A COMPARATIVE STUDY FOR THE REMOVAL OF HUMIC ACIDS FROM POWER PLANT MAKE-UP WATERS

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DECLARATION BY CANDIDATE

I, Gerhard Gericke, declare that unless indicated, this dissertation is my own and that it has not been submitted for a degree at another University or Institution.

G Gericke

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DEDICATION

To Marinda, Corne-Mari, Simonne and Reinette

ABSTRACT

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GERHARD GERICKE

There is an ever-increasing need to improve the quality of make-up water to power plants. One area of research that has received a lot of attention in recent years is the question of the removal of natural organic matter from boiler feed-water. The sources and impacts of organic material have been discussed as well as the possible techniques to remove or reduce the levels of natural organic matter from surface waters used as make-up water. For this study, four treatment techniques were chosen to determine their efficacy in removing humic acid. These are: enhanced coagulation, photo-oxidation, chemical oxidation and anodic oxidation. Due to the lack of readily available analytical chromatographic techniques to identify and quantify the humic acid concentration of the model compound used, the methods for comparing the various treatment techniques were limited to total organic carbon, spectrophotometric and chemical oxygen demand analyses. The results showed that enhanced coagulation would still be the preferred method in removing natural organic matter from surface water until a cost effective alternative technique has been identified. However anodic oxidation showed potential as an efficient oxidation technique in reducing natural organic matter in surface water, but further research in this field needs to be undertaken to develop this technology into a full scale industrial process. The research will have to be supported by the development of suitable analytical techniques such as HPLC and LC/MS to facilitate the qualitative and quantitative studies of the complex humic acids and their oxidation by-products.

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GLOSSARY OF TERMS AND ABBREVIATIONS

ALARA	As low as reasonably achievable
Alum	Aluminium sulphate
Caustic	Sodium hydroxide solution
COD	Chemical oxygen demand
Demin water	Water treated by a demineralisation process
DOC	Dissolved organic carbon concentration
EPRI	Electrical Power Research Institute
NOM	Natural organic matter
OA	Oxygen absorbed
pH	The negative logarithm of the hydrogen ion activity measured at a defined temperature, usually at 25 0C
ppb	Parts per billion, (μg/l)
ppm	Parts per million, (mg/l)
TDS	Total dissolved solids
THM	Trihalomethane
TOC	Total organic carbon concentration
USEPA	United States Environmental Protection Agency
VGB	Vereinigung der Grosskraftwerksbetreiber

CHAPTER 1:

INTRODUCTION

Water treatment forms an integral part of thermal electric power generation (coal fired as well as nuclear power stations). There are generally two main water cycles associated with thermal power generation, namely the steam/water cycle that uses demin water for the production of steam and the cooling water circuit, which is used for condensing the steam back to water. The two cycles are isolated from each other and exchange heat via a condenser.

Power station make up water treatment plants have traditionally been designed to produce water of a very high quality (free from inorganic salts) by synthetic ion exchange resins. Raw water quality (mainly TDS, OA and silica) is the key factor in the design of the plant. Any deterioration of raw water quality during the life cycle of the plant, which is currently a South African and worldwide phenomenon, will inevitably have a negative impact on treatment plant performance and plant integrity. In order to meet the specifications of the water quality required for proper plant operation, an extra burden, as well as associated treatment costs, will therefore have to be placed on existing treatment processes to compensate for change in feed water quality.

Apart from increasing salt concentrations in raw waters, there are indications that NOM present in the water is also increasing. This is becoming a concern for industries requiring high purity water and a number of industries, including the power industry, have embarked on programmes to set a target value for TOC in demin water. Over the past few years, Eskom has studied alternative methods to reduce organic matter prior to demineralisation by optimising flocculation/coagulation processes. This research also included studies into advanced oxidation processes (catalysed UV, ozone and peroxide) and it was demonstrated that some degree of organic reduction could be achieved by employing these techniques.

Lowering the target value for TOC might have a negative impact on the costs of demineralised water production, especially if such a decision is not supported by scientific facts. An area that has been a topic of contention for quite some time is the fate of organic matter in steam/water circuits and the impact of these compounds and their breakdown products (organic acids and carbon dioxide) on materials of construction.

In this **chapter**, the water quality requirements and treatment processes as required for Eskom (the largest power utility in South Africa) are discussed, followed by the impact of NOM on these specifications and existing treatment processes.

1.1 DEMIN WATER SPECIFICATIONS AND TREATMENT PROCESSES EMPLOYED BY ESKOM

Modern high-pressure power generating plants require very high purity feed water to ensure plant integrity and to reduce the failure of plant components. Strict guidelines are enforced by the power industry with regard to make-up water quality (**Table 1.1**).[1]

Table 1.1: Demin water specifications for coal fired power stations measured at the mixed outlet

Parameter	**Target**	**Limit**
Turbidity (FTU)	<0.1	0.2
Specific conductivity (μS/cm @ 25 ^{0}C)	<0.08	0.1
Sodium (μg/l as Na^+)	<1	2
Silica (μg/l as SiO_2)	ALARA	10
Chloride (μg/l as Cl^-)	<1	2
Sulphate (μg/l as SO_4^{2-})	<1	2
TOC (μg/l as C)	100	250

These specifications were developed over the years by institutions such as EPRI and the VGB and were traditionally limited to the inorganic species only, but recently the specifications were broaden to also include TOC values. These values were however chosen as guidelines only with the intention that they could be increased or decreased as more knowledge is gained with regard to the impact of organic contamination in plant systems.[2,3,4,5,6]

Eskom power plants obtain their water as surface water from mainly three river systems, namely the Komati, Usuthu and Vaal Rivers. The Komati River supplies Arnot, Hendrina and Duvha Power Stations. Kendal, Kriel and Matla's main supply is from the Usuthu River and Lethabo and Tutuka Power Stations get their water from the Vaal River. These systems are interlinked to form what is known as a transfer scheme and it is possible for stations to also get water blends from the various sources, however this is more the exception than the norm and is determined mainly by dam levels and conditions of severe drought.[7]

Various sources differs in quality (**Table 1.2**) and water treatment plants are designed with this in mind.

Table 1.2: Average water quality from the Komati, Usuthu and Vaal rivers

Parameter		**Komati River**	**Usuthu River**	**Vaal River**
Turbidity	(FTU)	20.7	1.7	88.2
pH	(@ 25 ^{0}C)	8.06	8.55	7.93
Specific conductivity	(µS/cm @ 25 ^{0}C)	164	59	187
Sodium	(mg/l as Na^+)	7.35	4.5	12.21
Potassium	(mg/l as K^+)	1.23	2.0	4.02
Calcium	(mg/l as $CaCO_3$)	11	12	37
Magnesium	(mg/l as $CaCO_3$)	10	10	36
Total hardness	(mg/l as $CaCO_3$)	21	22	73
Total alkalinity	(mg/l as $CaCO_3$)	66.8	19	65
Chloride	(mg/l as Cl^-)	5.52	3.4	6.1
Sulphate	(mg/l as SO_4^{2-})	12.36	5.8	11.9
Nitrate/Nitrite	(mg/l as N)	0.11	0.10	1.5
Phosphate	(mg/l as N)	0.15	0.2	0.2
Silica	(mg/l as SiO_2)	7.6	1.2	23
OA	(mg/l O_2)	10.1	2.3	15
TOC	(mg/l as C)	4.8	5.9	5.2

A typical water treatment plant at Eskom power stations is shown in **Figure 1.1**. The exception to the rule is the Koeberg Nuclear Power Station that receives potable water from the Cape Metropoliton Council, which is then further treated on site to produce demin water.

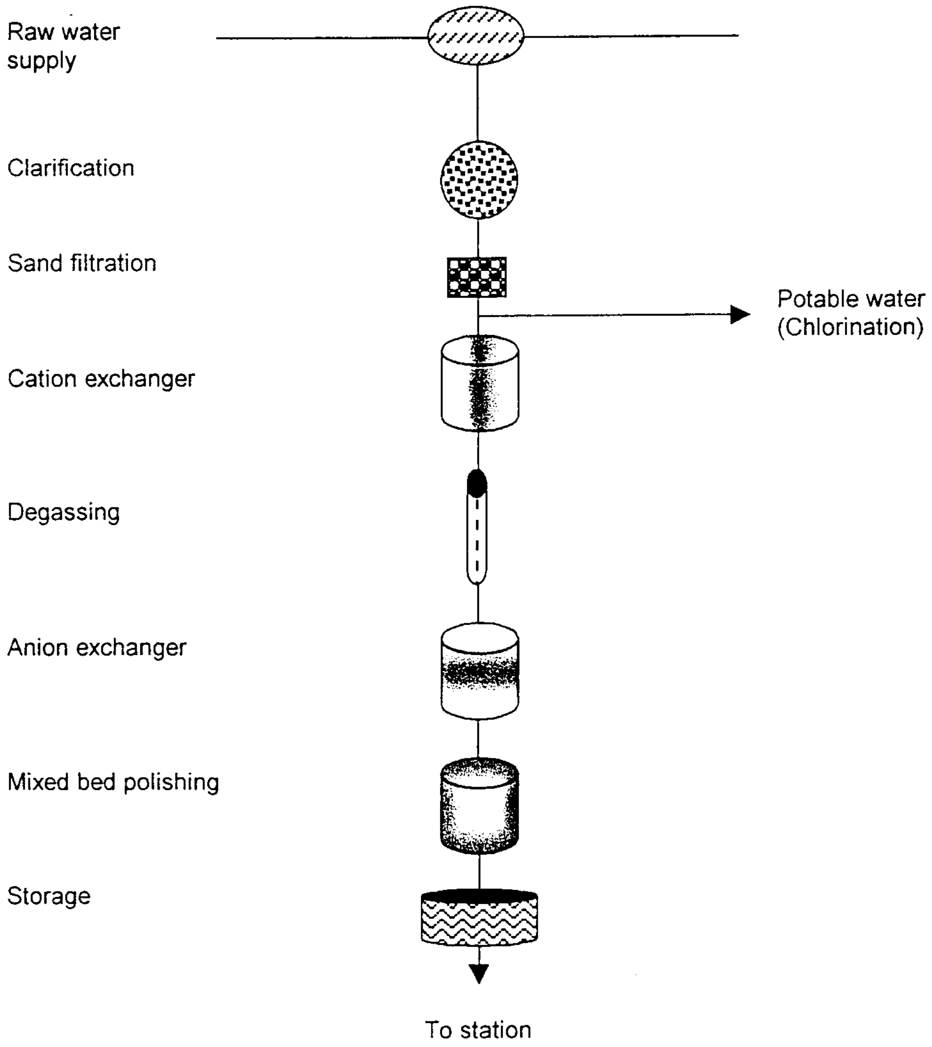


Figure 1.1: Typical water treatment plant employed at Eskom power stations

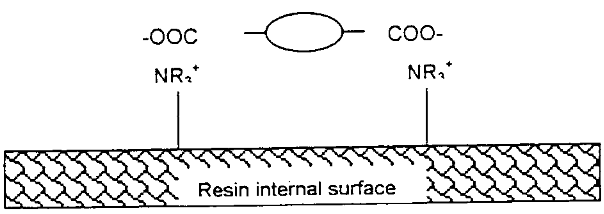
These treatment plants are primarily designed to:

- Firstly remove the turbidity (suspended solids) from the raw water by flocculation and filtration and
- Secondly, to remove the dissolved or ionic inorganic and organic species from the water by demineralisation.

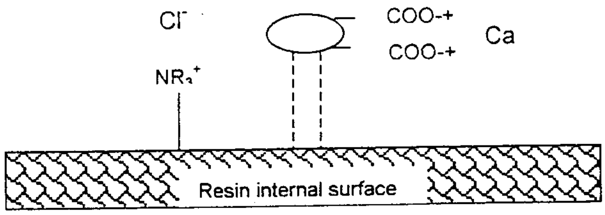
1.2 IMPACT OF NOM ON DEMINERALISATION PROCESSES

Although water demineralisation processes can cope very well with the removal of ionic inorganic compounds from raw water, the removal of organic species poses a greater problem. Most demineralisation processes can remove organics to a certain degree, but fouling of the anion exchange resin (reversible as well as irreversible fouling) normally occurs during this process.[8,9,10]

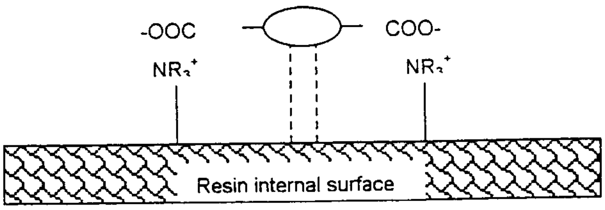
The majority of NOM present in natural waters is acidic in nature and is therefore only partly removed by cation exchange resins. These compounds are however strongly absorbed by anion exchange resins. It has been postulated that the removal of organic compounds by anion exchange resins can take place by either electrostatic forces and ion exchange or adsorption onto the resin matrix via van der Waal's forces or a combination of the two mechanisms (**Figure 1.2**).[9,11]



(1) Removal by ion exchange



(2) Removal by van der Waals forces



(3) Removal by both mechanisms

Figure 1.2: Various mechanisms for the removal of organic matter by ion exchange

During the regeneration process (caustic for anion exchange resin) the organic compounds are not completely removed due to the high affinity of the resin for the organic molecules. Gradual fouling of the resin takes place over a period of time and the resin starts to show the following symptoms:[8,9]

- The rinse water requirements increase,
- The carboxyl groups of the organic compounds interact with the Na^+ ion of the caustic to form sodium carboxylate (Figure 2.2) which eventually hydrolyses back to the free acid releasing sodium ions into the product water,
- Gradual increase in product water conductivity and decrease in pH due to organic acid leakage,
- Gradual silica leakage,
- A gradual decline in exchange capacity over a period of time and
- Shortened operating times.

To overcome this problem, caustic brine washes need to be carried out from time to time and the frequency of these cleanup procedures will increase with increasing fouling levels.

The phenomenon of sodium and TOC leakage from fouled anion exchange resin can clearly be seen from results that were obtained from a demineralisation unit at Matimba Power Station which had a design specification of 9 Ml (**Figures 1.3 and 1.4**).

Figure 3: Sodium leakage levels from various stages in the demineralisation proce

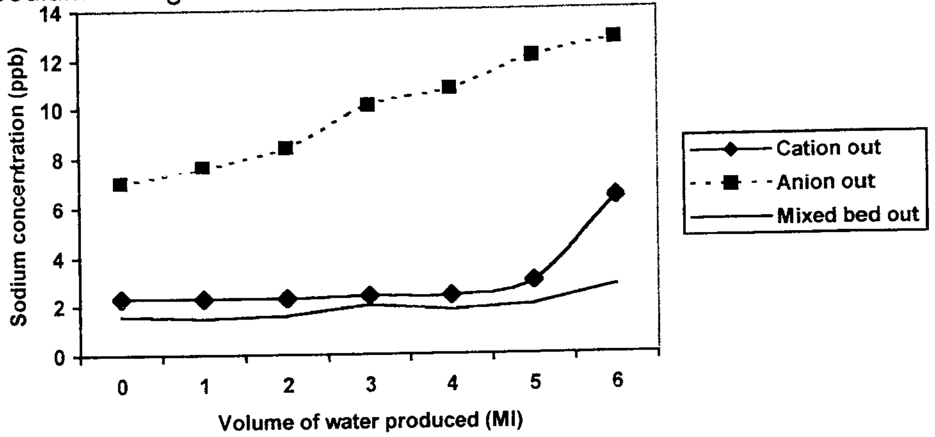


Figure 1.3: Sodium leakage levels from various stages in the demin process

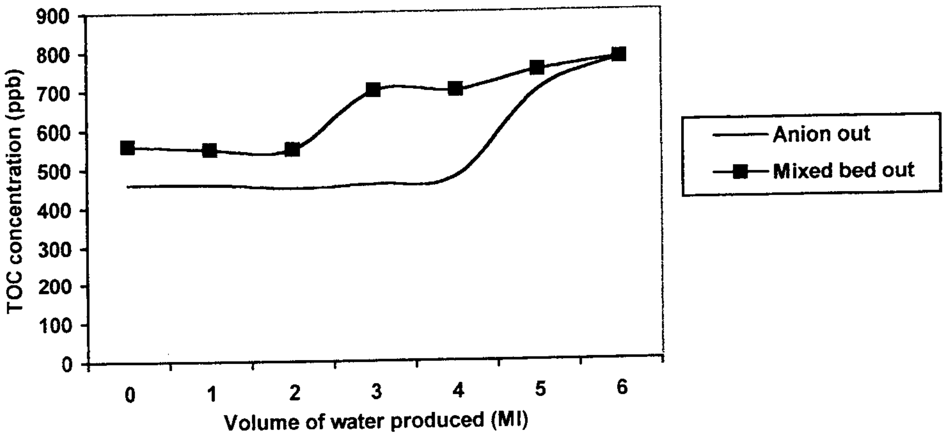


Figure 1.4: TOC leakage levels from various stages in the demin process

Those organics that are not removed (usually colloids), normally find their way into the steam/water circuit where they are decomposed through thermo-hydrolytic processes into carbon dioxide, short chain organic acids and inorganic species associated with the original organic compounds.[8,9] The impact of these transformations will be discussed in more detail in the following **section**.

1.3 THE FATE OF ORGANICS IN STEAM/WATER CYCLES

Owing to the high operating temperatures and pressures, there is an ever-increasing need to maintain the highest purity in the cycle fluid of modern power plants. In addition to the minimisation of inorganic impurities in the steam/water cycle, it has been recognised that the presence of organic compounds can contribute to the impurities in the power plant cycle chemistry.[12,13,14,15,16] Inorganic species can typically be present in the steam at concentrations in the very low ppb range whereas organic species at concentrations near 100 ppb have been reported.[12]

There are a large number of possible sources and pathways through which organic matter can enter the steam/water cycle of a power plant:

- Make up water,
- Ion exchange resin,
- Condenser inleakage,
- Pre-operational preservatives,
- Bacteria,
- Lubricating oil,
- Water treatment and
- Chemical cleaning.

Of all these sources, the raw water is the most likely source of contamination. Ion exchange resin can produce water that appears to be very pure from a conductivity measurement point of view, however most organic compounds show little or no electric conductance. The product water can still be polluted with organic contamination as discussed under **Section 1.2**.

It is generally accepted that organic matter will undergo thermal decomposition upon entering the steam/water circuit forming carbon dioxide and lower molecular weight organic acids. Superheated steam often contains low concentrations of volatile acids which can range from sub-ppb to ppb levels.[4,5,6,15,17,18,19,20,21]

In many cases inorganic compounds associated with the organic molecules will also be released in the form of inorganic acids. Organics in the raw water for instance, will react with chlorine during the treatment process forming halogenated organic compounds that are not removed by the ion exchange process. When decomposed, these organics will not only form the lower molecular weight organic acids and carbon dioxide, but also hydrochloric acid. This will give rise to a lowering of the pH and increase in conductivity in the regions of first condensate formation on the low pressure stage of the turbine.[18,19] It is these regions that are more susceptible to acidic attack.

Although steam/water circuits are operated at an alkaline pH level through the addition of ammonia (pH 8.9-9.2), localised corrosion in the turbine can occur in the region of first condensation (the so-called Wilson line). The first condensation "washes" all volatile impurities out of the steam, provided that the distribution coefficients of these impurities between the liquid phase and steam phase are small. Hydrochloric acid, sulphuric acid, acetic acid, silicic acid etc have low distribution coefficients and hydrochloric acid concentrations as high as 20 % have been reported in water droplets present in the first condensate. The distribution coefficient of the ammonia is such that it stays in the steam phase and is therefore not able to effectively neutralise these acids.[17,19]

Although most organic acids are relatively weak acids (weaker than inorganic acids), they are sufficiently ionised to corrode certain metals. *Bodmer*[17] has shown how a mixture of organic acids (including acetic acid) has contributed to stress corrosion cracking of a 60 MW_e turbine. The organic acids were breakdown products originating from the NOM present in the surface water that was used for demin production.

To illustrate the breakdown products that could be derived from demin water, a sample of demin water from Kriel Power Station was subjected to photocatalytic decomposition. Ion chromatographic analyses, for which the results are given in **Table 1.3**, were performed on the sample before and after oxidation.[21]

Table 1.3: Increase in ionic species concentration after photocatalytic oxidation of demineralised water

IONIC SPECIES	CONCENTRATION PRIOR TO OXIDATION (ppb)	CONCENTRATION AFTER OXIDATION (ppb)
Chloride	8	24
Nitrite	<0.1	<0.1
Nitrate	0.2	30
Bromide	<0.1	2
Sulphate	6	17
Oxalate	<0.1	18

There was a marked increase in the concentrations of the chloride, nitrate and sulphate concentrations after oxidation. These ions were associated with the organic compounds, but were undetected by standard chemical techniques.

Further evidence of organic breakdown under pressure and temperature was collected from Kendal Power Station, which has a history of TOC related problems since commissioning. The following observations were made:

- Polysaccharides originating from algal and cellular material and which could be associated with amino acids and proteins are present in the raw water,
- The polysaccharides have a negative influence on the performance of the demineralisation plant's ability to remove TOC (even after a brine wash) although the feed water to the plant has a relatively low TOC concentration (**Table 1.4**) and
- A relatively high TOC concentration in the superheated steam which was accompanied with a high cation conductivity.

Table 1.4: TOC removal before and after brine wash of ion exchange resin at Kendal Power Station

SAMPLE POINT	TOC BEFORE BRINE (ppb)	TOC AFTER BRINE (ppb)
Cation inlet	1230	1400
Cation outlet	1340	1390
Weak base outlet	1170	571
Strong base outlet	496	385
Mixed bed outlet	481	380

The brine treatment included a brine wash of the mixed bed, but as the results in **Table 1.4** indicate, the treatment had little effect on the performance of the mixed bed resin and an overall drop in TOC concentration of only 100 ppb could be achieved. This was mainly due to the marginal improvement in the performance of the strong base ion exchange resin. There was however a vast improvement in the performance of the weak base anion resin. From the results it is also clear that before the brine wash, loading of TOC onto the strong base occurred.

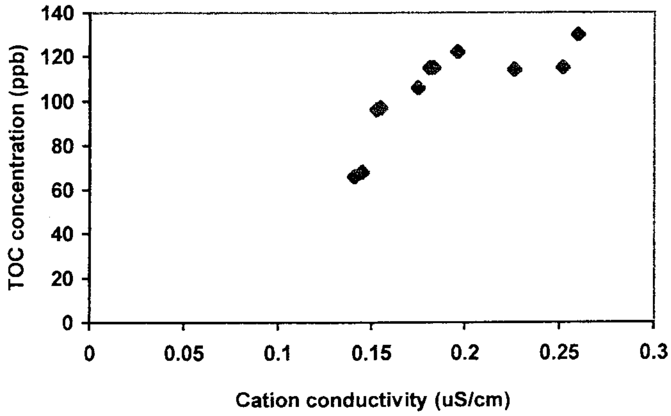


Figure 1.5: TOC concentration versus cation conductivity in superheated steam

From **Figure 1.5** it appears that there is a strong correlation between the cation conductivity and the TOC concentration in the superheated steam. Chloride and sulphate concentration for this particular situation was within specification and did not contribute significantly to the cation conductivity. Although no speciation of the TOC was carried out, it is safe to conclude that the organic compounds were sufficiently ionised as to impact on the cation conductivity.

1.4 THE NATURE AND ORIGIN OF NOM

NOM is present in all natural water sources and is as a result of the decay of vegetal matter. It is normally quantified and expressed as TOC, which is defined as the sum of the dissolved organic carbon (DOC), non-purgeable organic carbon (NPOC), particulate organic carbon (POC) and volatile organic carbon (VOC) fractions.[12,22]

The DOC fraction consists of humic and fulvic acids (collectively known as humic substances and is the predominant fraction of NOM), which are high molecular polyfunctional weak organic acids.[9] Humic substances are responsible for the brown or yellow colour in surface waters containing high levels of NOM (10-30 mg/l C). By definition, DOC is classified as that fraction of humic substances that can pass through a 0.45 μm filter. They contribute to 5-10 % of all anionic species in natural waters and their anionic character is due to the dissociation of carboxylic acid groups. Calcium and sodium ions are normally the counterions associated with the negative groups. When phenolic groups are present, metal ions can chelate or bond to the structure.[23] Humic substances can be divided into three main groups of organic compounds:[24]

- *Humic acid*: that fraction of humic substances that is not soluble in water under acidic conditions (pH < 2.0),
- *Fulvic acid:* that fraction that is soluble in water under all pH conditions and finally
- *Humin:* That fraction that is not soluble in water at any pH level.

The presence of humic substances in natural waters is undesirable for a number of reasons:[23]

- They possess ion exchange properties,
- They can act as a transport mechanism for toxic, water insoluble compounds,
- They react with chlorine to form chlorinated organic compounds such as THM's,
- They stabilise dispersed and colloidal particles during coagulation processes and
- They can precipitate in water distribution systems.

The presence of organic compounds can therefore, based on the above, have a major impact on the performance of a water treatment plant.

CHAPTER 2:

NOM REMOVAL TECHNIQUES

The levels of organic matter in water can be minimised by either removal or destruction. The removal of organics can be achieved through processes such as adsorption, separation and sedimentation and include technologies such as:

- Flocculation and clarification,
- Membrane processes,
- Ion exchange,
- Filtration and
- Activated carbon.

The destruction of organic matter is normally achieved through oxidation (catalytic, oxidation agents or thermal) processes which include technologies such as:

- Ozonation (O_3),
- Hydrogen peroxide (H_2O_2),
- Sonochemistry,
- Photocatalytic oxidation,
- Supercritical water oxidation and
- Anodic oxidation.

All of the aforementioned techniques can either be employed on their own or can be used in combination with each other. For the purposes of this study, the following techniques were chosen to compare their efficacy in removing/minimising a model humic substance from water:

- Coagulation and flocculation,
- Photochemical oxidation,
- H_2O_2 oxidation and
- Anodic oxidation.

This **chapter** will describe each one of the selected technologies in more detail.

2.1 COAGULATION AND FLOCCULATION

2.1.1 Basic principles of coagulation and flocculation

The coagulation and flocculation treatment is normally employed where suspended solids (turbidity) need to be removed from water. This in principle, involves the addition of chemicals (coagulants) to the water with rapid mixing and the settling of the flocs (larger particles) under gravity to produce a lower turbidity water.[26,27]

Suspended particles or colloids in water normally carry a negative electrical charge, Zeta potential (the measure of the force that indicates how closely particles can approach each other), which keeps the particles apart. These particles or colloids also have van der Waal's forces acting between them that tend to pull the particles together. As long as the Zeta potential is greater than the van der Waal's forces, the particles will stay in suspension. If, on the other hand, the van der Waal's forces exceed the Zeta potential, the suspended matter will be attracted to each other and combine to form larger, heavier particles (the flocs) that can grow in size and eventually sink to the bottom of the containment.[26,27,28]

Due to the negative character of the suspended matter, coagulant chemicals are invariably positively charged metal ions that destabilise the net charge on the particles, forcing them to be attracted to each other. The metal ions commonly used in water treatment are the sulphate and chloride salts of trivalent aluminium (Al^{3+}) and iron (Fe^{3+}).[26,28]

Since alum is more commonly used in water treatment, its interaction on suspended matter will be considered.[27,28,29] When alum is added to the water to be treated, it will undergo hydrolysis to form a series of multivalent hydrous oxide species (a similar scheme exists for Fe^{3+}):

$$[Al(H_2O)_6]^{3+} + H_2O \Leftrightarrow [Al(H_2O)_5OH]^{2+} + H_3O^{3+}$$

$$[Al(H_2O)_5OH]^{2+} + H_2O \Leftrightarrow [Al(H_2O)_4(OH)_2]^{+} + H_3O^{3+}$$

This reaction will continue until the neutral species, $[Al(H_2O)_3(OH)_3]$ has been formed, which is insoluble in water. The positively charged hydrated aluminium ions can thus effectively destabilise the negative charge on the suspended matter. This normally occurs within one or two seconds after the chemical has been added to the water. At this point, the particles start to come together to form tiny floc particles, which eventually grow to form the larger heavier flocs that settle out. The process is generally affected by the alkalinity of the water, since the available Al^{3+} concentration depends on the hydroxyl portion of the compounds that constitutes the alkalinity. In low alkalinity waters, the alkalinity might have to be increased prior to the flocculation process to increase efficiency.

The process can be further enhanced by the addition of coagulant aids such as organic polymers (cationic, anionic and non-ionic) which help in the formation of heavier, more settleable flocs. The most common of these are the cationic polymers for the obvious reason to assist in the destabilisation of the negative charge that exists on the suspended matter.

2.1.2 The role of coagulation and flocculation in the removal of NOM

Although the coagulation/flocculation/clarification process has traditionally been used to clarify turbid water, it has also been recognised to remove organic matter from raw water to a large degree.[27,28,30,31,32,33,34] In this application, the process is termed as *"Enhanced coagulation"* and has been referred to by the USEPA as the *"Best generally available technique"* in the reduction of THM formation which forms as a result of the reaction between chlorine and the residual organic matter in the water.[28] The process involves the addition of excess dosing of coagulant chemicals, over and above the amount required to achieve optimum clarification, in order to reduce NOM to a minimum.

The NOM removal process by enhanced coagulation, according to *Jacangelo et al*[30], involves:

- Colloid destabilisation accompanied by charge neutralisation,
- Precipitation and
- Coprecipitation.

NOM comprises particulate matter and DOC. The particulate matter will be removed by colloid destabilisation whilst the DOC portion is removed by precipitation or coprecipitation. The authors also proposed a model by which the NOM coagulation process can be characterised (**Table 2.1**).

From the model, it is clear that NOM characterisation, treatment selection and plant optimisation are the key elements in the effective removal of NOM by coagulation and flocculation.

Rebhun et al[34] demonsrated that NOM promotes floc formation of mineral particulates and vice versa when the flocculant demand is determined by the NOM present. In a publication by *Croue et al*[32] it was shown that 32 to 47 % of DOC (measured by UV absorbance at 254 nm) could be removed by coagulation and flocculation. More recent work indicated that removal levels in excess of 70 % could be achieved.[35] for TOC levels of up to 10 ppm. The reason for the improvement in the removal of the DOC levels is not known at this stage, however it is thought be due to the improvement of water treatment chemicals, NOM characteristics or improved plant optimisation or a combination of these factors.

Table 2.1: Conceptual model of NOM coagulation

Parameter	Results
Interaction	
NOM + H^+	Precipitation of humic acid if pH = 1; enhanced coagulation effective up to a point beyond which protons inhibit interaction between NOM and metal hydrolysis products, render NOM molecules smaller in size and more hydrophobic, enhance GAC adsorption
NOM + metal hydrolysis products	Precipitation of NOM whose solubility is exceeded; adsorption of NOM on metal hydroxide solids; some anions (OH^- and SO_4^{2-}) interfere by competing for sites; cations able to bind to NOM can replace metal hydrolysis products, reducing coagulant dosing demand
NOM + cation	Precipitation of NOM whose solubility is exceeded; reduction in the concentration of metal hydrolysis products needed for precipitation or coagulation
NOM characteristic	
Increased hydrophobicity	Increased removal
More binding sites per molecule	Increased removal; greater coagulant demand; sharper increase in removal as coagulant dosage increases
Higher molecular weight	Increased removal
Increased heterogeneity	A more gradual increase in removal as dosage increases
Treatment	
Coagulation	Remove larger molecular weight and more hydrophobic NOM; extended activated carbon bed life, reduced gel formation on membranes , reduced oxidant demand
Ozonation-oxidation	Decrease hydrophobicity, decrease molecular weight; could hinder or assist coagulation
Softening	Removes much of the coagulable NOM by precipitation and co-precipitation

2.2 PHOTOCATALYTIC OXIDATION

The use of photocatalytic processes for the oxidation of organic pollutants and for the disinfection of potable water is becoming a popular technology in water treatment. The process generally involves the formation of the highly reactive hydroxyl radical (OH•). The OH• radical has a much stronger oxidising potential compared to other more common oxidising agents (**Table 2.2**) and is second in reactivity when compared to fluorine.[36]

Table 2.2: Comparative oxidation potentials

Species	Volts
Fluoride	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Hypochlorous acid	1.5
Chlorine dioxide	1.5
Chlorine	1.4
Oxygen	1.2

The photocatalytic process occurs during the excitation of an active surface by photo-radiation. During the process electrons are transferred from the valence band to the conductance band of light active species. This transfer of an electron leaves a hole (h+) in the valence band and subsequently creates a negative charge (e') in conductance band (**Figure 2.2**). The separation between the highest energy level in the valence band and the lowest energy level in the conductance band is known as the band gap. The band gap corresponds to the threshold wavelength (minimum photo energy) at which promotion of the electron will take place. The formation of the h+/e' pair results in the creation of a redox reaction, providing that the reaction occurs prior to the electron back transfer.[37,36]

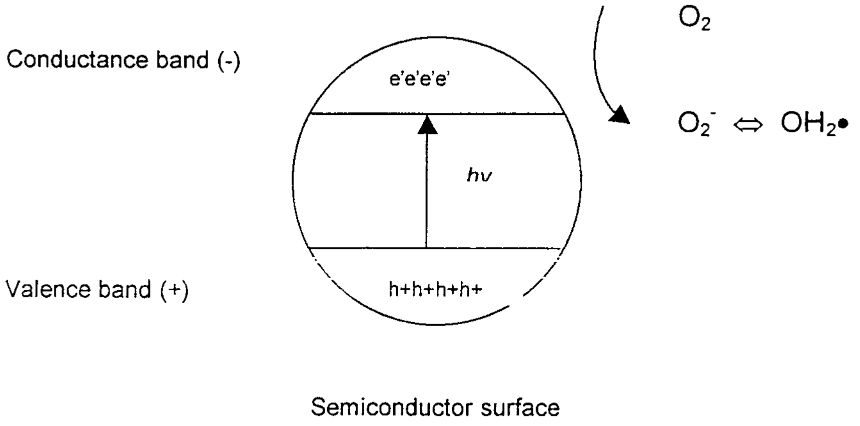


Figure 2.2: A typical semiconductor particle cell

Oxidation of a suitable donor will take place at the holes or valence band while the reduction of a species will take place at the conductance band.

Figure 2.2 illustrates how the dissolved oxygen in the water can take up the electrons at the conductance band to form a superoxide ion (O_2^-) which will readily convert in the water to the OH• radical.[38] Many organic compounds have redox potentials that are higher than the valence band edge of most semiconductors and they can therefore act as electron donors at the valence band region where they will be oxidised. It is this characteristic of organic compounds that makes photocatalytic oxidation a suitable technique for the destruction of undesirable organics.[38,39]

A large number of metal oxide coatings can be used to create the active surface, however titanium dioxide (TiO_2) powders have proven to be quite successful for the treatment of organically polluted water and air. The wavelength most commonly used is in the UV range. [37,38,39,40,41]

Although numerous kinetic equations have been proposed for the oxidation rates of the various pollutants, it has been recognised that there are number of factors that influence the reaction mechanisms and rate constants. Some of these include:[38]

- The rate of photo absorption at a given wavelength,
- The quantum yield of h^+/e^- generation,
- The rate of recombination of electrons and holes,
- The number of active sites and
- The lifetime of the radicals.

Based on these uncertainties, studies are still underway to determine the exact pathways by which most of these compounds are being oxidised. As the purpose of this **study** is not to determine the mechanisms and pathways of the various oxidation processes, a simplified approach will be adopted.

2.2.2 Application of photocatalysis in the oxidation of organic matter in water

Organic contamination in water has traditionally been removed by separation processes such as:

- Adsorption by activated carbon,
- Ion exchange,
- Air stripping and
- Flocculation.

However, these technologies suffer from the disadvantage that they merely transfer the organic compounds from one phase to another, raising the issue of how to dispose of the waste. Oxidation or mineralisation of the organics on the other hand, results in the formation of CO_2, water and small amounts of acids. A further advantage of photocatalytic oxidation of organic pollutants is that the process operates at or near ambient temperature and pressure.[42]

The mineralisation or decomposition of a large number of organic compounds has already been studied and a summary of the results has been published by *Pichat*.[38]

These compounds include:

- Alkanes, alkenes and halogenated derivatives,
- Alcohols, aldehydes, ketones, ethers and esters,
- Substituted aromatic compounds,
- Pyridine
- Chlorinated biphenyls,
- Dyes and
- Surfactants.

Halogens, sulphur and bromide are converted to the corresponding mineral acids. (See **Section 1.3, Table 1.3**).

As has been shown previously (**Section 2.2.1, Figure 2.2**) the conductance band reaction (reduction) with oxygen and water yields the OH• radical. A very simplified mechanism for both the conductance band and valence band reactions has been described by *Pichat*:[39]

$O_2^{-\bullet} + H^+$ (from water dissociation) $\Leftrightarrow HO_2\bullet$ ($pK_a = 4.8$)
$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
$H_2O_2 + O_2^{-}\bullet \rightarrow OH\bullet + OH^- + O_2$
$H_2O_2 + e' \rightarrow OH\bullet + OH^-$

(It should be noted that this reaction is pH dependant.).

The valence band reaction (oxidation) has been described by the following reaction:

$$H_2O + h^+ \rightarrow OH\bullet + H^+$$
$$OH^- + h^+ \rightarrow OH\bullet$$

Based on the above, two further simplified versions of the oxidation/mineralisation of organic compounds by photocatalysis, which has been demonstrated by *Anderson*[43] and *Kerzhentsev et al*[44] respectively, are given:

$$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3CHO_2 \rightarrow CO_2$$

$$C_9H_{12}O_5NPS + 13/2O_2 \rightarrow 9CO_2 + 3H_2O + NO_3^- + SO_4^{2-} + H_2PO_4^- + 4H^+$$

2.3 ELECTROCHEMICAL OXIDATION

The electrochemical oxidation of aqueous organic compounds comprises the oxidation of the organic material at the anode. This oxidation can lead to the complete mineralisation (to CO_2) of the material or a degree of mineralisation accompanied by the formation of new carbon containing compounds. It has been reported that the degree of TOC reduction by electrochemical methods is higher than that obtained by chemical oxidation techniques.[45,46] as with chemical oxidation techniques, the electrochemical oxidation technique also result in the formation of intermediate products.[47]

Comnellis et al[46] reported that the oxidation products formed during chemical and electrochemical oxidation are almost identical and concluded that both reactions occur via the same mechanism. The mechanism can be summarised as the electrophilic attack of the OH• radical on the organic compound or its oxidation products. The mechanism for the electrochemical oxidation process on the electrode surface involves the following three steps:

- Radical formation

  $2H_2O \rightarrow 2OH\bullet + 2H^+ + 2e'$

- The OH• radicals are adsorbed on the surface of the electrode where it reacts with the organic compound or with water to produce oxygen

  $Org + OH\bullet \rightarrow$ oxidation product *(Rate 1)* or

  $2OH\bullet \rightarrow H_2O + 1/2O_2$ *(Rate 2)*

- The adsorption of the organic compound on the electrode surface where it will be oxidised to CO_2

  $Org \rightarrow CO_2 + H_2O$ *(Rate 3)*

The rates 1 to 3 strongly depends on the anode material used.

A number of electrolytic catalysts such as metal oxide have been identified that can oxidise organic matter through anodic oxidation, which include:[47,48]

- Titanium dioxide (TiO_2)
- Manganese dioxide (MnO_2)
- Cobalt oxide (Co_2O_3)
- Iron oxide (Fe_2O_3)
- Chrome oxide (Cr_2O_3)
- Copper oxide (CuO)
- Tin oxide (SnO_2)
- Antimony oxide (SbO_2)
- Vanadium pentoxide (V_2O_5) and
- Platinum and platinum alloys.

The efficiency of the electrochemical oxidation processes depends on a number of factors, which include:[49]

- Choice of electrode material,

- Current densities,
- Concentration of the pollutant,
- pH of the solution and
- Salt concentration of the solution.

CHAPTER 3:

EXPERIMENTAL METHODS

The humic acid substance considered for this study was a sodium salt of humic acid of which a 10 mg/l (as total C) solution of the substance was used in all experiments. The choice for the specific humic acid used was purely based on the fact that it was readily available. A 1000 ppm stock solution was prepared from the pure compound in demin water. All test solutions were diluted from the concentrated stock solution. This chapter will detail the steps followed in preparing the test solutions, the technologies employed to reduce the humic acid concentration and the analytical techniques used to determine the efficiency of the reduction process.

3.1 PREPARATION OF HUMIC ACID STOCK SOLUTION

1 g of the humic acid compound was dissolved in demin water and the undissolved phase was filtered off through a 0.45 μm membrane filter by means of vacuum filtration. The TOC concentration of the stock solution was determined by means of an ASTRO® 2100 TOC analyser. The sample was combusted at a temperature of 600 °C in a stream of ultra high purity oxygen (99.999 %). The carbon content was determined as CO_2 by an infra-red detector. All analyses were performed in triplicate.

A 10 mg/l as TOC humic acid working solution was prepared by the appropriate dilution of the stock solution in demin water.

3.2 CHARACTERISATION OF THE SOLID HUMIC SUBSTANCE

Approximately 100 mg of the solid humic acid substance was analysed by a LECO® CHN-1000 analyser to determine the % carbon, hydrogen and nitrogen composition of the substance. The sample was combusted at a temperature of 1050 ^{0}C in a stream of ultra pure (99,999%) oxygen. The liberated hydrogen and carbon (as CO_2) gases were analysed by an infra-red detector, whilst the nitrogen gas was analysed by a thermal conductive detector. A maximum detection time of 5 minutes was allowed. Five replicate samples were analysed.

A further sample of the compound was ashed at 900 °C and the residue was subjected to elemental analysis by means of a SEM.

3.3 ANALYSIS OF THE WORKING SOLUTION BY HPLC

Although the initial intention was to follow the removal or oxidation of the humic acid concentration and the formation of oxidation by-products by HPLC, no suitable method for this purpose could be found. It was recommended[50] to replace the HPLC method by spectrophotometric measurements at 254 nm and 430 nm. The costs for developing a suitable HPLC method would have been in the order of R 100 000 and no guarantee could be given that a fully validated method would be completed within one year. This had a major impact on the study as inferred methods of quantification had to be used and the identification and quantification of intermediate/by-products could not be carried out.

3.4 UV/VIS CALIBRATION CURVES

A series of calibration standards were prepared from the humic acid stock solution to cover a range from 0.5 to 10 ppm as TOC. A quartz glass sample cuvette with a pathlength of 1 cm was filled with the calibration solution. The absorbance of the solution was measured at a wavelength of 430 nm (visible range) and 254 nm (UV range) respectively using a Phillips® PU-8700 UV/Visible spectrophotometer. Two calibration curves were constructed. One each for the different wavelengths.[50,51]

3.5 COD ANALYSIS

A 10 000 ppm COD stock solution was prepared by dissolving 8.503 g of potassium hydrogen phthalate (dried at 120^0 C) in 1000 ml of demin water. From the stock solution a series of calibration standards ranging from 50 to 300 ppm were prepared. The standards and samples analyses were carried out by means of a SKALAR SAN+™ flow injection analyser equipped with a data handling station.

3.6 REDUCTION OF HUMIC ACID BY COAGULATION/FLOCCULATION

1 liter samples containing 10 ppm humic acid (as TOC) solution were poured into glass beakers, which were placed in a jar test apparatus (Phipps and Bird®) equipped with mechanical stirrers. Bentonite was added to each beaker to give a resultant turbidity of 20 NTU to resemble the turbidity of average surface water.

The flocculant (alum) was added at various concentrations to the water and the solution was "flash" mixed for 1 minute at about 120 rpm followed by a slow mix for 20 minutes to allow floc formation. The floc was allowed to settle without stirring for an additional 20 minutes. An aliquot was removed from just below the water line[52] for TOC, UV/VIS and COD analysis. The experiment was carried out in triplicate at three pH levels (pH = 4, pH = 7 and pH = 9).

3.7 REDUCTION OF HUMIC ACID BY PHOTO-OXIDATION

3.7.1 Photo-Oxidation By UV Alone

A 200 ml sample containing 10 mg/l humic acid (as TOC) was placed in a glass reactor (**Figure 3.1**) equipped with a low pressure UV lamp with wave length of 254 nm. Samples were exposed to the UV radiation for 5, 10 15 and 20 minute time periods whilst mechanically being stirred by a magnetic stirrer. At the end of the variuos time periods, the samples were analysed by UV/VIS, TOC and COD techniques. The experiment was carried out in triplicate at three pH levels (pH = 4, pH = 7 and pH = 9).

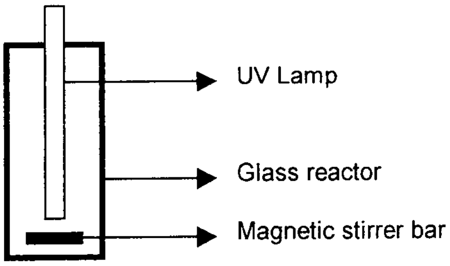


Figure 3.1: UV reactor

3.7.2 Photocatalytic Reduction Of Humic Acid

A similar procedure as described in **Section 3.5.1** was followed. In this case the inside of the glass reactor was covered with a TiO_2 coated mesh which acted as a catalyst.

3.8 CHEMICAL OXIDATION BY HYDROGEN PEROXIDE

H_2O_2 was added to 1 liter humic acid solution (10 mg/l as TOC) and mechanically stirred for until no residual H_2O_2 could be detected. The presence of H_2O_2 was determined by using MERCK™ test strips. The H_2O_2 concentration was varied between 10 and 200 ppm. The solution was finally analysed by UV/VIS, TOC and COD techniques. The experiment was carried out in triplicate at three pH levels (pH = 4, pH = 7 and pH = 9).

3.9 REDUCTION OF HUMIC ACID BY ANODIC OXIDATION

The humic acid solution was passed through an anodic oxidation chamber (**Figure 3.2**)[53] and the permeate was collected for TOC, UV/VIS and COD analyses. The anode was covered with a platinum catalyst and a constant potential of 2.5 volt was applied over the electrodes. The flow rate of the humic acid solution was varied between 100 and 400 $l/m^2/h$. The experiment was carried out in triplicate at three pH levels (pH = 4, pH = 7 and pH = 9).

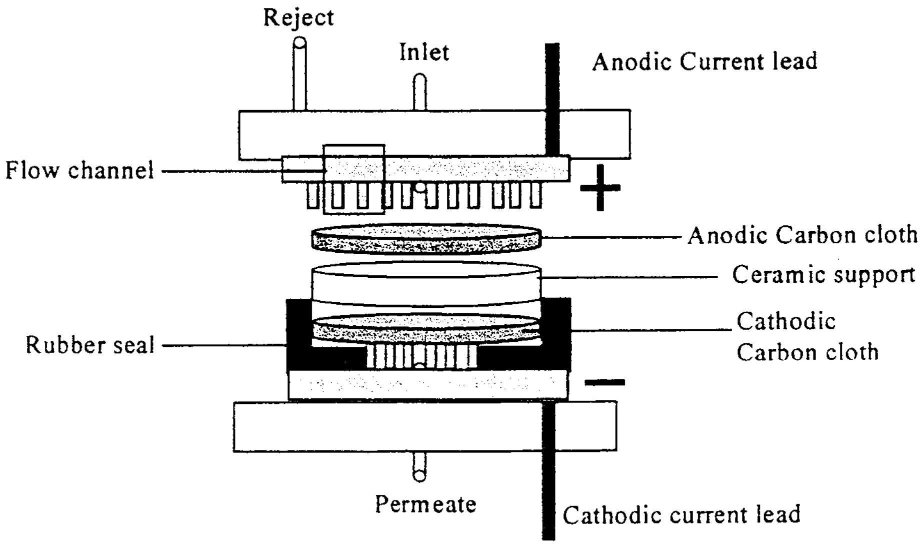


Figure 3.2: Schematic of flat electro-membrane reactor

CHAPTER 4:

RESULTS

In this **chapter** the results obtained will be given and discussed in detail.

4.1 CHARACTERISATION OF THE SOLID HUMIC SUBSTANCE

The major chemical composition of the solid humic and the results of the ash elemental analysis is given in **Tables 4.1** and **4.2** respectively.

Table 4.1: Major composition of the solid humic substance

Component	**Concentration (%)**
Inherent moisture	17.5
Ash	22.9
Carbon	39.9
Nitrogen	0.52
Hydrogen	2.57
Total sulphur	0.38
Oxygen	14.03
Carbonate (as CO_2)	2.20
Total	100.00

Table 4.2: Ash elemental analysis

Component	**Concentration (%)**
Silicon (as SiO_2)	11.8
Aluminium (as Al_2O_3)	3.7
Iron (as Fe_2O_3)	20.7
Titanium (as TiO_2)	0.5
Calcium (CaO)	12.17
Magnesium (MgO)	4.95
Sodium (as Na_2O)	37.1
Sulphur (as SO_3)	8.49
Managanese (as MnO)	0.31
Total	99.72

The insoluble phase observed during the preparation of the stock solution can be attributed to the high mineral content (ash) of the humic substance. This was the main reason for expressing the humic acid concentration in terms of TOC, as it was not possible to prepare accurate humic acid concentrations from the solid substance.

4.2 UV/VIS CALIBRATION CURVES

Figures 4.1 and **4.2** depict the calibration curves at 430 nm and 254 nm respectively. These curves were used to measure the residual humic acid concentrations after the various treatment techniques.

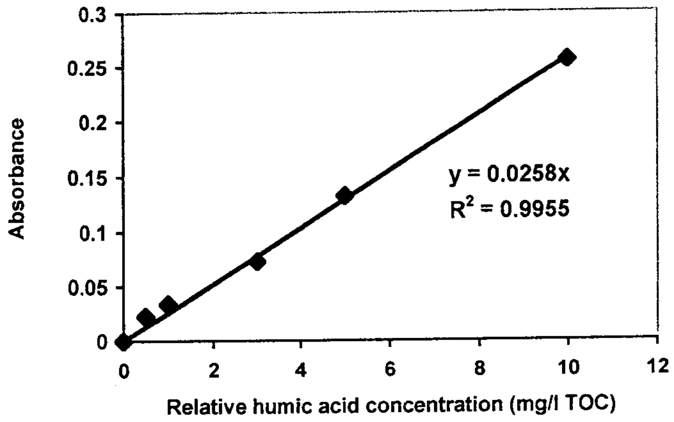


Figure 4.1: Humic acid calibration curve at 430 nm

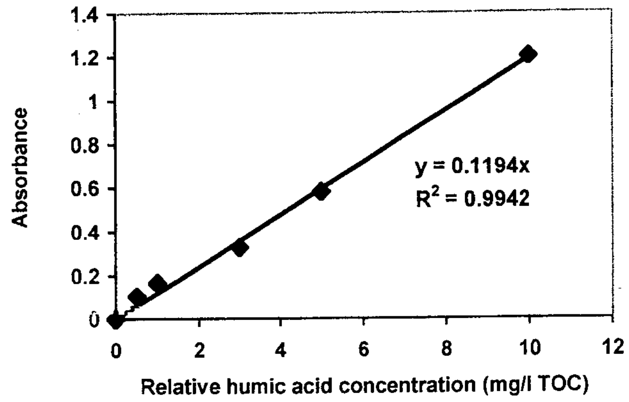


Figure 4.2: Humic acid calibration curve at 254 nm

Both calibration curves showed excellent linearity over the working range for which it was intended. The absorbances measured in the UV range (254 nm) were much more sensitive (38.8 times) than those obtained in the visible range (430 nm). This can be attributed to the fact that the absorbance at 254 nm is an indication of the total DOC whilst the measurement at 430 nm is more an indication of the colour of the solution due to the humic acid concentration.

4.3 HUMIC ACID REDUCTION BY FLOCCULATION

The results of the humic acid reduction terms of TOC, UV/VIS absorbance and COD by means of flocculation are depicted in **Figures 4.3** to **4.6**.

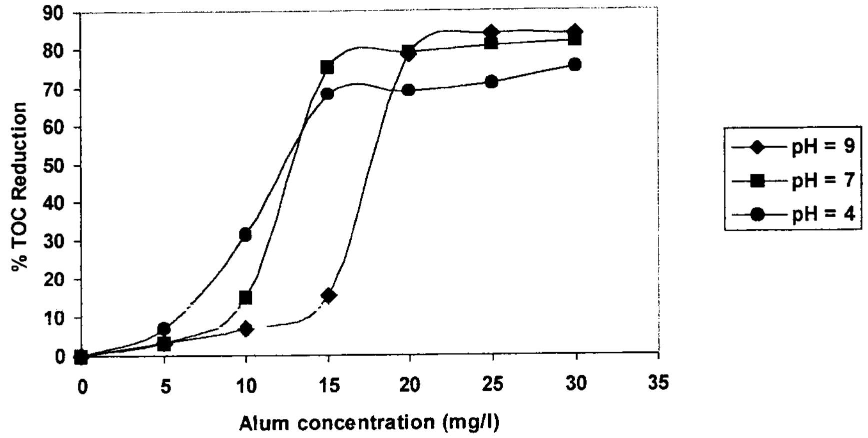


Figure 4.3: TOC reduction as a function of alum concentration at pH = 4, pH = 7 and pH = 9

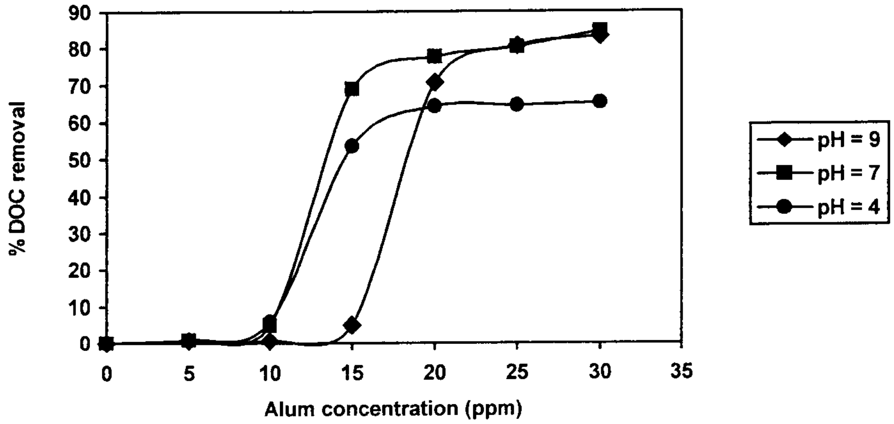


Figure 4.4: Humic acid reduction (DOC) as a function of alum concentration measured at 254 nm for solutions at pH = 4, pH = 7 and pH = 9

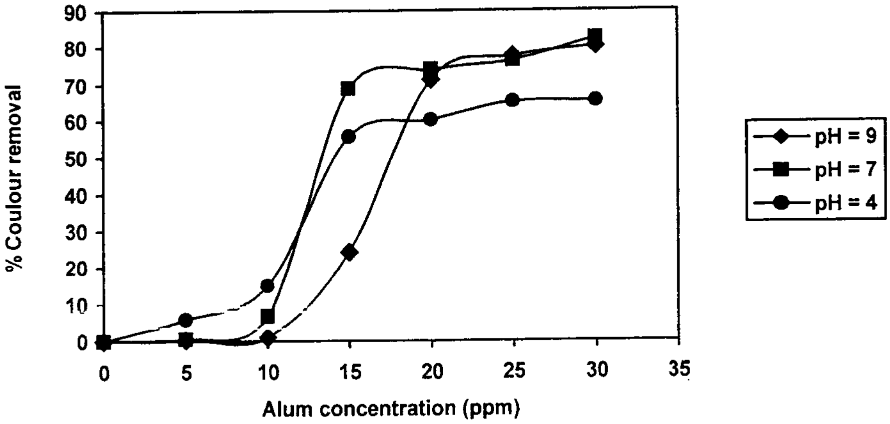


Figure 4.5: Humic acid reduction (colour) as a function of alum concentration measured at 430 nm for solutions at pH = 4, pH = 7 and pH = 9

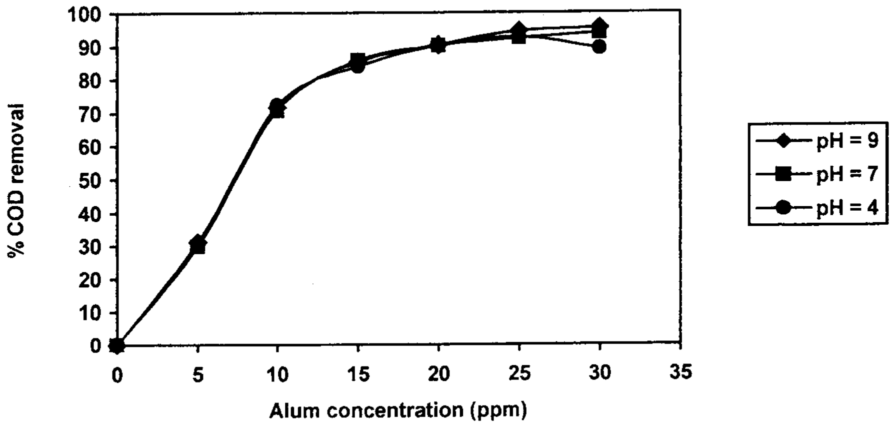


Figure 4.6: COD reduction as a function of alum concentration for solutions at pH = 4, pH = 7 and pH = 9

The TOC measurement and both spectrophotometric measurements showed that maximum humic acid removal was achieved at a neutral to alkaline pH range although the solution at a pH of 9 required more alum to show a significant change. This can be attributed to the fact that excess alum was initially required to neutralise the alkalinity before effective floc formation could be achieved. This observation is supported by results published by *Hecht*[54]. The significantly lower efficiency in humic acid removal at pH = 4 through the coagulation/flocculation process can most properly be attributed to the explanation given by *Jacangelo et al*[30] and which is summarised in **Table 2.1**: "..*enhanced coagulation is effective up to a point beyond which protons inhibits interaction between NOM and metal hydrolysis products.*"

The results depicted in **Figures 4.3** to **4.4** also show a strong correlation between TOC measurements and spectrophotometric measurements as a means to analyse for humic acid concentrations.

The results obtained for the COD reduction as a function of alum concentration did not show any significant differences in the efficiency of the coagulation process at various pH levels. It should however be pointed out that the correlation between TOC and COD has been reported to be generally very poor[55.] No comparisons in terms of curve shapes, rate of reduction and direct concentrations of the residual analyte should be made without recognising the fact that TOC and COD are measuring different species. The former is an indication of carbon concentration due to total organic compound concentration and the latter is an indication of the ease of oxidation of the species present in the water (this can also include inorganic compounds, especially metal ions).

The good correlation in terms of the maximum level of organic reduction showed by all four the measuring techniques used, is primarily due to the fact that the flocculation process is a physical removal process in which the organic matter is removed from the water. As the test solutions were prepared demin water, no other species were present that could influence the measurements.

From the results (**Figures 4.3** to **4.6**) it can also be seen that for the test solutions having a turbidity of 20 NTU and a humic acid concentration of 10 mg/l (as TOC) there would be little advantage to increase the alum concentration (both from a financial and efficiency point of view) beyond 20 mg/l. This will however change with changing water quality, especially where TOC/turbidity ratios and TOC/alkalinity ratios varies as is the case with natural waters where these ratios are source and seasonally dependant.

4.4 HUMIC ACID REDUCTION BY CHEMICAL OXIDATION

Figures 4.7 to **4.10** shows the results obtained for the reduction in humic acid in terms of TOC, UV/VIS and COD.

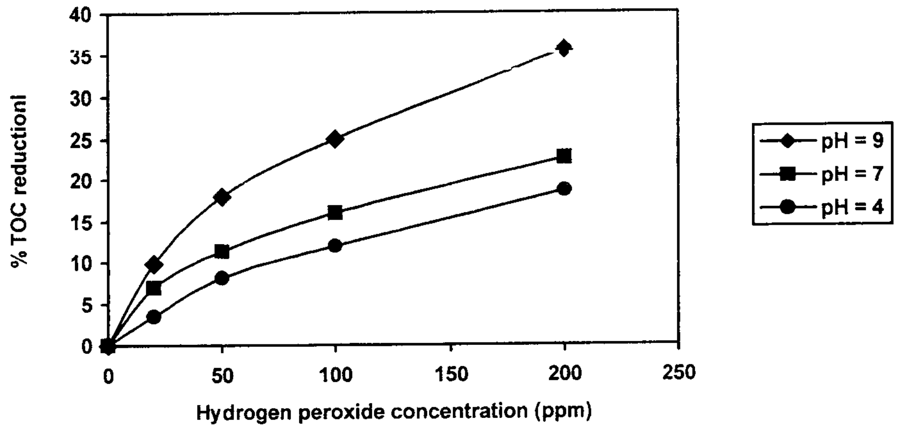


Figure 4.7: TOC reduction as a function of H_2O_2 concentration for solutions at pH = 4, pH = 7 and pH = 9

The results depicted in **Figure 4.7** indicate that the addition of H_2O_2 has led to the oxidation of the organic matter and that a degree of mineralisation of the organic substance to CO_2 has taken place. There is also strong evidence that interaction of the peroxide on the humic substance was strongly pH dependant. The higher the pH, the higher the degree of mineralisation, which indicates that OH• formation took place more readily in an basic environment and which is supported by literature[39,46] (**Section 2.2.2** and **2.3**).

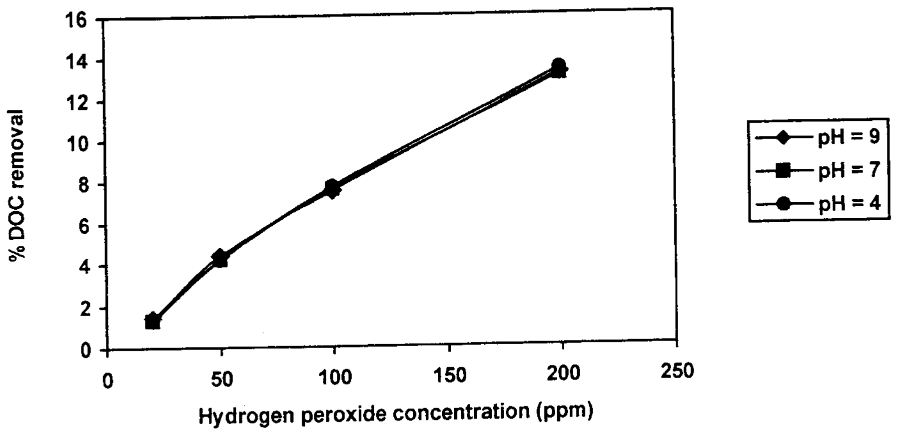


Figure 4.8: Humic acid reduction (DOC) as a function of H_2O_2 concentration measured at 254 nm for solutions at pH = 4, pH = 7 and pH = 9

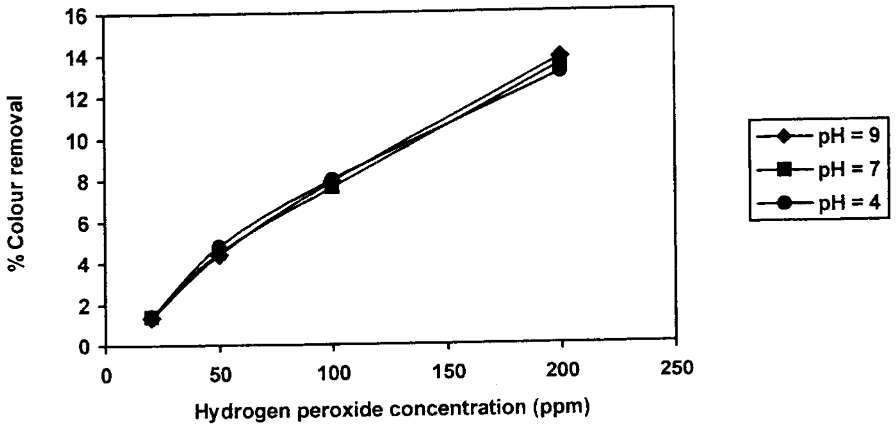


Figure 4.9: Humic acid reduction (colour) as a function of H_2O_2 concentration measured at 430 nm for solutions at pH = 4, pH = 7 and pH = 9

Both spectrophotometric determinations showed about the same degree of humic acid removal and the percentage reduction showed an almost linear response to the concentrations of H_2O_2 added. The degree of humic acid reduction as colour and as DOC was much lower than that experienced with the coagulation process. However it supports the findings in terms of TOC reduction (**Figure 4.7**) and is further evidence that a high degree of mineralisation within the peroxide dosing range could not be achieved. The conversion of the initial complex humic acid structure to lower molecular weight organic compounds such as organic acids should not be ruled out and should be considered as a strong possibility (**Chapter 2**). The concentration and type of intermediates formed was however beyond the scope of this study. The spectrophotometric analysis did however not show any pH dependence on the degree of humic acid reduction and can most probably be attributed to the formation of the intermediates and the fact that these measuring techniques are not species specific. . Based on this, one should at this stage be careful to try and distinguish between humic acid reduction and organic reduction. For this reason, all spectrophotometric results reported from here onwards will refer to percentage organic reduction.

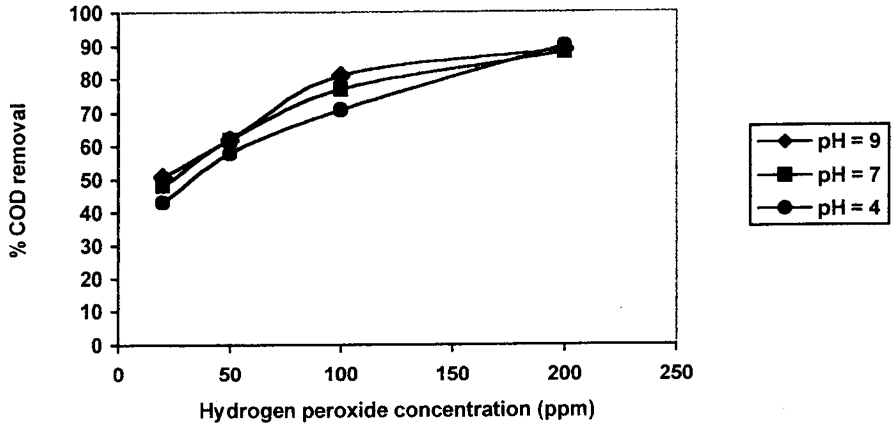


Figure 4.10: COD reduction as a function of H_2O_2 concentration for solutions at pH = 4, pH = 7 and pH = 9

Figure 4.10 shows a very high degree of COD reduction, but it should not be compared to the similar high degree of reduction as reported in **Section 4.3, Figure 4.6** where the COD reduction was primarily due to the physical removal of the humic substance from the water. The results reported in **Figure 4.10** are merely a confirmation that residual organic compounds are present as lower molecular mass organic intermediates, which can be more readily oxidised by the hot chromic acid solution used in the COD determination as was the case with the untreated humic acid solution.

4.5 HUMIC ACID REDUCTION BY PHOTO/PHOTO-CATALYTIC OXIDATION

4.5.1 Humic Acid Reduction By Photo-Oxidation

Figures 4.11 to **4.14** show the results obtained for the reduction in organic substances in terms of TOC, UV/VIS and COD through UV radiation at 254 nm.

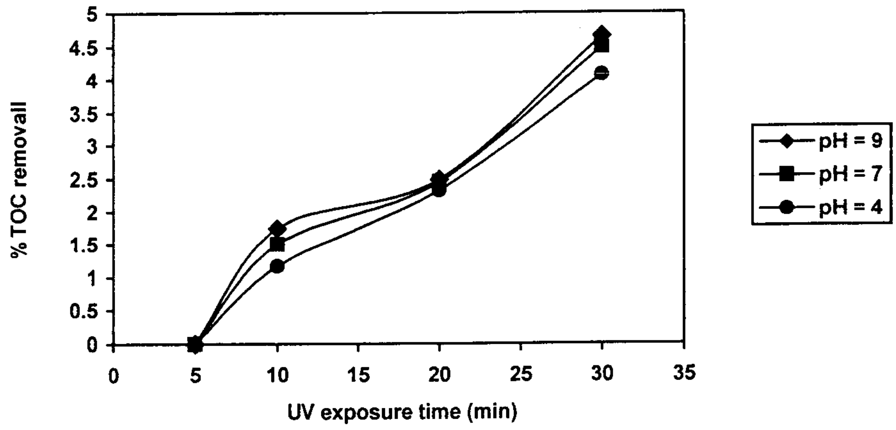


Figure 4.11: TOC reduction as a function of UV exposure time for solutions at pH = 4, pH = 7 and pH = 9

Very poor TOC removal was observed when the humic acid solution was subjected to UV radiation. At this low level of TOC reduction, no strong pH dependency could be observed although the results do indicate a very marginal increase in TOC reduction with increasing pH. It was expected that OH• formation would occur more readily in basic solutions (**Chapter 2**).

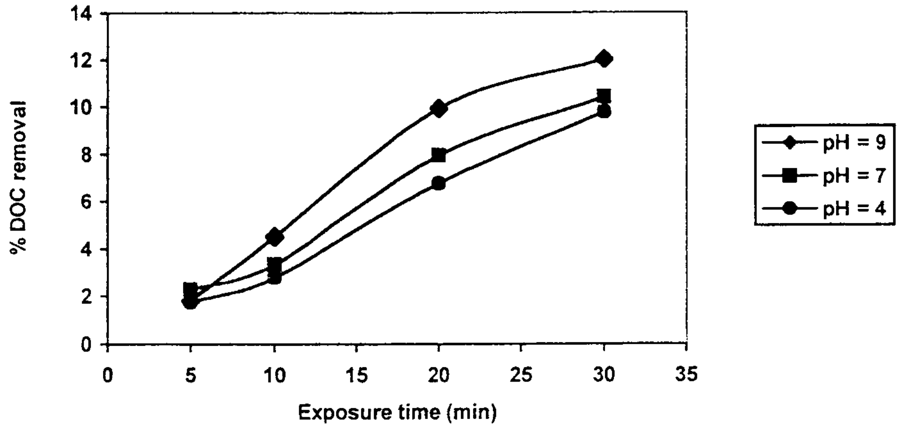


Figure 4.12: Organic reduction (DOC) as a function of UV exposure time measured at 254 nm for solutions at pH = 4, pH = 7 and pH = 9

There was a steady increase in the degree of the reduction of the organic compound concentration with increasing exposure time as can be seen from **Figure 4.12**. The results do show pH dependency, ie the higher the pH, the higher the degree of reduction, which confirms to a certain extent the observations made in **Figure 4.11** in terms of OH• radical formation

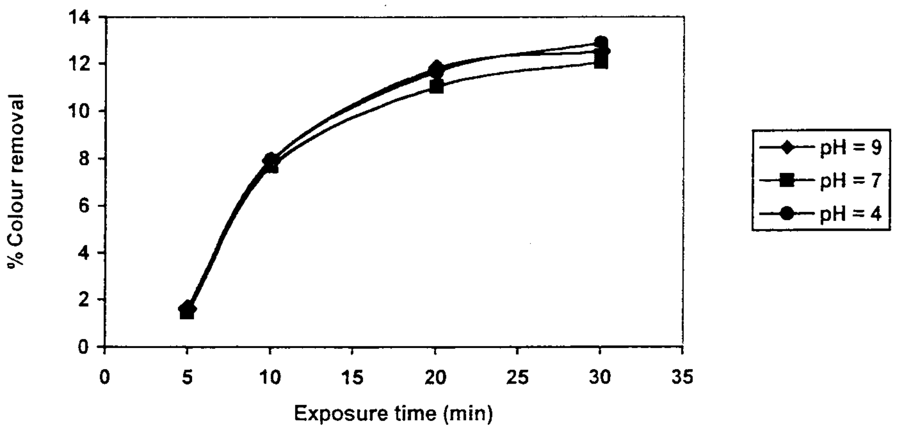


Figure 4.13: Humic acid reduction (colour) as a function of UV exposure time measured at 430 nm for solutions at pH = 4, pH = 7 and pH = 9

The spectrophotometric analysis carried out at 430 nm also showed some degree of organic reduction although pH dependency is not as pronounced, as was the case with the measurements taken at 254 nm. The initial degree (between 5 and 10 minute exposure) of reduction measured at 430 nm showed a faster response than was experienced with the measurements taken at 254 nm.

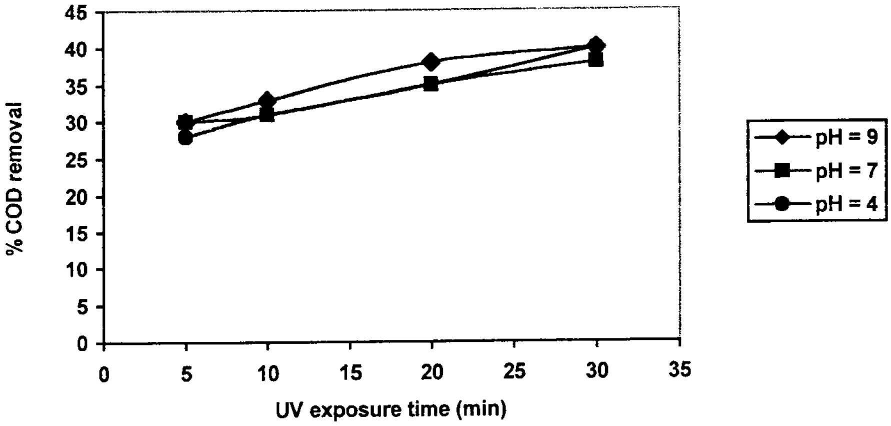


Figure 4.14: COD as a function of UV exposure time for solutions at pH = 4, pH = 7 and pH = 9

4.5.2 Humic Acid Reduction By Photo-Catalytic Oxidation

Figures 4.15 to **4.18** show the results obtained for the reduction in humic acid in terms of TOC, UV/VIS and COD through catalysed UV radiation at 254 nm.

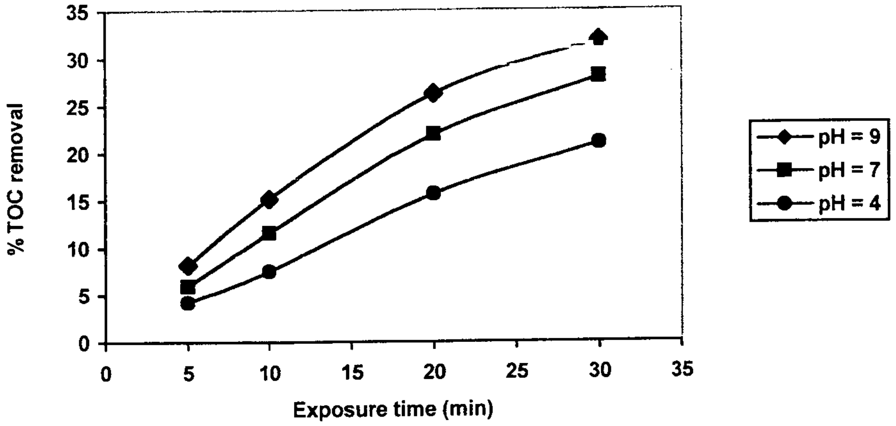


Figure 4.15: TOC reduction as a function of catalysed UV exposure time for solutions at pH = 4, pH = 7 and pH = 9

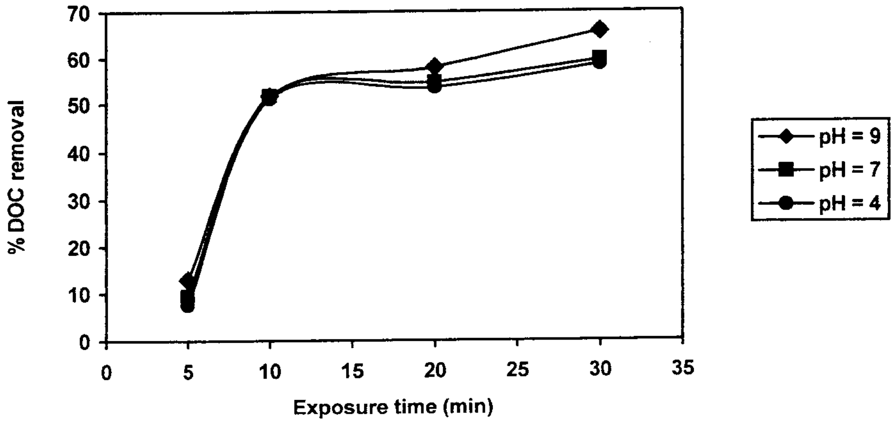


Figure 4.16: Organic reduction (DOC) as a function of catalysed UV exposure time measured at 254 nm for solutions at pH = 4, pH = 7 and pH = 9

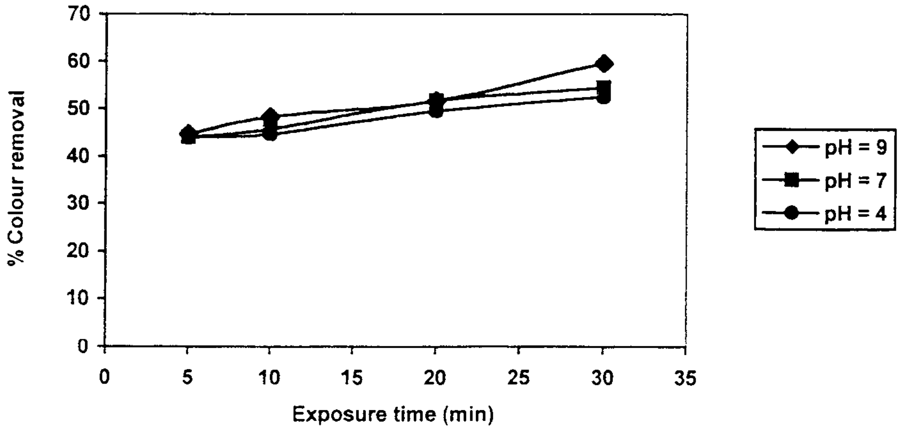


Figure 4.17: Humic acid reduction (colour) as a function of catalysed UV exposure time measured at 430 nm for solutions at pH = 4, pH = 7 and pH = 9

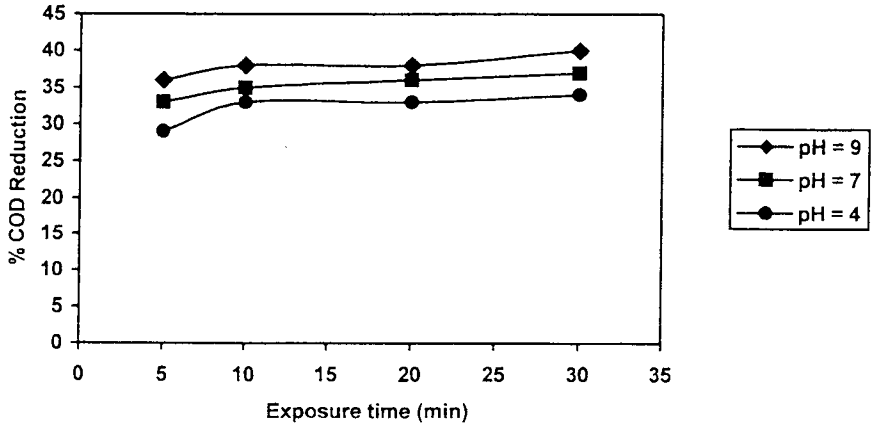


Figure 4.18: COD as a function of catalysed UV exposure time measured at 254 nm for solutions at pH = 4, pH = 7 and pH = 9

The presence of the catalyst has vastly improved the oxidative power of the UV radiation in terms of TOC reduction compared to the non-catalised UV radiation. The results were comparable with those obtained during the oxidation of the humic acid with H_2O_2, both in terms of the degree of mineralisation and pH dependency.

A significant increase in organic reduction measured at both 254 nm and 430 nm was also observed when compared to the H_2O_2 and uncatalysed UV treatment. The reason for the difference in the results between catalysed UV and the H_2O_2 treatment cannot be explained at this stage. One possible explanation could be that different oxidation mechanisms are involved between the H_2O_2 and humic substance and the catalysed UV and the humic substance, which could result in a difference in the intermediates being formed which in turn can influence the absorbance characteristics of the intermediate species. As indicated in **Section 2.2,** there are still a number of uncertainties in terms of metal catalysed organic oxidation that need to be studied to fully understand the pathways involved. It should also again be pointed out that the spectrophotometric analyses are not species specific, but a mere indication of the presence of lower molecular weight organic compounds.

The COD results showed in **Figure 4.18** are comparable with those obtained for the uncatalysed UV oxidation. The same argument that was used for the previous COD results still holds for these results in that during the flocculation process physical removal of the humics took place. During the oxidation processes discussed up to this point, intermediate organic products were formed and that COD results obtained are an indication of the ease of oxidation of the residual organic species and not necessarily an indication of the degree to which the organic species concentrations were reduced.

4.6 HUMIC ACID REDUCTION AS A RESULT OF ANODIC OXIDATION

Figures 4.19 to **4.22** show the results obtained for the reduction in humic acid in terms of TOC, UV/VIS and COD through anodic oxidation.

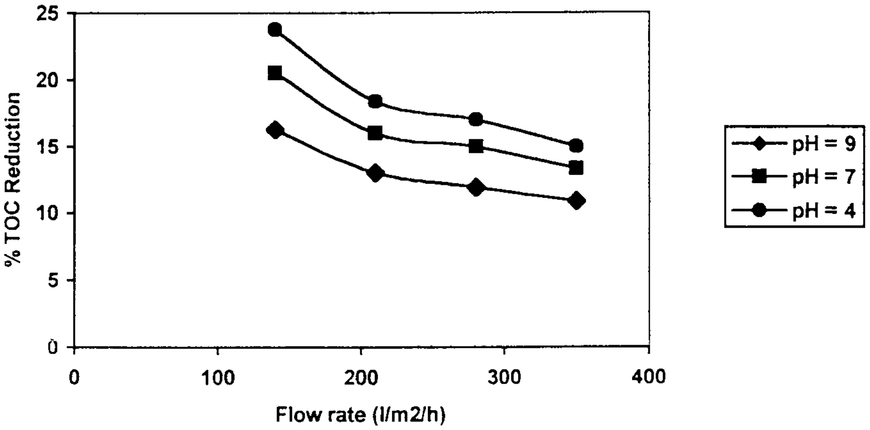


Figure 4.19: TOC reduction as a function of flow rate for solutions at pH = 4, pH = 7 and pH = 9

The results depicted in **Figure 4.19** show the level of TOC reduction that could be achieved by a single pass of the humic acid solution through the anodic decomposition reactor chamber. A definite pH and flow dependency on the degree of mineralisation can be seen. In this case however (compared to the oxidation techniques discussed thus far), the more acidic the solution, the higher the degree of mineralisation. This is in agreement with the theoretical explanation given in **Section 2.4** and results reported by *Maluleke et al* [53].

The formation of a brownish "floc" or resin like substance was also noticed in the samples collected from the permeate side of the reactor at all pH levels. A similar observation was reported by *Maluleke et al*[53] in studying the anodic oxidation of phenol. During the oxidation of the phenol, the 'floc" formation was however limited to the neutral to alkaline pH range only.

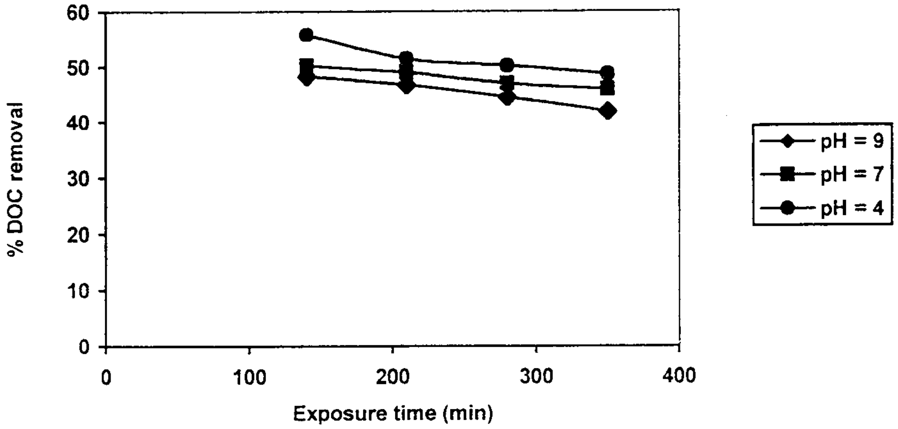


Figure 4.20: Humic acid reduction (DOC) at 254 nm by anodic oxidation as a function of flow rate for solutions at pH = 4, pH = 7 and pH = 9

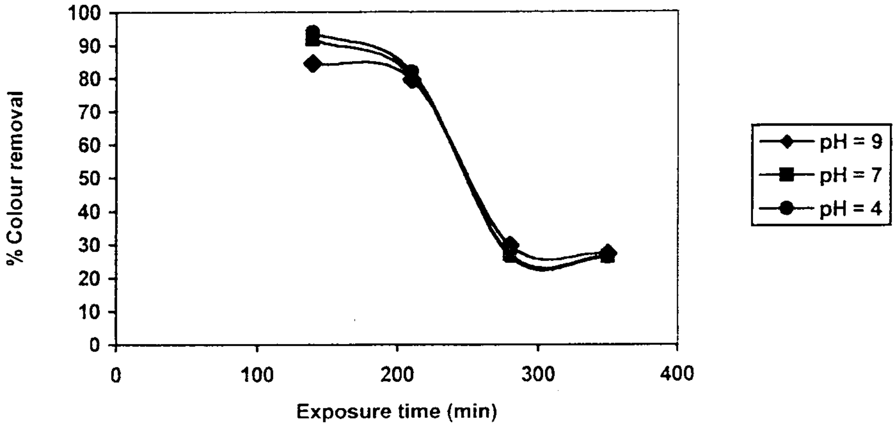


Figure 4.21: Humic acid reduction (colour) at 430 nm by anodic oxidation as a function of flow rate for solutions at pH = 4, pH = 7 and pH = 9

The spectrophotometric analyses at 254 nm and 430 nm showed a much improved degree of organic removal (at the flow rate where maximum TOC removal was observed) in comparison with the other oxidation techniques evaluated. A maximum of 95 % humic acid reduction (in terms of TOC) was observed at 430 nm. This compared favourably with similar results obtained during the flocculation tests. Lower molecular weight organic matter (as intermediates) is still present as indicated by the measurements taken at

254 nm, but it would appear to be less than what was observed during the H_2O_2 and UV/catalysed UV oxidation. The nature of the organic species will however have to be identified once the mechanism for the anodic oxidation of humic acid has been studied in more detail. It is anticipated that much improved results (higher degree of mineralisation) will be achieved through a multi-pass system.

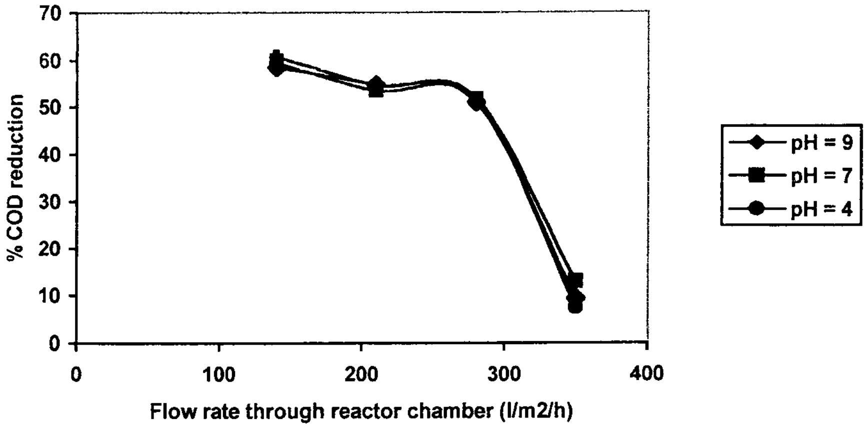


Figure 4.22: COD reduction by anodic oxidation as a function of flow rate for solutions at pH = 4, pH = 7 and pH = 9

The degree of COD reduction after anodic oxidation as a function of flow rate is shown in **Figure 4.22**. The results clearly show a flow dependency although no definite influence of pH could be seen. The reduction in the COD can be two-fold:

- Mineralisation of the humic substance to CO_2 and
- The formation of intermediate low molecular weight reaction by-products, possible short chain organic acids.

As with the other oxidation techniques, no direct comparisons should be made with results obtained from the different analytic techniques employed as the mechanisms and types of intermediates still need to be studied. It should be pointed out at this stage that the decomposition of the humic substance (as measured at 430 nm) by anodic oxidation was much more pronounced when compared to the oxidation by H_2O_2, UV and catalysed UV. The relatively low currents measured during the anodic oxidation process (**Table 4.1**) are also encouraging, as this will have a direct implication on operational costs. It would appear that there is a direct relationship between the degree of oxidation/mineralisation and the current as a function of pH, ie the lower the pH, the higher the current, the higher the degree of humic acid decomposition. Relatively high currents were recorded at the point of maximum degree of humic acid decomposition (140 l/m^2/h) compared to the higher flow rates where the degree of oxidation was reduced.

Table 4.1: Current measurement at flow rate and pH during the anodic decomposition of humic acid

pH	Flow rate (l/m^2/h)	Current (mA)
9	140	36
	210	29
	280	21
	350	20
7	140	55
	210	45
	280	22
	350	21
4	140	68
	210	50
	280	30
	350	25

CHAPTER 5:

CONCLUSIONS

This **chapter** will mainly deal with the conclusions derived from the results obtained in comparing the four techniques evaluated for the removal/minimisation of humic acid from water in terms of their applicability to the power industry.

5.1 COAGULATION/FLOCCULATION OF HUMIC ACID

This technique has a two-fold advantage in that it reduces the turbidity of the raw water as well resulting in a high degree of humic acid removal and subsequent TOC and COD reduction. The variability in turbidity, TOC and pH levels of natural waters would however determine the dosage required to achieve maximum TOC removal. An additional advantage of the technique is that no intermediate products are formed, which can result in low molecular weight organic compounds present that would require additional treatment other than the standard demin process. An issue that will have to be borne in mind is that the use of enhanced coagulation will result in the production of excess sludge in the treatment process, which will have to be disposed of. This could be the prime motivation to investigate alternative techniques for future use such as oxidation/mineralisation techniques.

5.2 CHEMICAL OXIDATION BY H_2O_2

Although a high degree of COD reduction was observed, TOC reduction ranged from below average to average at high dosage levels. The difference in the degree of TOC reduction and COD reduction is attributed to the formation of intermediate or reaction by-products such as low molecular organic acids. These compounds will still be present as TOC and have an absorbance at 254 nm and 430 nm, hence the poor results observed using spectrophotometric measuring techniques as an indication of humic acid reduction.

5.3 PHOTO-OXIDATION

UV oxidation at 254 nm had very little impact on the oxidation of the humic compound, although the use of the TiO_2 vastly improved the degree of TOC reduction (again the formation of lower molecular organic compounds was evident). This efficacy of this technique strongly depends on contact time. Although basic research to explain thc theory behind the process is well documented, little attention has been given as to the practical implementation of the technique in industry, ie reactor design for high flow requirements, energy consumption and the impact of possible OH• scavenging compounds that could be present in natural waters. During this **study**, the influence of just pH on the reduction of TOC was clearly demonstrated.

5.4 ANODIC OXIDATION

Although there was a below average reduction in the TOC concentration after a single pass of the humic acid containing water through the anodic oxidation chamber, the spectrophotometric and COD measurements showed a much improved state of affairs when compared to the results obtained for the photo-oxidation and chemical oxidation techniques. The results that were observed for the 430 nm and COD measurements were in fact comparable to those obtained during the coagulation/flocculation tests.

From this, the immediate conclusion would be that on average 90% of the humic acids were oxidised (**Figure 4.21**). However due to the lack of information regarding the nature of the "floc" that formed during the oxidation process, it would be pre-mature to base this high degree in humic acid and COD reduction (**Figures 4.21** and **4.22** respectively) purely on oxidation. The possibility that a chemical reaction could have occurred between the anode and the humic compound resulting in the humic acid actually precipitating out of solution, rather than being oxidised, should not be ruled out at this stage.

In conclusion, the results obtained for anodic oxidation indicate that there would be merit in exploring this technology further, provided that suitable analytical techniques are available to study the mechanisms involved in the oxidation of humic substances.

5.5 GENERAL CONCLUSIONS

The following general conclusions can be made at this point in time:

- Enhanced flocculation/coagulation is a suitable and practical technology to remove humic substances from natural waters, especially where conventional infra-structure is available,
- From the oxidation techniques studied, anodic oxidation shows great promise for further exploitation,
- The lack of suitable analytical methodology such as HPLC and LC/MS, would hinder any mechanistic studies with regard to the oxidation of humic substances or the formation of lower molecular weight organic compounds,
- Techniques such as spectrophotometric and COD measurements are no indication of the degree of mineralisation of organic compounds during oxidation,
- The lack of the commercial availability of the oxidation techniques studied (except for H_2O_2) prohibits any techno-economic comparisons to be made at this stage and
- The lack of sufficient documented data on the mechanistic oxidation of humic substances and the complexity of these humic substances had a negative impact on this research.

CHAPTER 6:

RECOMMENDATIONS

From the results obtained and observations made during this study, the following recommendations are made:

- In the absence of technologically matured oxidation techniques, enhanced coagulation should continue to be used as a means to control and minimise NOM,
- Enhanced coagulation/flocculation should be used as a bench mark against which the performance of oxidation techniques are being evaluated,
- Fundamental research in the use of anodic oxidation as a means to reduce NOM in natural waters should continue as the technique showed very positive results,
- The future research should include real samples,
- The above research should be accompanied by developing suitable analytical techniques to study the oxidation of humic substances and the reaction by-products/intermediates formed during oxidation and
- Future research with regard to anodic oxidation will have to include reactor designers to address the need of the industry in terms of application.

The above recommendations are also true for any oxidatioin technique developed for the treatment of natural waters and are supported by similar recommendations made during 1998 at an international workshop held in Lausanne, Switzerland.[55] Some of these recommendations included:

- The development of standard comparative tests for oxidation techniques,
- A full understanding of the radical and redox chemistry of oxidation techniques,
- Understanding, eliminating or inhibiting the chemical and the physical processes that reduce the efficiencies of oxidation techniques,
- Conducting multi-discipline research involving engineers, chemists and biologists to improve oxidation techniques,
- Modelling studies for scale-up and predicting of oxidation techniques,
- Establish figures of merit to compare the performance of oxidation techniques,

- Identification of undesirable by-products,
- Innovation in reactor design and
- Conducting research on real samples not only model compounds.

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APPENDIX A:

In **Appendix A** a publication from the author as published in the VGB PowerTech Journal, Volume 82/2002 (ISSN 1435–3199), March 2002 is presented. The publication was titled: "Plant optimisation: A Key Factor in Minimising Natural Organic Matter in Power Station Make-up Water. A list of the Editorial Staff, Scientific Editorial Advisory Board and Technical Editorial Advisory Board is also presented.

VGB POWERTECH

3/2002

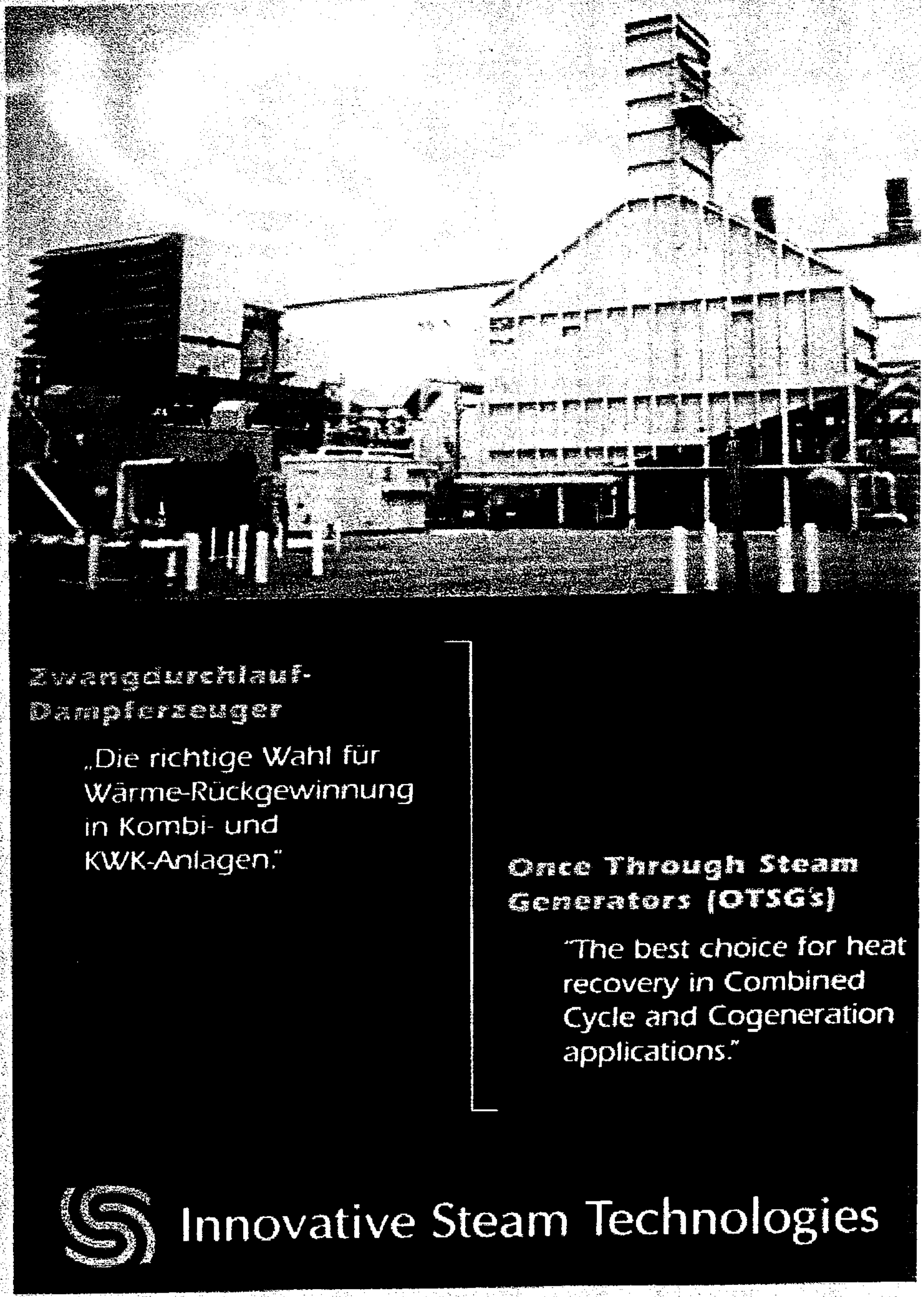
[illegible] Elektrotechnik

[illegible] Changing U.S. Electricity Market

[illegible] Decentralized Generation

[illegible] Pipeline-Verdichterstationen

Is there a future for Coal?



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International Edition

Plant Optimization: A Key Factor in Minimizing Natural Organic Matter in Power Station Make-up Water

Kurzfassung

Anlagenoptimierung: Ein wesentlicher Faktor in der Minimierung natürlicher Organika in Kraftwerkszusatzwasser

Der zunehmende Einsatz von Hochtemperatur- und Hochdruck-Kessel- und -Turbinenanlagen, die mit hohen Drücken und hohen Temperaturen arbeiten, zwingt die Kraftwerke, ständig an der Verbesserung der Qualität von Kondensat und Speisewasser zu arbeiten. Ein Forschungsgebiet, das sehr aktuell geworden ist, ist das Abscheiden von natürlichen Organika aus dem Kraftwerkszusatzwasser. Im Trinkwasser können organische Stoffe den Geschmack beeinflussen und zu einer Verfärbung führen. Sie können das Bilden von Keimungsnebenprodukten einleiten und verteilte und kolloidale Teilchen im Klärvorgang stabilisieren. Obwohl sich Rohwasser durch die Demineralisierung von anorganischen Salzen befreien lässt, ist das Abscheiden organischer Stoffe weitaus schwieriger.

Einige organische Verbindungen lassen sich im Ionenaustausch herausfangen, jedoch verschmutzt dabei das Anionentauschharz und in geringerem Umfang auch das Kationentauschharz. Das kann wiederum den Gesamtwirkungsgrad der Wasseraufbereitung mindern. Die nicht entfernten Organika finden ihren Weg in den Wasser-Dampf-Kreislauf, wo sie unter thermohydraulischen Einflüssen zerfallen. Die Zerfallsprodukte stören die Qualität von Dampf und Kondensat. Zwar ist eine Reihe moderner Oxidationsverfahren zur Herabsetzung oder Beseitigung organischer Stoffe aus Wasser bekannt, jedoch war man bei Eskom zuerst bestrebt, mit betrieblichen Maßnahmen zu Ergebnissen zu kommen. Es zeigte sich, dass durch eine sorgfältige Auswahl von Flockungs- und Ausfällmitteln sowie einen optimierten Zusatz dieser chemischen Stoffe die vorhandene Organika-Abscheidung in der Anlage um bis zu 300 % gesteigert werden konnte.

Introduction

Utility Background

Eskom is the national electricity utility for South Africa and the fifth largest electricity generating company in the world. It is generating more than half of the electricity produced on the African continent. Its nominal capacity of 37 840 MW is distributed via a power line network of 241 802 km fed by 10 fossil-fired power plants, one nuclear power plant and some hydro-electric and pump storage schemes. The fossil power plants burn about 76 million metric tonnes of coal per annum.

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Water Supply to Eskom

Eskom power plants obtain their water as surface water from mainly three river systems, namely the Komati, Usuthu and Vaal Rivers. These systems are interlinked to form what is known as a transfer scheme and it is possible for stations to also get water blends from the various sources, however this is more the exception than the norm and is determined mainly by dam levels and conditions of severe drought [1].

The turbidities of the water for the three main sources range from 1.7 to 88.2 FTU with an average total organic carbon (TOC) concentration of about 6 ppm. It should be noted that these values are subject to seasonal changes and TOC values as high as 16 ppm have been recorded during the rainy seasons.

The water treatment processes employed by Eskom to produce boiler make-up water consist mainly of:

- pre-chlorination of the raw water,
- coagulation and clarification,
- sand filtration, and
- demineralization.

The specifications for demineralized water as per the Eskom Chemistry Guidelines [2] is given in Table 1.

Rational for Organic Specification and Control of Natural Organic Matter

Owing to the high operating temperatures and pressures, there is an ever increasing need to maintain the highest purity in the cycle fluid of modern power plant. In addition to the ubiquitous inorganic contaminants, it is also recognized that the presence of organic matter contributes to the impurity of the power plant cycle chemistry as documented by a number of authors over the years [3 to 7].

There are a number of possible sources through which organic matter can enter the water/steam cycle of a power plant:

- make-up water,
- ion exchange resin,
- condenser inleakage,
- pre-operational preservatives,
- bacteria,
- lubricating oil, and
- water treatment and chemical cleaning agents.

Of all these sources, the raw water is the most likely source of contamination, because all natural waters contain natural organic matter (NOM) in the form of humic substances. Although water demineralization processes can cope with the removal of inorganic salts from raw water, the removal of organic matter poses a far greater problem. Some organic compounds can be removed via the ion exchange process, however fouling of the anion exchange resin, and to a lesser extent the cation exchange resin, occurs during this process. This can have an impact on the overall performance of the water treatment plant. Those organics that are not removed will find their way into the water/steam circuit where they are decomposed through thermo-hydraulic processes forming carbon dioxide and lower molecular weight organic acids, contributing to cation conductivity levels [4 to 10].

This paper will discuss two case studies experienced by Eskom with the influence of natural organic matter on the water treatment plant, the effect on the quality of water produced and the actions taken to minimize the impact.

Table 1. Demin water specifications for coal-fired power stations measured at the mixed bed outlet.

Parameter		Target	Limit
Turbidity (FTU)		< 0.1	0.2
Specific conductivity	(µS/cm at 25 °C)	< 0.08	0.1
Sodium	(ppb as Na^+)	< 1	2
Silica	(ppb as SiO_2)	ALARA	10
Chloride	(ppb as Cl^-)	< 1	2
Sulphate	(ppb as SO_4^{2-})	< 1	2
TOC	(ppb as C)	100	250

Impact of NOM on Water Treatment Plant and Water Quality

Sodium and TOC Leakage

The majority of NOM present in natural waters is acidic in nature and is therefore only partly removed by cation exchange resins. These compounds are however strongly absorbed by anion exchange resins. It has been postulated that the removal of organic compounds by anion exchange resins can take place by either electrostatic forces and ion exchange or adsorption onto the resin matrix via van der Waals forces or a combination of the two mechanisms [11, 12].

During the regeneration process (caustic for anion exchange resin) the organic compounds are not completely removed due to the high affinity of the resin for the organic molecules. Gradual fouling of the resin takes place over a period of time and the resin starts to show the following symptoms [11]:

- the rinse water requirements increase,
- the carboxyl groups of the organic compounds interact with the Na^+ ion of the caustic to form sodium carboxylate which eventually hydrolyses back to the free acid releasing sodium ions into the product water,
- gradual increase in product water conductivity and decrease in pH due to organic acid leakage,
- gradual silica leakage,
- a gradual decline in exchange capacity over a period of time, and
- shortened operating times.

To overcome this problem, caustic brine washes need to be carried out from time to time and the frequency of these clean-up procedures will increase with increasing fouling levels.

The phenomenon of sodium and TOC leakage from organically fouled anion exchange resin can clearly be seen from results and shortened operating times that were obtained from a demineralization unit which had a design specification of 9 Ml (Figures 1 and 2).

Fouled Sand Filters, TOC Carry Over and Silica Slippage

Figure 3 shows the TOC results of a treatment plant that suffered from poor organic removal sludge carry over from the clarifiers and anaerobic conditions in the sand filters.

Apart from the high TOC levels measured at the outlet of the mixed bed, an average oxygen absorbed concentration of 1.3 ppm was also measured. A sudden silica slip of about 100 ppb was also observed halfway through the service cycle, where after the train was taken out of service.

Upon investigation, it was found that the clarifier suffered from sludge carry over for a period of time, fouling the sand filters and the cation inlet sump. The sand filters were neither backwashed nor sanitized regularly. This eventually led to the creation of anaerobic conditions in the sand and the sludge carried into the sump which contributed to severe resin fouling and hence the slippage of TOC and silica.

Reduction of NOM through Enhanced Coagulation and Plant Optimization

There are a number of ways through which TOC levels can be reduced during water purification, which include the application of the following technologies:

- advanced oxidation processes (AOP),
- activated carbon,
- organic scavenging resin,
- membrane processes, and
- enhanced coagulation.

Eskom evaluated all of the above technologies as options to minimize the impact of NOM on its plant. AOP was ruled out from both a cost benefit and effectiveness point of view. It was found that under AOP treatment higher molecular weight compounds were only broken down to lower molecular weight organic species without having a significant impact on the TOC levels.

Activated carbon, organic scavenging resin and membrane processes would need to be retrofitted to existing plant resulting in additional capital outlay and water treatment costs.

Evaluation of existing plant operating procedures showed that if the plant operation could be optimized with respect to operating conditions together with the application of enhanced coagulation, TOC reduction of to 70 % could be achieved across the primary treatment process without excessive additional costs incurred. Enhanced coagulation can roughly be defined as the optimum addition of coagulation chemicals (1.5 to 7 times the requirement for turbidity removal) to reduce TOC levels to a minimum. Enhanced coagulation has been identified by the United States Environmental Protection Agency as the *"Best Available Method"* for not only reducing TOC levels via flocculation, but also to minimize tri-halomethane precursors in potable water [13 bis 17].

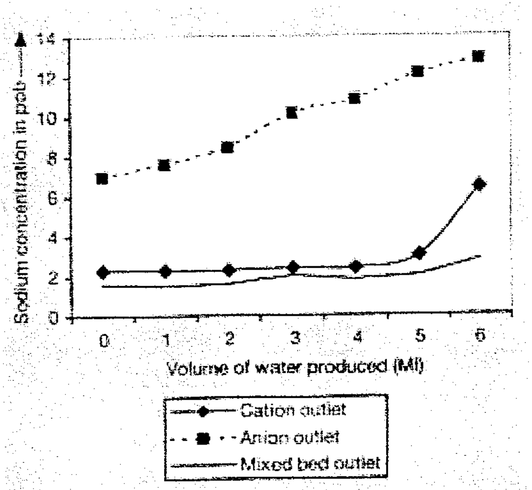


Figure 1. Sodium leakage levels from various stages in the demineralization process.

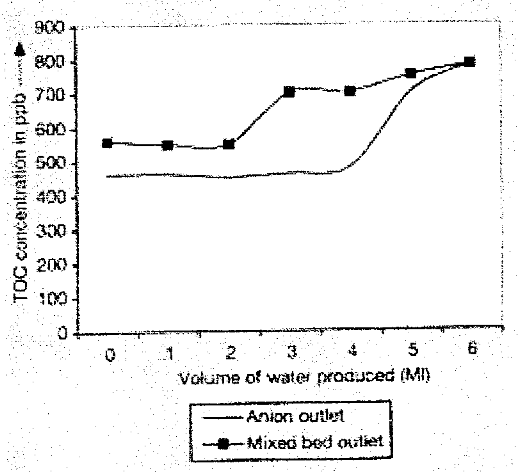


Figure 2. TOC leakage levels from various production stages in the demineralization process.

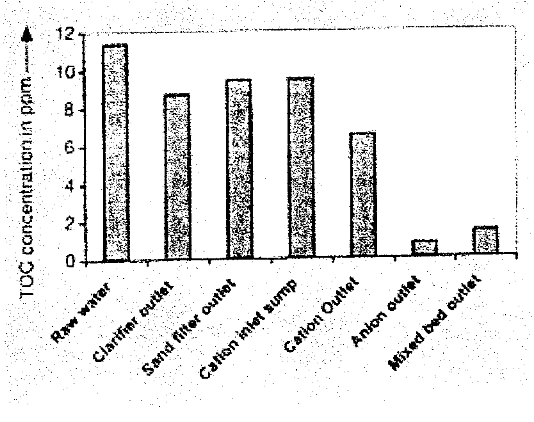


Figure 3. TOC concentration at various stages in the demineralization process.

The programme introduced by Eskom entailed:

- the evaluation of coagulants and flocculants available on the South African market,
- the dosing levels required,
- the application, and
- the measurement of the effectiveness of the treatment programme, which was done by UV-254 nm measurements supplemented by TOC and High Performance Liquid Chromatography analysis.

Figure 4 shows typical dissolved organic carbon (DOC) removal results obtained from a water treatment plant before the application of the enhanced coagulation (coagulant dosage based on turbidity removal only) and after applying enhanced coagulation.

Recently, DOC removal levels of up to 90 % have been achieved, which corresponds to about 60 % TOC removal.

Traditionally, aluminium sulphate (alum) was primarily used as coagulant, but with the introduction of enhanced coagulation, the alum was replaced by poly-aluminium chloride (PAC) to avoid excess sulphate burden on the demineralization plant. The PAC and poly-electrolyte are dosed as separate products (not blends as commonly used for potable water treatment) to avoid the over dosage of poly-electrolyte, which can be carried over into the demineralization plant where it can foul the cation exchange resin. Excess, unreacted poly-electrolyte can also increase the TOC concentration of the water to be treated. Experience has shown that this is especially true when water quality or flow rates change and dosage levels have to be adjusted accordingly.

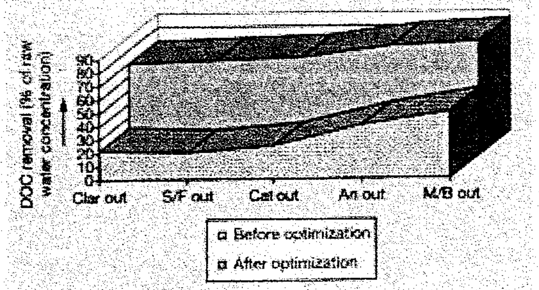


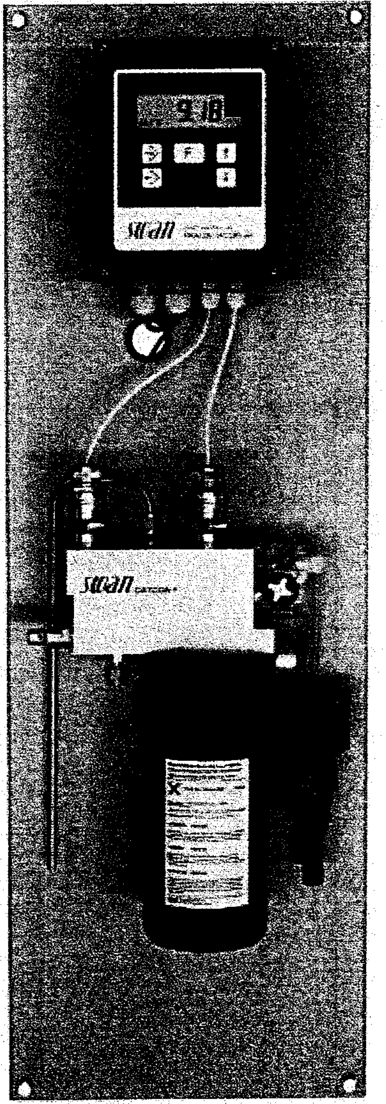
Figure 4. DOC concentration at various stages in the demineralization process before and after enhanced coagulation.

Apart from the correct flocculant selection, a number of key plant operating parameters also need to be addressed to obtain the full advantage of enhanced coagulation:

- measurements and control of raw water and chemical dosing,
- the proper chemical selection, preparation and application (sufficient reaction time is important),
- TOC/DOC and turbidity monitoring,
- stop/start operation of clarifier (the start up procedure is very important to prevent any sludge carry over),
- sand filter operation, backwashing and sanitizing,
- control over the upflow rate in the clarifier,
- sludge management and control,
- seasonal changes in TOC and turbidity levels, and
- temperature changes and the impact on the clarifier performance (during cold spells there might be a requirement to increase the dosage levels).

Conclusion

The practice of enhanced coagulation, coupled to a plant optimization and a resin manage-



ment programme can be highly successful in educing TOC levels across the conventional reatment processes employed to produce power plant make-up water of high quality.

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Mitteilungen der VGB-Geschäftsstelle

Mieten statt kaufen – auch bei Energieerzeugung

Europamarkt für die Vermietung von Energieerzeugungsanlagen

Immer weniger Unternehmen investieren in der Zukunft in den Bau eigener Energieanlagen, viele setzen stattdessen auf Miete. Entsprechend soll der Umsatz auf dem Europamarkt für die Vermietung von Energieerzeugungsanlagen von über 360 Mill. US-$ im Jahre 2000 auf rund 550 Mill. US-$ im Jahre 2007 ansteigen. Zu diesem Ergebnis kommt die Unternehmensberatung Frost & Sullivan in einer neuen Analyse.

Angesichts der aktuellen Wirtschaftslage drosseln viele Unternehmen ihre Investitionen und orientieren sich stärker auf kurzfristige Renditen. Das Mieten von Energieerzeugungsanlagen, meist von Dieselaggregaten, ist dabei nach *Ian French*, Marktforschungsanalyst bei Frost & Sullivan, eine kostengünstige Möglichkeit, Energie einzusetzen, ohne in Anlagen investieren und Personal vorhalten zu müssen. Kurzzeit-Energieversorgungsverträge erfreuen sich deshalb wachsender Beliebtheit. Vorübergehende Energieengpässe, steigender Energiebedarf und Kostenvorteile durch Mieten tragen zur Attraktivität dieser Lösung bei. Entsprechend ist in sämtlichen Abnehmerbranchen mit einem deutlichen Wachstum zu rechnen, wobei Bauwesen, Industrie und die Veranstaltungsbranche mit zusammen mehr als 65,5 % des Gesamtumsatzes im Jahre 2000 auch in Zukunft die lukrativsten sein dürften.

Vorteile des Mietens müssen besser an Kunden kommuniziert werden

Obwohl der Markt in den nächsten 10 Jahren kräftig wachsen soll, bleibt eine Reihe von Hindernissen zu überwinden. Vor allem müssen die Industriekunden noch besser mit den Vorteilen des Mietens von Energieerzeugungsanlagen vertraut gemacht werden. Ein weiteres Wachstumshemmnis ist die Tatsache, dass Bauunternehmen in Regionen wie Deutschland und Skandinavien Energie aus dem Netz beziehen können.

Insgesamt dominieren aber auf dem Gesamtmarkt die positiven Triebkräfte.

Hohe Margen locken neue Anbieter

Eine Anlage bringt während ihrer Lebensdauer bis zum 10-fachen der Investitionskosten ein. Eingerechnet ist dabei normalerweise auch ihr Verkauf auf dem Gebrauchtanlagenmarkt. Allerdings überholen einige Anbieter ihre Anlagen und erzielen dann wieder 60 bis 70 % des Neupreises. Solche Margen ziehen immer mehr Unternehmen an, und immer mehr konzentrieren sich auf den Bau- und den Veranstaltungssektor. So ist zu erwarten, dass sich der Markt in den nächsten Jahren erheblich konsolidieren wird. Dabei werden die Marktführer ihre Positionen durch Fusionen und Übernahmen festigen. Die meisten Opfer dürften unter den Unternehmen zu finden sein, die sich auf Anwendersektoren am unteren Ende der Preisskala wie Bauwesen und Veranstaltungsbetrieb beschränken. Mit der Verschärfung des Wettbewerbs wird das Preisniveau sinken, wodurch das Mieten für die Anwender noch attraktiver werden dürfte.

Marktführer: Aggreko

Marktführer auf gesamteuropäischer Ebene ist Aggreko, doch verfügen auch andere Marktteilnehmer über nennenswerte Marktanteile in bestimmten Länder- oder Regionalmärkten. Einige größere Unternehmen verfolgen Strategien zur Ausdehnung ihrer Aktivitäten über ihre bisherigen Geschäftsfelder hinaus. Mit dem Wachstum des Marktes haben sie sich auf Mehrwertdienstleistungen wie Kühlung, Spezialanlagen und technische Beratung konzentriert.

Titel der Analyse:
The European Power Generation
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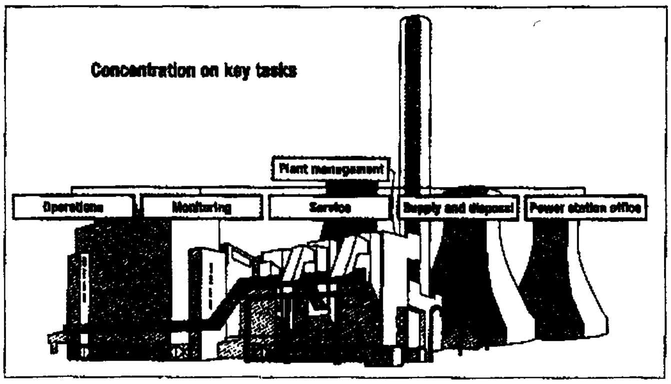
Preis € 5500,–

Das neue KWK-Gesetz bringt Klimaschutz voran

Endlich Rechtssicherheit für Investitionen

Als wichtigen Beitrag zur effizienten Förderung der Kraft-Wärme-Kopplung (KWK) und damit zum Klimaschutz bewertet der Verband der Elektrizitätswirtschaft (VDEW), Berlin, das am 25. Januar 2002 vom Bundestag verabschiedete neue KWK-Gesetz. „Endlich wird das geltende, unzulängliche Gesetz abgelöst. Damit ist der Weg frei für Investitionen zur Modernisierung und zum Ausbau der energiesparenden und umweltschonenden Technik", betont VDEW-Präsident *Günther Marquis*.

Der VDEW-Präsident hatte die intensiven und langwierigen Verhandlungsrunden zwischen den acht beteiligten Verbänden und mit der Politik koordiniert. „Das lange Ringen um den Kompromiss hat sich gelohnt – auch wenn der Wirtschaft erhebliche Zugeständnisse abverlangt wurden", hebt *Marquis* hervor. Schließlich sei das neue KWK-Gesetz ein wichtiger Baustein der Selbstverpflichtung der Industrie zum Klimaschutz. Danach ist zugesagt, die jährlichen CO_2-Emissionen



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