

Thermal analytic study of the influence of oxidative water pretreatment on adsorbate characteristics in spent activated carbon*

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Abstract

A method was developed to characterize the influence of liquid phase oxidative pretreatment on the ultimate solid phase adsorbate distribution and implied regenerability of activated carbon. This method is based on thermal analysis principles and consists of heating the spent carbon in a nitrogen atmosphere up to 850°C, whilst simultaneously monitoring mass loss. Adsorbate fractions were characterized with respect to temperature intervals. A specific advance in adsorbate characterization is the possibility to quantify the highly volatile adsorbate fraction (desorbing at temperatures below 180°C), by distinguishing between moisture and adsorbate in this temperature range. The comparison of chlorination, oxygenation and ozonation for liquid phase pretreatment showed that low dosage (3 mg/l) preozonation resulted in the most favourable adsorbate thermal response pattern. Adsorbates desorbing below 600°C were maximized, and those above 600°C (especially >850°C) were minimized.

Introduction

The term 'thermal analysis' covers a range of experimental techniques which have a similar operating principle and can be used to identify or characterize materials and to study chemical or physical transition in them as a function of temperature. A physical parameter particularly suitable for studying changes in a material is the decrease in sample mass which occurs as volatile reaction products are lost. Continuous measurements of sample temperature and mass are made as the temperature of the sample is raised at a predetermined rate in the technique known as *thermogravimetric analysis* (TGA). The resulting graph of mass against temperature is termed the *thermogravimetric curve*.

TGA was considered a potentially useful technique for studying spent activated carbon. Essentially, TGA, when conducted in a steam atmosphere, simulates the thermal regeneration process, and precise mass loss rates as a function of temperature can be recorded. However, mass loss during reaction with steam is not a reliable measure of extent of regeneration, because some base (virgin) activated carbon is also gasified, and it is not readily possible to differentiate between adsorbate and base carbon in this regard. Moreover, Chihara *et al.* (1981) have shown that the steam-motivated gasification rates of base activated carbon and residual pyrolyzed adsorbate (for sucrose) are the same; total mass loss rate could therefore embody a substantive, yet undefined loss of base carbon. The difficulty in distinguishing the contributions in the reactions of the two carbonaceous materials detracts from the efficacy of using a steam environment for TGA studies on spent activated carbon.

The nature of adsorbate associated with spent carbon, in the context of thermal regeneration considerations, can be suitably characterized through TGA studies conducted in an inert (e.g. N₂) atmosphere. The various reactions that occur within a spent activated carbon under a rise of temperature (in an inert atmosphere), are ideally categorized as follows:

Type I: thermal desorption of volatile organic compounds initially adsorbed on the activated carbon, but not irreversibly bound to active surface sites;

Type II: thermal decomposition (cracking) of organic compounds, which are not sufficiently volatile for thermal desorption and/or which are tenaciously bound to surface sites, forming volatile fragments;

Type III: carbonization of remaining organic compounds with the concomitant deposition of a carbonaceous residual, at e.g. 800°C. Compounds which partake in this type of reaction are most critical to regeneration considerations, insofar as the carbonaceous residual has to be removed selectively, in practice, by way of endothermic steam or carbon dioxide oxidation at comparatively high temperatures (>800°C). This regeneration temperature domain is best avoided, since energy losses increase significantly, equipment specifications become more stringent (and costly), and base activated carbon losses invariably occur concurrent with the oxidation of carbonized adsorbate residuals.

In reality, many organic adsorbates will display combinations of Types I to III behaviour. Urano *et al.* (1981) analyzed thermogravimetric curves for various pure (single component) adsorbates on activated carbon, and classified them as shown in Table 1.

Suzuki *et al.* (1978) classified organic adsorbates in a similar fashion (see Table 2), and considered the possible influence of various adsorbate properties (boiling point, aromaticity, oxygen content, molecular mass and chemical functional groups) on thermal treatment response. Boiling point and aromaticity (i.e. the ratio of aromatic to total carbon atoms in a molecule) appear to most significantly characterize the behaviour of an adsorbate during (inert) thermal treatment; in particular the extent to which carbonaceous residuals will be deposited upon heating to 800°C. Organic compounds with high boiling points and of appreciable aromatic content, will likely exhibit Type III behaviour with concomitant excessive carbonaceous residuals at 800°C. These residuals have to be endothermically and selectively oxidized (normally under steam) at temperatures in excess of 800°C, thus posing the greatest difficulty of thermal regeneration. Prime examples of such intractable adsorbates are humic acids (which act as precursors for the formation of organohalogen compounds upon chlorination), lignin, phenol and substituted phenols. If liquid phase pretreatment could have the ultimate effect of shifting the adsorbate thermal response pattern, to reduce or eliminate Type III behaviour, then much benefit would be derived from such pretreatment: the relative intensity of regeneration conditions would be reduced.

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TABLE 1
THERMAL TREATMENT RESPONSE OF SELECTED ADSORBATES (AFTER URANO *ET AL.*, 1981)

Adsorbate	Molecular mass	Boiling point °C	Aromaticity*	Carbonaceous† residual (fraction) at 700°C	Thermal treatment response (under N ₂)
Toluene	92	111	0,86	0	Type I: complete vaporization or sublimation until about 300 °C
Nitrobenzene	121	211	1,00	0	
Propionic acid	74	141	0,00	0,01	Type I & II & III: desorbed partially by vaporization and thermal decomposition, with some carbonaceous residual at 700°C
Benzoic acid	122	249	0,86	0,03	
Salicylic acid	139	256	0,86	0,13	
Aniline	93	185	1,00	0,34	
Phenol	94	180	1,00	0,36	
Chlorophenol	129	214	1,00	0,40	
Nitrophenol	139	215	1,00	0,34	
Resorcinol	110	277	1,00	0,50	
2-naphthol	144	288	1,00	0,62	
Benzene sulphonic acid	156	-	1,00	0,36	Type II & III: desorbed partially by thermal decomposition, leaving carbonaceous residual at 700°C
Dodecyl benzenesulphonic acid	348	-	0,33	0,30	

*Aromaticity = ratio of aromatic to total carbon atoms in molecule.

†The fraction of the original adsorbate remaining as carbonaceous residual at 700°C under N₂. Estimated from figures presented by Urano *et al.* (1982) Heating rate = 17°C/min.

The approach in this study has been to monitor heterogeneously spent activated carbon mass (adsorbate) loss, under N₂, as a function of temperature using thermal analysis techniques. Traditional TGA, which is incapable of distinguishing between desorbed water and volatile organic adsorbates in the relatively low temperature range (<180°C), was extended to include such discernibility, thereby enabling the

determination of a complete adsorbate thermal treatment response profile, ranging from the highly volatile (desorbed <180°C) to those yielding carbonaceous residuals at elevated temperatures.

A further objective was to elucidate the effect of liquid phase pretreatment (oxygenation, chlorination, ozonation at different levels) on ultimate solid phase adsorbate thermal treat-

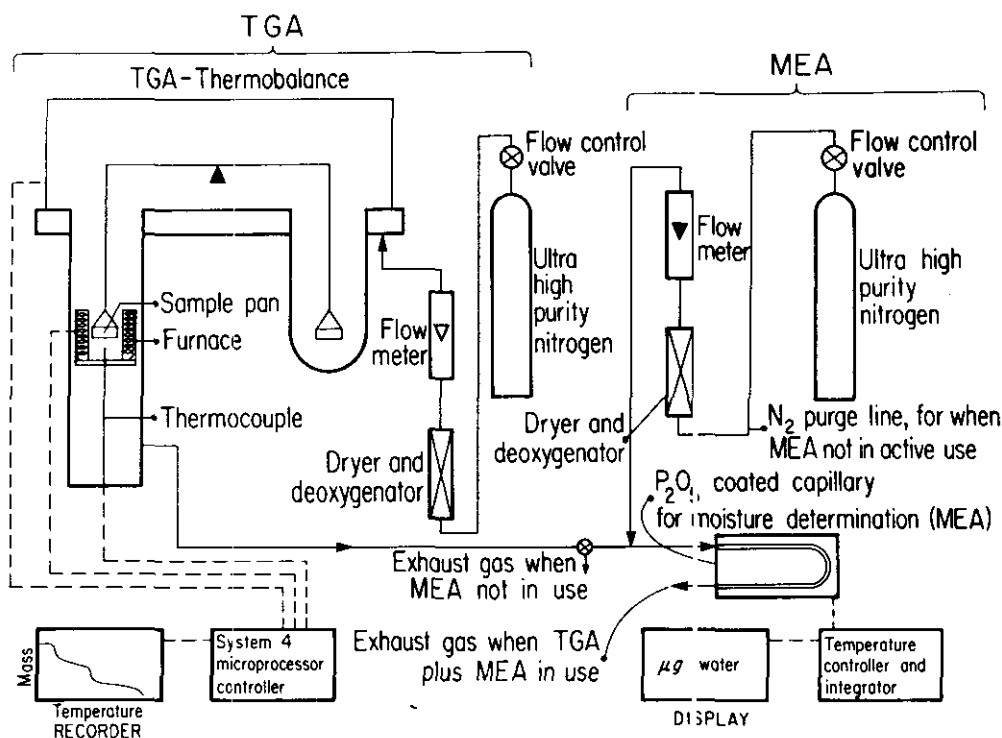


Figure 1
Arrangement of TGA and MEA equipment.

ment response. Grady *et al.* (1984), for example, have shown that ozonation can significantly effect the molecular mass distribution of dissolved organic compounds; Van Leeuwen *et al.* have shown that overall adsorber performance (1983), solute adsorbability (1984a) and biodegradability (1984b) are all influenced by the nature and extent of oxidative liquid-phase pretreatment. It is therefore conceivable that these influences will impact upon the nature of the resultant adsorbate, thus affecting the regeneration requirements of the spent activated carbon.

Experimental

Experimental arrangement

The TGA and moisture evolution analyzing (MEA) equipment arrangement is shown in Fig. 1. The TGA section comprises a Perkin Elmer model TGS-2 thermobalance (Perkin Elmer Corporation, Norwalk, Connecticut) with its control unit, including a microfurnace with heater control unit. A Perkin Elmer System 4 temperature controller enables comprehensive temperature programming capability (e.g. starting temperatures, heating rates; with up to four sequential program stages). A Perkin Elmer first derivative computer (FDC) determines the rate of mass loss of the sample in the microfurnace, and the outputs of the balance (mass change) and the FDC (rate of mass change) are simultaneously recorded on an X-Y-Y' recorder. High purity nitrogen gas is passed through a molecular sieve cartridge filter which scavenges oxygen and water vapour, and is then used as microfurnace atmosphere and carrier gas.

Two modes of operation are possible. If information on sample moisture content (desorbed < 180°C) is not required, the TGA section is used independently, and the carrier gas exiting from the microfurnace is vented to the atmosphere. The Du Pont moisture evolution analyzer 903 (Du Pont Company, Wilmington, Delaware) is then kept under continual purified nitrogen purge (from a separate source), in order to maintain a stable baseline for this instrument. If the sample moisture content is required (in order to determine the highly volatile adsorbate fraction, by subtracting moisture content from total mass loss up to 180°C), the carrier gas exiting from the microfurnace and laden with moisture and volatiles from the sample, is routed to the MEA unit. (The N₂ purge through the MEA unit is discontinued for the duration of such moisture determination). Within the MEA unit, the carrier gas transports the moisture to an electrolytic cell, where a thin film of phosphorous pentoxide, deposited between two parallel, helically-wound electrodes, absorbs the water, thus rendering the film electrically conductive. The adsorbed water is promptly electrolyzed by a current flowing between the electrodes, converting the water to hydrogen and oxygen gases which are discharged through a vent with the carrier gas, coulometrically regenerating the phosphorous pentoxide. The charge required to completely regenerate the P₂O₅ is integrated and displayed as total moisture content (0.99 999.9 µg H₂O).

All gas connections are made of PTFE and stainless steel tubing, with brass couplings.

Spent carbon samples

Spent carbon samples were collected from a pilot experiment

TABLE 2
THERMAL TREATMENT RESPONSE OF SELECTED ADSORBATES (AFTER SUZUKI *ET AL.*, 1978)

Adsorbate	Molecular mass	Boiling point, °C	Aromaticity*	Carbonaceous† residual (fraction) at 800°C	Thermal treatment response (under N ₂)
n-Pentane	72	36	0,00	0	
n-Hexane	86	69	0,00	0	
n-Heptane	100	98,4	0,00	0	
n-Decane	142	174	0,00	0	
Benzene	78	80	1,00	0	Essentially Type I (vaporization or sublimation), with little or no residual upon heating to 800°C
Toluene	92	110,6	0,86	0	
p-Xylene	106	114	0,75	0,03	
Butyric acid	88	164,1	0,00	0,01	
Butanol	74	118,0	0,00	0,02	
Hexanol	102	157,5	0,00	0,04	
Octanol	130	194,5	0,00	0,03	
Tetraethyleneglycol	194	-	0,00	0	
Caproic acid	116	205,4	0,00	0,04	Essentially Type II (thermal decomposition), with little or no residual upon heating to 800°C
Benzoic acid	122	250	0,86	0,15	
Humic acid	-	-	-	0,26	
p-Oxybenzaldehyde	122	310	0,86	0,35	
Lignin	165δ	-	0,60δ	0,45	Essentially Type III, with high residual upon heating to 800°C
p-Hydroxydiphenyl	170	308	1,00	0,49	
Methylene blue	320	-	0,38	0,58	
Phenol	94	182	1,00	0,61	
β-Naphthol	144	285	1,00	0,68	

*Aromaticity = ratio of aromatic to total carbon atoms in molecule.

†The fraction of the original adsorbate remaining as carbonaceous residual at 800 °C under N₂. Heating rate = 6 °C/min.

δSoft wood (coniferous), monomeric unit (Pearl, 1967).

(discussed in greater detail by Van Leeuwen, 1983), designed to study the effects of liquid phase oxidative pretreatment (ozonation at different levels, oxygenation, chlorination) on adsorber performance, adsorber service time, water quality, solute biodegradability and adsorbability. The pilot plant treated activated sludge plant (Bardenpho) effluent, and had been in operation for 6 months at the time of spent carbon sampling. The adsorber columns were operated in an upflow mode, had an empty bed contact time of 16 min and were sampled (250 cm³ each) near the process water inlet. Each adsorber contained 19 l of 8 x 30 mesh bituminous coal based granular activated carbon, and was immediately preceded by a dual medium filter.

Table 3 summarizes the conditions pertaining to the different pretreatment procedures at the pilot plant and the corresponding spent activated carbon sample codes. A part (20 cm³) of each spent carbon sample was centrifuged and immediately deep frozen, to arrest the possible loss of volatile adsorbate, biological activity or other adsorbate conversions, with a view to

subsequent determination of the highly volatile (desorbed < 180°C) adsorbate fraction, plus affording extended storage possibility. The remainder of each spent carbon sample was predried at 110 °C for 24 h, and stored in sealed containers.

Sample preparation and analysis

TGA only mode of analysis.

This mode of analysis, i.e. not including the moisture evolution analyzer (MEA), is used to characterize the thermal treatment response of all adsorbates, excluding the highly volatile fraction which desorbs along with water. A preliminary study was conducted with respect to TGA operating conditions, in order to establish an analytical protocol for future use. The following main parameters were considered:

- Carrier gas: (N₂) flow rate
- Spent carbon sample particle size
- Microfurnace heating rate.

Spent carbon samples were ground to a fine powder (95% < 75 μm) as part of this programme, in a blender type mill. On completion of this study a further refinement was introduced, i.e. using a centrifugal ball mill (Model S2 mill, Retsch KG, Düsseldorf), with two 50 ml grinding jars (each with three 20 mm grinding balls).

The following TGA analytical protocol was ultimately established (see: Results and Discussion for details):

- Temperature range : 25°C to 850°C
- Heating rate : 45°C/min
- Sample particle size : 95% < 75 μm
- Carrier gas (N₂) flow rate : 50 ml/min
- Operation mode : % sample.

Virgin and spent activated carbon particle densities (after having been dried at 180°C) were determined by means of mercury displacement (Autopore 9200 porosimeter, Micromeritics, Inc., Georgia). These densities were used to calculate total adsorbate loading (t_{1m}) as follows:

Liquid phase treatment	Spent Carbon Sample Code
No oxidative pretreatment, filtration, carbon (control)	BFC
Low (≅ 3 mg/l) ozone dosage, filtration, carbon	BO ₃ FCL
Medium (≅ 5,2 mg/l) ozone dosage, filtration, carbon	BO ₃ FCM
High (≅ 8 mg/l) ozone dosage, filtration, carbon	BO ₃ FCH
Chlorination (≅ 0,5 mg/l free residual), filtration, carbon	BCl FC
Oxygenation (≅ 3 mg/l), filtration, carbon	BO ₂ FC

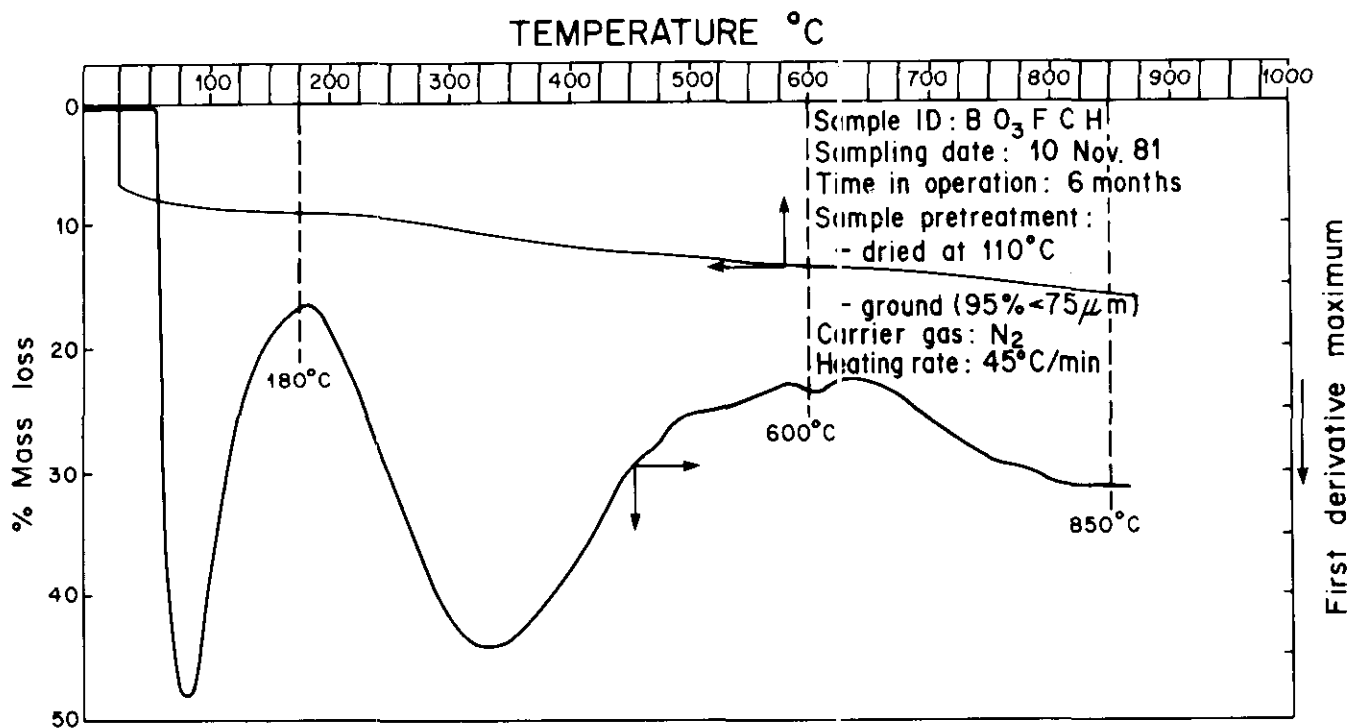


Figure 2
Example of thermogravimetric and first derivative curves.

$$q_{tm180} = \frac{1\,000(\rho ps_{180} - \rho pv_{180})}{\rho pv_{180}} \text{ mg adsorbate/g of base activated carbon} \quad (1)$$

where

ρps_{180} = particle density, spent carbon dried at 180°C, g/cm³
 ρpv_{180} = particle density, virgin (base) carbon dried at 180°C, g/cm³

TGA plus MEA mode of analysis

The TGA and MEA instrumentation (Fig. 1) are used in series for the simultaneous determination of both total mass and moisture loss (desorbed < 180°C), in order to calculate, by difference, the highly volatile adsorbate fraction.

A centrifuged and frozen spent carbon sample is ground manually in a low temperature room (4°C) to minimize the loss of highly volatile adsorbate as a result of frictional heat. The ground sample to be analyzed is kept briefly in a sealed sample holder at 4°C until it is required for analysis. Otherwise it is deep frozen again for extended storage purposes. For analysis a 3 to 4 mg sample is transferred to the TGA thermobalance and heated at the rate of 2.5°C/min up to 110°C. Then the rate is increased to 14°C/min up to 180°C and held at this temperature for 5 min. This temperature programme is used in order to avoid overloading of the electrolytical cell of the moisture evolution analyzer.

During moisture determination the N₂ carrier gas which has passed over the heated sample is routed to the moisture evolution analyzer where the cumulative moisture content is measured. Moisture content and total mass loss (between 25° - 180°C) are therefore determined simultaneously.

MEA calibration is done regularly, using AR grade disodium tartrate as standard, which has a fractional water content of 0,1566 (<180°C). A pronounced drift in the calibration per-

formance usually signals the need to recondition or replace the electrolytical cell of the MEA.

Results and discussion

TGA analytical protocol

The thermogravimetric curves determined during the *orientation* study for spent carbon sample BO₃CL, were divided into the following temperature intervals: 30°C to 215°C and 215°C to 800°C, based on the existence of minima (at ~ 215 and ~ 800°C) on the rate of mass loss curve generated by the FDC unit. These minima represent temperatures at which the desorption/reaction rate is minimal, where an intermediate step has been complete and/or a next step becomes more important (see Fig. 2 for illustrative purposes).

Influence of carrier gas (N₂) flow rate.

For a fixed particle size fraction (1 700 to 2 000 μm) and a fixed heating rate (80°C/min), TGA analyses were done at carrier gas flow rates varying from 30 ml/min to 60 ml/min. The 30°C to 215°C fraction, comprising highly volatile adsorbates remaining after predrying at 110°C plus traces of water vapour adsorbed during handling, was insensitive to carrier gas flow rate, as shown in Fig. 3. The 215°C to 800°C fraction increased gradually with gas flow rate, although it seemed to level off somewhat at higher flow rates. Carrier gas flow rate is constrained at the lower and upper levels by the need to remove desorption/reaction products, and by the onset of physical disruption of the sample or sample pan, respectively. Mass loss rate is expected to increase as desorption reaction products, whose presence in the immediate surroundings of the sample can suppress desorption kinetics, are removed as they are released from the sample particles. A carrier gas flow rate of 50 ml/min has been selected for all subsequent TGA work.

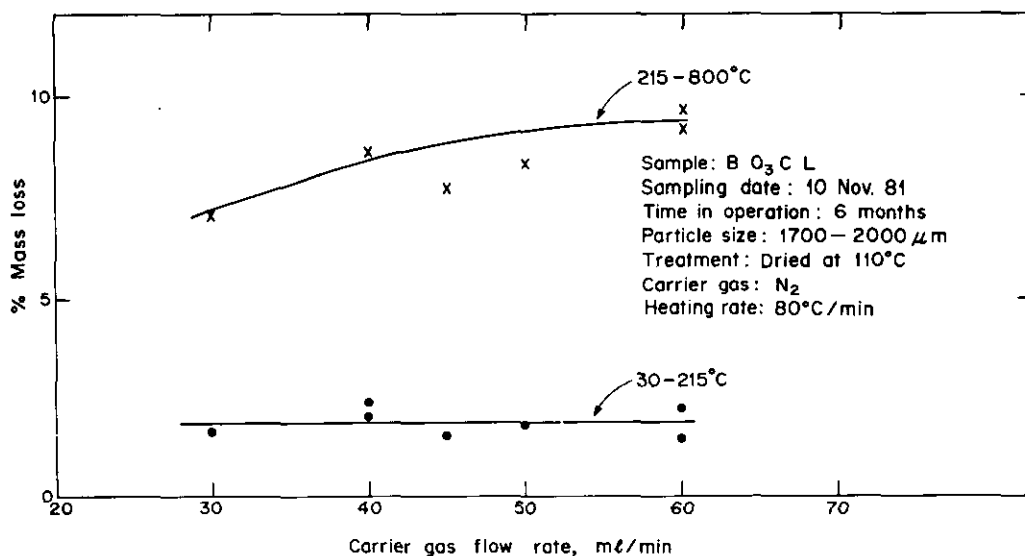


Figure 3
 Influence of carrier gas flow rate on TGA.

Influence of adsorbent particle size.

Fig. 4 shows the marked effect of sample particle size on TGA mass loss levels. Mass loss for both the 30°C to 215°C and 215°C to 800°C particle size intervals increases sharply as particle size decreases, indicating that activity increases inversely with particle size. This heterogeneity of adsorbate loading with respect to par-

ticle size posed a serious problem when 1 to 4 mg samples, typically a few particles, had to be analyzed by TGA. Different approaches were followed in an attempt to overcome this problem, as summarized in Table 4. The procedure comprising mechanical grinding (and blending) to 95% < 75 μm produced the best results and has been adopted for subsequent work (with the exception of the ensuing heating rate study).

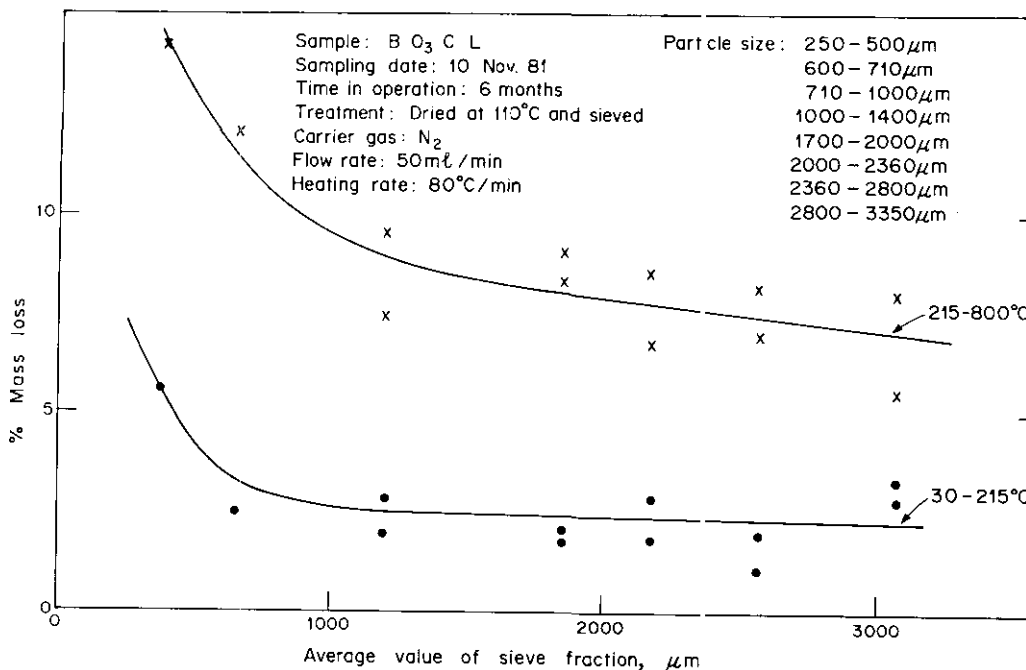


Figure 4
Influence of adsorbent particle size on TGA.

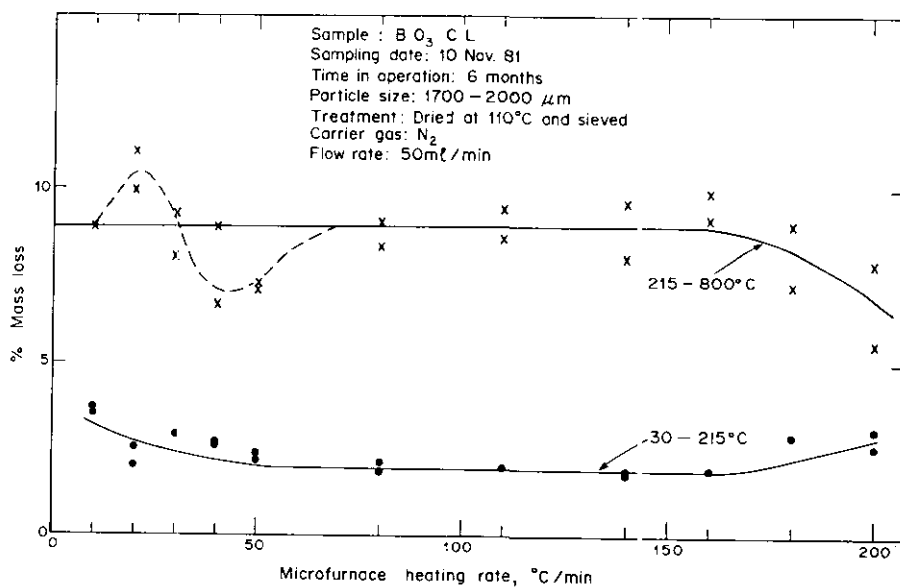


Figure 5
Influence of microfurnace heating rate on TGA.

TABLE 4
EFFECT OF SAMPLE HANDLING PROCEDURE ON MASS LOSS STATISTICS FOR TGA UNDER N₂ AS CARRIER GAS, FOR THE 215 TO 800°C TEMPERATURE INTERVAL. (SPENT CARBON SAMPLE BO₃CL; HEATING RATE = 80°C/MIN)

TGA mass loss statistics	All particle sizes (250 to 3350 μm) included in population sampled for TGA	Manual grinding, plus selection of the 150-250 μm size fraction for TGA sample	Manual grinding to 95% < 150 μm then sampled for TGA	Mechanical grinding (and blending) to 95% < 75 μm, then sampled for TGA
Average per cent mass loss	8,8	7,0	6,5	7,7
Standard deviation	2,3	2,3	1,5	0,4
Coefficient of variation	26%	33%	23%	5%

Influence of heating rate.

Fig. 5 shows the influence of microfurnace heating rate on mass loss for the temperature intervals 30°C to 215°C and 215°C to 800°C. By and large, mass loss is relatively insensitive to heating rate over a wide range. There may well be some perturbation for the 215°C to 800°C fraction between 20°C/min to 60°C/min, but the trendline remains essentially constant. At heating rates above 160°C/min, the 30°C to 215°C fraction increases, with a concomitant pronounced decrease in the 215°C to 800°C fraction. It is likely that equilibrium desorption conditions are not being attained in this rapid heating rate range. If heating rate exceeds the volatilization and intraparticle diffusion rate of adsorbate in the 215°C to 800°C interval, for example, then adsorbate could be partially carbonized prior to escape from the particle. The result will be a smaller amount of mass loss in this temperature interval, with more carbonaceous residuals to deal with at higher temperature. A heating rate of 45°C/min, which would not be uncommon in an actual regeneration context, has been selected for all subsequent TGA work.

Calculation principles

All calculations have been referred to dry (at 180°C) and adsorbate free *base* carbon. Firstly, because for all the ensuing actual TGA studies, conducted according to the analytical protocol as developed above, a distinct and recurring FDC (i.e. mass loss rate) minimum was encountered at 180°C, signalling the conclusion of desorption of highly volatile adsorbate and moisture (see Fig. 2 as example). At this point, the rate of mass loss is minimal, and mass loss accordingly is insensitive to minor experimental variations in temperature. Secondly, dry carbon is required for particle density determination by mercury displacement (see equation 1), and a reference drying temperature of 180°C satisfies this requirement.

For the ensuing TGA studies, the following temperature intervals have been selected, and the respective intervals have conveniently been termed as follows:

- 25°C to 180°C (excluding moisture) : highly volatile adsorbate (hv)
- 180°C to 600°C : medium volatility adsorbate (mv)
- 600°C to 850°C : low volatility adsorbate (lv)
- > 850°C : non-volatile adsorbate (nv)

The following equations have been used to calculate the different adsorbate fractions, based on TGA, MEA and particle density determinations. (A series of blank TGA runs were conducted with virgin carbon, and the resultant minor mass loss profile was taken into consideration; i.e. the ensuing spent carbon adsorbate profiles have been based on *net* increments).

Adsorbate loss (hv) between 25°C and 180°C is calculated as:

$$q_{25-180} = \frac{(\Delta\% M_{25-180} - \% H_2O_{25-180}) \times 100}{(100 - \Delta\% M_{25-180})} \times 10 \times \frac{\rho_{PS180}}{\rho_{PV180}} \dots (2)$$

Adsorbate loss (mv) between 180°C and 600°C is calculated as:

$$q_{180-600} = \frac{(\Delta\% M_{180-600}) \times 100}{(100 - \Delta\% M_{25-180})} \times 10 \times \frac{\rho_{PS180}}{\rho_{PV180}} \dots (3)$$

Adsorbate loss (lv) between 600°C and 850°C is calculated as:

$$q_{600-850} = \frac{(\Delta\% M_{600-850}) \times 100}{(100 - \Delta\% M_{25-180})} \times 10 \times \frac{\rho_{PS180}}{\rho_{PV180}} \dots (4)$$

The non-volatile residual (nv), (> 850 °C) is calculated as:

$$q_{>850} = q_{tm180} - (q_{180-600}) - (q_{600-850}) \dots (5)$$

The total adsorbate loading is calculated as:

$$Q_{>25} = q_{25-180} + q_{180-600} + q_{600-850} + q_{>850} \dots (6)$$

Where:

- % H₂O₂₅₋₁₈₀ = Percentage water loss between 25 and 180°C (MEA)
- Δ% M₂₅₋₁₈₀ = Mass loss between 25 and 180°C, in per cent (TGA)
- Δ% M₁₈₀₋₆₀₀ = Mass loss between 180 and 600°C, in per cent (TGA)
- Δ% M₆₀₀₋₈₅₀ = Mass loss between 600 and 850°C, in per cent (TGA).

All 'q' values and 'Q' are in units of mg adsorbate/g of base (virgin) activated carbon.

Adsorbate thermal treatment response studies

Effect of type of liquid phase pretreatment.

The effect of type of oxidative pretreatment, as described in Table 3, is shown in Fig. 6 and Table 5. Between 3 and 5 analyses were done in respect of each treatment alternative. None of the pretreatment alternatives was capable of eliminating the q_{>850} non-volatile adsorbate fraction, which would have been most desirable from a regeneration point of view. Oxygenation had very little effect on the adsorbate distribution, except for a moderate increase in the q₂₅₋₁₈₀ highly volatile adsorbate frac-

tion. The *direction* of change, however, was for the fractions below 600°C to increase, and those above 600°C to decrease, which is favourable. Total adsorbate loading was also somewhat higher.

The direction of change for all adsorbate fractions, in the case of a low ozone dosage, was identical as for oxygenation and therefore favourable in a regeneration perspective. Moreover, the extent of change was considerably greater for all fractions, and the low ozone dosage actually resulted in the most favourable adsorbate distribution for all the pretreatment possibilities in this study. Total adsorbate loading further increased (relative to preoxygenation).

Prechlorination further increased the total adsorbate loading, to a high level ($Q_{>25} = 254$ mg adsorbate/g base carbon). With the exception of a slight decrease in the low volatility $q_{600-850}$ adsorbate fraction, the dominant tendency was for the resultant adsorbate loadings to increase as a result of prechlorination.

Effect of preozonation dosage level.

Preozonation at various dosage levels had a non-linear effect on the thermal treatment response patterns for the various adsorbate ranges (Fig. 7), and the total adsorbate loading increased monotonically with dosage. From a regeneration point of view, the ideal preozonation level is at 3 mg/l (low), since those adsorbates desorbing below 600°C are maximized, and those above 600°C (especially $q_{>850}$) are minimized. Total adsorbate loading at this point is about 20% higher than with no preozonation, and an overall minimum residual adsorbate fraction at 850°C ($q_{>850}/Q_{>25}$) of 0,31 is attained here.

The non-volatile adsorbate residual ($q_{>850}$) is most sensitive to preozonation dosage levels increasing above 3 mg/l; it increases about threefold for the transition from the low (3 mg/l) to a high (8 mg/l) preozonation level. A maximum residual adsorbate fraction ($q_{>850}/Q_{>25}$) of 0,63 is reached at the high preozonation level, which is comparable to the highest pure-

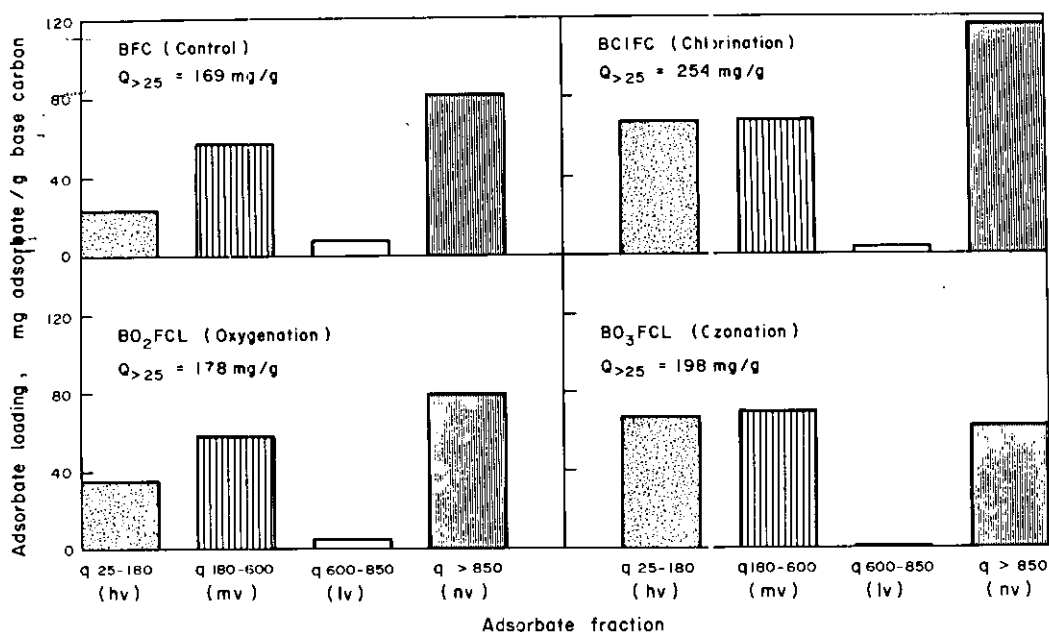


Figure 6
Adsorbate thermal treatment response as a function of type of liquid phase pretreatment.

Sample code	Solid phase adsorbate loading, mg adsorbate/g base carbon					Residual fraction at 850°C	
	q_{25-180} (hv)	$q_{180-600}$ (mv)	$q_{600-850}$ (lv)	$q_{>850}$ (nv)	$Q_{>25}$	$\frac{q_{>850}}{Q_{>25}}$	
BFC	23	57	7	82	169	0,49	
BO ₃ FCL	67	69	0	62	198	0,31	
BO ₃ FCM	48	53	0	115	216	0,53	
BO ₃ FCH	47	52	3	175	277	0,63	
BC/FC	67	68	3	116	254	0,46	
BO ₂ FC	35	58	5	80	178	0,45	

component values found by Suzuki *et al.* (1978) namely 0,61 for phenol; 0,68 for β -naphthol, Table 2, and undesirable as far as regeneration is concerned.

A t-test based statistical analysis was conducted to ascertain the significance of differences for the influence of preozonation dosage level (depicted in Fig. 7), in view of the potential practical importance of these findings. Each preozonation dosage level was individually compared with the control (BFC) which represented no oxidative pretreatment. The comparison was done in respect of each adsorbate fraction. The differences shown in Fig. 7 were acceptably significant at the 0,005 level for the highly volatile (hv) fractions, 0,010 for the non-volatile fractions (nv) and 0,025 for the medium volatility (mv) fraction. The differences shown for the low volatility (lv) fraction were significant only at the 0,300 level; however, this fraction makes a virtually inconsequential contribution to the overall mass-balance and is therefore not

of primary concern.

In studying the effects of preozonation from a liquid phase point of view, Van Leeuwen (1983), 1984(a), 1984(b)) identified various diverse influences (e.g. biodegradability and adsorbability changes), the net effect of which was also non-linear with an optimum preozonation dosage level of about 4 mg/l. A compromise dosage objective of 3 to 4 mg/l would adequately suit the requirements of both solid and liquid phases.

Summary and conclusions

A battery of activated carbon adsorbers was fed with activated sludge plant (Bardenpho) effluent which had been pretreated with several oxidants such as ozone, chlorine and oxygen. A method was developed to characterize the influence of such ox-

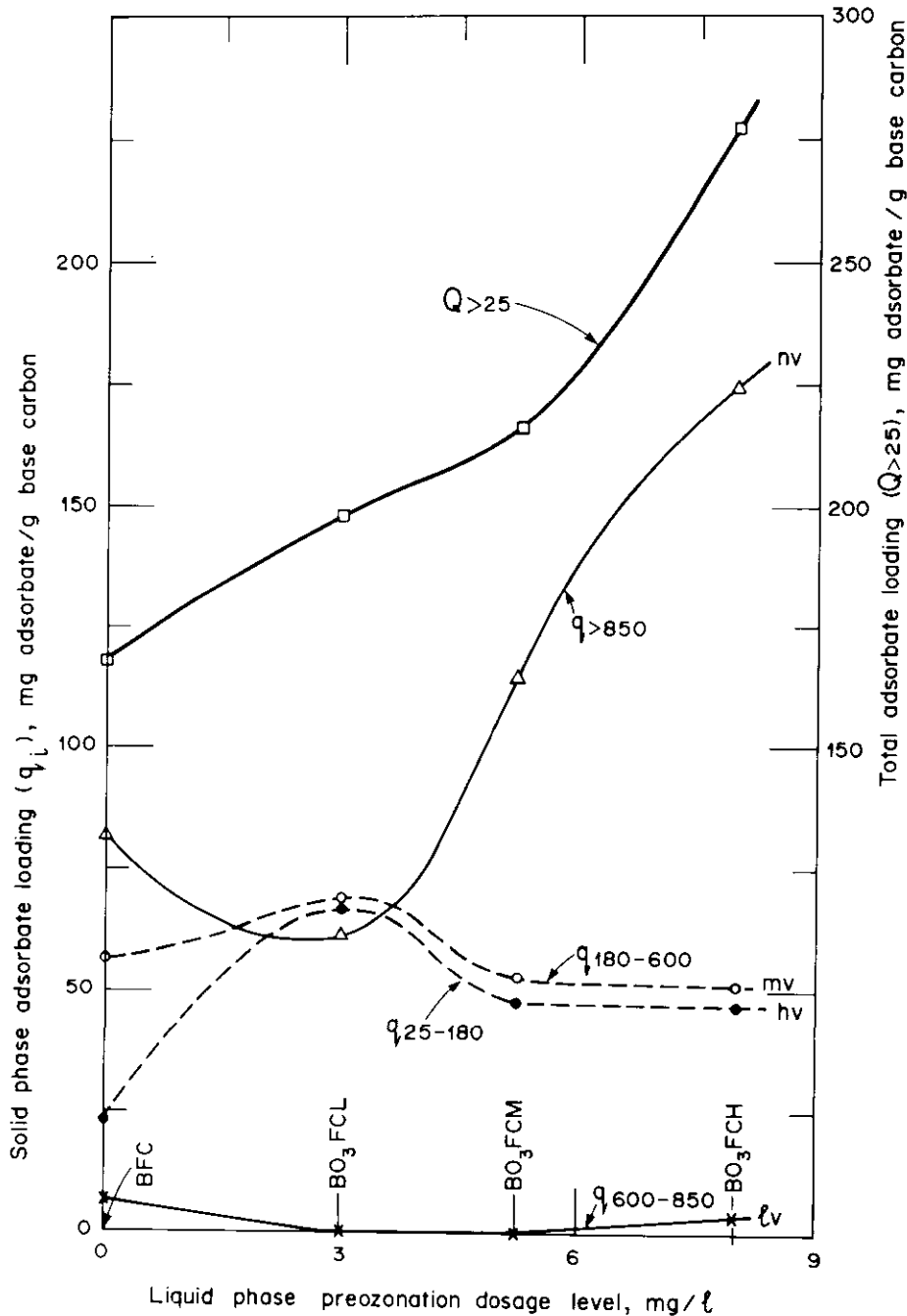


Figure 7
Adsorbate thermal treatment response as a function of preozonation dosage level.

idative pretreatment on the ultimate solid phase adsorbate distribution, and implied regenerability of the activated carbon. This method is based on thermal analysis principles and consists of heating the spent carbon in a nitrogen atmosphere up to 850°C, whilst simultaneously monitoring mass loss. Adsorbate fractions were characterized with respect to temperature intervals. The temperature range in question has been divided into the following intervals: 20°C – 180°C (highly volatile), 180°C – 600°C (medium volatile), 600°C – 850°C (low volatility) and > 850°C (non-volatile). The resultant analytical protocol is precision orientated, and requires exact control of sample heating rate (45°C/min), carrier gas flow rate (N₂ at 50 ml/min) and sample particle size (95% < 75 µm). A specific advance in adsorbate characterization is the possibility to quantify the highly volatile adsorbate fraction (desorbing at temperatures below 180°C), by distinguishing between moisture and adsorbate in this temperature range.

None of the pretreatment alternatives was capable of eliminating the non-volatile adsorbate residual (> 850°C), which would have been most desirable from a regeneration point of view.

The comparison of chlorination, oxygenation and ozonation for liquid phase pretreatment, showed that low dosage (3 mg/l) preozonation resulted in the most favourable adsorbate thermal treatment response pattern. Adsorbates desorbing below 600°C were maximized, and those above 600°C (especially > 850°C) were minimized.

An overall minimum non-volatile adsorbate residual was obtained at the low preozonation dosage level. The non-volatile adsorbate residual is most sensitive to preozonation dosage levels increasing above 3 mg/l; it increases about threefold for the transition from low to high (8 mg/l) dosage level. Expressed as a fraction of total adsorbate loading, the non-volatile residual reached an overall minimum of 0,31, and maximum of 0,63 at the low and high preozonation dosage levels, respectively.

In a spent carbon regeneration perspective, the low preozonation dosage level effects the most suitable adsorbate thermal treatment response pattern. This strategy is in adequate agreement with liquid phase treatment requirements.

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Mention of commercial products or trade names does not constitute endorsement or recommendation for use.

References

- CHIHARA, K., MATSUI, I. and SMITH, J.M. (1981) Steam-carbon reactions (Part II). *A.I.Ch.E. J.* 27 (2) 220-225.
- GRADY, C.P.L., KIRSCH, E.J., KOCZWARA, M.K., TRGOVICH, B. and WATT, R.D. (1984) Molecular weight distributions in activated sludge effluents. *Wat. Res.* 18 (2) 239-246.
- PEARL, I.A. (1967) *The Chemistry of Lignin*. Marcel Dekker, New York.
- SUZUKI, M., MISC, D.M. KOYAMA, O. and KAWAZOE, K. (1978) Study of thermal regeneration of spent activated carbons: Thermogravimetric measurement of various single component organics loaded on activated carbons. *Chem. Engng. Sci.* 33 271-279.
- URANO, K., YAMAMOTO, E. and TAKEDA, H. (1981) Regeneration rates of granular activated carbons containing adsorbed organic matter. *Ind. Eng. Chem., Process Des. and Dev.* 21 (1) 180-185.
- VAN LEEUWEN, J., PRINSLOO, J. and VAN STEENDEREN, R.A. (1983) The optimization of ozonation and biologically activated carbon (BAC) in the water reclamation context. *Ozone Science and Engineering* 5 (6) 171-181.
- VAN LEEUWEN, J., STREETER, J.H. and VAN STEENDEREN, R.A. (1984a) Optimization of the removal of organic substances in a water reclamation plant. Presented at the 4th meeting of the South African Institution of Chemical Engineers, Potchefstroom, South Africa, 14-15 March.
- VAN LEEUWEN, J., NUPEN, E.M. and CARSTENS, P.A. DU T. (1984b) The influence of ozone, oxygen and chlorine on biological activity on biological activated carbon. Presented at the IOA/NIWR International Conference, Pretoria, South Africa, 26-29 March.