

## CHAPTER 25

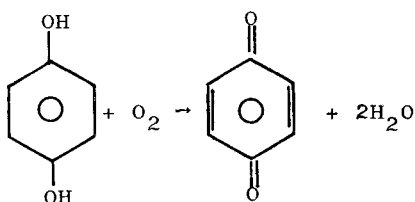
## THE PHOTOCHEMICAL INDUSTRY

## CHARACTERISTICS OF THE WASTE WATER

The waste water from the photochemical industry contains several toxic compounds such as silver, hydroquinone and methol.

The silver is recovered as silver chloride by a precipitation process. Although silver chloride has a solubility product of  $10^{-10} \text{ mol}^2/\text{l}^2$ , the waste water still contains 0.1-1.0 mg silver/l, a concentration which is above the toxic limit for fish and above the WHO's limit for drinking water.

The  $\text{LD}_{50}$  of hydroquinone for fish is 0.3 mg/l and for methol 5 mg/l. Furthermore, the toxicity of hydroquinone and methole is synergistic. A concentration of 0.1 mg/l hydroquinone and 0.6 mg/l methol corresponds to the  $\text{LD}_{50}$  value. Hydroquinone also consumes oxygen according to the following process:



A typical analysis of waste water from the photochemical industry is shown in Table 25.1.

It is seen from the analytical data that adjustment of the pH is required.

Furthermore, the high ammonium ion and ammonia concentration is toxic at this pH.

TABLE 25.1

A typical analysis of waste water from the photochemical industry

Component	Concentration
Colour	black/red
Odour	as benzaldehyde
pH	9.6
Dry matter (mg/l)	6500
Suspended solid (mg/l)	107
Dissolved dry matter (mg/l)	3400
Total alkalinity (mg calcium carbonate/l)	1705
COD (mg/l)	1800
BOD <sub>5</sub> (mg/l)	1000
Phenols (mg/l)	5
Hydroquinone (mg/l)	200
Methol (mg/l)	100
EDTA (mg/l)	2
Sorbitol (mg/l)	5
Salicylic acid (mg/l)	6
Cyanide (mg/l)	0.5
Sulphate (mg/l)	1200
Na <sup>+</sup> (mg/l)	4000
Thiosulphate (mg/l)	3000
Silver (mg/l)	1
Lead (mg/l)	10
Thiocyanate (mg/l)	60
Halogenides (mg/l)	200
Nitrate (mg/l)	300
NH <sub>4</sub> <sup>+</sup> and NH <sub>3</sub> (mg/l)	60

Treatment methods

Fig. 25.1 is a flow-sheet for the treatment of waste water from the photochemical industry.

By the addition of aluminium sulphate it is possible to remove a substantial part of the organic components and reduce the loading of the BOD<sub>5</sub>.

Before addition of the flocculant the pH of the waste water is adjusted. This pH adjustment is carried out in a large tank which simultaneously unifies the composition of the waste water which often varies considerably with time. The sludge obtained by settling after the flocculation can be treated by filtration.

The biological treatment of photochemical waste water after the chemical precipitation step must be adapted to the special composition characteristic of the waste water from the photochemical industry. Adaptation can take up to several months for the biological culture.

In most cases a mixture of municipal waste water and waste water from the photochemical industry is treated in the biological step. It is hardly possible to adapt the micro-biological culture to 100% waste water from this industry.

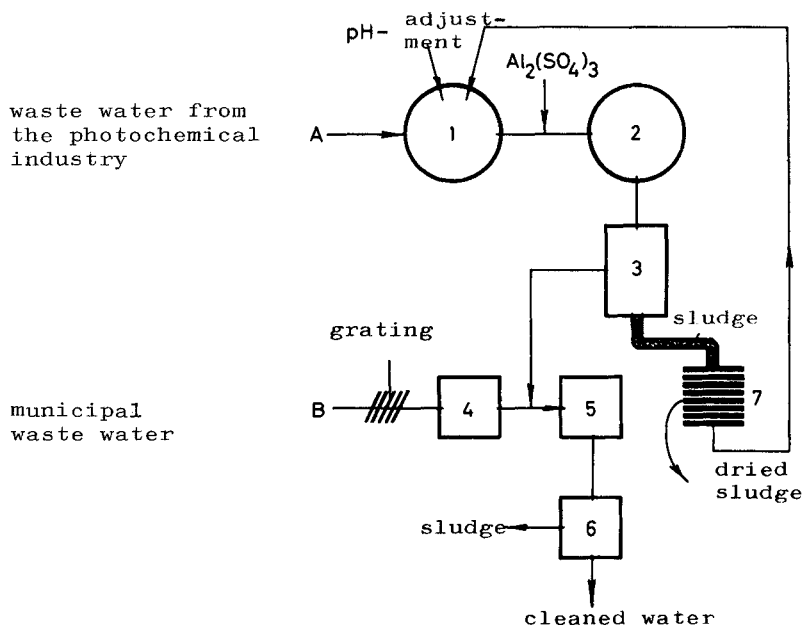


Fig. 25.1. Flow-sheet for treatment of waste water from the photochemical industry. (1) pH adjustment; (2) flocculation; (3) sedimentation; (7) filtration. (4) sedimentation; (5) biological treatment; (6) sedimentation of sludge.

Ozone is particularly useful in breaking down certain developer components that are slowly biodegraded. Such compounds include colour developing agents such as phenidone and hydroxylamine sulphate. Breakdown of these ingredients by ozone proceeds more rapidly and to a greater extent than with biological treatment.

Suggested uses of ozone are therefore (Boba et al., 1975).

1. As a preliminary treatment for overflow colour developer solutions.
2. As a preliminary treatment for other solutions that may contain substantial amounts of thiocyanate, formate, EDTA and black and white developing agent.

3. As a tertiary treatment and disinfectant for the combined waste after it has first been treated biologically. When a mixed waste is first treated biologically to remove most of the oxygen demand, ozone posttreatment is an effective way of destroying organic compounds that are biodegraded slowly, removing colour, odour and disinfecting the waste.

Silver in a photoprocessing effluent is either in the form of an insoluble precipitate, or in a water-soluble thiosulphate complex that has a very low order of toxicity for biological treatment plants and aquatic organisms.

A secondary treatment plant will remove most of the silver and the little that passes through will be in an insoluble particulate form that has a very low level of toxicity (Bart et al., 1976).

Dilution of the processing effluent with the total waste water flowing to a treatment plant will further lower the silver concentration entering the plant and ultimately the treated effluent leaving the plant. The low toxicity associated with the silver present in photographic processing effluent leads to the conclusion that this silver presents no hazard to secondary waste treatment plants or to water receiving the effluent.

Photographic processing wastes often contain iron(III)- and iron(II)cyanide. Iwano et al. (1975) have suggested a new procedure using a weakly basic resin for eliminating these components. The complexed cyanides recovered by the resin are then chemically decomposed to non-toxic substances by alkaline hypochlorite.

#### REFERENCES

- Bart, C.C. et al., 1976. Silver in photoprocessing effluents. J. Wat. Poll. Contr. Fed., 48: 389.
- Boba, T.W. and Dagon, T.J., 1975. Ozonation of photographic processing wastes. J. Wat. Poll. Contr. Fed., 47: 2114.
- Iwano, H., Shimanura, I. and Abe, A., 1975. Elimination of ferri- and ferrocyanide from photographic processing wastes by ion exchange resin. Photographic Science and Engineering, 19: 219.