Recent developments in effluent purification/colour stripping

Demonstrated in the second part of the article series: purifying, colour stripping, minimizing and re-using dyehouse effluent, are recent developments in this area, presenting processes which are to some extent already state of the art today, together with those practised up to now only on the laboratory, technical college and pilot scales.

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Oxidative dyestuff destruction with the aid of "Fenton's reagent", ozone or hydrogen peroxide has already been presented (ITB 4/95), though oxidative dye destruction and other organic effluent content substances can be effected by other methods and substances.

UV light or a combination of UV light and H_2O_2

In the first case, there is only the photo-oxidative effect of UV light, while, additionally in the latter, the chemo-oxidative effect of the hydroxyl radicals produced by UV catalysis from the peroxide is applicable.

Oxidative dyestuff destruction by electro-chemical processes

Chemical-free, oxidative dyestuff destruction and minimisation of the effluent charge by electro-chemical processes, e.g. by the Klose Abwassertechnik GmbH (D) electrolytic effluent purification processes *(Figs. 2 + 3)* and conventional electrolytic methods.

By way of water electrolysis with corrodable iron anodes (alternatively: aluminum anodes), the electroflotation process developed by Klose produces chemical reaction-forming, highly reductive hydrogen at the cathode, and chemical reaction-forming, highly oxidative oxygen, together with Fe(II) ions which have an additional catalytic effect, at the anode. Additionally, a pH change near the iron anode makes possible the additional precipitation of Fe(II) and Fe(III) hydroxides (with Al anodes: AL(III) hydroxide precipitation), which flocculates the organic residual charge. The resultant flocs are separated from the aqueous phase by flotation via the O_2 and H_2 gases produced at the electrodes following the addition of auxiliary flotation agents (collectors, foams, controllers and activators), the moisture removed and compressed by a chamber filter press, and pressed into a compact filter cake.

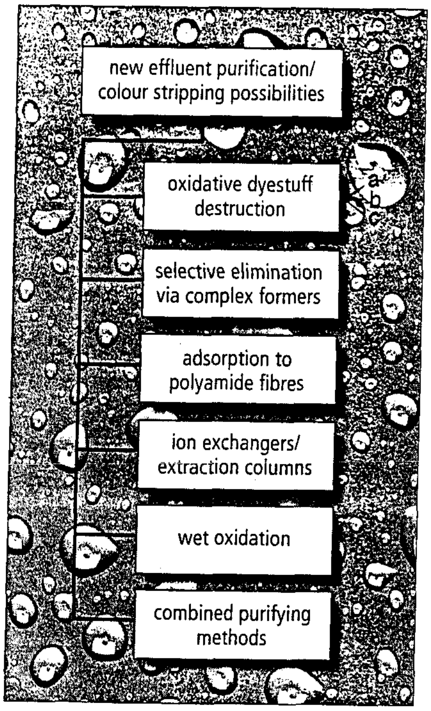

Fig. 1: Future-qualified technology
a = UV light
b = combination of UV light and H_2O_2
c = electro-chemical processes

Photograph: ITB

This German process is now tremendously important, and has clearly outstripped the comparable American "Brinecell" electrolytic process, which produces in chloride-containing effluent oxidative chlorine, chlorine dioxide, ozone and OH radicals (AOX problem!).

With conventional electrolysis with corrodable anodes, the so-called direct method, which works without the addition of auxiliary chemicals (so-called mediators), and owes its purifying effect exclusively to the respective oxidative and reductive effects of the emergent chemical reaction-forming gases oxygen and hydrogen, has relatively little effect.

In contrast, with the "indirect" method, despite incorrodable electrodes, the effect of corrodable electrodes is guaranteed however in that auxiliary substances (mediators) are used, small quantities of iron (II) sulphate (approx. 0.5 g/l) plus larger quantities of triethanolamine (3 to 20 g/l) generally being involved. One great disadvantage of this method is the obviously high chemical cost.

Selective elimination by complex formation

This process employs so-called macrocyclic (and macroreticular) compounds (ligands). Dyestuff can be selectively eliminated by incorporation in macrocyclic compounds based on cucurbituril. Other effluent charges (e.g. textile auxiliary agents and basic chemicals) are not (or at least hardly) agglutinated because of the dyestuff selectivity of cucurbituril. Nevertheless, in the sense of quantitative dyestuff elimination, the process should be carried out with a superstoichiometric quantity of cucurbituril. Up to now, this method has been successfully applied on the laboratory, technical college and pilot scales with hydrolysed and non-hydrolysed reactive, direct, acid and disperse dyes.

Advantages over conventional precipitation with iron or aluminium salts are a far higher bonding capacity for dyestuffs and considerably easier operation (with flocculating agents, a marked surplus has a redissolving effect). Moreover, cucurbituril, as a solid "dye absorbent", like activated carbon filters, can be regenerated again by oxidative (e.g. with peracetic acid) and reductive (e.g. with sodium dithionite) processes, minimizing the special waste disposal problem.

Incidentally, a highly acid complex solution (for extracting the dyestuff from the chelate) has recently been tested for regenerating cucurbituril with subsequent dyestuff separation by ion pair extraction. The regeneration results of this method are allegedly better than those with oxidizing and reducing agents.

The insolubility of cucurbituril also has the advantage that no surplus is carried along with the effluent. In fact, excessive flocculating agents themselves constitute effluent pollution.

Heavy metal ions (also from metal-containing dyestuffs) can be selectively bonded by macrocyclic compounds based on special polymer-fixed azakrone ether or cryptands. This means for example that Cr(III) ions exclusively are selectively bonded to these solid ion exchangers. After regeneration (with acid), the result is pure Cr(III) salt for instance, which can be reused as valuable material.

Finally, there are also special macrocyclic calixarene-based compounds or compounds based on formaldehyde or chromotropic acid cycling products, which are able to complex AOX relevant substances (halogen-containing, adsorbable to activated carbon organics).

Adsorption

Polyamide fibres (Man-made fibre industry waste), PA gels, alums, thermally activated aluminium oxide, silica gel, bentonite (Na-Al silicate), biofilters (peat, wood, lignin, chitin, mod. guarana, carbonized wool etc.) and other solid sorbents in the fixed bed and fluid bed processes, involving newer alternatives to conventional carbon adsorption, all of which are still practised on the laboratory and pilot scales. Interesting in connection with PA adsorption is the extraordinarily good agglutination of reactive dye hydrolysate in a highly acid medium.

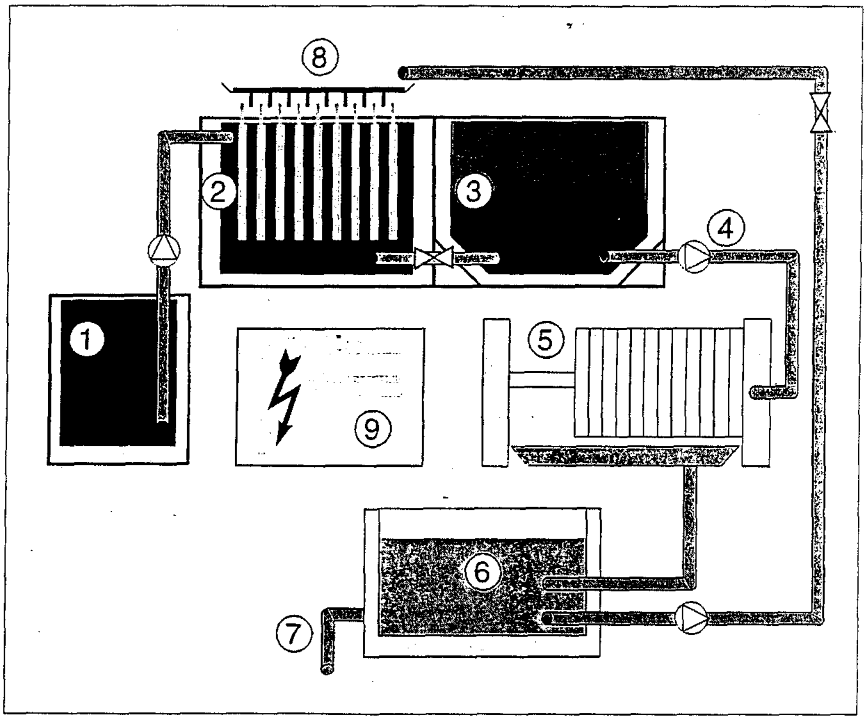

Fig. 2: The "Clearox" process
1 untreated water tank, 2 "Klose-Clearox" reactor, 3 floc container, 4 charging filter pump, 5 chamber filter, 6 clean water tank, 7 recycling or duct, 8 foam precipitation unit, 9 SPS control unit and current converter Photograph: Klose Abwassertechnik GmbH

On this point, this method of conventional carbon adsorption, which, for the most part, guarantees no satisfactory colour stripping with reactive dye hydrolysate, is clearly superior.

The latest possibilities of filtration, including reverse osmosis and electrodialysis, have already been reported in the ITB 4/95 edition.

Purification via ion exchangers and extraction columns

Conventional ion exchange with synthetic anionic and/or cationic polymers is not customary in effluent colour stripping and purification (in contrast to the preparation of only slightly contaminated water), and also has very little effect. The same applies to the so-called "direct extraction" process.

On the other hand, successfully used on the laboratory scale, and now therefore on the technical college scale, for removing sulphogroup-containing dyestuffs from highly polluted effluent, is ion pair extraction (BASF). Here, an addition compound of dye and an added water-insoluble long-chain aliphatic amine (trioctylamine) in a two-phase water/hydrocarbon (xylol) mixture moves into the organic phase.

The prerequisite here is a pH below 7, at which the amine is present in protonized form, i.e. cationic, thus forming a salt bond with the anionic dyestuff (after separation of the organic phase, the dyestuff is then precipitated from it with NaOH (in addition to a small quantity of water) or Ca $(OH)_2$.

Fig. 3: Arrangement of electrode plates in the "Klose-Clearox" *system reactor*
Photograph: Klose Abwassertechnik GmbH

Trials in which the liquid organic sorbent (xylol) is replaced by a solid organic one have recently been conducted. The results are still awaited.

Recently, experiments have been carried out with cationized cellulose for effluent colour stripping in general and also with liquid ion exchangers, especially for the total (simultaneous) removal of all heavy metals from effluent (twin-phase reactive extraction).
More detailed information on these processes, which have certainly not yet moved on from the laboratory and technical college scales, is not yet available however.

Wet oxidation

In the case of wet oxidation, also called "wet combustion", all effluent content substances are catalytically "wet combusted" in a reactor at 120 to 300 °C and under more or less high pressure by blowing in air or by added hydrogen peroxide, and consequently fully mineralized. A distinction is drawn here between high pressure nitrogen (effect of compressed air at 50 to 150 bar, 200 to 300 °C with the use of Cu catalysts) as well as the more important, as of course weaker but technically markedly less expensive, low pressure nitrogen (3 to 20 bar, 120 to 200 °C; as the "Loprox" process using compressed air, iron (II) salts and quinone-forming organic substances; as the "Clear-Finish" process using hydrogen peroxide, iron (II) salts and milk of lime and caustic soda respectively).

This process, which is carried out in an aqueous medium, is not to be confused with the (economically more unfavourable for smaller effluent quantities) high temperature combustion of effluent by atomizing effluent in special gas or oil burners, i.e. oxidation, which takes place in a special vapour-type medium (gas plasma oxidation process). The "Katox" and "Palmer-Nohl" processes are unpressurized biochemical variants of wet oxidation at close to ambient temperature.

Combination of cleaning methods:

The meaningful combination of processes in effluent colour stripping/purification leads naturally to a markedly increased synergistic effect, providing for a high degree of purifying efficiency, as already demanded by direct introducers. Generally in this respect, substance destroying (e.g. oxidizing and/or reducing processes) and substance separating processing stages (e.g. filtration, precipitation, adsorption) are placed alternately in certain sequences (serially) and, if necessary, next to each other (parallel).

Due to the countless successful purifying sequences published to date, only three processes, which are of special interest to direct textile introducers, or are successfully practised by them, are mentioned by name: these are the "Scholl", "Wisa" and "ITV" processes.

Effluent purification/effluent recycling at the dyeing machine

Finally, let us now point to the possibility of effecting effluent purification (possibly coupled with the regeneration of adsorptive purifying agents like activated carbon or macrocyclic ligands with simultaneous chemical recycling) plus heat recovery directly at the dyeing machine.

This provides the possibility of the (repeated) re-use of even deeply dyed and organically charged effluent (e.g. in reactive dyeing).

Read in the next ITB edition about effluent purification/colour stripping for the direct introducer.

Literature references can be requested under reader service No. 5-412. ■