The increasing importance of assessing toxicity in determining sludge health and management policy

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(Paper presented to BHr Group Seminar on 'Sludge Management', Cranfield 23 May, 2001)

SYNOPSIS

The harm caused by toxic industrial effluents to sewage treatment works, has been recognised for many years. These can cause reduction in biodegradable efficiency, with an associated requirement for longer treatment time, and in extreme cases, toxic shock can kill off the secondary tanks.

Currently, the presence of harmful industrial effluents is made evident by their effects on the overall treatment cycle at the works. An increasing frequency of incidents has led to a call to establish or improve methods of detecting toxicity of effluents accepted for treatment.

This paper describes the causes and effects, discusses economic and operational penalties, and reviews the current approach to, and methods of detection. The paper ends with an appraisal of the likely advances over the next few years and the ways in which improved detection can lead to a toxicity management strategy for the operation of sewage treatment works.

INTRODUCTION

The effective management of the activated sludge of a biological treatment plant is of critical importance in order to minimise treatment costs and to avoid contamination by effluents of receiving waters. Even in well managed treatment systems, it is not uncommon for influent characteristics to change rapidly and unexpectedly as a result of changes in upstream discharges. Plants that treat industrial waste may find that toxic or inhibitory chemicals can pass through treatment systems with little effective removal (1,2,3). Storm flows can introduce toxins from leachates and other urban runoffs. The reduction of treatment plant efficiency resulting from the effects of toxicity on the activated sludge bacteria can therefore result in unacceptable levels of effluent toxicity.

Toxicity can also give rise to operational problems such as changes to the sludge settling characteristics, and this may take a significant time to recover. Settling problems can be caused by both filamentous bulking and by deflocculation. Both of these can be induced by toxic shock loads (4). Filamentous bulking may be detected by microscopic examination, enabling corrective action to be taken. However, the only indication of toxicity-induced deflocculation may be a rapid increase in effluent suspended solids. This may result in significant activated sludge washout before the cause and source of the problem have been identified.

The relationship between the observed consequences of toxicity shocks of this sort and the way in which the toxins affect the metabolic processes of the sludge bacteria is not well understood. This is unfortunate, since toxicity detection methods inevitably have to be based upon knowledge of this sort. The bacteria break down organic compounds in the mixed liquor, thereby reducing BOD and COD. The carbon removed is used either for the respiration of the bacteria or is incorporated into new biomass, as a result of growth. Any stage in the chain of metabolic reactions involved in both respiration and growth, can be poisoned by different toxic chemicals. As the respiration rate and growth rate is inhibited, the rate of breakdown of the carbon compounds of the mixed liquor decreases. As a result, the rate of BOD removal decreases. So toxic shocks can result in increases in effluent BOD and COD levels unless remedial action is taken. Similar effects on the nitrifying bacteria result in increases in ammonia levels in the effluent. In extreme cases the bacteria are killed by the toxicity. The restoration of a plant which has experienced total killoff, involving cleanout and reseeding, is a costly operation.

The role of toxicity management in treatment works is now receiving more attention from plant managers, largely as a result of the introduction of recent environmental legislation. However, there are also good economic and operational reasons for doing this. In this paper procedures and methods which are becoming available for the management of toxicity will be reviewed.

TOXICITY AND LEGISLATION

Most legislation is directed towards regulation of discharges to the receiving environment, rather than to wastewater treatment works. However, Annex 1 of the EU Urban Waste Water Treatment Directive (1991) states 'Industrial wastewater entering collecting systems and urban waste water treatment plants shall be subject to such pre-treatment as is required in order to: … - ensure that the operation of the waste water treatment plant and the treatment of sludge are not impeded'. This has been largely overlooked and has not been the subject of secondary legislation, although in the UK some water companies do use toxicity-based discharge consents in some instances.

The more recent EU Water Framework Directive (2000) is concerned primarily with protecting receiving waters from pollution. The scope of regulation will increase beyond existing levels to place more emphasis than hitherto on reduction of toxic chemicals entering receiving waters. Currently some discharge consents are based upon concentration limits of known toxic chemicals. However in recognition of the fact that very often a discharger does not know the exact composition of the waste stream, and also that the toxicity of many of the discharged chemicals is not known, a more pragmatic approach will be used. Using a series of Direct Toxicity Assessment (DTA) tests, the toxicity of end-of-pipe effluents to a series of prescribed organisms from marine or freshwaters, can be measured. Tests of this sort have undergone several years of field trials by the Environment Agency, SEPA and representatives of the chemical industry. Although the date and manner in which these will be used in formulating discharge consents has not yet been announced, it is likely that future IPPC consents will incorporate these DTA tests.

In the United States, the Environmental Protection Agency (EPA) regulates discharges to both receiving waters and to publicly owned treatment works (POTW's). Paradoxically, whilst discharges to receiving waters are subject to direct toxicity testing (Whole Effluent Toxicity or WET tests) the discharge to POTW's is not. The consents for discharge to POTW, which are prescribed in the EPA's National Pretreatment Program (5), are still based upon concentration limits of some 129 registered toxic chemicals.

TOXICITY EVENTS AND OPERATIONAL CONSEQUENCES

Records of total kill-off of secondary tanks are largely anecdotal. Recently however, instances of partial and chronic toxicity events have appeared in the literature. In Sweden, it was found that 60% of 109 treatment works investigated showed inhibition of nitrification, some with more than 20% inhibition (6). In another study in Greece, up to 50% inhibition of nitrification was attributable to industrial wastewater (7). In the UK, chronic nitrification inhibition levels of approximately 15% were found in a plant receiving a mixture of domestic and industrial waste, with occasional peaks of up to 50% (8).

Whilst nitrification inhibition will have its major effect on the quality of the effluent, with potential consequences for failed discharge consents, respiration inhibition is an indicator of problems with biodegradation of BOD. In Sao Paulo elevated BOD was correlated with filamentous bulking in a treatment plant which received large volumes of industrial waste water (9). The Antwerp treatment works showed almost continuous inhibition of respiration rate of the activated sludge over a 10 day monitoring period. Peaks were up to 30%, with an average of 10% respiration inhibition. No deterioration of effluent quality was observed during this period. However during a second 10 day period, there was a 48 hour increase in toxicity with peaks of up to 43% and this was accompanied by a substantial washout of solids (10).

Computer modelling can be useful in predicting the consequence of toxicity events. A computer model simulation, using the Activated Sludge Model No 1 (11), and process layout and influent pattern of the COST 624 simulation benchmark (12,13,14), was used to model the effects of a non-soluble non-biodegradable toxic substance which caused inhibition of the respiration rate. The model used a treatment plant consisting of 5 completely mixed aeration tanks and a secondary settler. It was found (Figures 1 & 2) that at the lower concentration used in the simulation, there was a 50% decrease in respiration rate and this caused a 3-4 fold increase in the effluent COD. Increasing the toxin concentration fourfold increased the respiration inhibition to approximately 80%, with a consequential increase in effluent COD of 150% (15).

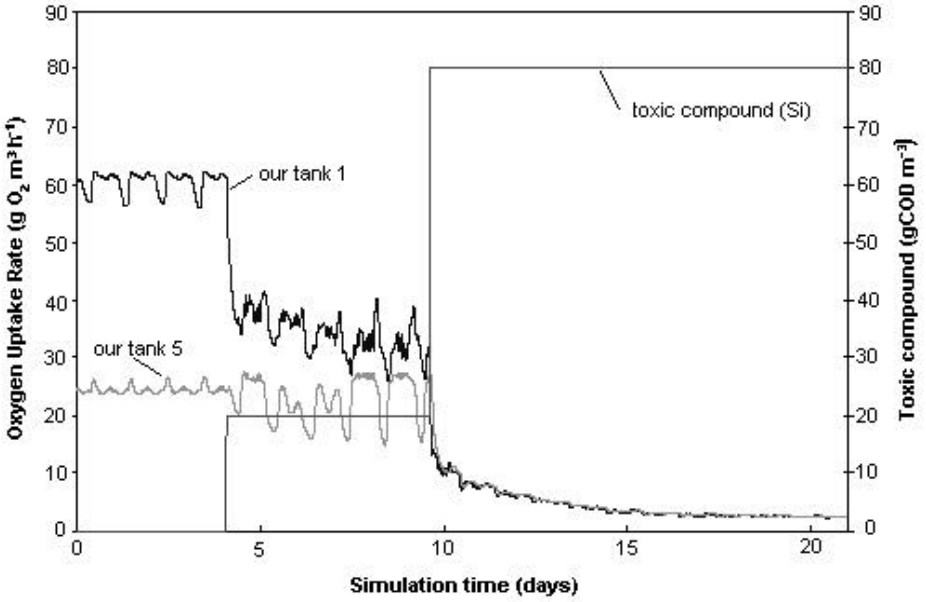

Figure 1 Computer model simulation of the effect of influent toxicant on respiration rate in 1st and 5th aeration tank (15).

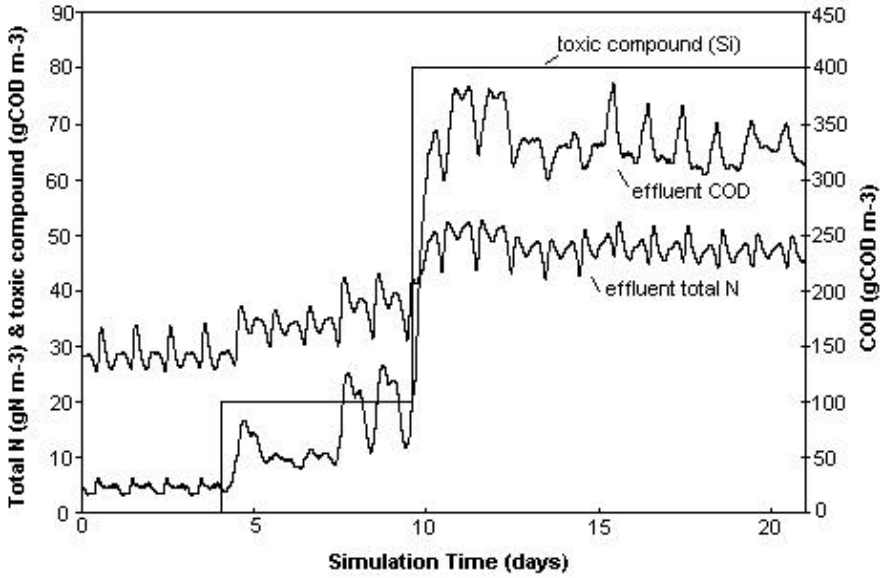

Figure 2 Computer model simulation of the effect of influent toxicant on effluent N and COD concentrations (15).

Since respiration inhibition results in a lower rate of breakdown of degradable compounds, this has to be compensated for by an increase in the retention or treatment time, where this is feasible. Aeration costs may increase as a result, although this will to some extent be offset by a lower aeration requirement, as the rate of oxygen consumption by the bacteria decreases. In some European countries charges are levied according to the BOD or COD of the discharged effluents. In these cases, if retention time cannot be increased in order to keep BOD and COD within limits, there will be increased costs imposed upon the treatment works.

Information on the economic costs of toxicity events at sewage treatment plants is sparse. However, in the Netherlands in the year 2000, a 95000 p.e. municipal plant was subject to a 50% decrease of biomass activity due to an oil spill. The recovery of the plant took 5 days and the costs were approximately 45000 Euros (16). On another occasion, the cost of recovery of an industrial wastewater works treating an average of 1400 m^3 d^{-1} of waste from a chemical plant, was reported to be 40,000 Euros (16).

PROCEDURES FOR TOXICITY MEASUREMENT

There are three main approaches to the measurement of wastewater toxicity: on-line devices; in-situ devices; and laboratory instruments. They have complementary roles in the management of toxicity at treatment plants.

On-line devices

These attempt to alert the plant operators to the presence of toxic substances in the influent before it is discharged into the plant. This allows diversion of the influent stream to storage tanks, giving time for consideration of whether detoxification can be undertaken or whether to slow-feed the waste into the plant. The role of on-line devices is therefore in protection against unexpected toxic slugs.

Ideally these devices should be continuous, taking measurements in real time. However a number of systems, by the nature of the measurement principle, are discrete-sampling systems. Influent will continue to enter the plant for the length of time required to take the measurement on the sample taken. Since the total amount of toxicity entering during this time will be small in relation to the volume of the receiving tanks, in most cases this is not a serious issue. Examples of on-line monitors are the Rodtox and Stiptox which measure respiration inhibition, and Amtox which measures nitrification inhibition. On-line early warning devices have recently been reviewed by a WERF working party. They evaluated the advantages and disadvantages of the various systems available and made recommendations for their further development (17).

Whilst on-line devices have the benefit of protecting treatment plants from incoming toxicity, those currently available are widely recognised to be prone to false positives. Furthermore they cannot provide information on the nature nor the source of the toxicity. Laboratory tests are therefore required to achieve these.

In-situ devices

In operational terms, these occupy the niche between on-line and laboratory devices. They sample the actual sludge in the aeration tanks - on a discrete-sampling basis in the case of respirometers - and monitor the presence of toxicity in the tanks. This is a useful approach in that it provides information to the operators which can be used in process control.

Laboratory instruments

These use batch tests, and ideally should give information on toxicity to the activated sludge bacteria which will receive the waste. Laboratory tests are used for evaluating the toxicity of tankered waste before acceptance for treatment. They should be used, as noted above, in conjunction with on-line devices to check for false alarms, but his is not yet widely practiced. Laboratory tests may be used in toxicity tracking to locate the source of toxicity, and for evaluation of toxicity of new streams before discharge. Although this is not yet widely practiced, laboratory procedures of this sort could be used as a basis of toxicity-based consents. This would enable the treatment works manager to be aware of the actual toxicity of wastewater which will be received via sewer. It could also be used to determine a treatment cost strategy. The MOGDEN formula currently in use, undoubtedly undercharges a producer of low BOD, but highly toxic and damaging waste. Finally, laboratory instruments can be used to test procedures for reducing the toxicity of highly toxic materials before discharge to sewer.

PRINCIPLES OF LABORATORY TOXICITY TESTING

The principles involved in three most commonly used groups of laboratory instruments are: bacterial luminescence, nitrification inhibition and activated sludge respiration inhibition. Other procedures involve the use of biosensors (Biosense) and enhanced chemiluminescence of solutions of enzymes in solution (Eclox, Aquanox)

Bacterial luminescence

Here different concentrations of the wastewater are mixed with a culture of a marine luminescent bacterium. The decrease in light output is a measure of toxicity. In principle, this is similar to measuring respiration inhibition, since luminescence is a measure of the rate at which the bacteria produce ATP in the course of their respiratory metabolism. Well known examples of this method are Microtox and Toxalert. The method has the advantage that it has been in use for a long period of time during which a large amount of toxicity data has been generated. However, the test requires expensive consumables, and since it is based upon the luminescence of cultures of a single marine bacterium, it does not provide information on the toxicity to the actual bacteria of the receiving activated sludge. It follows from this that in some instances the test will fail to detect actual toxicity. Of equal importance is that it may be oversensitive to some mildly toxic substances.

Nitrification inhibition

This detects inhibition to the nitrifying bacteria *Nitrobacter* and *Nitrosomonas*, often using pure cultures to achieve this. An example of this is Amtox, which measures changes in the concentration of ammonia resulting form nitrification when the bacteria are incubated with toxic wastewater. Nitrification inhibition is often regarded as a very sensitive test for toxicity, since nitrifying bacteria are generally more prone to poisoning by toxins, and because efficient nitrification is required in order to meet ammonia effluent limits. However, these tests do not provide information on the heterotrophic bacteria which form the bulk of the sludge biomass and which are involved in BOD removal. It follows therefore that in non-nitrifying plants, these tests would have a lack of relevance. Furthermore in many treatment plants, nitrification takes place in tertiary treatment tanks subsequent to BOD removal. In these cases use of nitrification inhibition tests on the influent wastewater entering the treatment works may result in over-estimation of toxicity to the nitrifiers, since some of the toxic substances may be biodegraded in the course of treatment in the secondary tanks.

ACTIVATED SLUDGE RESPIRATION INHIBITION

These tests measure the inhibition of the total oxygen uptake by the activated sludge bacteria when mixed with toxic wastewater. In sludge from secondary tanks which also nitrify, the rate of oxygen uptake is a measure of both the respiration of the heterotrophic bacteria and of the oxidative reactions involved with the nitrification of ammonia to nitrite and nitrate. Respiration rate is a measure of the energy metabolism of the bacteria, and most of this energy is used for their biosynthesis and growth. Oxygen uptake rate is therefore a good estimator of the biomass growth rate and of the 'health' of the activated sludge. Both respiration rate and growth rate are also highly correlated with the rate of biodegradation of the complex organic carbon compounds in the sewage.

Respiration inhibition tests, involve the measurement of the concentration of wastewater causing a 50% (or other selected percentage) inhibition of the respiration rate. They are therefore of direct relevance to the processes taking place in the treatment works. Examples of activated sludge respirometers are the Emeris and Strathkelvin ASR, produced in the UK, and several others, of which the Arthur is probably the best known, in the USA.

Although the advantages of respirometry have been well known for some time, activated sludge respiration inhibition tests have not been widely applied. This appears to be due to the commonly held view that respirometry is time-consuming and difficult. This in turn has stemmed from the lack of a dedicated instrument designed for the purpose. Strathkelvin Instruments has now brought to market an Activated Sludge Respirometer which has been designed to offer speed, simplicity and accuracy in operation (Figure 3).

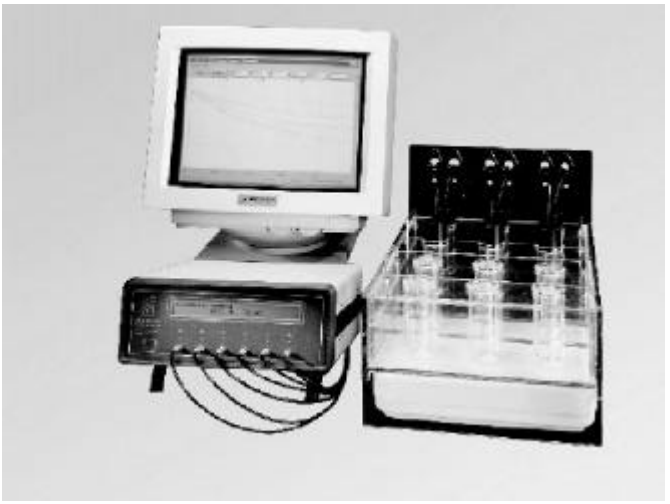

Figure 3 The Strathkelvin Activated Sludge Respirometer which utilises 6 oxygen electrodes connected via an interface to the pc loaded with dedicated respirometry software.

The oxygen sensors of the respirometer are Clark-type polarographic electrodes. Other respirometers which have been used for activated sludge have depended upon the use of a single electrode. The associated protocols have involved measurement of the rate of oxygen depletion of a sample of the sludge in a closed container, followed by re-aeration to the starting oxygen level again. This process was repeated several times creating a series of respirograms. The procedure is time-consuming and is not readily adaptable to the measurement of the effects of different concentrations of the wastewater on the sludge respiration rate. The Strathkelvin respirometer results from a technology transfer from respirometry applications in the biomedical field, and uses 6 oxygen electrodes simultaneously. In order to make the instrument compact, sludge sample volumes have been reduced to 20 mls. The variation in respiration rates between 6 samples from the same batch of sludge is very small. The rates measured on these 20 ml samples are almost identical to those measured in a 1 litre sample.

The use of 6 oxygen electrodes enables the respiration rate of a control sample of sludge to be measured at the same time as that of samples of the same sludge mixed with 5 different concentrations of wastewater. Using sludge with a MLSS of approximately 4000 mg/l, the respiration rate of the 6 test samples can be recorded in only 5-10 mins. The dedicated respirometry software allows the analysis of the traces to be carried out automatically at the termination of the run (Figure 4).

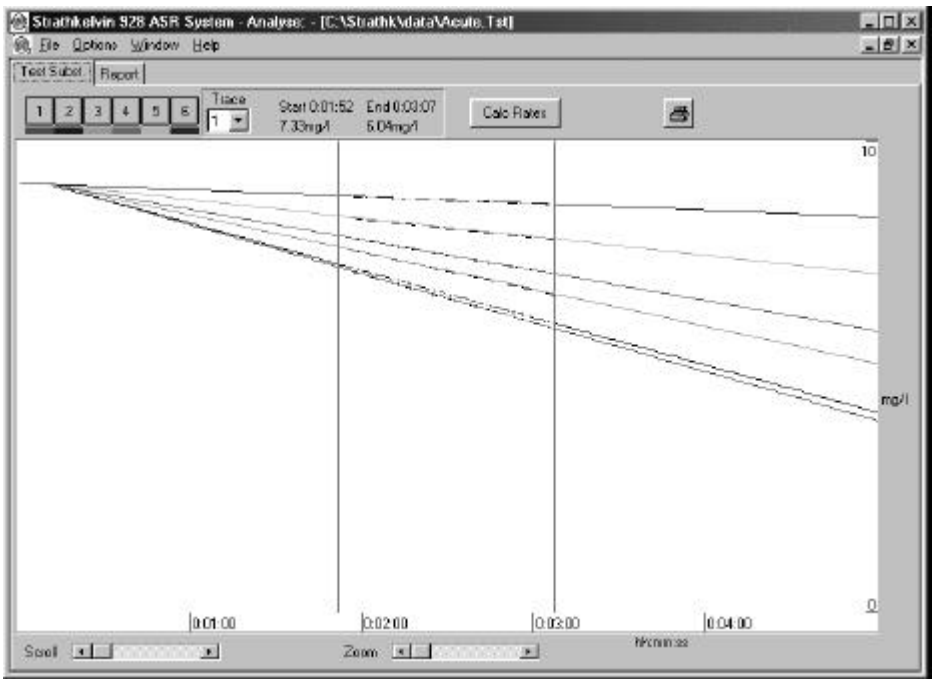

Figure 4 The analysis screen showing the results of a respirometry run. Clicking the 'Calc Rates' button transfers the calculated results to the Report page.

The results of the test are displayed as a fully audited Report in a locked spreadsheet. The report shows values for EC_5, EC_{10}, EC_{20} and EC_{50} i.e. the concentrations which produce a 5%, 10%, 20% or 50% inhibition of the respiration rate. These values can be used by the treatment plant manager, as shown below, to determine the rate at which the wastewater should be allowed to enter the plant, in order to minimise the effects of toxicity on the activated sludge.

In addition to the toxicity test, the software offers a sludge respirometry test which simply outputs MLSS-normalised respiration rates. These data can be used to check for chronic toxicity in the secondary tanks by daily monitoring of the 'health' of the sludge. The test can also be used to yield data on aeration requirements for process control optimisation.

CASE STUDY OF A RESPIRATION INHIBITION TOXICITY TEST

This example shows the result of a test on tankered waste of unknown composition, which was delivered for treatment at a biological treatment plant.

Acute test

Test substance: ES Plant Date: Tue Jan 23 2001

Control respiration rate

	Respiration Rate (mg/l/h)
Control	124.5

Temperature

20.0 °C

Test substance: **ES Plant**
(Datafile: C:\Strathk\Data\testmanual.tst)

Comments: Line 3 effluent

	Concentration (%)	Respiration Rate (mg/l/h)	% Inhibition
Sample 1	20	120.2	3.4
Sample 2	40	94.4	24.1
Sample 3	60	77.3	37.9
Sample 4	80	47.2	62.1
Sample 5	100	17.2	86.2

Concentration causing inhibition of:
5% (EC5) = 21.1 %
10% (EC10) = 24.9 %
20% (EC20) = 34.8 %
50% (EC50) = 69.3 %

Figure 5

Figure 5 shows an extract from the Report, it can be seen that with a 20% concentration of the wastewater, the respiration rate at 120.2 mg O_2/l/hr is 3-4% below the respiration rate of the control sludge. With increasing concentration, the percentage inhibition progressively increases. The plot of the relationship is shown in Figure 6.

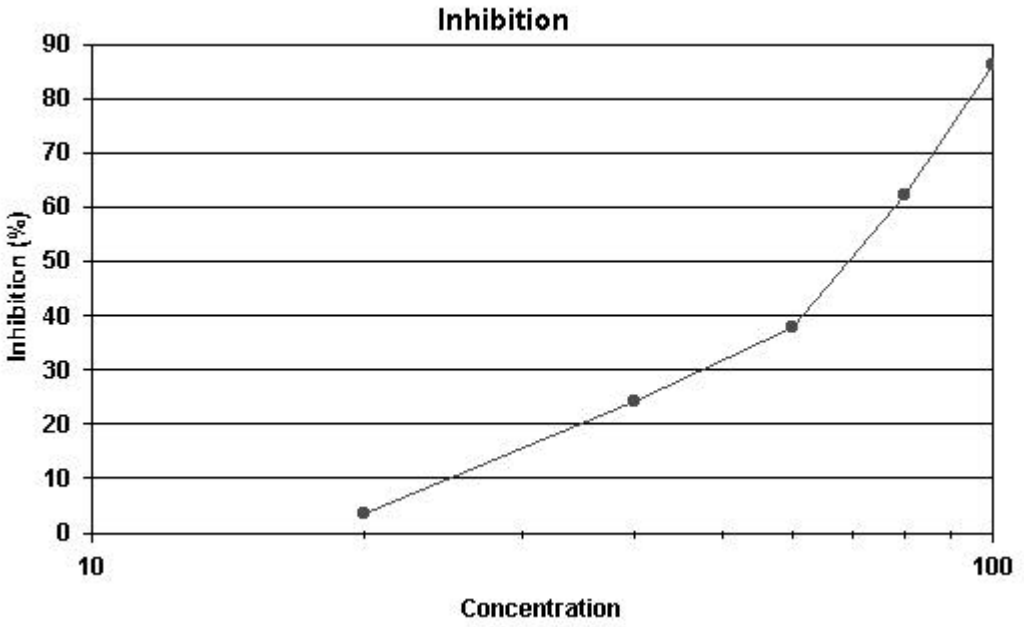

Figure 6 The plot of inhibition v concentration from the Report.

The software has calculated the concentration causing 5% inhibition (EC_5) to be 21.1% whilst the EC_{10} is 24.9% and the EC_{20} is 34.8%. These values clearly show that the waste is toxic. The plant manager then has to decide what level of inhibition is acceptable in the treatment tanks. In the study carried out at the Antwerp sewage treatment works, an average 10% inhibition did not appear to affect the quality of the effluent. Probably most managers will opt for a more cautious approach and accept a 2-5% inhibition. Unfortunately there is still a dearth of information on the effects of low levels of toxicity on the treatment process. It may be that process control models such as the Activated Sludge Model 1 (7) referred to above will, in time, be adapted to assist in decisions of this sort.

The final stage involves the calculation of the dilution of the waste which would be achieved when discharged into the system, from knowledge of tank volumes and flows. From this it is then possible to calculate the rate of discharge required to achieve the acceptable level of inhibition.

SUMMARY

The management of toxicity at sewage treatment works is becoming of increasing importance in view of the increasingly more stringent environmental legislation which is being enacted. Whilst the legislation is targeted primarily to control of the quality of effluents discharged to receiving waters, there is a knock-back effect on the management of biological treatment plants.

Evidence is already accumulating of toxicity affecting the functioning of treatment works which accept significant quantities of industrial wastewater. It seems likely that in the years ahead, toxicity management strategies, perhaps integrated into process control software programs will become increasingly common. These will rely upon more sophisticated on-line monitors to protect treatment plants, and upon data obtained by the new generation of laboratory respirometers which measure toxicity from the respiration inhibition of the receiving activated sludge.

From information which is now available, it seems likely that toxicity effects will increase the operating costs of biological treatment. Paradoxically, except for a small number of documented cases of catastrophic toxic shock, there appears to be virtually no information on these costs, in the public domain. Information of this sort is urgently needed in order for treatment plant managers to make informed decisions on how best to manage toxicity emanating from industrial wastes.

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