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Abstract: The focus of this paper is on the influence of natural organic matter (NOM) in the Eskom power generation plants of South Africa and the strides taken by the Eskom power utility to deal with the challenges presented by the occurrence of NOM. A review of recent literature concludes the impact of NOM on power plant chemistry and the detrimental impact of NOM in the power industry was highlighted. This paper concludes the research programme that was established by Eskom to identify and address the organics presents in the raw water and their impact on power plant operation. Characterization of South African raw water sources was done by extensively sampling eight different water treatment plants (waste and potable water treatment) located within the five major source water types in South Africa. The NOM composition of all the samples was studied first by applying conventional (industrial) techniques (UV, DOC, SUVA-254 and bulk water parameters). NOM characterization was further conducted using advanced techniques (BDOC, PRAM and FEEM) which were aimed at developing rapid assessment protocols. The treatability and removal of the NOM in a water treatment train was investigated by determining the character and composition of the NOM samples taken at various stages of the water treatment process. Identification of NOM in Eskom Identification of NOM in Eskom raw water supplies was performed by making use of LC-OCD and SUVA-254 to determine the treatability of the water from the various catchments supplying the Eskom power plants. The use of nanotechnology for the removal or reduction of NOM was pursued by synthesizing and applying Pd-modified N-co-doped TiO₂ for the photocatalytic degradation of NOM fractions. The results presented in this study clearly demonstrated the high variability of NOM at the South African Water Treatment Plants. The nitrogen, palladium co-doped TiO₂, through photodegradation, effectively removed NOM (up to 96%) when compared to commercial TiO₂.

Key words: cooling water, liquid chromatography organic carbon detector, natural organic matter, nanotechnology, photodegradation, power generation

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 demineralized 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 stations' make-up water treatment plants have traditionally been designed to produce water of a very high quality (free from inorganic salts) by synthetic ion

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exchange resins. Raw water quality, mainly total dissolved solids (TDS), oxygen absorbed (OA) and silica are the key factor in the design of a 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 place on existing treatment processes to compensate for change in feed water quality.

The presence of NOM in surface water is largely due to the decay and leaching processes of organic materials from plants, animals and microorganisms and their transfer into water [1]. In order to reduce NOM from water in a water treatment train, the composition of the NOM in the source water must be taken into account, since its composition at any given time may depend on the local prevailing conditions. One of the objectives of this study was therefore to characterize NOM present in South African source waters through extensive sampling of representative water types at identified regions in the country and develop a rapid NOM characterization protocol.

Apart from the increasing salt concentrations in raw waters there are indications that NOM present in the water is also increasing, prominently during specific seasons [2, 3]. 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 total organic carbon (TOC) in demineralised water. The major component of NOM is humic substances (derived from soil or produced by chemical and biological processes) [1], of low to moderate molecular weight and has both aromatic and aliphatic components [4]. Over the past few years, Eskom has studied alternative methods to reduce organic matter (humic substances) prior to demineralisation by optimising flocculation/coagulation processes [5, 23]. 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.

2. Impact of NOM in the Water Industry

2.1 Impact of NOM within the Water Treatment Plant

Having a polydisperse and divergent structure [6] NOM is often described as a complex mixture of organic components which are inevitably present in all surface waters and having highly variable composition in water bodies. NOM in its natural environment; surface water, does not pose a challenge however, during water treatment NOM mostly affects the quality of drinking water by permitting the formation of disinfection by-products (DBPs) in the final drinking water when residual NOM reacts with the disinfectant predominantly during the disinfection process [7]. Microbial regrowth in the distribution system, odour, taste and colour problems of the final treated water are some of the key complications faced with poor removal of NOM by the water treatment process [8]. The reduction of NOM affects the capacity of other treatment processes remove organic to micro-pollutants or inorganic species that may be present in the water. To allow further characterization of NOM, separation of NOM based on hydrophobicity has been the main objective of several studies [9-11]. The separation of NOM allows for the fractioning of organic matter into hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) NOM fractions with hydrophobic referring to humic substances consisting of greater aromaticity [12].

2.2 Impact of NOM within the Power Industry

Three classical case studies is summarized in the following section to indicate the impact of NOM on power plant water chemistry.

2.2.1 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 [5, 13-15].

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:

• The rinse water requirement 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 Na⁺ 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 (Figs. 1 and 2).

2.2.2 Fouled Sand Filters, TOC Carry Over and Silica Slippage

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



Fig. 1 Sodium leakage due to organic fouling.



Fig. 2 Organic leakage during a production run.



Fig. 3 Organic carry over due to incorrect operation and poor maintenance.

2.2.3 Impact of Trihalomethane on Power Plant Steam/Water Cycle

Traditionally, raw water was pre-chlorinated to reduce algal growth within the clarifiers and sand filters. This practice was however terminated due to the formation of trihalomethane (THM) which cannot be removed via the ion exchangers. These compounds would then thermally break down within the steam water circuit resulting in an increase in chloride ions. This situation is quite evident at Koeberg Power Station as the station receives potable water that requires treatment for station make-up. By the time the water reaches the station it already contains THM. This water is then further chlorinated resulting in even higher THM concentrations.

Chloride in contact with metal surfaces has a detrimental effect on the structural integrity for power plants. Inconel, a metal alloy consisting of nickel, chromium and iron is used for the manufacture of steam generator tubes of Pressurised Water Reactors worldwide because of its physical properties. Steam generator tubing is by far the most vital component of this type of nuclear power plant and Inconel is susceptible to chloride induced pitting corrosion. Chloride also causes stress corrosion cracking in austenitic stainless steels that constitute the balance of the plant systems. For these reasons it is imperative that plant chemists must continue to strive to keep the chloride concentration as low as achievable [16].

Table 1 shows the chloride concentrations obtained in the make-up water (ultra-pure water) after UV/TiO_2 oxidation [16].

From the results it is evident that pre-chlorination in the flocculation/coagulation step prior to demineralisation leads to the formation of THM which are not retained by the ion exchange resin. These compounds will enter the steam/water circuit where it will undergo thermo/hydraulic decomposition to chloride ions and low molecular weight organic acids. This is an undesirable situation in power plant systems.

2.2.4 Impact of NOM on the Calcium Precipitation Potential in Cooling Water Systems

The role of the cooling water system at large steam generating plants is to cool down the exhaust steam (used to turn the turbines) for recycling. The cooling water flows through condenser tubes and the steam passes over these cold tubes which enables condensation. Due to the high TDS concentration, scaling of the condenser tubes can occur and result in decreased thermal efficiency [17].

Various studies shown that the presence of NOM can influence the precipitation potential in cooling water systems. Metal complexation with NOM differs depending on the type of metal present, size and type

Table 1 Chloride levels detected in demineralized water after UV/TiO_2 oxidation.

Pre-UV oxidation	Pre-UV oxidation	Х
Chloride (ug.1 ⁻¹)	Chloride (ug.1 ⁻¹)	Increase
0.41	111.0	271
0.46	80.4	175
1.22	756.0	620
0.83	59.7	72

of the organic molecule, pH and temperature of the water [18]. This complexation of metals with organics affects the scaling potential of the water [19]. Visual MINTEQ is a modelling programme that takes this metal complexation into consideration when calculating the saturation index of the cooling water and was used during the Eskom study [17].

Due to evaporation and concentration of chemical species in the water, NOM values in excess of 70 mg/l C (as TOC) commonly measured in Eskom power Traditionally Eskom used the EDTA plants. complexation method to determine Ca and Mg concentrations in the cooling water system and based on the results would adjust the chemical dosing to prevent scaling if required [20]. To protect the plant material from acid attack, Eskom opted for a slight scaling regime. In recent years however, inductively coupled plasma emission spectroscopy (ICP-OES) is being used to determine the Ca and Mg concentrations. By adjusting the chemical dosing and control, plant operators found that they cannot maintain the thin scale layer in the pipe work anymore resulting in bare metal being exposed to the harsh cooling water conditions.

Upon investigation it was found that the ICP method reported higher Ca/Mg values than what was measured through titration. The reason for this was that Ca/Mg complexation rendered these ions unavailable for the complexation with EDTA. Due to the high plasma temperature of the ICP the organic-metal complex was broken, resulting in the total Ca/Mg concentration being measured.

The impact on Langelier Saturation Index (LSI) due to the different analytical techniques can clearly be seen in Table 2.

Average	Average	Average	Average	Average	Average	LSI	LSI
Temp.	pH	Alkalinity	TDS	Ca ²⁺	Ca ²⁺	Ca ²⁺	Ca ²⁺
(°C)	_	(mg.l ⁻¹	$(mg.l^{-1})$	(ma.1 ⁻¹	(ma.l ⁻¹ as	ICP	Titration
		Ca ²⁺ as	-	as Ca2+)	Ca^{2+})		
		CaCO ₃)		ICP	Titration		
25.00	8.50	148.67	3.30	375	195.30	2.04	1.93
42.73	8.37	148.67	3.30	372.33	195.33	2.10	1.85

Table 2	Effect of LSI (usi	ng ICP Ca ²	+ and	titrated	Ca ²⁺	
concentrations) at different temperatures.						

Through additional studies conducted, it was concluded that metals do bind with NOM in the water. The results from this study clearly indicated that the organics in the water play an important role when it comes to determining whether the water has a potential to scale (Scaling Index, SI). The raw water quality in particular greatly affects the cooling water in terms of the scaling potential. The higher the dissolved organic carbon (DOC) concentration in raw water, the lower the SI indicating a decrease in the scaling potential of the water. It is important to note that when using Visual MINTEQ and calculating the SI, the total Ca concentration (ICP Ca) must be used.

When calculating the LSI the Ca concentration obtained using EDTA titration method must be used to obtain accurate results. Visual MINTEQ has shown to be a powerful tool when it comes to studying the chemical behaviour of water in terms of scaling when elevated concentrations of NOM is present.

3. Methodology

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 and the performance of the

 Table 3 Demineralised water specifications for coal fired

 power stations measured at the mixed bed cation/anion

 exchange outlet.

Parameter	Target	Limit
Chloride (ug/l as Cl ⁻¹)	< 0.1	0.2
Sulphate (ug/l as SO_4^{2-})	< 0.08	0.1
TOC (ug/l as C)	< 1	2

demineralize ion exchange resin as documented by a number of authors over the years [5, 13-15]. 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 [5]. To address these issues, Eskom embarked on a research programme to identify and quantify the organics present in the raw water in order to determine their impact on power plant operation.

Research approach to date:

The methodology section of this paper will focus on objectives (6) to (9) while the programme consisted of the following tasks:

(1) Evaluation of selected water treatment chemicals (coagulants and flocculants) on various raw water streams using standard laboratory jar tests to determine the efficiency of organic removal.

(2) Subject the most suitable treatment chemicals to plant trials to determine their efficacy in terms of organic and turbidity removal.

(3) Optimisation of the operating conditions for each water plant [15].

(4) Determination of the impact of pre-chlorination on the demineralisation plant performance in terms of organic leaching [5, 16] using UV/TiO₂ oxidation and ion chromatography.

(5) Treatability of various water streams in terms of NOM removal through clarification and flocculation.

(6) Identification of NOM within surface waters throughout South Africa.

(7) Quantification of NOM in Eskom raw and treated waters by liquid chromatography organic carbon detector (LC-OCD).

(8) NOM removal by eight South African water treatment plants.

(9) Use of nanotechnology for the reduction of NOM by making use of photocatalytic degradation of NOM fractions.

3.1 Identification of NOM in South African Source Waters

Source water samples were collected from eight different water treatment plants broadly located within the five major source water types of South Africa between the periods of February 2013 to June 2014 in five sampling rounds. The sampling campaigns were planned and timed in order to accommodate the dry and the rainy seasons. The water treatment plants sampled were: Loerie (L) Water Treatment Plant, Midvaal (M) Water Treatment Plant, Olifantsvlei (O) Wastewater Treatment Plant, Plettenberg Bay (P) Water Treatment Plant, Rietvlei (R) Water Treatment Plant, Umzoniana (U) Water Treatment Plant, Vereeniging (V) Water Treatment Plant, and the Wiggins (W) Water Treatment Plant.

Conventional (industrial) techniques for the characterization of the bulk properties of NOM in the samples was done by ultra-violet (UV) analysis, DOC analysis, specific ultra violet absorbance (SUVA) measurements and the studying of bulk water properties such as pH, turbidity, conductivity, temperature, hardness and analysis of ions. The use of advanced NOM characterization techniques gave further insight into the composition and character of NOM in the samples. This was done through fluorescence excitation emission matrices (FEEM), dissolved biodegradable organic carbon (BDOC) analysis and the modified polarity rapid assessment method (PRAM).

3.2 NOM in Eskom Water Supplies

Specific ultra violet analysis at 254 nm (SUVA-254) has been used to determine the treatability of the water from the various catchments supplying Eskom power plants [21]. Quantification of NOM in Eskom raw and

treated waters was performed by making use of LC-OCD).

3.3 NOM Removal in Eight South African Water Treatment Plants

At each water treatment plant, two to four samples were collected at different stages of the water treatment train taking into account the water treatment procedures employed at that particular water treatment plant, namely; a raw water sample, an intermediate sample before sand filtration and a final sample after sand filtration. One wastewater treatment plant was targeted for sampling at which only two types of samples were taken during the five sampling rounds i.e. a sample taken before and one after the maturation ponds. For seven drinking water treatment plants, raw water samples, an intermediate sample before sand filtration and a third sample after sand filtration were collected. For the waste water treatment plant (the Olifantsvlei wastewater treatment plant), only two samples were taken, i.e., samples were taken before and after the maturation ponds.

3.4 Nanotechnology — Photocatalytic Degradation of NOM Fractions

A preliminary study was carried out to investigate the use of nanotechnology for NOM removal. This was done by synthesizing and applying Nitrogen, palladium co-doped TiO₂ for the photodegradation of NOM and NOM fractions fractionated by the modified PRAM. The N, Pd co-doped TiO₂ efficiency was then compared with commercial TiO₂ for the photodegradation of NOM and its fractions.

4. Results and Discussion

4.1 NOM in South African Source Waters

UV, DOC and SUVA results indicated that the P samples were highly aromatic in nature as they had SUVA values greater than $4 \ell \cdot m^{-1} \cdot mg^{-1}$ while the rest of the samples were less aromatic with SUVA less than $4 \ell \cdot m^{-1} \cdot mg^{-1}$. The turbidity of the water samples was used

as an indicator for the amount of clay particles and the samples were found to have varying turbidities, with the V samples having very high turbidity values (up to 99.8 NTU) and the W water having low turbidity values (as low as 1.0 NTU). The bulk water parameters also revealed the character of the NOM. The hardness of the sampled water could be grouped into three categories — low hardness (L, P, V, W), medium hardness (O, R, U) and high hardness (M).

FEEM indicated that all the samples had hydrophobic acids, humic and humic-like material but in varying proportions, with the P samples having the highest concentrations of these while the W sample contained the least amounts of humic substances. The BDOC results indicated that the percentage DOC removal ranged between 20% and 65%, with the highest removal noted for the P samples and the least for the W and M samples. The lower percentage DOC removal was noted in water that had low SUVA values (implying low humic substances). The PRAM fractionation showed that DOC-fraction distribution varied substantially depending on the source water and type of treatment process employed when one considers samples taken from the treatment train. The P samples had the hydrophobic (HPO) fraction being the most dominant ranging between 32-74% in DOC, whereas the transphilic (TPI) fraction appeared to be the second most abundant fraction, constituting 3-28% of the total NOM samples. The other sampling sites

Table 4 SUVA-254 nm values of Eskom raw water.

had an almost equal spread between the TPI and the hydrophilic (HPI) fraction, with slightly higher amounts of the HPO fraction.

4.2 Quantification of NOM in Eskom Water Supplies Using LC-OCD

Traditionally, organic matter or the concentration thereof has been measured and expressed as either by the "permanganate number", oxygen absorbed (OA) or chemical oxygen demand (COD) [20]. These results generally used by engineers to design are demineralisation and reverse osmosis plant; however the techniques suffer from the ability to identify the organic species present. Further it is also not possible to find a linear relationship between the two parameters as the results are based on the ability of the oxidising agents (permanganate in the case of OA and dichromate in the case of COD) to oxidise the species present. Although TOC or DOC analysis has been issued to supplement aqueous organic measurements it also suffers from non-specifity, i.e., it only measures the number of carbon atoms present [20].

The real questions for water treatment are however the treatability of the water and the impact of the NOM on the treatment process. SUVA-254 was used to determine treatability of the water from the various catchments supplying Eskom power plants and the results are depicted in Table 4.

Catchment	$\frac{\text{SUVA-254}}{(1 \cdot \text{m}^{-1} \cdot \text{mg}^{-1})}$	Composition	Treatability
Komati	4.89	Mostly aquatic humic substance	Good NOM removal, 50% with alim
Usuthu	2.78	Mixture of aquatic humic substances and other NOM	Fair to good removal, between 25 and 50% with alum
Lower-Vaal	2.8	Mixture of aquatic humic substances and other NOM	Fair to good removal, between 25 and 50% with alum
Crocodile-West	3.2	Mixture of aquatic humic substances and other NOM	Fair to good removal, between 25 and 50% with alum

Based on these results targets can now be set for organic removal at a power station based on the raw water supply to that specific station. Measurements put in place entails maximum removal across the clarifiers through enhanced coagulation using poly aluminium chloride and to ensure that sand filters are kept clean and free from organic matter and biological growth through proper sanitation. Proper chemical selection

and mixing as well as optimised clarifier operation (sludge control and up flow rate selection) is also of importance. The results of addressing the above factors can be seen in Fig. 4.

The SUVA-254 value of the raw supplied to this particular power station is in the region of 4.89 $(\ell \cdot m^{-1} \cdot mg^{-1})$.



Fig. 4 Percentage DOC removal across a power plant water treatment facility before and after optimisation.

In order to fully understand the impact of NOM on power plant operations, proper identification of the species has become of importance which was facilitated in this study by making use of LC-OCD identification. This work will in future be supported with fluorescence emission excitation matrix (FEEM) measurements. Fig. 5 depicts the changes in organic species concentration through a typical water treatment plant. The LC-OCD chromatograms clearly indicated the efficiency of the various steps in the pre-treatment process to reduce specific organic compounds. The identification and quantification of the various NOM species is far superior to a standard total organic carbon analysis. By monitoring the individual species, problem areas within a process can be highlighted and action can be taken. This is also a valuable tool in plant optimization.



Fig. 5 LC-OCD identification of NOM in power station treated water.

4.3 NOM Removal in Eight South African Water Treatment Plants

The highest DOC removal (85%) was achieved at the P (G) water treatment plant, which had highly humic and coloured water. For the P water UV_{254} removal ranged from 78% to 88% with an average of 83%. For the O samples the UV_{254} removal by the maturation ponds ranged from 3% to 14% with an average UV_{254} removal of 7% while the other plants had an average UV_{254} removal of 19% of the raw water.

4.4 Nanotechnology — Photocatalytic Degradation of NOM Fractions

For the bulk NOM, photodegradation percentages lower than 50% were obtained with the N. Pd co-doped TiO_2 while very minimal (< 5%) NOM reduction was attained with the commercial TiO₂. Using the N, Pd co-doped TiO₂, the highest photodegradation of the NOM fractions was achieved with the hydrophobic fraction (71% to 96%). The least NOM reduction occurred in the transphilic fraction (14% to 15%). Using commercial TiO₂, the hydrophobic fraction was reduced by 5% to 34% and the transphilic fraction was reduced by a 5% to 7%. These results are far better than those achieved by most NOM removal methods such as coagulation, whose NOM removal efficiencies are in the range of about 75%. The hydrophobic fraction showed the highest degradation efficiency of 96% because of increased interaction with the nanoparticles The results obtained in the photodegradation studies suggest a potential for using nanotechnology, in the latter stages of the water treatment train, for the reduction of NOM from water.

5. Conclusions

The differing levels and composition of NOM in South African water sources within the different geographical regions suggests that a water treatment strategy by a treatment plant should address the issues relating to specific NOM occurring in the source water and its treatability. The use of LC-OCD for NOM identification on the treated water at the Eskom power station indicated the efficiency of the various steps in the pre-treatment process to reduce NOM compounds. This identification and quantification of the various NOM species is far superior to a standard TOC analysis. By monitoring individual organic matter species (specifically using LC-OCD), problem areas within a process can be highlighted and action can be taken towards plant optimisation to improve removal of the identified fractions.

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