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Catalytic strategies for industrial water re-use

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Abstract

The use of catalytic processes in pollution abatement and resource recovery is widespread and of significant economic importance [R.J. Farrauto, C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, Blackie Academic and Professional, 1997.]. For water recovery and re-use chemo-catalysis is only just starting to make an impact although bio-catalysis is well established [J.N. Horan, Biological Wastewater Treatment Systems; Theory and Operation, Chichester, Wiley, 1990.]. This paper will discuss some of the principles behind developing chemo-catalytic processes for water re-use. Within this context oxidative catalytic chemistry has many opportunities to underpin the development of successful processes and many emerging technologies based on this chemistry can be considered [Vogelpohl and Geissen (Eds.), in: Proceedings of the Conference on Water Science and Technology, Clausthal-Zellerfeld, Germany, May 1996, J. Int. Assoc. Water Quality, Pergamon, 1997]. Specifically, redox catalysis with active oxygen transfer oxidants has advantages and this paper will consider the design of such technologies [Vogelpohl and Geissen (Eds.), in: Proceedings of the Conference on Water Science and Technology, Clausthal-Zellerfeld, Germany, May 1996, J. Int. Assoc. Water Quality, Pergamon, 1997; F.E. Hancock et al., Catalysis Today 40 (1998) 289; F. King and F.E. Hancock, Catalysis Today, 40 (1998) 289; J. Hollingworth et al., J. Electron Spectrosc., in press]. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Industrial water re-use in Europe has not yet started on the large scale. However, with potential long term changes in European weather and the need for more water abstraction from boreholes and rivers, the availability of water at low prices will become increasingly rare. As water prices rise there will come a point when technologies that exist now (or are being developed) will make water recycle and re-use a viable commercial operation. As that future approaches, it is worth stating the most important fact about wastewater improvement – avoid it completely if at all possible! It is best to consider water not as a naturally available cheap solvent but rather, difficult to purify, easily contaminated material that if allowed into the environment will permeate all parts of the biosphere.

A pollutant is just a material in the wrong place and therefore design your process to keep the material where it should be – contained and safe. Avoidance and then minimisation are the two first steps in looking at any pollutant removal problem. Of course avoidance may not be an option on an existing plant where any changes may have large consequences for plant items if major flowsheet revision were required. Also avoidance may mean simply transferring the issue from the aqueous phase to the gas phase. There are advantages and disadvantages to both water and gas pollutant abatement. However, it must be remembered that gas phase organic pollutant removal (VOC

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combustion etc.,) is much more advanced than the equivalent water COD removal and therefore worth consideration [1].

Because these aspects cannot be over-emphasised, a third step would be to visit the first two steps again. Clean-up is expensive, recycle and re-use even if you have a cost effective process is still more capital equipment that will lower your return on assets and make the process less financially attractive.

At present the best technology for water recycle is membrane based. This is the only technology that will produce a sufficiently clean permeate for chemical process use. However, the technology cannot be used in isolation and in many (all) cases will require filtration upstream and a technique for handling the downstream retentate containing the pollutants. Thus, hybrid technologies are required that together can handle the all aspects of the water improvement process [6,7,8].

Hence the general rules for wastewater improvement are:

1. Avoid if possible, consider all possible ways to minimise.
2. Keep contaminated streams separate.
3. Treat each stream at source for maximum concentration and minimum flow.
4. Measure and identify contaminants over complete process cycle. Look for peaks, which will prove costly to manage and attempt to run the process as close to typical values as possible.

This paper will consider the industries that are affected by wastewater issues and the technologies that are available to dispose of the retentate which will contain the pollutants from the wastewater effluent. The paper will describe some of the problems to be overcome and how the technologies solve these problems to varying degrees. It will also discuss how the cost driver should influence developers of future technologies.

2. The industries

The process industries that have a significant wastewater effluent are shown in Fig. 1. These process industries can be involved in wastewater treatment in many areas and some illustrations of this are outlined below.

- Refining
- Chemicals
  - Intermediates, Speciality
- Petrochemicals
- Pharmaceuticals
- Agrochemicals
- Food and Beverages
- Pulp and Paper
- Municipal Waste Water Treatment

Fig. 1. Process industries with wastewater issues.

2.1. Refineries

The process of bringing oil to the refinery will often produce contaminated water. Oil pipelines from offshore rigs are cleaned with water; oil ships ballast with water and the result can be significant water improvement issues.

2.2. Chemicals

The synthesis of intermediate and speciality chemicals often involve the use of a water wash step to remove impurities or wash out residual flammable solvents before drying.

2.3. Petrochemicals

Ethylene plants need to remove acid gases (CO_2, H_2S) formed in the manufacture process. This situation can be exacerbated by the need to add sulphur compounds before the pyrolysis stage to improve the process selectivity. Caustic scrubbing is the usual method and this produces a significant water effluent disposal problem.

2.4. Pharmaceuticals and agrochemicals

These industries can have water wash steps in synthesis but in addition they are often formulated with water-based surfactants or wetting agents.

2.5. Foods and beverages

Clearly use water in processing and COD and BOD issues will be the end result.

2.6. Pulp and paper

This industry uses very large quantities of water for processing – aqueous peroxide and enzymes for bleaching in addition to the standard Kraft type processing of the pulp.

It is important to realise how much human society contributes to contaminated water and an investigation of the flow rates through municipal treatment plants soon shows the significance of non-process industry derived wastewater.

3. The technologies

The technologies for recalcitrant COD and toxic pollutants in aqueous effluent are shown in Fig. 2. These examples of technologies [2,6,8] available or in development can be categorised according to the general principle underlying the mechanism of action. If in addition the adsorption (absorption) processes are ignored for this catalysis discussion then the categories are:

1. Biocatalysis
2. Air/oxygen based catalytic (or non-catalytic).
3. Chemical oxidation
1. Without catalysis using chemical oxidants
2. With catalysis using either the generation of $^{\bullet}$OH or active oxygen transfer.

Biocatalysis is an excellent technology for Municipal wastewater treatment providing a very cost-effective route for the removal of organics from water. It is capable of much development via the use of different types of bacteria to increase the overall flexibility of the technology. One issue remains – what to do with all the activated sludge even after mass reduction by de-watering. The quantities involved mean that this is not an easy problem to solve and re-use as a fertilizer can only use so much. The sludge can be toxic via absorption of heavy metals, recalcitrant toxic COD. In this case incineration and safe disposal of the ash to acceptable landfill may be required.

Air based oxidation [6,7] is very attractive because providing purer grades of oxygen are not required if the oxidant is free. Unfortunately, it is only slightly soluble in water, rather unreactive at low temperatures and, therefore, needs heat and pressure to deliver reasonable rates of reaction. These plants become capital intensive as pressures (from ∼10 to 100 bar) are used. Therefore, although the running costs maybe low the initial capital outlay on the plant has a very significant effect on the costs of the process. Catalysis improves the rates of reaction and hence lowers the temperature and pressure but is not able to avoid them and hence does not offer a complete solution. The catalysts used are generally Group VIII metals such as cobalt or copper. The leaching of these metals into the aqueous phase is a difficulty that inhibits the general use of heterogeneous catalysts [7].

Chemical oxidation with cheap oxidants has been well practised on integrated chemical plants. The usual example is waste sodium hypochlorite generated in chlor-alkali units that can be utilised to oxidise COD streams from other plants within the complex. Hydrogen peroxide, chlorine dioxide, potassium permanganate are all possible oxidants in this type of process. The choice is primarily determined by which is the cheapest at the point of use. A secondary consideration is how effective is the oxidant.

Possibly the most researched catalytic area is the generation and use of $^{\bullet}$OH as a very active oxidant (advanced oxidation processes) [8]. There are a variety of ways of doing this but the most usual is with photons and a photocatalyst. The photocatalyst is normally TiO_2 but other materials with a suitable band gap can be used [9,10]. The processes can be very active however the engineering difficulties of getting light, a catalyst and the effluent efficiently contacted is not easy. In fact the poor efficiency of light usage by the catalyst (either through contacting problems or inherent to the catalyst) make this process only suitable for light from solar sources. Photons derived from electrical power that comes from fossil fuels are not acceptable because the carbon dioxide emission this implies far outweighs and COD abatement. Hydroelectric power (and nuclear power) are possible sources but the basic inefficiency is not being avoided.

Hydrogen peroxide and ozone have been used with photocatalysis but they can be used separately

- Total Solutions
  - Adsorption (GAC, Polymer resin)
- Chemical oxidation
- Wet Air oxidation
- Catalytic Wet Air oxidation
  - Homogeneous or heterogeneous
- Supercritical Water Oxidation
- Biotreatment
- UV/H_2O_2/O_3

- Partial Solutions
  - Adsorption (GAC)
  - Flocculation, Sedimentation
  - Hydrogenation

Fig. 2. Potential technologies for COD removal.

or together with catalysts to effect COD oxidation. For ozone there is the problem of the manufacturing route, corona discharge, which is a capital intensive process often limits its application and better route to ozone would be very useful. It is important to note at this point that the oxidants discussed do not have sufficient inherent reactivity to be use without promotion. Thus, catalysis is central to their effective use against both simple organics (often solvents) or complex recalcitrant COD. Hence, the use of Fenton's catalyst (Fe) for hydrogen peroxide [11].

In terms of catalysis these oxidants together with hypochlorite form a set of materials that can act has 'active oxygen transfer (AOT) oxidants' in the presence of a suitable catalyst. If the AOT oxidant is hypochlorite or hydrogen peroxide then three phase reactions are avoided which greatly simplifies the flowsheet. Cheap, catalytically promoted oxidants with environmentally acceptable products of oxidation that do not require complex chemical engineering and can be produced efficiently would appear to offer one of the best solutions to the general difficulties often observed.

3.1. Redox catalysis and active oxygen transfer

The mechanism of catalytically promoted oxidation with hydrogen peroxide or sodium hypochlorite cannot be encompassed within one concept, however there are general similarities between the two oxidants that allows one to write a series of reactions for both (Fig. 3) [5]. This type of mechanism could be used to describe a broad range of reactions for either oxidant from catalytic epoxidation to COD oxidation. The inherent usefulness of the reactions is that;

1. The reactions take place in a two-phase system.
2. High pressure and temperature are not required.
3. The catalytic surface can act as an adsorbent of the COD to be oxidised effectively increasing the concentration and hence the rate of oxidation.

The simple mechanism shows the selectivity issue with this type of processes. The oxidant can simply be decomposed by the catalyst to oxygen gas – this reaction must be avoided because dioxygen will play no role in COD removal. Its formation is an expensive waste of reagent with oxygen gas ($20/Te) compared to the oxidant ($400–600/Te). To be cost competitive

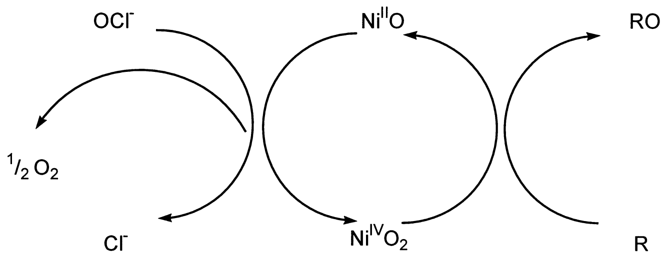

Fig. 3. The redox cycle for nickel and hypochlorite in the oxidation of COD (represented by R).

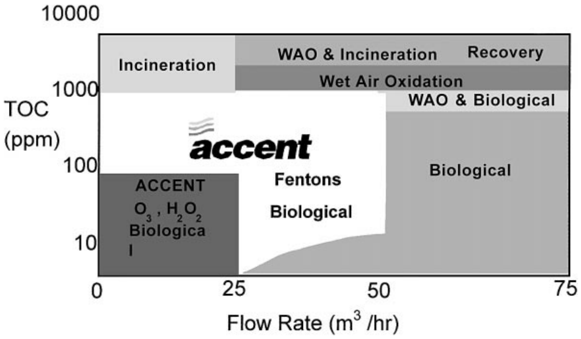

Fig. 4. The technology map.

with alternative processes redox catalysis needs excellent selectivity.

3.2. Technology mapping

The technologies so far described can be mapped [12] for their applicability with effluent COD concentration (measured as TOC) and effluent flow rate ($m^3\,h^{-1}$). The map is shown in Fig. 4. The map outlines the areas where technologies are most effective. The boundaries, although drawn, are in fact fuzzier and should be only used as a guide. Only well into each shape will a technology start to dominate. The underlying cost model behind the map is based on simple assertions – at high COD mass flows only air/oxygen will be able to keep costs down because of the relatively low variable cost of the oxidant. At high COD concentrations and high flows only biological treatment plants have proved themselves viable – of course if done at source recovery becomes an option. At low flows and low COD levels redox AOT catalysis is an important technology – the Synetix Accent[1] process being an example of this type of process (see Fig. 5 for a simplified flowsheet).

The catalyst operates under very controlled conditions at $pH > 9$ and hence metal leaching can be avoided (<5 ppb). The activity and selectivity aspects of the catalyst displayed in Fig. 3 can be further elaborated to look at the potential surface species. This simple view has been extended by a significant amount of research [3,4,5]. Now the mechanism of such a catalyst can be described in Fig. 6. The key step is to avoid recombination of NiO holes to give peroxy species and this can be contrasted with the hydrogen peroxide situation where the step may be characterised as oxygen vacancy filled. From both recombination will be facilitated by electronic and spatial factors.

The range of application of the process is outlined below. From laboratory data some general types of chemical have been found suitable – sulphides, amines, alcohols, ketones, aldehydes, phenols, carboxylic acids, olefins and aromatic hydrocarbons.

From industrial trials recalcitrant COD (non-biodegradable) and sulphur compounds have been successfully demonstrated and a plant oxidising sulphur species has been installed and is operational.

4. Conclusions

Wastewater treatment processes are in the early stages of development. The key parameters at present are effectiveness and long term reliability. Many processes operating are in this stage, including the redox

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[1] Accent ™ is a trademark of the ICI Group of Companies.

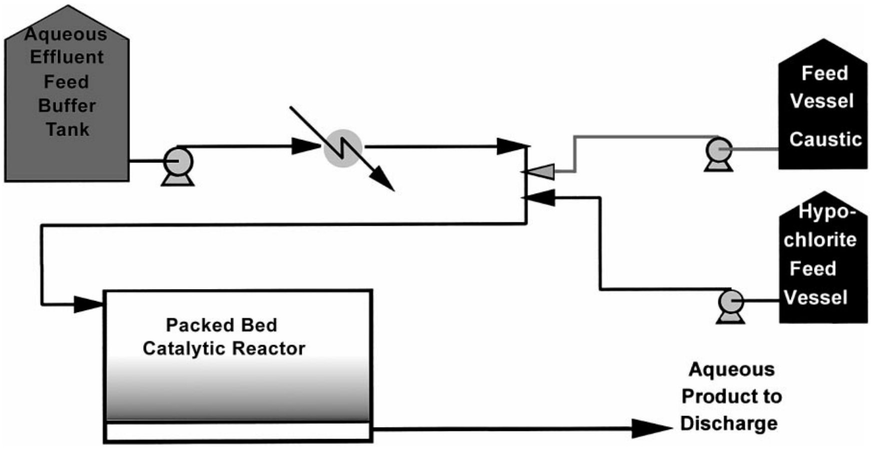

Fig. 5. The accent process flowsheet.

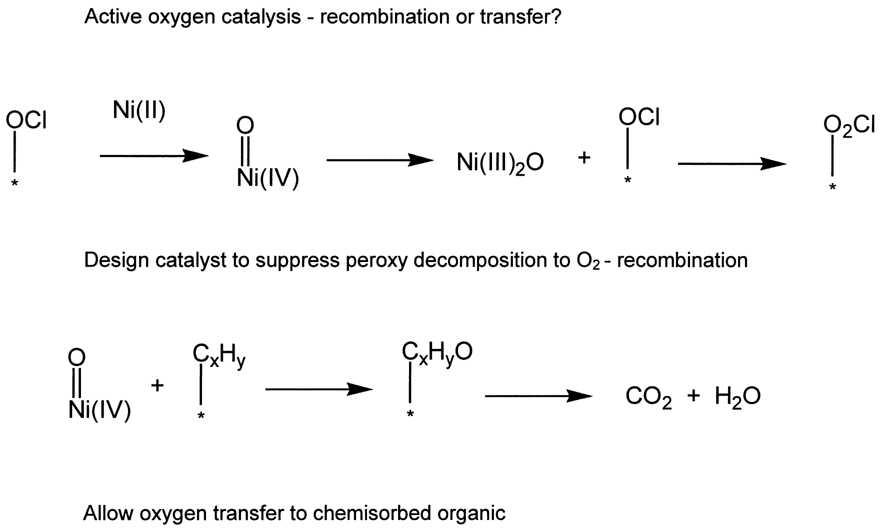

Fig. 6. The defect mechanism of redox catalysis.

catalysis systems. However, once proven, redox catalysis offers many advantages for COD removal from wastewater:

1. The low capital cost of installation.
2. Simple operation that can be automated.
3. Flexible nature of the process – can be easily modified to meet changing demands of legislation.

Hence it will be expected to develop into an important technology in wastewater improvement.

Acknowledgements

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