TREATMENT OF INDUSTRIAL EFFLUENTS

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Preface

One of the hallmarks of an advanced civilisation is its concern for the disposal of its society's waste products in a safe and environmentally acceptable manner. The controlled treatment of waste-waters in the UK, as in other countries, had its conception in the aftermath of the epidemics of cholera and other diseases in the middle and late nineteenth century. The major pollutants then were 'natural' compounds which owed very little to the ingenuity of the industrial chemist. This is now not so. In many countries the wastes from industrial processes are not only being produced in ever increasing amounts, but also can contain toxic and poorly degradable compounds. They are often considerably stronger than domestic sewage, which many of the present treatment systems were only designed to handle. In addition, the consumption of water for domestic and industrial use has increased to such a degree that nowadays it is not unusual to find that the rivers receiving treated effluents cannot give the dilution necessary for their survival as good quality watercourses, a problem aggravated during periods of drought.

The technological hardware for treating waste-waters has not kept pace with the changes in the complexity of effluents, though there have been considerable advances in the understanding of the biochemistry and microbiology of the biological processes which still form the main routes for purification. This book examines such developments and how this knowledge should assist the rational development of industrial treatment processes and the control and legislation concerning them. Since each industrial waste can present its own particular set of problems chapters dealing with the peculiarities of many different types of waste have been included besides those involved with general principles. Thus this book was designed to be both a textbook for all students of water resources technology, a guide for water quality engineers practising as multifunctional scientists in Regional Water Authorities and for those involved with or concerned about the effluents which their industry produces.

Contents

Chapter One

Microbes and Effluent Treatment

1.1 INTRODUCTION

Some form of biological treatment of human and farm wastes has been well established since late neolithic times, and certainly was a feature of the early cities of the fertile crescent and other centres such as Mohenji-Dara in the Indus basin, where waste treatment relied on its digestion in cess pits. Systems utilising waste in farming were also highly developed early in China. Early septic tanks, sewage farms and self-purification, by dilution into rivers or the sea, were probably based on the empirical observation that the waste slurries became less offensive when so treated, though it is doubtful whether the consequent improvement in community health was associated with these methods of waste disposal until our own time.

Such methods were largely neglected in the medieval cities of the west, and it was not until the population pressures which arose during the industrial revolution that they were taken up and developed. The first activated sludge plants began to be operated by 1900 AD. Although aimed primarily at the disposal of potentially offensive wastes, in recent years an additional objective has been the up-rating of water quality, either because the water courses form the final depository or the water in the effluent is to be reused. Solid residues then became an embarrassment, in contrast to China where they still make an important contribution to agriculture and fish farming.

Until the middle of the last century the main problem of effluent treatment was one of scale. With the growth of industry, especially the chemical industry, new problems appeared owing to the addition of so-called unnatural products to water systems. It is a tribute to the flexibility of microbial genetics and metabolism that our modern biological effluent treatments continue to work efficiently.

Biological treatment of wastes in water is based on the quite simple and readily repeated observation that polluted water left standing and open to the air undergoes chemical changes which finally can result in clarification; the water can even become potable after decantation or sand filtration. Such changes are chemically similar to putrefaction which was associated with the presence of and later the activities of microbes. All biological effluent treatment systems are based on this seemingly simple process whereby a range of microbes utilise the organic compounds in polluted water as food; they grow, and are then separated from the water, which can then be considered as clean. The engineering developments in recent years have been associated with the preparation of the effluent by separating inorganic and other solids which slow down the purification process, and designing systems in which the microbes and nutrients, including oxygen, are kept in intimate contact and then separated from the water at the end of the process.

Two main systems are used. The first employs microbes which adhere to a solid substrate over which the effluent flows. Rapid-flow synthetic-support systems and more recently fluidised beds are now being employed to improve throughput. The alternative reactor system is analogous to a chemostat with arrangements to return the organisms produced by growth, the biomass, to the treatment tank and the excess to waste. Many plants also include a pretreatment by anaerobic digestion. This reduces many of the larger polymers, such as cellulose, to smaller fragments which are more readily assimilated by microbes. Methane is a useful end-product of anaerobic digestion, but its presence illustrates the fact that in the absence of oxygen little mineralisation of pollutants takes place and they appear as other end-products, such as fatty acids and alcohols. Although not originally a design feature of treatment systems, it is desirable that during treatment most of the pathogens found in human and animal excreta are killed. This is an important factor in environmental health. The higher temperatures at which digesters operate (40–45° C) are less favourable for pathogens and aid their destruction.

A chemostat is a device for growing microbes continuously at rates somewhat below their maximum specific growth rate, μmax. It applies generally only to organisms that can be maintained in a reproductive growth cycle. This can often be achieved even for organisms such as the fungi, whose life cycles are often more complicated. The underlying principle is that medium in which one essential constituent is made growth limiting is continuously added to a reactor vessel. In effluent treatment the limiting growth substrate is often the carbon source. This means that other nutrients serving as sources of nitrogen, sulphur, phosphorus, etc. are in excess and appear in the effluent, to be either diluted or removed by tertiary treatment. At dilution rates below 0.01–0.02 h^{-1}, the kinetics are complicated by the rate at which the microbes are dying, partly due to lack of energy; this means that the assumption that growth is exponential does not hold.

It must be remembered that often dead organisms (that is those that have lost the ability to reproduce) can metabolise substrates for considerable periods at rates above those obtaining in viable ones where metabolism is carefully regulated to the requirements of growth.

Although the principles, briefly stated above, are relatively simple in concept, some fundamental biological principles are often neglected. These may be considered by first examining the basic processes as related to the final objectives. The efficiency of any plant may be measured by the rate at which the organic material can be removed with the minimum possible production of microbes, so that the final effluent contains the minimum of dissolved or solid residues. This means that the carbon pollutants are to be completely mineralised to CO_2 and H_2O. Thus the plant is a wet oxidation system in which the catalysts are the microbes. In teleological terms the 'aims' of the microbes are to utilise the substrate to grow and reproduce at the maximum rate. Thus in this respect the aims of the microbes and the desires of the engineer are opposed and a compromise position has evolved empirically. This has been arrived at by feeding the effluent to an established colonial microbial mass at such a rate (often expressed as the residence time) that maximum oxidation of organic carbon takes place. In practice residence times of 20 h are equivalent to quite low dilution rates (0.02 h^{-1}) in a chemostat. This means that very low concentrations of substrates are maintained with a consequence that reproduction rates are also low. These conditions appear to favour the growth of microbes which tend to flocculate but it also means that the death rate is high. For instance, in a typical activated sludge system only about 2–5% of the total microbes present are able to reproduce when placed in favourable conditions. One other consequence of such low dilution rates is that the system is very sensitive to shock conditions such as alteration in the flow rate and changes in the concentration of components. Not only do chemical and population changes take place when such perturbations occur, but the system may take a long time, days or weeks depending on their ability, to recover. One immediate method of overcoming shock changes is to use as buffers holding (and mixing) tanks into which the raw effluent is fed before passing on for treatment; however, this can be employed only on relatively small systems. An understanding of the mechanisms of responses to perturbation of the steady state is essential in plant control and for achieving better efficiency.

1.2 POPULATION DYNAMICS

According to classical ecological theory, a mixture of a wide variety of substrates should support a rich and varied population, while single substrates will, by selective pressure, give rise to a restricted population. It may seem surprising therefore that effluents containing few or even single substrates give rise to a comparatively varied population, often not differing widely from those of normal plants treating domestic sewage. This is mainly because of the release of cell contents upon the death of cells under starvation conditions and the support of growth of a variety of heterotrophs by so-called cannibalism (Fig. 1.1). Under such starvation conditions competition is severe. Although heterotrophs will be selected predominantly, the maintenance of a low carbon content means that some autotrophs are able to coexist and to flourish. It is on this that we rely for nitrification and the removal of inorganics such as thiocyanate and cyanide, though heterotrophs can also be involved in some of these processes.

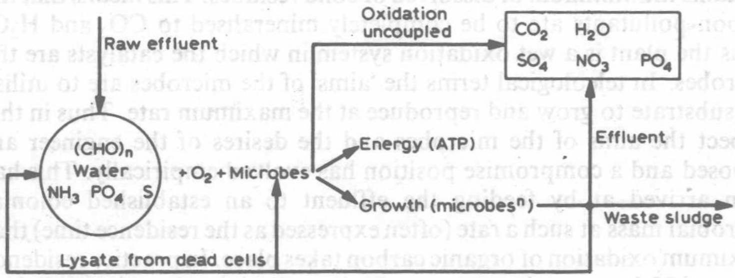

Fig. 1.1 *Outline of the transformations which occur during biological effluent treatment*

Changes in the concentration of substrates, unless severe, are unlikely to cause marked changes in the population composition. The addition of new substrates is however likely to produce such changes, and throughput will have to be adjusted until the change is accomplished. The source of the new microbe may be from the low numbers already present, by chance contamination or by deliberate inoculation from a rich source of microbes such as soil, mud or an appropriate sludge from another plant. The rate at which the new organism establishes itself will depend on its growth characteristics, mainly on its reproduction time (mean generation time) which may be from about twenty minutes in the case of some pseudomonads to several days for *Mycobacteria* or *Nocardia*. Major changes are rarely found except under 'shock' conditions. For instance, a sudden increase in carbohydrate onto a filter bed often gives rise to a massive overgrowth of micro-fungi, organisms not normally found in large numbers elsewhere in effluent treatment plants.

Short-term fluctuations in oxygen availability are buffered by the presence of facultative anaerobes. However prolonged anaerobiosis will produce marked population changes, not only due to the loss of the aerobes but also to the accumulation of fermentation end-products. Recovery to the state prior to the prolonged anaerobiosis may be slow.

Inter-relations within the mixed microbial population include, in addition to the competitions for substrate, prey–predator relationships and antibiosis. Unlike the soil, antibiosis is not likely to be of major importance in effluent treatment because in such a mixed environment antibiotics produced by one type of organism are freely available as a foodstuff for another. However, prey–predator relationships are of major importance, and that between the protozoa and the bacteria on which they feed has been the subject of considerable study from which mathematical models have been evolved which evaluate treatment conditions (see Chapter 9). This system is one which readily lends itself to rapid enumeration of the protozoa involved and has therefore proved of use. Most other methods of enumerating specific microbes are too time consuming and difficult to be of use in plant regulation and control. For this reason methods which estimate the activity of the population as if it were composed of a single organism are proving more attractive. They depend essentially on some measurement of enzymic activity and the manner in which this responds to perturbations is now considered below.

1.3 ENZYMIC CHANGES

An assessment of enzyme activity can consist of measuring an overall activity such as CO_2 production, acid production or respiration where oxygen uptake is measured, as in the BOD test. Alternatively single key enzymes may be estimated—for instance, an oxygenase in effluent plants treating phenols. It must be stressed, however, that little has yet been done in this field with single enzymes despite its promise.

Changes in enzyme activity rapidly respond to substrate concentrations, often over a wide range of activities. This may be simply by the laws of mass action, where product and substrate both regulate the rate; the time scale here is seconds or less. In addition, more subtle changes controlling rates are found, particularly in linked enzyme systems where the end-products of a series of reactions feed back and inhibit the first enzyme of the series. Certain key intermediates may also act as regulators of enzyme rates (eg. ATP, NAD, citric acid) (see Chapter 8). Such regulatory systems are of major importance in maintaining the growth of the microbes at their optimum, and are therefore of major importance in the balance between oxidation and biomass production, the central problem of effluent treatment.

In addition to these changes in enzyme rates which occur over periods of seconds and minutes, there are slower changes which may take place over periods of hours or days. These essentially are changes in the enzymic composition of the microbial population which are ultimately determined by the population's genetic composition. Changes in substrate may cause new enzymes to appear (induction) and other enzymes to disappear (repression) (see Chapter 8). The ability of any sludge to respond to changes in substrate composition can therefore be evaluated by measuring its ability to make the necessary enzymes. The best sludges in this respect are those that maintain the widest 'gene bank' and are therefore likely to consist of a wide range of species.

Processes such as contact stabilisation are thought to help establish