Effective cleaning of industrial waste water

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Stricter requirements are continually being set for the cleaning of industrial waste water. Whether new legal specifications or operational modifications, there is a demand for concepts and processes which ensure maximum flexibility for the cleaning facilities. Oxygen processes offer large performance reserves which allow existing plants to be adapted for new tasks without elaborate structural extensions or investments.

In addition to goals such as increased reliability in compliance with prescribed effluent values or ensuring adequate effluent quality for recycling in the plant, the demand for space plays a major role, particularly in the industrial sector. Biological filters, static bed plants and membrane biologies therefore represent an interesting addition to conventional plant concepts where the extension or replacement of existing plants is concerned. Here too, the potential can only be fully exploited with pure oxygen (O_2).

For the neutralization of alkaline waste water, carbon dioxide (CO_2) offers many advantages. For partial flows polluted with persistent contaminants, ozone (O_3) is the remedy of choice.

This article describes, on the basis of current application examples, how the potential of modern process engineering can be optimally exploited by using the technical gases O_2, CO_2 or O_3.

Oxygen in waste water treatment technology

Pure oxygen is "concentrated atmospheric oxygen" without the nitrogen ballast. This makes its optimizing potential very clear:

- oxygen can be dissolved in water more quickly and using less energy. That permits a flexible response, even to large fluctuations in demand.
- Only approx. 4% of the volume of air has to be introduced when pure oxygen is used. This results in the following advantages:
- such as correspondingly lower apparatus costs for the gas input,
- minimal aerosol formation and less stripping of odor-intensive substances,
- fewer hydraulic breakdowns in the operation of filter plants,
- no disturbance of settling processes through unintended flotation (supersaturation of nitrogen in deep aeration tanks leads to gassing out in the final sedimentation).

Fig. 1: Pure oxygen input technique developed by Messer: Gassing hose (left), Injector (center), Oxidator (right)

Oxygen input systems

The economic advantages of a pure oxygen supply can only be used optimally with suitable plant technology. In practice, special hose aerators, injectors and oxidators (Fig. 1) have proven their worth.

The choice of system or system combination depends largely on the application and the local circumstances. Important parameters are, for example, the tank geometry and the local availability and cost of electrical power.

Title picture: BASF waste water treatment plant Ludwigshafen (7 million EW)

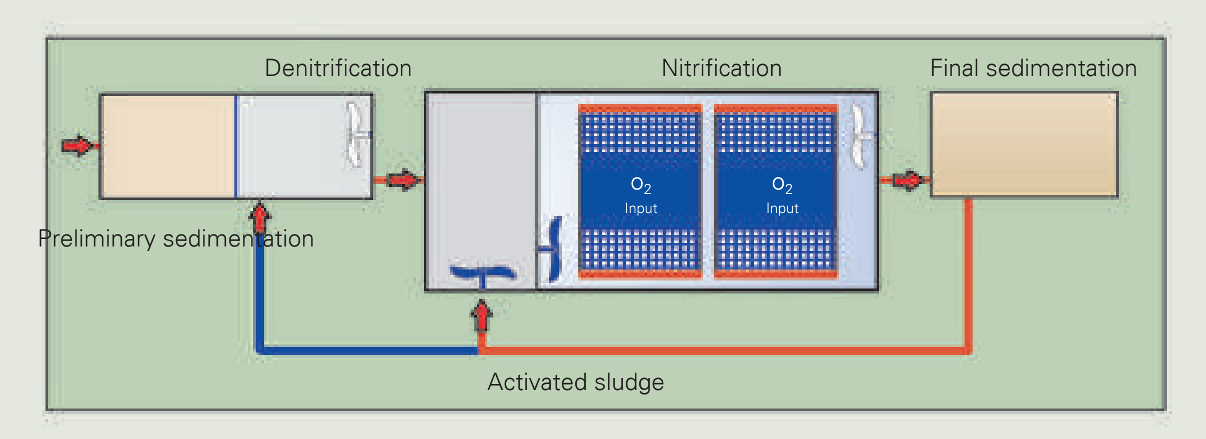


Fig. 2: Diagram of the conversion of a water treatment plant to the Biox®-N process

Problem solving in practice

Peak load coverage through partial oxygen gassing (POG)

Odor problems at a water treatment plant usually indicate a lack of oxygen. Since 1981, because extreme short-term fluctuations in the oxygen demand were causing odor problems, the Emschermündung Water Treatment Plant in Germany has been successfully operated for over 20 years with an additional pure oxygen supply, eliminating the need for further measures.
In another example, a potato processing plant in Mecklenburg, an increase in performance was needed. In spite of an extension of the treatment plant to include a Sequence Batch Reactor (SBR), the required effluent values could not be complied with. The one of two reactors was provided with an additional supply of pure oxygen. For this purpose, one half of the existing dome aerators was refitted for pure oxygen, while the other half was still operated with air. After this conversion to POG operation, effluent values well below the limits could be achieved in the converted reactor alone. For batch processes like batch tanks or sequence batch reactors, which have proven themselves many times in the food industry, high oxygen demand peaks are characteristic at the introduction of fresh waste water batches. In a dairy water treatment plant in Saxony, in spite of a generously dimensioned aeration system, peak overloads of up to 280% of the nominal values regularly led to a temporary lack of oxygen. The oxygen supply is now provided by a pure oxygen plant (POG) which also reliably covers the phases of maximum oxygen demand.

Better performance for nitrification and denitrification

For the elimination of nitrogen in the third cleaning stage, as demanded by legislation, Messer has developed the Biox® process. The performance of the biological stage is considerably enhanced through support or replacement of the conventional aeration with pure oxygen while, at the same time, increasing the biomass present in the system (Fig. 2). It is then often possible to separate a sufficient volume from the existing tank for the denitrification. One of the largest industrial water treatment plants in the world also uses pure oxygen for nitrification. Here the oxygen is brought into solution by means of Messer aeration mats.

Nitrogen supersaturation/Flotation: Problem solved with pure oxygen

In deep tanks and in so-called tower biologies, the aeration can lead to such high concentrations of dissolved nitrogen (which is not consumed by the microorganisms like oxygen) that it sporadically gases out in the shallower sedimentation tank. Flotation then occurs in the sedimentation tank, resulting in a great deterioration in effluent values. With a water depth of 10 m in the aeration tank, a nitrogen supersaturation of 150% was measured in the sedimentation tank of a 3000 EW pilot plant. When the deep tanks were supplied continuously or intermittently with pure oxygen instead of compressed air, the supersaturation with nitrogen was reduced and the sedimentation tank operated without problems.

Compact cleaning in oxygen gassed filters

If waste water is to be free of particles and have stable, low effluent values (e.g. for ammonia), biofiltration processes are used for cleaning or aftercleaning. One particularly economical and compact system is the two-stage continuous sand filter, in which quartz sand is used as the filter medium and carrier for the biomass.

The plants are suitable both for permanent and for temporary use. When the aerobic first stage is supplied with pure oxygen, optimum operation is ensured, i.e.:

- disturbance-free filtration thanks to small gas volume flow
- no channel formation in the sand bed
- reduced stripping out of odor-intensive constituents
- no unwanted lime precipitation.

The total solids content remaining in the waste water is well below 10 mg/l. This makes possible the direct recycling of the cleaned waste water in production processes.

Application examples:

- In the context of soil remediation and dewatering, continuous sand filters with short residence time (less than 10 minutes) have achieved elimination rates of over 99 % for MAH (= monocyclic aromatic hydrocarbons) and over 92 % for PAH (= polycyclic aromatic hydrocarbons). The effluent values for MAH and PAH were less than 3 µg/l.
- In the waste paper processing industry, a sand filter was connected after an anaerobic treatment stage. For sulfide loads of up to 2.7 kg S/m3 • d, the degree of degradation was over 97% and the sulfide effluent value below 1 mg/l. The elimination rate for solids (TSS) reached 80% to almost 100% and resulted in TSS effluent values below 20 mg/l. The COD reduction in the filter was about 50%.

Membrane biology: Safety in minimum space – ideally with oxygen

Waste water purification in membrane biologies, in which a microfiltration through membranes replaces conventional sedimentation (Fig. 3) is particularly space-saving and safe. The active sludge content is run higher by a factor of from 3 to 8 than in conventional plants.

So, apart from the sedimentation, the biological stage is also considerably compacter. The effluent quality of a membrane biology is free of solids and complies hygienically with the bathing water standard, so the reutilization possibilities for the water are very good.

The potential performance of a membrane biology can only be fully exploited, however, if pure oxygen gassing systems supplement or replace the conventional aeration. The mixture of waste water and activated sludge in membrane biologies is extraordinarily viscous, which makes the absorption of oxygen from a fine bubble pressure aeration system considerably more difficult. Messer has developed an oxygen injection system especially for this highly viscous activated sludge, with which even the highest oxygen input rates can be realized economically. In a direct comparison in a membrane biology, this system achieved a dissolving efficiency more than 2.5 times higher with a 2.5 times lower energy consumption than with air injection. In the case of reactors operated under pressure, the energy savings are even more drastic. In a landfill seepage water plant, the system has also proven itself for supplementary oxygen supply on the occurrence of peak loads: Here it was possible to improve the cleaning performance directly by 40 %.

Advantages of pure oxygen in industrial waste water treatment plants:

- general increase in cleaning performance
- sudden loads and continuous overloads are reliably countered
- safe nitrification
- considerably lower odor emissions
- oxygen input takes place silently
- higher operational reliability
- suitable for emergency use in the case of aerator failure
- no costly and time-consuming extension of the plant
- can be used as a transitional or interim solution
- lower investment costs than conventionally constructed plants

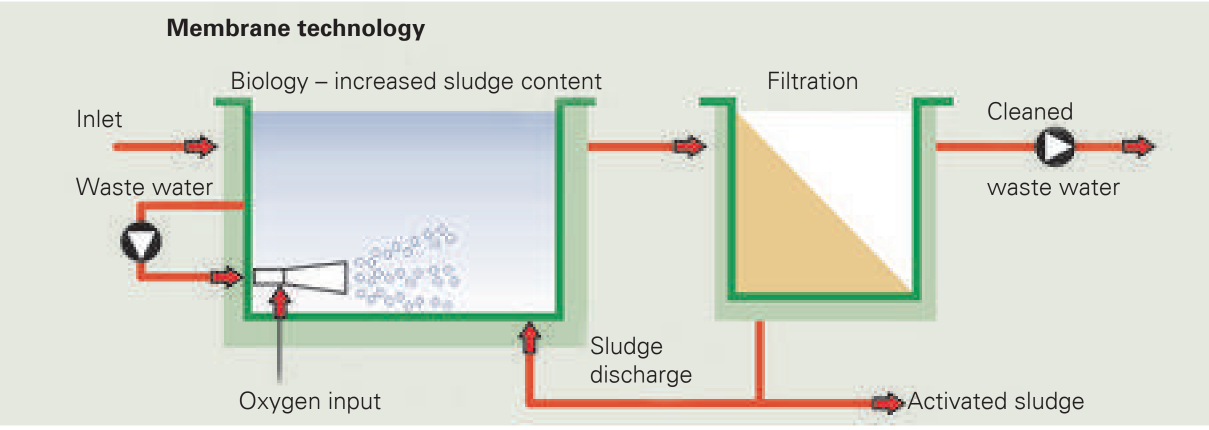
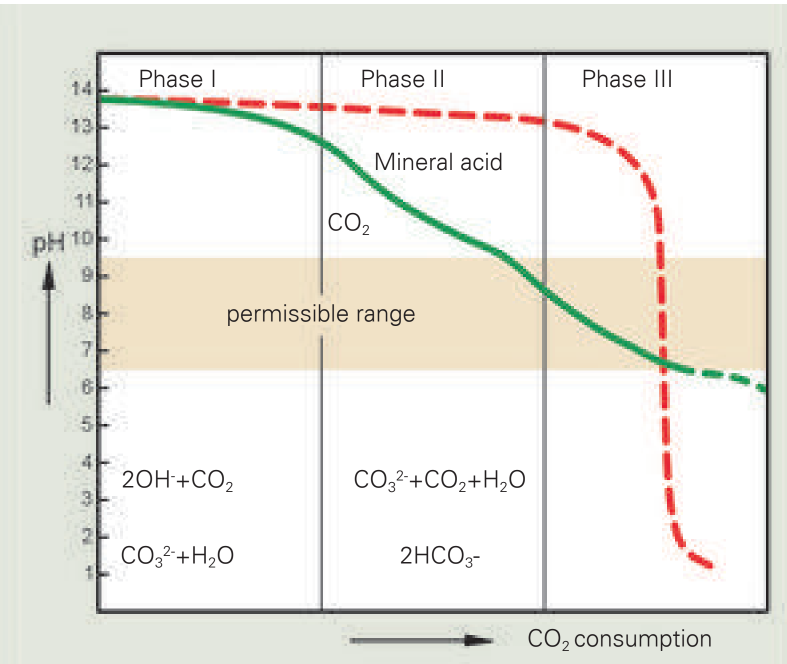


Fig. 3: Space saving through a membrane biology

Fig. 4: CO_2 operated construction site neutralization at Berlin's Main Station, former Lehrter Station.

Neutralization and pH regulation with CO_2: no salination in the water circulation

Alkaline waste water has to be neutralized before it is passed into a biological waste water purification plant. Here, neutralization with CO_2 is rightly growing in importance:



- A comparison of the stoichiometric consumption values between CO_2 and the mineral acids with complete utilization is particularly favorable for CO_2. This is one reason why a cost comparison also often results in favor of CO_2.
- Lower salt contents are not only important for the waste water charges, but also for the multiple use of (almost) closed water circulations: In the case of CO_2, salination with chlorides or sulfates and the associated corrosion problems are avoided.
- Fig. 5 shows the neutralization curve of a mineral acid in comparison with carbonic acid. The shallower neutralization curve of CO_2 means that its addition, even in the range around the neutral point, only has a slight effect on the pH value, which practically excludes over-acidification (unlike mineral acids). Consequently, elaborate regulation technology can be dispensed with for CO_2.

Fig. 5: Diagram of neutralization curves for the use of CO_2 and mineral acids

Fig. 6: Neutralization components used by Messer:
Aeration hoses (left), Batch tank constructed by customer (center), Liquid feed (right)

For the input and dissolving of CO_2 in water, Messer uses a variety of systems:
tube reactors, jet systems, static mixers, ejectors or even aeration mats. The technique used depends on the water quality, for example the water hardness, and the local circumstances.

Messer supplies every user with the optimum tailor-made process with the best CO_2 utilization, so the best economy. Here, Messer can draw on practical experience with over 150 neutralization plants (Fig. 4 and 7).

Fig. 7: Neutralization of alkaline waste water from the textile industry with CO_2

Neutralization and pH regulation with CO_2 – Advantages at a glance:

- No salination due to chlorides, sulfates etc., so
- environmentally friendly
- no charges for increased salt content
- better suited for reutilization in circulation
- over-acidification practically excluded
- no corrosion problems
- low operating costs
- controlled precipitation of heavy metals or hardness components possible

Neutralization with CO_2 has already been carried out in the following sectors of industry:

- Drinks industry
- Dairies
- Paper and cellulose industry
- Galvanic processes
- Metallurgy
- Textile and leather industry
- Chemicals
- Glass
- Power plants
- Laundries
- Construction site neutralization

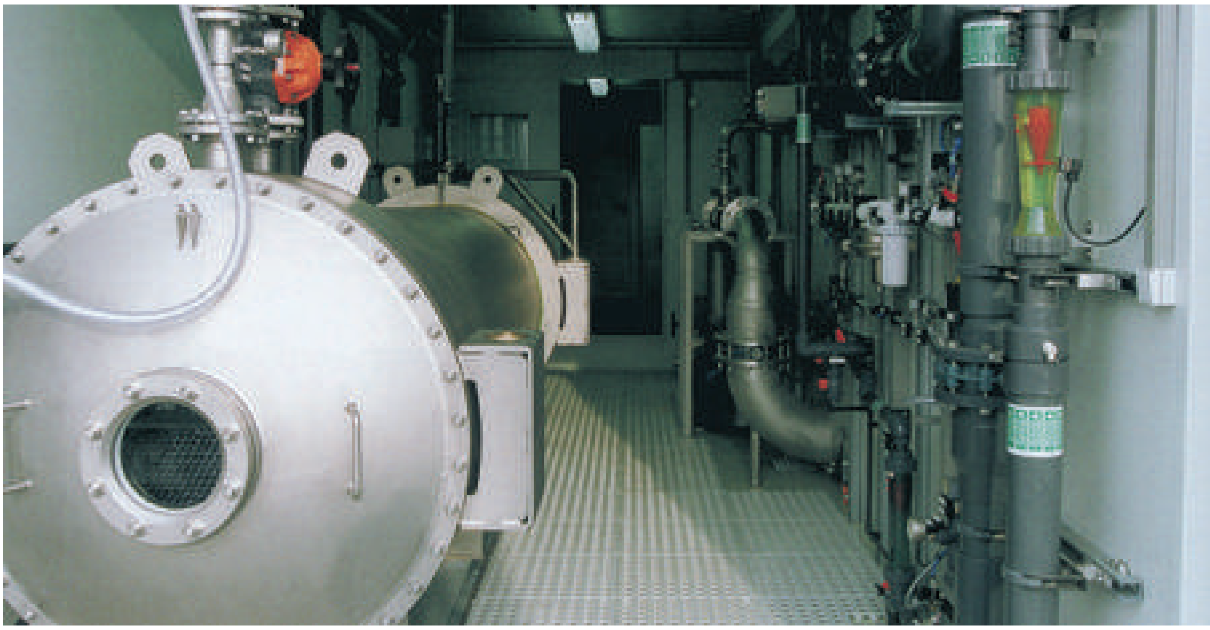


Fig. 8: Ozone plant for waste water partial flow oxidation (Photo: Wedeco)

Ozone - Oxidation and disinfection without salination

If the waste water contains organic substances resistant to biodegradation or if the biological activity in the circulation water has to be limited, an ozone treatment is often the process of choice. After fluorine, ozone is the most powerful oxidant. However, it reacts to form relatively unproblematic oxidation products and oxygen, and does not cause salination of the treated water.

Ozone cannot be stored, so it is always produced from oxygen in ozone generators on site (Fig. 8). For industrial applications, ozone concentrations of 10 to 14% by weight can be realized with energy consumption well below 10 kWh/kg ozone. These high concentrations, only achievable with pure oxygen, are beneficial because the mechanical and energy costs for dissolving the ozone in the water are lower and the reactions take place more quickly. The following application examples illustrate the advantages of ozone:

Ozone in combination with aerobic biological treatment stages

In order to attack degradation resistant substances directly with ozone, the ozone treatment is usually connected after a biological cleaning stage. In partial oxidations, ozone cracks persistent constituents remaining in the effluent and, in this way, makes them accessible to further, inexpensive biological purification. A measure for the degradability of waste water constituents is the ratio of COD to BOD_5 (chemical oxygen demand to biological oxygen demand). The smaller this ratio, the better the waste water can be biologically cleaned. In the waste water from a cellulose factory, the COD/BOD ratio in the first stage effluent was reduced from 8 to 3 and, in this way, the COD related cleaning performance of the whole system was raised from 45% to over 80%. In the textile industry, an ozone stage after the treatment plant is used to remove the color from the effluent. In the pharmaceuticals sector, ozone is primarily used for disinfection and the deactivation of pathogenic organisms.

Ozone for the treatment of circulated/ process water

If, for economic and ecological reasons, production water is recirculated, the organic contamination of the water through biological activity may lead to sliming. Here, ozone is the biocide of choice, as it does not contribute to salination and, even in relatively low dosage, effectively inhibits the biological activity.

Ozone for cooling water treatment

The advantages of the use of ozone in open cooling water circulation systems are so convincing that Messer is successively equipping all its own production plants accordingly. Even in low specific quantities of 0.1 g per m^3 circulation water, ozone leads to:

- a drastic reduction of microorganisms and algae growth
- avoidance of scaling in all system components and, thus, among other things, to an
- increase in the efficiency and/or service life of heat exchangers and, thus, to
- clear savings, according to branch, in energy consumption
- greatly reduced maintenance costs (many times the service life in some cases)
- lower salination in comparison with conventional technology, so a clear saving of additional water.

Ozone is therefore a valuable complement to existing treatment techniques. As the exhaust gases from ozone stages (when using pure oxygen) are generally highly enriched with oxygen, further utilization, for example in aerobic treatment stages or for enrichment in incineration stages, is of particular interest.

For the following processes, ozone is used with the corresponding effects:

Cellulose bleaching

- Ozone replaces chlorine in the bleaching process
- Improved degree of whiteness
- Avoidance of AOX in the effluent

Paper, textile, printing and plastics industries

- Bleaching of paper and textile fibers
- Ozone as an auxiliary for the coating of paper
- Improved adhesion in the manufacture of drinks packaging material

Chemicals industry

- Ozone as oxidizing agent for chemical processes
- Manufacture of base substances for the pharmaceuticals and cosmetic industries

Textile waste water

- Bleaching
- Avoidance of AOX in the effluent

Cooling water

- Microbiological cleaning of cooling water systems without the use of organic biocides or chlorine compounds
- Reduction of corrosion
- Avoidance of AOX in the effluent

Foodstuffs

- Disinfection of foodstuffs, store-rooms, packaging aids, production machines and seawater for mussel farming

Summary

In industrial firms, the waste water treatment often consists of a combination of different biological, chemical and diverse physical processes. With the increasing trend to closed water circulations, the technique described here has assumed central significance.
Messer not only delivers the gases for the purpose, but also offers complete service packages, ranging from consulting to design, equipment, installation and commissioning. Here, Messer works in close consultation with users and, by preference, with local engineering firms.

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