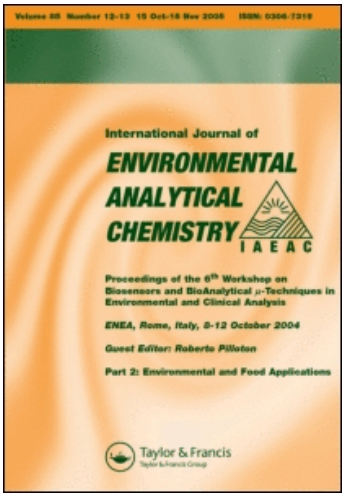

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The Use of Fast Atom Bombardment (FAB) Mass Spectrometry for Monitoring Petrochemicals

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The Use of Fast Atom Bombardment (FAB) Mass Spectrometry for Monitoring Petrochemicals†

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In recent years ionisation by Fast Atom Bombardment (FAB) has been developed to enable mass spectrometric (MS) analysis to be performed on samples containing polar, involatile compounds without any pre-derivatisation. This makes FAB MS an ideal candidate for the analysis of polar petrochemical waste products. In addition, the soft ionisation induced by FAB minimises fragmentation, enabling complex mixtures to be screened routinely without lengthy sample work-up. Confirmatory identification of components can be obtained at high MS resolution. The present study reports the use of FAB MS to monitor specific petrochemicals in the aqueous effluents from certain coastal plants.

KEY WORDS: FAB mass spectrometry, petrochemicals, phenols, phthalates, derivatisation.

INTRODUCTION

Possibly the most significant advance in mass spectrometry in recent years has been the development of a new form of soft ionisation called fast atom bombardment (FAB). This liquid phase method enables samples to be analysed by mass spectrometry without first being vaporised. The technique was first reported by Barber, Bordoli and Sedgwick[1] as a modification of the technique of secondary ion

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mass spectrometry (SIMS). The FAB method overcomes the problems inherent to SIMS, such as short spectral lifetime and surface charging, by utilising a beam of fast atoms/ions (typically Xenon at 2–8 keV), to bombard the sample placed on a target in solution in a liquid matrix. The ionisation induced is of low energy which therefore minimises fragmentation enabling valuable information concerning the molecular ion to be obtained.

The FAB technique has been refined by workers such as Morris[2] mainly for the study of biochemicals, particularly high molecular weight (up to 8,000 amu) biopolymers. Although the uses of FAB mass spectrometry are diversifying there is no reported study of its use in environmental studies.

The present work utilises FAB mass spectrometry to examine polar organic compounds present in the aqueous effluents of two plants at coastal sites. The FAB results are compared with those obtained by conventional gas chromatography-mass spectrometry (GLC/MS) of the effluent extracts both before and after derivatisation.

Site 1 manufactures PVC, polyester resins and synthetic rubbers. Aqueous effluents from this site is discharged into the upper tidal stretch of a river, which flows for *ca.* 150 m before entering a small bay. Future work will include the analysis of the river water, sea water and foreshore sediments.

Site 2 is a large production complex manufacturing a range of organic acids, intermediates and plasticisers. Effluent from the plant is discharged *ca.* 10 m offshore into a creek in the intertidal sediments of an estuary. Sediment samples have also been taken from a grid of sites around the effluent outfall for future work on the analysis of the receiving environment.

EXPERIMENTAL

Samples

Two pre-cleaned 2.7 litre glass bottles ("Winchester" type) were used to collect aqueous effluent from both sites. The bottles were sealed with PTFE lined screw caps and transported immediately to the laboratory where they were extracted within 24 hours of sample collection. The results are assumed representative; detailed replication studies are planned.

Extraction

Acid fractions were obtained by adjusting the pH of the effluent to 2, using pre-extracted hydrochloric acid (6N) and extracting with dichloromethane ($2 \times 100\,cm^3$). The sample bottle was rinsed with dichloromethane ($100\,cm^3$) and the organic extracts combined. The combined extract was transferred to a 1 litre separating funnel and washed with pre-extracted hydrochloric acid ($200\,cm^3$; 1N). The organic extract was evaporated to dryness at ambient under vacuum (Buchi Rotavap R) to provide an acidic fraction.

Derivatisation

Fifty percent of each acid fraction was derivatised using N-methyl N-trimethylsilyltrifluoroacetamide (MSTFA). The solution was kept at 40°C for a minimum of 30 min before GLC/MS analysis of the resulting trimethylsilyl (TMS) derivatives.

Electron impact (EI) gas chromatography-mass spectrometry

The effluent fractions from Site 1 were examined with a Finnigan 3200 quadrupole mass spectrometer incorporating a 6100 data system. The instrument was scanned at 1 cycle every 2 seconds over the mass range 50–550 amu with emission current at 300 μA and an ionisation voltage of 70 eV. Gas liquid chromatography (GLC) used a $20\,m \times 0.3\,mm$ i.d. OV-1 WCOT glass column with a Gröb split/splitless injector and oven temperature programme of 40°C to 300°C at $6°C\,min^{-1}$.

The effluent fractions from Site 2 were analysed on a VG Analytical ZAB HF mass spectrometer with an integrated Hewlett Packard 5790 capillary gas chromatograph and a VG Analytical 11–250 data system. The mass spectrometer was scanned over the mass range 500–35 amu once every 1.7 seconds with the trap current at 200 μA, ionisation voltage at 70 eV and an accelerating voltage of 8 kV. Mass resolution was set at approximately 2,000. GLC was carried out on a $30\,m \times 0.26\,mm$ i.d. DB-1 (OV-1 equivalent, J. & W. Scientific Inc.) WCOT fused silica column with a Gröb split/splitless injector and oven temperature programme of 40°C to 320°C at $8°C\,min^{-1}$.

FAB mass spectrometry

FAB was carried out using a VG Analytical ZAB HF mass spectrometer using Xenon as the primary ionising beam with a beam energy of 8 keV. The underivatised acid extract was loaded onto a glycerol-coated probe tip which was subsequently dosed with 1 μl of thioglycerol. Positive and negative spectra were obtained over the mass range 1,500–50 amu using a scan speed of 5 seconds/decade and recorded using an on-line VG Analytical 11–250 data system.

RESULTS AND DISCUSSION

Site 1 effluent—GLC/MS

GLC/MS analysis of the underivatised acid fraction from the Site 1 effluent showed 7 peaks (A–G, see below), of which the largest was due to phenol. Five of the remaining 6 peaks showed mass spectra that were similar to those of nitrophenol and the methyl and C_2 homologues of phenol and nitrophenol. The latest eluting peak displayed a mass spectrum with an apparent molecular ion at m/z 174 but no structure was confirmed at this stage.

The GLC/MS total ion current (TIC) trace of the derivatised acid fraction is shown in Figure 1. It is clear that derivatisation has allowed the detection of higher molecular weight components (J, K and L) in addition to the components A–G that were also seen in the analysis of the underivatised fractions. By comparing the mass spectrum of component J with the NBS reference spectra library in

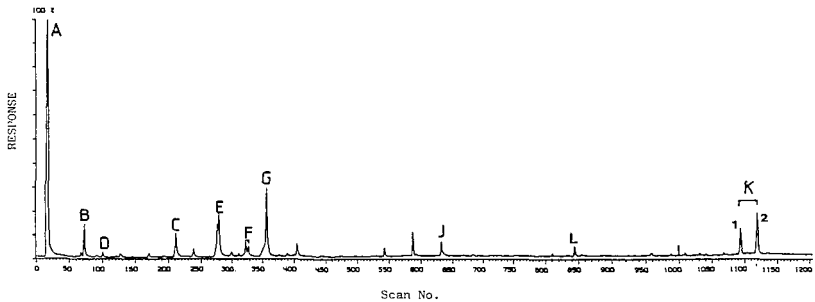


FIGURE 1 GLC/MS total ion current trace of Site 1 effluent acid fraction—TMS derivatives (peak identifications given in Table I).

an INCOS data system a library match was obtained with the di-TMS derivative of methylenebisphenol (Table I). By subsequent comparison of this spectrum with those of other components in the mixture, possible structures have been postulated and are shown in Table I. Components K1 and K2 have similar mass spectra but shown no molecular ion. A partial structure, based on the fragment ions in the spectrum, has been postulated. The higher molecular weight components seen in the GLC/MS analysis of the derivatised acid fraction are thought to correspond to the oligomeric condensations of phenol, formaldehyde and furfural, all of which were in use at Site 1 at the time of sample collection.

Site 1 effluent—FAB

The positive ion FAB mass spectrum of the underivatised acid extract showed no major ions apart from those of the glycerol matrix. The negative ion FAB spectrum is shown in Figure 2. In the negative ion mode the ions detected generally correspond to the loss of a proton from the molecular ion. Thus the ion at 93(A) is probably due to the loss of a proton from phenol (molecular weight 94). There are FAB ions corresponding to $[M-H]^-$ for all except one of the major components (A–L) previously seen as TMS derivatives by GLC/MS. The component that responds best to FAB ionisation has an $[M-H]^-$ of m/z 425 corresponding to a molecular weight of 426. It is thought that this may correspond to components K1 and K2, above. On this basis a full structure for the two K isomers has been postulated (Table II).

In addition to the components seen in the GLC/MS analysis (Table I) there are other major ions in the negative ion FAB spectrum that possibly correspond to the molecular anions of dinitrophenol (M) and a component (N) resulting from the condensation of one phenol and two furfural moieties. There are also ions at m/z 59 and m/z 73 which may indicate the presence of acetic and propionic acids respectively. The identity of these four previously undetected components is only tentative at the present, but confirmation of their molecular formulae could be obtained by accurate mass measurement of their $[M-H]^-$ ions. As FAB spectra generally have a relatively long lifetime in the instrument, several ions can be accurately mass measured during one analysis.

TABLE I

CGCMS analysis of trimethyl silyl derivatives of phenols in Site 1 discharge.

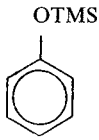
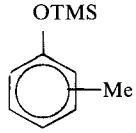
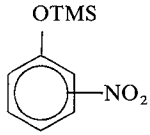
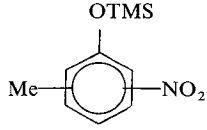
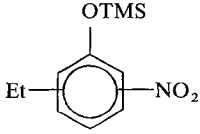
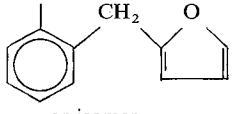
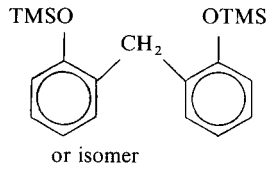
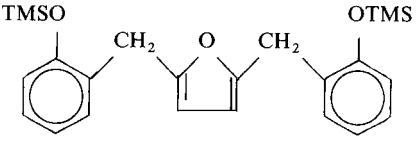
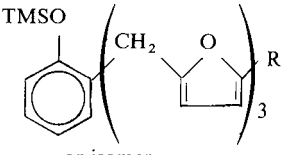
Component	Scan no.	Molecular weight	Molecular formula	Structural assignment
A(TMS)	20	166	$C_9H_{14}SiO$	Phenol TMS 
B(TMS)	73	180	$C_{10}H_{16}SiO$	Cresol TMS 
C(TMS)	212	211	$C_9H_{13}SiNO_3$	Nitrophenol TMS 
E(TMS)	278	225	$C_{10}H_{15}SiNO_3$	Nitrocresol TMS 
F(TMS)	324	239	$C_{11}H_{17}SiNO_3$	Nitroethylphenol TMS 
G(TMS)	359	246	$C_{14}H_{18}SiO$	TMSO  or isomer

TABLE I (continued)

Component	Scan no.	Molecular weight	Molecular formula	Structural assignment
J(TMS)	633	344	$C_{19}H_{28}Si_2O_3$	 or isomer
L(TMS)	845	424	$C_{24}H_{32}Si_2O_3$	 or isomer
K1(TMS)	1095	?	?	 or isomer
K2(TMS)	1121	?	?	As K1(TMS)

Site 2 effluent—GLC/MS

The TIC trace obtained from GLC/MS analysis of the underivatised acid fraction from Site 2 effluent is shown in Figure 3. The majority of components have been identified by successful comparison of their mass spectra with those in the NBS spectrum library of the VG Analytical 11-250 data system (Table III). By far the largest component in the trace (C) is thought from its library spectrum match to be a trimethyl cyclohexenone possibly resulting from the condensation of three acetone molecules. Components G, I, O and P (Figure 3), four of the largest remaining peaks in the trace, have been identified as dimethyl, diethyl, dibutyl and dioctyl phthalates respectively. Moreover, the mass fragmentogram of the m/z 149 ion, characteristic of phthalates, showed an additional homologous

TABLE II

Interpretation of the major ions seen in the negative ion FAB spectrum of the acid extract of Site 1 discharge water.

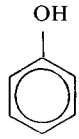
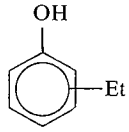
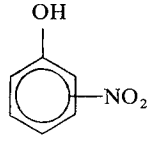
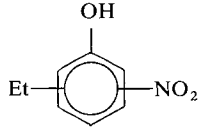
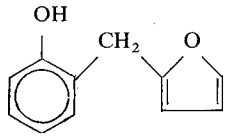
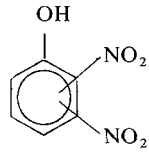
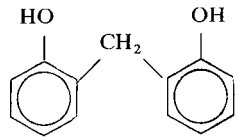
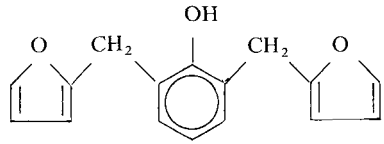
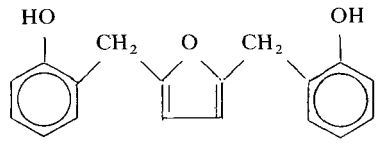
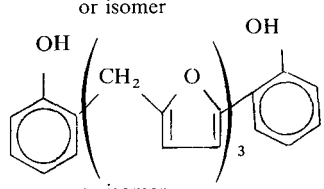
Component	Ion (m/z)	Molecular weight	Molecular formula	Structural assignment
A	93	94	C_6H_6O	Phenol 
B	121	122	$C_8H_{10}O$	Ethylphenol(s) 
C	138	139	$C_6H_5NO_3$	Nitrophenol 
F	166	167	$C_8H_9NO_3$?	Nitroethylphenol? 
G	173	174	$C_{11}H_{10}O_2$	 or isomer

TABLE II (continued)

Component	Ion (m/z)	Molecular weight	Molecular formula	Structural assignment
M	183	184	$C_6H_4N_2O_5$	Dinitrophenol? 
J	199	200	$C_{13}H_{12}O_2$	 or isomer
N	253	254	$C_{16}H_{14}O_3$	 or isomer
L	279	280	$C_{18}H_{16}O_3$	 or isomer
K	425	426	$C_{27}H_{22}O_5$	 or isomer

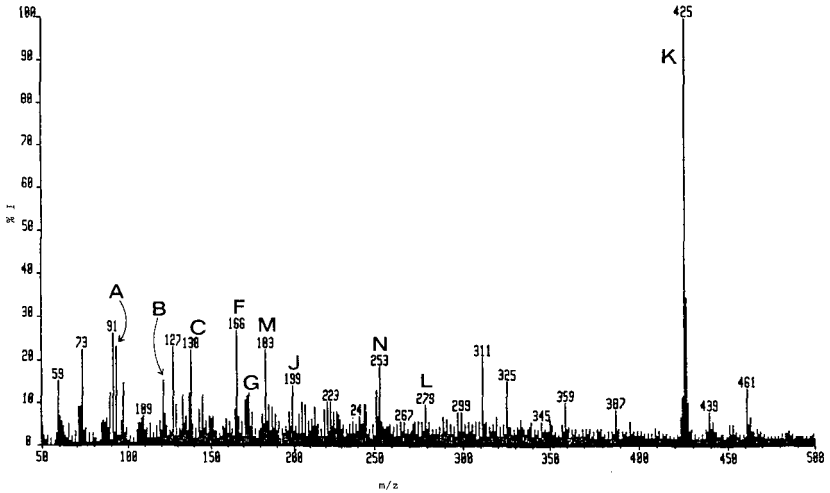


FIGURE 2 Negative ion FAB mass spectrum of Site 1 effluent acid fraction (peak identifications given in Table II).

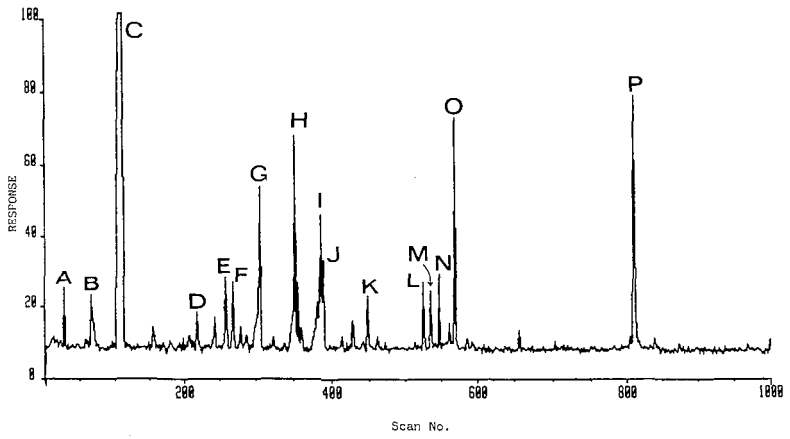


FIGURE 3 GLC/MS total ion current trace of Site 2 effluent acid fraction (peak identifications given in Table III).

series of phthalate esters from C_{15} (heptyloctyl phthalate) to C_{24} (didodecylphthalate). Although no data library match was obtained for Component H it is thought from its mass spectrum to be the oxidised form of the common antioxidant di-tert-butylmethyl phenol.

TABLE III
GLC/MS analysis of Site 2 effluent acid fraction.

Component	Scan no.	Molecular weight	Molecular formula	Structural assignment
A	28	120	C_9H_{12}	Trimethyl Benzene
B	67	130	$C_8H_{18}O$	2-Ethylhexanol
C	111	138	$C_9H_{14}O$	Trimethylcyclohexenone
D	218	140	$C_8H_{12}O_2$	Ethylcyclohexandione ?
E	259	178	$C_{12}H_{18}O$	Isomer of F
F	269	178	$C_{12}H_{18}O$	Trimethyl(2-propenyl)-cyclohexenone ?
G	306	194	$C_{10}H_{10}O_4$	Dimethyl Phthalate
H	353	218	$C_{15}H_{22}O$?	Oxidised antioxidant ?
I	386	222	$C_{12}H_{14}O_4$	Diethyl Phthalate
J	390	202	$C_{14}H_{18}O$	Tetramethyl Tetralone
K	449	218	$C_{15}H_{22}O$?	Not yet assigned
L	526	278	$C_{16}H_{22}O_4$	Diisobutyl Phthalate
M	536	276	$C_{18}H_{28}O_2$?	Methanobenzocyclo-octadiene-ol ?
N	547	258	?	Unknown
O	570	278	$C_{16}H_{22}O_4$	Dibutyl Phthalate
P	811	390	$C_{24}H_{38}O_4$	Dioctyl Phthalate

The remaining components are mainly cyclic and aromatic alcohols and ketones.

GLC/MS analysis of the TMS derivatives of the Site 2 acid fraction showed only minor differences to that of the underivatised fraction. Minor peaks due to phenol and some acyclic aliphatic alcohols were detected in addition to the components listed in Table III (derivatised as expected).

Site 2 effluent—FAB

The positive ion FAB mass spectrum of the acid fraction from Site 2 effluent was relatively simple, with the spectrum (Figure 4) dominated by an ion at m/z 149. This is thought to be a fragment ion of phthalate esters, which were detected in the GLC/MS analysis of the effluent, above.

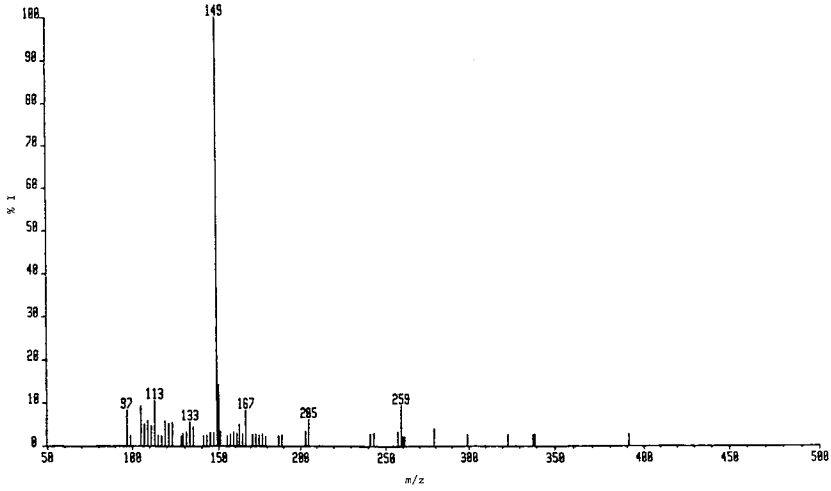


FIGURE 4 Positive ion FAB mass spectrum of Site 2 effluent acid fraction.

Figure 5 shows the negative ion FAB mass spectrum of the Site 2 effluent acid fraction. The ion at m/z 121 is thought to be the $[M-H]^-$ ion of benzoic acid. The two largest ions in the spectrum (m/z 221 and 277) are thought to represent the $[M-H]^-$ ions of C_4 and C_8 phthalate esters. As phthalate esters do not respond to the FAB technique in the negative ion mode it is thought that the peaks observed are due to phthalate mono-esters, the free acid group giving the expected response to negative ion FAB. The two major ions therefore probably represent the mono esters of the two major phthalates (dibutyl and dioctyl) observed in the GLC/MS analysis. Free phthalic acid (m/z 165) and the mono esters of the dimethyl and diethyl phthalates seen by GLC/MS are also indicated in the FAB spectrum (ions at m/z 179 and m/z 193). In addition there is an homologous series of ions m/z 263 to m/z 319 which probably correspond to the $[M-H]^-$ ions of C_7–C_{11} mono phthalate esters. The presence of these longer chain mono esters is consistent with the observation of long-chain diesters in the GLC/MS analysis.

The identity of the components giving rise to the higher ions (e.g. m/z 353) in the FAB spectrum has not yet been elucidated. Accurate mass measurement of these ions should help establish their molecular formulae.

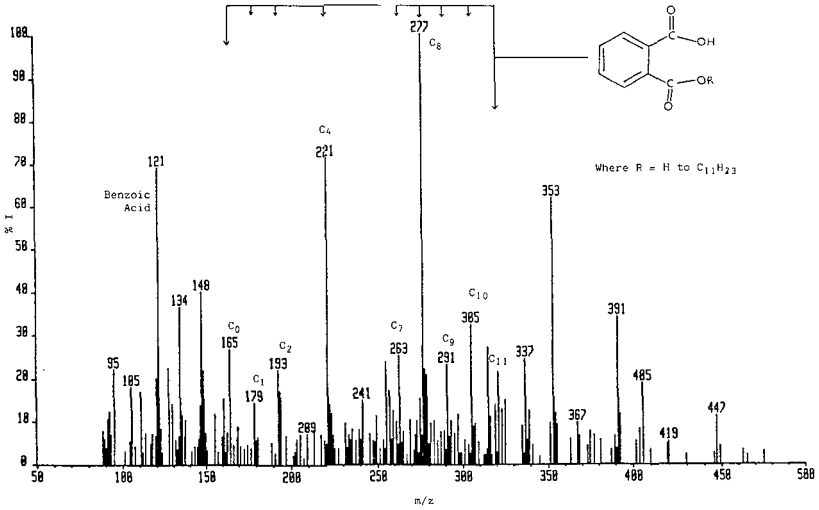


FIGURE 5 Negative ion FAB mass spectrum of Site 2 effluent acid fraction.

CONCLUSIONS

The results above, although of a preliminary nature, have shown that FAB/MS analysis of the underivatised acid extracts of petrochemical effluents can lead to the rapid detection of complex mixtures of components and that the results can be related directly to compounds identified by the slower GLC/MS technique.

The minimal sample preparation requirement and the short MS run time would suggest that FAB/MS screening may provide a convenient and cost-effective option for wide-scale environmental surveys around petrochemical outfalls. Initial characterisation by GLC/MS, however, will probably always be necessary.

In an extension of the present project it is planned to use the FAB technique to analyse sediments and waters from the receiving environment around the two effluent outfalls for those components identified in the present study of the effluents.

Acknowledgements

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