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JONAS S. ALMEIDA*, MARIA M. REIS*, JOÃO G. CRESPO*

DEVELOPMENT OF EXTRACTIVE MEMBRANE BIOREACTORS FOR ENVIRONMENTAL APPLICATIONS

The application of membrane bioreactors in drinking water denitrification as well as in detoxification of industrial wastewaters is discussed. The aim of this paper is to develop new types of membrane reactors involving selective membranes. These kinds of membrane bioreactors are suitable for particular applications in which selective removal of any given pollutant is required. The use of an anion-exchange membrane bioreactor in denitrification system is discussed. Several significant advantages of this bioreactor over the other biological bioreactors were found. It has also been proposed to use the membrane supported biofilm reactors for the treatment of industrial effluents containing volatile organic compounds. The system allows treatment of industrial effluents with extreme pH or high salinity without negative consequence for the biological culture involved. Nevertheless this process needs further investigation due to some problems with biofilm stability.

SYMBOLS

Fc,in – mass flux of pollutant entering wastewater compartment
Rc – rate of pollutant degraded in biofilm
Tc – flux of pollutant transferred across membrane
Fc,g – flux of pollutant leaving bioreactor unaffected via off-gas
Fc,l – flux of pollutant leaving biorector unaffected via liquid outlet
T – temperature
$Q_{b,l}$ – feed rate of mineral medium to the bioreactor
Q_{O2} – rate of oxygen supply to the bioreactor

INTRODUCTION

The increasingly frequent appearance of the term *membrane bioreactor* in the literature results from a confluence of efforts in the areas of membrane science, immo-

*Departamento de Química, Faculdade de Ciencias e Tecnologia, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal.

bilised biocatalyst engineering and semipermeable membrane technology. Multilayer membrane bioreactors can readily be constructed from several membrane films to which different biocatalysts have been attached or from combinations of permselective and catalytic membranes.

Most research work has been oriented to the development of reactors using permselective membranes impermeable to the biocatysts by size exclusion (Ferras et al., 1985; Barreiros et al., 1998). The final aim is to confine the biocatalyst to a restrict region, often using an ultrafilter. The number of papers and patents, over the last twenty years, dealing with the development and applications of this type of membrane bioreactors is quite significant. Unfortunately, the immense potential for combining different types of permselective membranes – acting not exclusively based on size exclusion – with catalytic membranes has not been explored.

The opportunity for development of new types of membrane bioreactors is quite clear: the demand for selective removal of defined pollutants requires new approaches in this field. This work discusses the use of two different kinds of selective membrane bioreactors for drinking water denitrification and for detoxification of industrial wastewaters.

WATER DENITRIFICATION

INTRODUCTION

Nitrate contamination of groundwater resources is becoming a problem in Europe as well as in the United States and Canada. In many areas the nitrate concentration in groundwater exceeds the nominal limit of 50 mg NO_3^-/L set by the World Health Organisation and European Community (ENV/91/24 March, 1992). Consumption of drinking water contaminated with nitrate may cause infant methemoglobinemia and contributes to cancer formation (Bouchard et al., 1992).

Biological denitrification leads to elimination of the pollutant (a complete reduction of nitrate), in contrast to other remediation processes where the pollutant is just transferred or concentrated. The biological denitrification process is based on the capability of some microorganisms to reduce nitrogen oxides, under anaerobic conditions, to molecular nitrogen using a carbon source as electron donor. Reduction of nitrate to nitrogen gas occurs in sequential steps according to the following sequence:

$$NO_3^- \rightarrow NO_2^- \rightarrow [NO](g) \rightarrow N_2O(g) \rightarrow N_2(g). \quad (1)$$

The kinetics of nitrogen oxides reduction and accumulation of intermediates depends on the microorganism and culture conditions used (pH, nitrate and nitrite concentration, dissolved oxygen concentration) (Lewandowski and Baltzis, 1992; Schafer and Conrad, 1993; Almeida et al., 1995a and 1995b).

Denitrifying bacteria are mostly heterotrophic and use organic substrates as electron donors. Heterotrophic denitrifying bacteria require an organic carbon source for respiration and growth. For drinking water denitrification an external carbon source has to be supplied due to the low carbon concentration present. Addition of non-fermentative compounds such as ethanol and acetate is the most common practice (Skrinde and Bhagat, 1982). The amount of carbon to be added depends on the nitrate concentration present in water, and should not exceed the stoichiometric concentration required for nitrate reduction in order to prevent additional water contamination by carbon. On the other hand, this amount should not be lower than the stoichiometric concentration required in order to avoid nitrite accumulation. In fact, the toxicity of nitrite is higher than of nitrate, with the nominal concentration admitted being set to 0.1 mg NO_2^-/L (ENV/91/24 March, 1992).

CARBON CONTROL IN DENITRIFICATION SYSTEMS

To develop a long-term stable process it is necessary to assure a high and constant denitrification efficiency even if the composition of the influent to be treated changes with time. Nitrate concentration in drinking water supplies may vary with environmental and climate changes and consequently the amount of carbon to be added should follow the changes of nitrate concentration in order to maintain the C:N ratio. This can be accomplished by on-line monitoring of nitrate concentration and using a control system which regulates the amount of carbon to be added as function of the nitrate concentration in the feed. This control strategy was already implemented in a cell recycle membrane reactor system.

Another alternative is the development of membrane bioreactors that exclude the direct contact of the microbial culture and the added carbon source with the water stream to be treated. With this aim an anion-exchange membrane bioreactor was developed.

The anion exchange membrane is used as a selective barrier between the nitrate contaminated water compartment and the biological compartment. The membrane facilitates diffusion of the monovalent negatively charged molecular species (namely nitrate) through its fixed carrier matrix. Besides excluding the passage of microorganisms, the anionic membrane also selectively excludes the transport of cationic and non-ionic molecules. The exclusion of non-charged molecules, such as the carbon source (e.g.: ethanol) used for biological denitrification and other metabolic by-products which may be excreted by the microorganisms involved, reduces the extent of soluble organic matter contamination in the treated water stream (Figure 1).

These selective transport characteristics imply that this bioreactor requires a less accurate dosage control of organic carbon feed than other denitrification systems. Hence, the system is of additional interest for small community-owned drinking water supply systems, where the municipality cannot afford having sophisticated carbon control systems. Furthermore, the exclusion of metabolic by-products in the form of

soluble organic carbon reduces the potential of disinfection-by-products (DBPs), as bacterial metabolic exudates were proven to serve as precursors to DBPs in drinking water reservoirs (Hozalski et al., 1992).

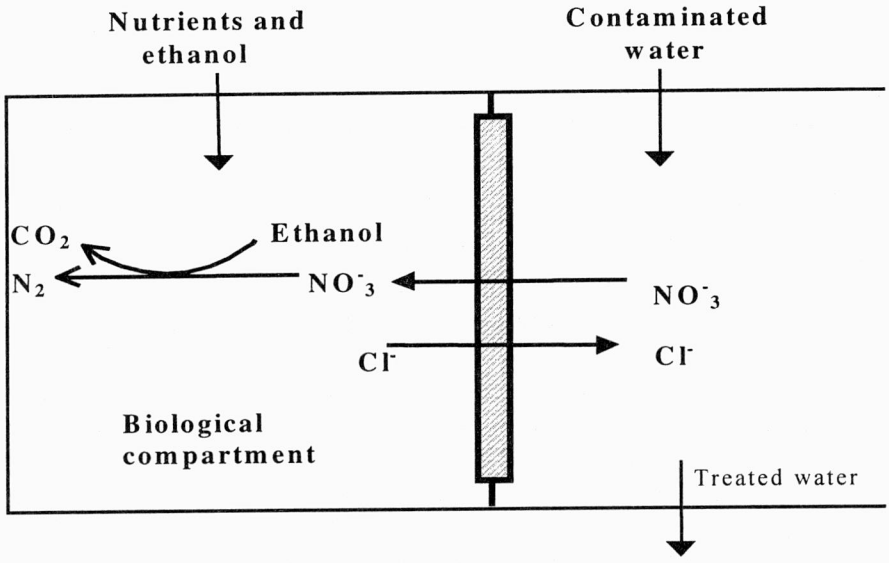

Fig. 1.Principle of ion-exchange membrane bioreactor for denitrification of drinking water

In this system, ethanol was used as a carbon source because it is a non-ionic compound. Chloride was used as a counter-ion to be exchanged for nitrate (Figure 2). Mass transfer coefficients for the transport of nitrate-chloride and ethanol were compared for seven different types of anion exchange membranes. Overall mass transfer coefficients for each membrane were determined in a highly stirred diffusion cell. The values obtained for the mass transfer coefficient of nitrate varied between 1.3×10^{-5} and 8.2×10^{-7} m/s. It was found that the degree of exclusion of ethanol varies significantly between different types of membranes. The overall transport rate for ethanol ranged between bellow detection (0 m/s) and 5×10^{-8} m/s.

It was found that phosphate and sulphate, two nutrients that are commonly added to the biological feed in denitrification processes, are not transported across the anion-exchange membrane and thus depletion of these compounds from the biological compartment is not a problem during operation of the reactor.

This configuration presents several significant advantages over other biological bioreactors:

- It allows for a complete isolation of the microbial culture in the biological compartment from the feed stream avoiding microbial contamination of the treated effluent.
- Contamination of the treated stream with microbial metabolic by-products or nutrients from the biological compartment is also avoided because these products are

generally hydrophobic and certainly not electrically charged and thus they are excluded by the membrane (ethanol is used as an electron acceptor during the denitrification process).

• The two previous advantages are particularly interesting when using Genetically Modified Organisms because this configuration guarantees that the treated stream will not be contaminated by the microorganism itself, by released plasmids or even by metabolic by-products.

• The removal of the charged target pollutant can be enhanced by facilitated transport across the ion exchange membrane using a selected ion for counter-ion transport (as is the case of chloride for the denitrification process). Conversion of the pollutant in the biological compartment keeps the driving force for pollutant transport.

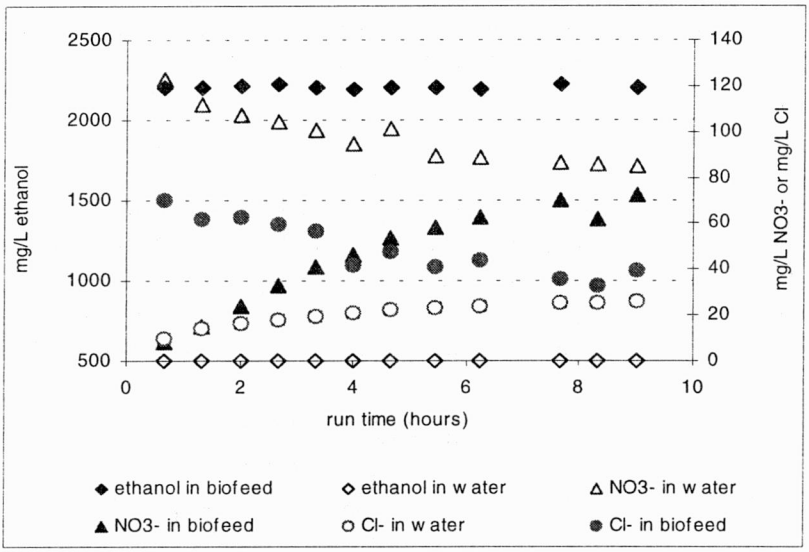

Fig. 2. Counter transport of nitrate and chloride across a ACM Neosepta membrane

• A high density culture can be obtained during a continuous operation process. The hydraulic residence time of the feed stream can independently be adjusted to the recirculation rate in the membrane module, allowing us to optimise individually the degree of pollutant extraction and the mass transfer conditions near the membrane. The cell culture can continuously (or semi-continuously) be fed with a concentrated nutrient media and purged if necessary.

DETOXIFICATION OF INDUSTRIAL WASTEWATERS

Discharges of volatile organic compounds (VOCs) have been subjected to increasing regulatory pressure over the last decade due to their potential to cause envi-

ronmental harm. On a local scale VOCs contribute to toxicity and odour problems. Once emitted into the environment they may be converted to photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight, which are toxic to humans and damage crops, and which may moreover contribute to global warming (Gibson et al., 1995).

A broad variety of VOC control techniques is available nowadays, merely focusing on cleaning up gaseous or liquid effluent streams. However, common abatement techniques employed (e.g. carbon adsorption and condensation) often have the disadvantage of only concentrating the pollutant in a different medium, thus needing further treatment steps. Biological degradation overcomes this problem by using microbial consortia capable of completely breaking down VOC into harmless compounds such as CO_2 and water. Membrane-supported biofilm reactors, for example, were found to be effective in degrading VOCs in wastewater while keeping volatilisation to a minimum (Freitas dos Santos et al., 1993, Rothemund et al., 1994).

EXTRACTIVE MEMBRANE BIOREACTOR (EMB)

Recently Livingston (Livingston, 1993) proposed the use of membrane-supported biofilm reactors in the treatment of industrial effluents containing volatile organic compounds. The reactor configuration proposed consists of a capillary membrane module with polidimethylsiloxane (silicone) fibers used in conjunction with a stirred tank. The effluent to be treated circulates inside the fibers while the biological phase,

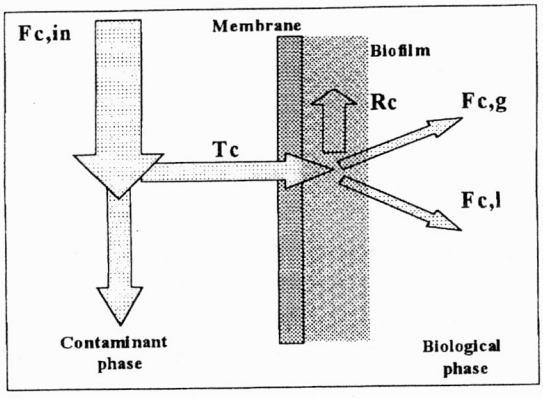

Fig. 3. Principle of the extractive membrane bioreactor. Fluxes of pollutant: Fc,in – mass flux of pollutant entering wastewater compartment; Tc – flux of pollutant transferred across membrane; Rc – rate of pollutant degraded in biofilm; Fc,g – flux of pollutant leaving bioreactor unaffected via off-gas (air stripping); Fc,l – flux of pollutant leaving biorector unaffected via liquid outlet

containing the microbial culture with ability to degrade the pollutant, circulates in the shell side of the module. Nutrients are fed to the bioreactor to replenish essential elements, and the overflow stream from the bioreactor acts as a purge to carry away inorganic elements (for instance chloride ion) that are released due to biodegradation of the pollutant.

This system allows treatment of industrial effluents with extreme pH values (acidic or alcaline) or with high salinity without negative consequences to the biological culture involved. This behaviour can be explained by the non-permeability of the hydrophobic silicone membrane to ions and hydrophilic compounds. The only chemical species transported through the membrane have a hydrophobic character, as happens with most of the volatile organic compounds in industrial effluents (see Figure 3).

Both wastewater and biological medium are continuously recycled over the membrane surface in a loop-like manner. The pollutant is thereby transferred across the membrane from the wastewater into the biological compartment. The pollutant transferred across the membrane is degraded by a biofilm that forms over the membrane. Thus, possible stripping effects due to aeration of the microbial culture in the biological reactor are also minimised.

RESEARCH NEEDS

Nevertheless, this process causes some problems that need to be studied further. The main difficulty lies on the use of pure bacterial cultures, as it has been done so far with this type of reactors (Freitas dos Santos et al., 1995). As a consequence the biofilms obtained are unstable and difficult to maintain under operation for long periods of time with a high efficiency. Also, the biofilm thickness cannot be controlled leading to production of excess biomass and development of an additional mass transfer resistance to pollutant transport.

Although commonly thought as bacterial, the vast majority of biofilms in nature include eukaryotic organisms. Natural assemblages of algae, fungi and protists are found, together with bacteria, on substrata in most hydrated environments. Pure prokaryotic biofilms are found exclusively as laboratory study systems or in rare ecological regimes (hot-springs or deep subsurface sites).

The second major problem is related to the bioreactor and biofilm monitoring. Non-invasive techniques for monitoring of biofilm growth and activity are rather difficult to apply to capillary membrane modules and thus, during operation under variable environmental conditions, as happens in industrial processes, information about the impact of those factors on the biofilm growth, activity and physiology status is rather scarce. In this work, a new on-line, non-invasive, monitoring technique was used to infer the biofilm development and activity during operation under changing environmental conditions.

SYSTEM MONITORING

Monitoring of the EMB performance is done following two entirely different approaches. Firstly, traditional 'off-line' analysis is applied by periodically withdrawing samples from several key locations in the system and monitoring the concentrations of the pollutant (dichloroethane was studied as a model pollutant) and its degradation product – chloride. Based on these, the dichloroethane (DCE) transfer and degradation rates are calculated.

The second approach uses 2D fluorimetry as a direct technique to monitoring the actual biofilm formed on the membrane. The idea behind this method is to monitor certain intra-cellular fluorophors in the biofilm whose fluorimetric responses change depending on biofilm growth and activity. The fluorimetric probe is thereby attached to the transparent wall of the cylindrical glass module of the EMB in direction of the membrane with biofilm which is fixed in the middle of the module.

In 1-dimensional fluorimetry a sample is excited at a single wavelength characteristic for the fluorophor which is to be monitored, and the fluorimetric response is then recorded over a range of emission wavelengths. In contrast to this, 2D fluorimetry does not focus on single fluorophor responses. Rather, it excites the sample over a range of wavelengths. The final result is a 3D fluorimetric map, the co-ordinates being excitation wavelength, emission wavelength and intensity. Figure 4 shows a typical fluorimetric map obtained from a scan of the biofilm in the EMB with two fluorphor peaks clearly distinguishable.

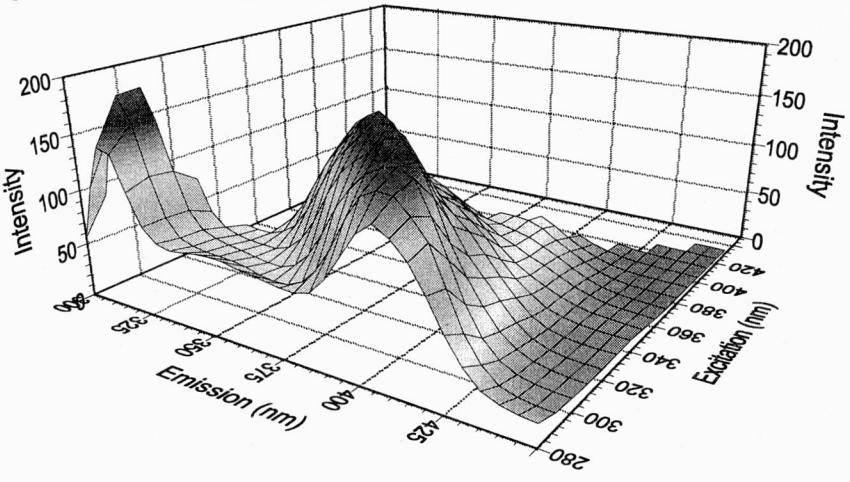

Fig. 4. Characteristic response obtained by 2D fluorimetric monitoring of a biofilm in an extractive membrane bioreactor

The advantage of 2D fluorimetry is that valuable information given by the fluorimetric map which might be contained in areas other than the immediate peaks is accessible, too. Therefore, what is of interest is the monitoring of shifts in the overall

fluorimetric map rather than looking at changes in single flurophor peaks. When comparing the two approaches to monitoring, fluorimetric analysis has the advantage of being on-line, non-invasive and yielding an immediate response which allows us to detect physiological changes in the biofilm long before the consequences of those changes are traceable by conventional off-line analysis.

However, the information obtained from the fluorimetric maps is very complex, which makes a simple deconvolution virtually impossible. In order to overcome this problem, a non-mechanistic approach to data interpretation is employed using Artificial Neural Networks (ANN) as mathematical tool.

ANN are capable of establishing associations between related sets of parameters without assumptions about underlying mechanisms. The relations are built exclusively from experimental data which are used to 'train' the network, thus creating an artificial system which 'learns from experience'. Applied to monitoring of the EMB, this mathematical methodology makes it possible to relate the information contained in the overall fluorimetric response map to the parameters determined off-line, e.g. DCE degradation rate in the biofilm. A valid ANN model, if trained with a sufficiently large set of experimental data, is capable of predicting system performance. In practical terms this means that the monitoring of the EMB could entirely be based on fluorimetry scans without having to carry out off-line analysis, as the ANN would automatically predict the correct associated off-line parameter from the fluorimetric map.

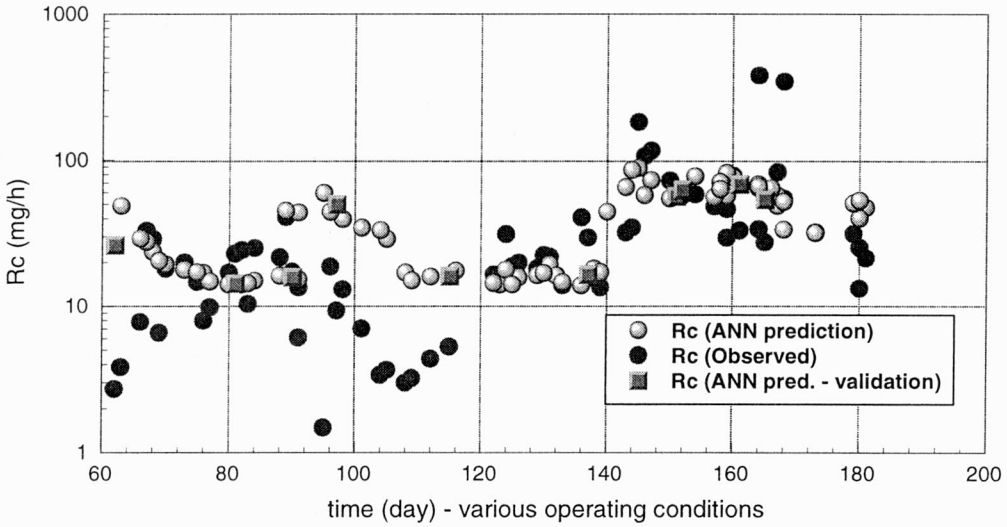

Fig. 5. Rate of DCE mineralisation: observed values (black circles) and values predicted by ANN (spheres) through association with fluorimetric response map. Experimental data used for model validation are represented by squares

Figure 5 shows the results of training an ANN with experimental data over a 120 day period, creating an association between fluorimetric map and rate of degra-

dation of DCE in the biofilm. The black circles represent the real observed rates of DCE mineralisation measured off-line, which were used to train the neural net. The spheres are the rates predicted by a single neural network with two hidden nodes. A number of rates observed in reality were left out when training the ANN, and were then used for model validation. Figure 5 proves that those values (represented by squares) were correctly predicted by the model found.

Overall predictions of process variables (Rc, Fc,g, Fc,l) from fluorimetric response maps were within a 6% average error. However, they were found unreliable for the lower range of the values observed experimentally (about 4% of total measured range).

SYSTEM MODELLING

In addition to system monitoring, Artificial Neural Networks can also be applied to model the performance of the STEMB. In contrast to conventional 'mechanistic' models comprising sets of *mathematical equations* which describe relationships between system variables, an ANN model consists of *relational maps* between those variables. An ANN was trained with the objective to model the performance of the STEMB by creating relational maps between key operational parameters (Q_{O2} and $Q_{b,l}$ and pH) and system variables (Rc, Tc, Fc,g, Fc,l). Data records over a 120 day monitoring period, where various operating conditions were employed, were used for the training.

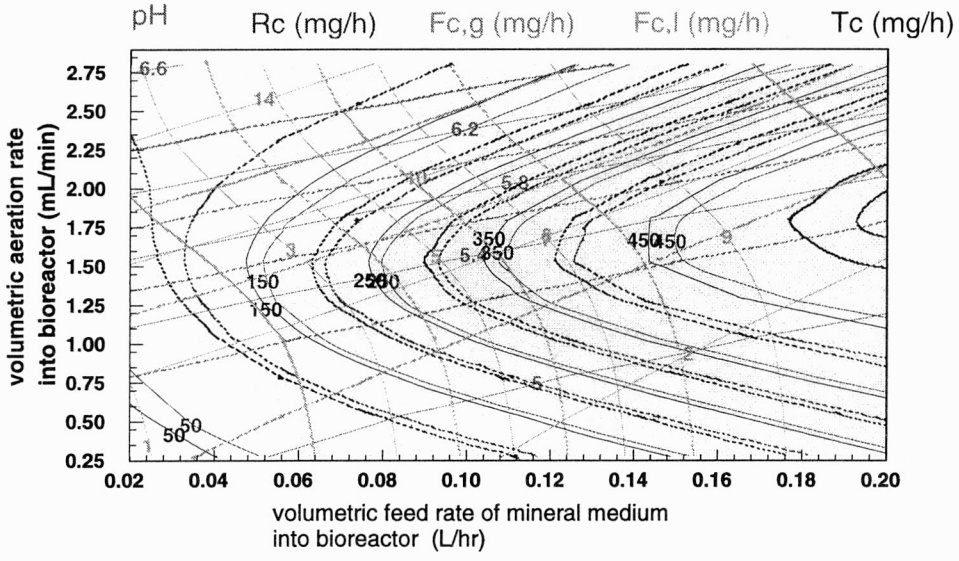

Fig. 6. Representation of process variables and pH as a function of oxygen supply rate and mineral medium feed rate

First it was verified that the ANN obtained satisfactorily mirrors experimental results. Prediction errors were below 5% when comparing the system parameters ob-

served and those predicted by the ANN (not shown). The associations between operational parameters and system variables inferred by this neural net were then represented by relational maps for single system variables. Subsequently, all the respective maps were compressed into a single representation (Figure 6) which makes it possible to identify optimum values for different operational modes. For example, if the flux of DCE leaving the bioreactor unaffected via the liquid outlet is to be kept under 5 mg/h, Figure 6 suggests that the optimum oxygen supply rate be 1.5 $l_{O2}/(l \cdot h)$.

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