC) must be applied when agreed upon with the client.

- DCS, model based process control, advanced process control systems should be assessed with regard to process optimisation, environmental pollution and product quality.

- Local panel, centralised or decentralised control of the plant must be considered.

- In an early design phase (feasibility/conceptual) the control philosophy should be regarded in respect with efficiency, quality and Safety, Health and Environmental requirements.

## 2.8. Overdesign factors

In the design of process-equipment, uncertainty factors in thermodynamic properties, design correlations and calculation methods are historically compensated for by 'overdesign factors'.

Overdesign should be used with caution, the use of indiscriminative arbitrary safety factors should be avoided.

The magnitude of the risk and consequences involved in a certain application will be reflected in the value of the appropriate safety factor. The justification of the overdesign of individual pieces of equipment will be made on the datasheets/duty-specifications.

For the following non critical equipment the overdesign has been agreed upon:

- pumps        10%   ( except the xxxxxx pump)          *(ETC)*

- For several streams in the material balance more than one condition will be shown for 'normal operation', and for 'design conditions'. In this latter balance overdesign factors have been applied on process uncertainties.

## 2.9. Fouling resistances for design

Fouling resistances shall be recorded explicitly, and shall be agreed with the client. The resistance values have to be selected according to the following priority schedule:

1.In the field measured specific values, under identical conditions;

2.Idem, under comparable conditions (c.q. same medium, different velocity, etc.);

3.Values based on guidelines applicable to a class of comparable media:

   - from corporate database or inhouse literature;

   - from preferred design standards i.e. HTRI, HTFS;

   - from different sources i.e.: TEMA, HEDH, VDI, other references.

For cooling water based on conditioned canalwater (viz. concentrated flocculated canalwater, full-conditioned with biofouling, corrosion and phosphate inhibitors) resistance values have to be taken from the report 'Richtwaarden voor vervuilings-coefficienten van behandeld koelwater', PT-RU/ RESEARCH N90.9397, oct.31 1990, grafiek bijlage 1C. The selected resistance value shall be in compliance with the cooling water conditioning programme and the effective linear velocity.

The conditioned cooling water shall be connected preferably to the tube side; the preferred velocity is 1.5 - 2 m/s and within this range as high as possible. If cooling water has to be connected to the shell-side, then an effective velocity, for definition see above mentioned report 'RESEARCH', of at least 0.7 m/s has to be pursued. According to report Research 91.9489 a fouling layer has to be taken into account when designing a shell-side cooling water heat exchanger.

In case of the conditioned river water, no flow-reducing control device(s) nor a bypass shall be installed in the cooling water stream. Throttling of the water flow can lead to:

- corrosion of carbon steel because of lack of corrosion inhibitors

- solid deposition and subsequent severe irreversible fouling;

- too high film temperatures and subsequent hydrolysis of phosphate, resulting in sludge deposition. The maximum allowed film temperature for this project is 50°C, this number should be used for a clean heat exchanger.

- chloride stress corrosion of austenitic stainless steel at elevated wall temperatures (>60 °C).

Use of coating at the tube side, to prevent fouling or corrosion, has to be checked with *WWTP Garmerwolde and RUG*.

The following fouling resistances will be used in this project:


| | | |
|---|---|---|
| Liquid process stream:A | 10000 | W/m$^2$ K |
| Vapour distillation column (clean ) | 6,700 - 10,000 | W/m$^2$ K |
| Steam 10,000 | W/m$^2$ K | |
| Demineralized water | 10,000 | W/m$^2$ K |
| Condensate, hot water | 10,000 | W/m$^2$ K |
| Chilled water | 10,000 | W/m$^2$ K |
| Brine   10,000 | W/m$^2$ K | |
| Untreated flocculated river water | 10,000 | W/m$^2$ K |

- Treated flocculated river water depends on method of treatment:

| | | |
|---|---|---|
| e.g. Cooling water | v = 1 m/s | 1667 W/m$^2$ K |
| v = 1.5 m/s | 3333 W/m$^2$ K | |
| v = 2 m/s | 5000 W/m$^2$ K | |
| plate heat exchanger (V > 1.5 m/s).......... | | W/m$^2$ K |
| spiral heat exchanger (V > 1.5 m/s).......... | | W/m$^2$ K |


## 2.10. Corrosion allowance


Basically corrosion allowance shall be granted in case of general corrosion attack. For critical process equipment, Engineering-Stamicarbon has to be consulted on this subject. Generally

the allowance shall not exceed 3 mm, for economical reasons. A more resistant construction material shall be selected when required, also considering the design lifetime. No corrosion allowance with respect to ambient (atmospheric) conditions shall be used.

All materials to be used for piping and equipment will be detailed in the Construction Material report, which is part of the Conceptual Process Design Package.

The corrosion allowance for utilities (equipment and piping):

| | |
|---|---|
| instrument air, mat. CS | : 0 (zero) mm |
| breathing air, mat. galvanised CS | : 0 (zero) mm |
| plant air, mat. CS | : 0 (zero) mm |
| nitrogen, mat. CS | : 0 (zero) mm |
| steam, mat. CS/alloy steel | : 0 (zero) mm |
| condensate, mat. CS | : 0 (zero) mm |
| cooling water, mat. CS | : 0 (zero) mm |
| demineralized water, mat. SS | : 0 (zero) mm |

The corrosion allowance for process streams will be 0 (zero) mm except for:

Fluid A, mat. CS                                                      : 0 (zero) mm

## 2.11. Economic criteria for optimisation of sub-systems

- An estimate of the production cost and preliminary economic analysis (pay-out time) including sensitivity analysis should be made in co-operation with the client.

For feasibility studies during the design the following prices (in Dutch guilders) will be used:

- (see editions of 'variabele verrekenprijzen Utilities' in order to obtain the prices).

Power :                          x.xx            Hfl/kWh

| | | | |
|---|---|---|---|
| LP steam (4 bar ) | : | x.xx | Hfl/t variable cost |
| MP steam (13 bar ) | : | xx.xx | Hfl/t variable cost |
| HP steam (27 bar ) | : | xx.xx | Hfl/t variable cost |
| natural gas | : | x.xx | Hfl/GJ |
| Potable water | : | x.xx | Hfl/t |
| canal water | : | x.xx | Hfl/t |
| demin. water | : | x.xx | Hfl/t |
| nitrogen | : | xx.xx | Hfl/t |
| plant air | : | x.xx | Hfl/t |
| instrument air | : | x.xx | Hfl/t |
| etc.  etc. | : | x.xx | Hfl/t |

## 2.12. Temperatures and pressures for mechanical design

Regarding temperatures and pressures for mechanical design of plant piping (excluding transmission lines outside battery limits) and equipment, reference is made to the latest revision of Process Design Guide 1.15: 'Determination of the design pressures and design temperatures'. The design conditions will be reported on the Equipment Design Condition Forms which are a part of the Conceptual Process Design Package.

## 3. GENERAL DESIGN DATA

### 3.1. Units of measurement

SI units shall be adhered to, and the use of the following specific units is preferred.

- pressure                      : bar  ($10^5$ N/m$^2$) absolute pressure unless stated otherwise

- flow               : kg/s, kg/h, m$^3$/s, m$^3$/h, Nm$^3$/s

- viscosity            : mPa.s

- power and heat flow     : Watt (W, kW)

- energy               : Joule (J, kJ)

- Nm$^3$ are defined at 0 °C and 1.01325 bar

### 3.2. Meteorological data (Limburg)

#### 3.2.1. Wind conditions

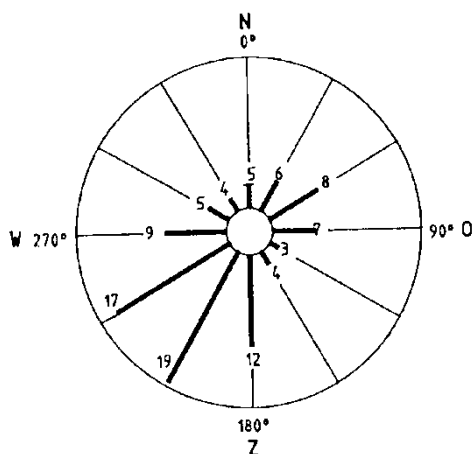Prevailing wind :  South West (see figure 3.1)

Figure 3.1 Compass-card for Beek (the Netherlands) detailing the occurrence of wind directions (in percentages). Data averaged over the period 1949 - 1970. Fluctuating wind conditions 1 %, no wind 2 %.

## 3.2.2. Wind speed

- For the design of structures, buildings etc. see the Project Specification.

- For the calculation of heat losses 10 m/s.

- For the calculation of gas dispersion in the atmosphere min. 2 m/s (Pasquill class F) for the

  MCA calculations.

## 3.2.3. Temperatures

In tanks, as caused by the radiation of the sun      : 25 °C

In tanks surrounded by a wall at approximate 2 m  : 30 °C

## 3.2.4. Air temperatures

Extreme max. dry bulb                                          : 35 °C

Minimum dry bulb                                          : -20 °C.

35 °C is exceeded during 10 minutes/year

30 °C is exceeded during 10 hours/year

## 3.2.5. Design air temperatures for equipment:

- Air compressor    - dry bulb     25 °C

        - wet bulb             18 °C

- Cooling tower     - dry bulb     25 °C

        - wet bulb             18 °C

- Air coolers                        27 °C     (27 °C is exceeded 44 hours per year)

- Air cooled turbine condensers    14°C      (14 °C is exceeded 2190 hours per year).

- Minimum air temperature       -20 °C

- air conditioning : according to HVAC specification.


### 3.2.6. Relative humidity

Average, summer            75 %

Design   - summer          85 %

          - winter          100 %


### 3.2.7. Barometric pressure

Maximum              1050 mbar

Minimum              950 mbar

Design                1030 mbar


### 3.2.8. Rain- and snowfall

Rain, maximum 0.8 mm/minute during 15 minutes (135 l/s/10.000 $m^2$ for 15 minutes)

Run off: 90 % on paved roads and roofs, 50% on unpaved roads.

Average annual rainfall 670 mm/year.

Average annual snowfall 300 mm/year.


### 3.2.9. Environmental conditions

The installations will be erected on *WWTP Garmerwolde and RUG* site at Garmerwolde, close to WWTP Garmerwolde. The ambient air is polluted with $NH_3$ , $SO_2$ , $CO_2$, nitrate, nitrous vapours and industrial dust. Copper or its alloys shall not be used, unless stated otherwise.