

DIFFUSE POLLUTION OF WATER SOURCES BY A NEWLY IDENTIFIED SILICONE BREAKDOWN PRODUCT

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ABSTRACT

Research on the mechanism of biological phosphate removal in the activated sludge process for wastewater treatment led to the discovery of a hitherto unknown pollutant of the water environment. Studies on the identity and nature of the unknown substance showed that it could exist in more than one oxidation state, depending on redox conditions, i.e. as precursor, intermediates and as an activated species. The activated species acts as a strong oxidant and is considered to be the final breakdown product of the precursors in biological wastewater treatment. Our studies over many years showed a link between the activated species and certain silicone breakdown products. Due to their exceptional chemical stability, silicones have long been considered as virtually inert in the environment. Subsequently, it has been reported by a number of researchers (1, 2) that silicones are degraded in the environment into silanols and eventually into harmless end products. However, our studies indicate that the activated silicone species could be the ultimate degradation product that occur widely in the water environment and that could have far-reaching implications on problems like global warming and acid rain.

Keywords :Silicone breakdown products, silanol, silane oxidant, diffuse pollution

INTRODUCTION

Silicones $[\text{Me}(\text{Me}_2\text{SiO})_n \text{SiMe}_3]$ (where Me refers to CH_3) are synthetic polymers that find wide application as lubricants, anti-foaming agents and in numerous other industrial and domestic applications. As a result of its exceptional chemical stability and very low solubility, silicone contamination of the environment and water sources is rarely mentioned as an environmental hazard in the literature. A number of studies however, showed that silicones are subject to degradation in the environment and that highly mobile hydrolysis products may find their way into the environment (1, 2, 3, 4). Silicone breakdown products such as dimethylsilanediol and siloxanols have been identified in studies relating to environmental degradation of silicones. The presence of these products as pollutants of the environment, however, has not been reported to date. Our studies show that there is good reason to believe that silicone breakdown products indeed occur widely in the water environment and that they may have far-reaching effects in the water environment and in water treatment systems.

The initial objective of this study was to establish whether redox reactions in the anaerobic and aerobic zones respectively of activated sludge plants used for the treatment of wastewater could influence biological phosphate removal in a chemical manner. The focus therefore was to find any substance that is chemically reduced in the anaerobic stage and then oxidised in the subsequent aerobic stage of activated sludge plants in such a way that it would facilitate phosphate removal by biological means. While conclusive evidence in this regard was obtained during the present study, another aspect became of much greater significance. In the search for the perceived chemical link, a picture emerged of a ubiquitous water and atmospheric pollutant that could have grave consequences for the world's environment.

METHODS

The unknown substance was first observed when an activated organic substance (AOS) was identified in the effluents of activated sludge and biological filter plants. The presence of AOS was demonstrated by addition of KI solution to an acidified effluent sample. Iodine is liberated from such samples when AOS is present. Concentration levels of the AOS proved to be about 10 times lower in activated sludge effluents than in biological filter effluents. The reason for this could be that activated sludge processes for the removal of phosphates include stages of high and low redox potential respectively and AOS is produced under conditions of relatively high redox potential and it is reduced under conditions of low (negative) redox potential.

It was discovered that the AOS could also be produced by chemical means. When settled sewage to which nitrate has been added, is left in contact with Fe metal, the AOS is produced within one hour. A similar procedure using tap water had the same result. This indicated that the substance (precursor) that was transformed to become the AOS under the reducing conditions was present not only in wastewater but also in tap water.

In laboratory activated sludge batch experiments it was demonstrated that chemical manipulation of AOS and its precursor directly influenced the efficiency of biological phosphate removal (5). The conclusion was that AOS could be a chemical link in the process of biological phosphate removal. Without this link there is little or no biological phosphate removal although all other factors for this process are favourable. However, this is not the most important finding of the present study. In the search for the chemical link, ubiquitous water and atmospheric pollutants which apparently have gone unnoticed to date, have been detected.

Having demonstrated the presence of the unknown substances in water and wastewater, our studies focussed on positive identification of these substances. Mass spectrometry appeared to be the obvious choice to identify AOS since it proved to be in a gaseous state when at room temperature and at low pH. (AOS can be stripped from an acidified distillate sample by aeration in a small column). The head-space method was used and samples of 500 μl and 1000 μl respectively were injected into the gas chromatograph via a thermal desorption module to cryofocus the volatile substances on the column for analysis.

RESULTS AND DISCUSSION

The MS spectrum for the most prominent peak in the chromatogram for AOS showed the base peak at mass number 44 and minor peaks at mass numbers 43 and 45. Similar peaks were found whether AOS was obtained from tap water or from effluent. The mass spectra were considered useful information but positive identification in this manner was not possible. In the search for further information on the nature and identity of AOS, we investigated the oxidative capacity and acidity of AOS. The AOS can be concentrated by means of distillation from an acidified solution. When 500 ml of such a solution is distilled, the AOS is concentrated in the first 100 ml of distillate. The distillate pH is typically around a value of 3.0. The relationship between the acidic and oxidative nature of the AOS can be established by titration with $\text{Na}_2\text{S}_2\text{O}_3$ and NaOH respectively. For the determination 0,025 N $\text{Na}_2\text{S}_2\text{O}_3$ and 0,02 N NaOH were used respectively. The ratio of 0,025N $\text{Na}_2\text{S}_2\text{O}_3$ titres to 0,02N NaOH titres proved to be 1,87:1 on average. This is considered an important clue regarding the identity of the AOS. If the H^+ ion of the AOS in a redox reaction is reduced to H^0 (hydrogen gas), i.e. a one electron transfer, the titration ratio would be 0,8:1. If, however, the H^+ ion is reduced to H^- , i.e. a two electron transfer, the ratio would be 1,6:1. The actual ratio found in our studies is close to 1,6:1, which is an indication that H^+ in this case is reduced to H^- . The only possible substances that could be involved therefore, are the hydrides and silanes. Because the AOS is a gas at room temperature, the only possible candidates are the silanes.

In order to demonstrate that there could be a link between AOS and silanes/silanols, dimethylsilanediol was prepared according to the procedure reported by Cella and Carpenter (6). It was found that dimethylsilanediol prepared in this manner was subject to polymerisation to form silicone when the ethylether used in the preparation, was evaporated. A sticky, brown residue was left when the ethylether was evaporated from a dish of aluminium foil. An IR spectrum showed that the residue after evaporation was indeed silicone with peaks at wavenumbers 802, 1036, 1073 and 1280 cm^{-1} that are typical of silicones.

The next objective was to find a suitable procedure whereby the suspected precursors of AOS in water could be isolated and identified by means of IR spectrophotometry. It was found that treatment at high pH produced the desired results. When water at pH 12,5 (through addition of NaOH) is left in contact with polythene surfaces (e.g. polythene tubing) for 96 hours, the oxidation test for AOS formation proved negative. When such an alkaline solution is acidified (pH 1 to 2) and extracted with chloroform, a greasy substance is obtained when the chloroform is evaporated. The IR spectra of the greasy substance showed characteristic peaks of silicone at wave numbers 802, 1024, 1081 and 1260 cm^{-1} (Figures 1A and 1B). In all the experimental work, great care was taken that no silicone products were used, e.g. for lubrication of stopcocks, etc. The results obtained indicated that polymerisation of the suspected contaminants in the water led to silicone formation under the experimental conditions. The fact that AOS formation was eliminated by the pre-treatment which led to polymerisation, indicates that there is a direct link between the AOS and the contaminants responsible for silicone formation under the experimental conditions.

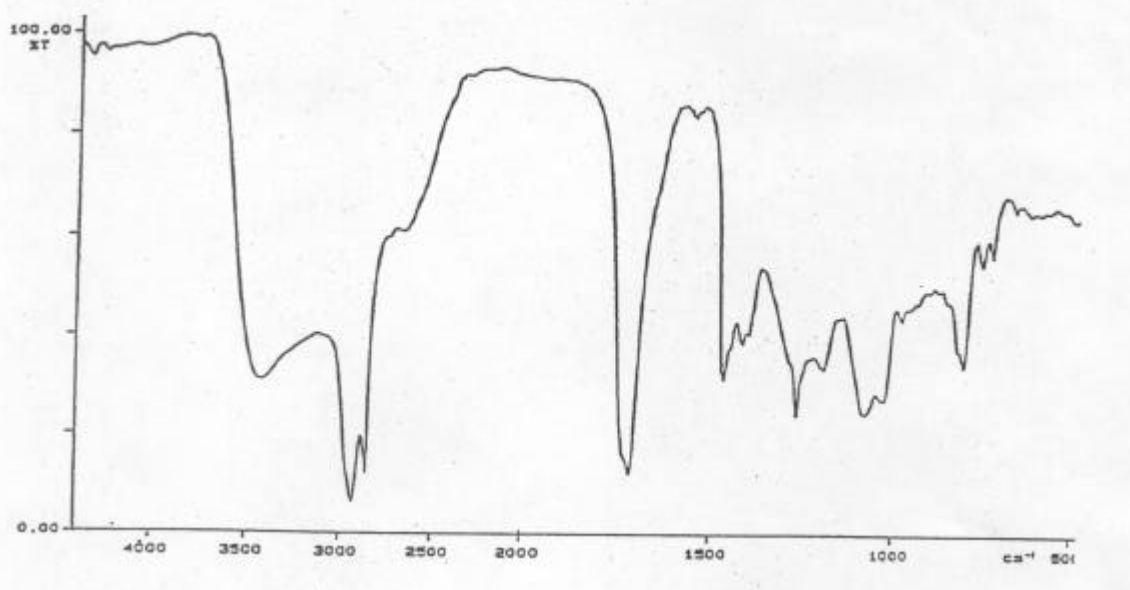


FIGURE 1A: IR SPECTRUM OF A CHLOROFORM EXTRACT.

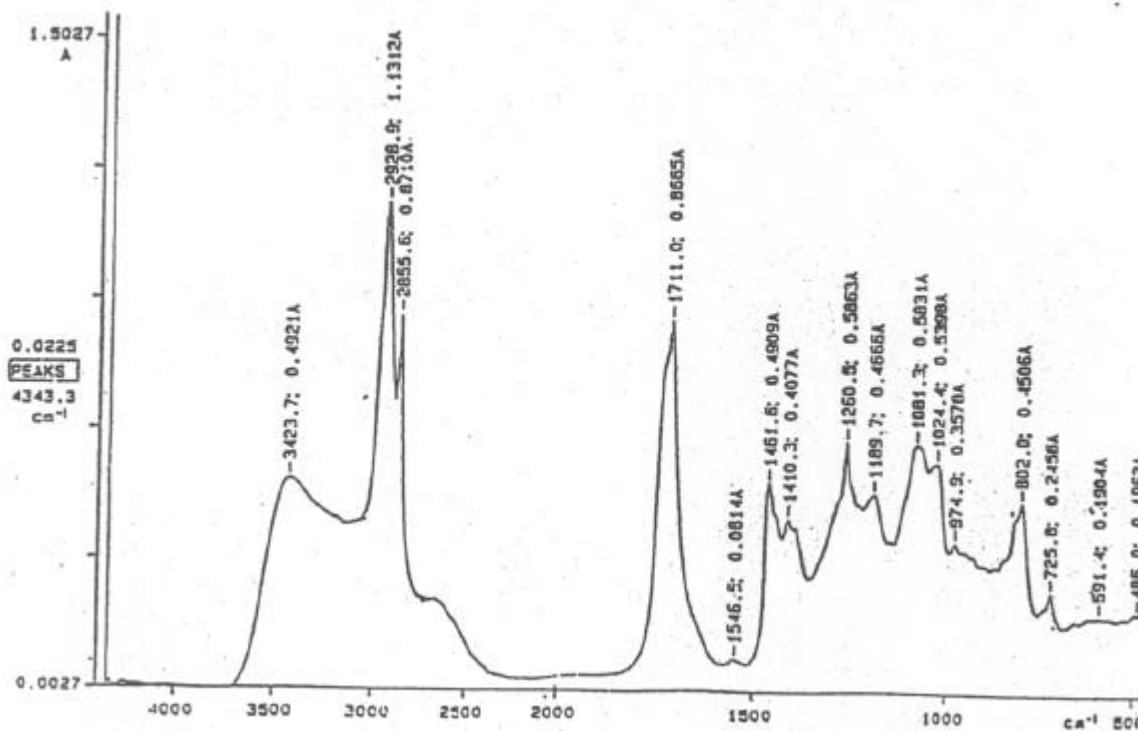


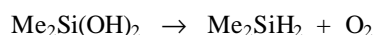
FIGURE 1B: INVERSE OF 1A, INDICATING PEAK WAVENUMBERS.

PROPOSED MODEL

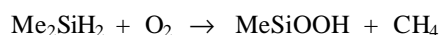
From the abovementioned experimental a model has been developed that offers an explanation for the observations. It is postulated that silicone degradation products such as trimethylsilanol Me_3SiOH and dimethylsilanediol $\text{Me}_2\text{Si}(\text{OH})_2$ can exist in water and wastewater in different oxidation states. Silane, e.g. trimethylsilane, is a strong reductant and can only exist as such in parts of activated sludge plants where a low redox potential exists, i.e. the anaerobic stages of the process. However, it became apparent that an oxidised variety of silane is present in wastewater, i.e. the AOS which is a strong oxidant and which is present in activated sludge plant effluents as well as biological filter effluents. Apart from being a strong oxidant, the AOS behaves like an organic acid: it can be distilled from acidified solutions but not from alkaline solutions.

It is postulated that the precursors of the AOS are trimethylsilanol and dimethylsilanediol. However, transformation to the AOS presumably involves the silanes as intermediates. In the case of the chemical procedure for AOS formation (Fe metal contact), the presence of nitrate is a prerequisite and AOS formation is accompanied by the quantitative reduction of nitrate to ammonia. The reductant in this case, the silanes, are oxidised in the process to become the AOS.

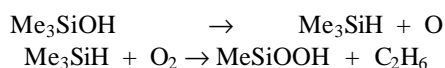
When dimethylsilanediol is considered as a candidate for AOS formation, there are possibly only two reaction pathways to consider. The most important consideration is that the ultimate reaction product behaves like an organic acid that dissociates to produce H^+ and an organic radical in solution. A possibility would be that silicon would fulfil a role exactly like that of carbon in organic acids, i.e. $-\text{SiOOH}$, which would dissociate like an organic acid, i.e. $-\text{SiOOH}^+$. However, since oxidant formation was accompanied by the reduction of nitrate to ammonia, it is suggested that the first step in oxidant formation is the formation of silanes, e.g. dimethyldisilane, under conditions of low redox potential. This reaction can be represented as follows:



AOS formation under conditions of relatively high redox potential, can be represented as follows:



In the case of trimethylsilanol, similar redox reactions can be represented as follows:



AOS formation with both dimethylsilanediol and trimethylsilanol would therefore have the same reaction product, Me SiOOH.

The MS spectra for the AOS displayed a base peak at mass number 44 and minor peaks at 45 and 43. The existence of the AOS has not been reported in the literature. Also, there is no product available that could serve as reference for the observed mass spectra in the present case. The boiling point of trimethylsilanol (99°C) is so close to that of water that it would evaporate with water from surface water supplies and find its way into the atmosphere as a contaminant of atmospheric water vapour.

AOS in the atmosphere

By using a simple technique of bubbling air through a small column of water at $\text{pH} \geq 7.0$ (40 ml in a flat 50 ml glass bottle), it was found that the AOS is also present in the atmosphere. Atmospheric samples taken at 8 different locations in South Africa tested positive for the AOS. Concentrations varied from $15 \mu\text{g}/\text{m}^3$ to $168 \mu\text{g}/\text{m}^3$. The presence of atmospheric AOS at different locations which varied from industrial complexes to rural communities, and from the coast to the remote inland is a clear indication that AOS is a ubiquitous pollutant that it is not confined to any specific region.

The mechanism for AOS formation in the atmosphere was simulated in the laboratory. It was observed that AOS could be produced when water that contains nitrate is exposed to UV radiation. A sample of distilled water containing $1 \text{ mg}/\text{l NO}_3\text{-N}$ left in a glass beaker under a UV lamp for 48 hours produced iodine when acidified and KI solution added. A control consisting of distilled water without any nitrates produced no iodine when treated in exactly the same way.

The presence of AOS and related compounds in the atmosphere could have far-reaching environmental effects. Whereas AOS formation in wastewater does not lead to acid formation (as it would be present as a salt similar to the salts of organic acids) in atmospheric water vapour it would result in free acid. The only requirement is that traces of nitrate are present. AOS formation could therefore result in the phenomenon of acid rain. Even more serious is the fact that the presence of these organic compounds in the atmosphere would contribute to the problem of global warming.

CONCLUSIONS

It has up to now not been possible to positively identify AOS using the standard types of methods that are available to identify organic compounds in solution. This means that the conclusions reached so far are based on indirect measurements and observations of the behaviour of the unknown substance. Studies are continuing to develop or adapt existing methods to positively identify the unknown substance.

From the available evidence it is concluded that AOS is a substance akin to known organic acids but that it is silicon and not carbon that constitutes the acid configuration, i.e. -SiOOH^+ . This is a completely new chemical concept and indeed a new complication in the field of environmental pollution. The implications to the environment on a global scale are far-reaching and merits intensive research to confirm our findings and to quantify possible effects.

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