Removal of Inorganic Pollutants from Wastewater During Reclamation for Potable Reuse

R. SMITH, M.L. SIEBERT and W.H.J. HATTINGH*
National Institute for Water Research of the Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, 0001

Abstract

The effectiveness of a pilot water reclamation plant for removing certain toxic and aesthetically undesirable inorganic chemical constituents from wastewater designed for potable reuse is described. Of the various stages in the process, the high lime and activated carbon treatments were shown to be the most significant for the removal of cadmium, copper, lead, mercury and zinc, while the chlorination stage proved to be the most effective for cyanide removal. Concentrations of all six substances investigated were reduced to below the detection limits of the analytical methods used.

Introduction

The unrestricted reuse of water depends on its suitability for the consumer, whether it be man, animal or plant. The safety of a water for human consumption in turn depends on the effective removal of microbiological and chemical contaminants, i.e. bacteria, parasites and viruses, together with organic and inorganic chemical compounds. The microbiological quality of a reclaimed water can be guaranteed as long as proper disinfection is practised (Grabow, Bateman and Burger, 1978), but it is not so easy to guarantee its chemical quality. Van Rensburg *et al.* (1978) have shown that a reclamation plant should and can remove toxic organic chemicals, for example, chlorinated pesticides, volatile chlorinated hydrocarbons, carcinogens, organo phosphates etc., but information on the removal of inorganic chemical substances in such a plant is relatively meagre.

This paper deals with an investigation into the ability of a pilot reclamation plant to remove certain undesirable inorganic chemical constituents from purified sewage effluent.

Experimental

The pilot plant used in the study is adjacent to the full-scale Stander water reclamation plant at the Daspoort sewage works, Pretoria, and was operated on secondary, biologically purified sewage effluent at a flow rate of 3,3 m^3/h (Fig. 1). This pilot plant was previously used for the development of the criteria for the Stander plant, and its mode of operation is identical to that of the Stander plant.

Four separate investigations were carried out:

(1) A mixture of copper and zinc plating solutions was obtained from a local plating shop, diluted with water, and fed to humus tank effluent at a rate of 36 dm^3/h to produce a feed solution containing 2,2 mg/dm^3 copper and 2,4 mg/dm^3 zinc.

(2) A synthetic solution of cadmium chloride in water was fed at the same rate as for the first investigation to give a feed solution containing 2,6 mg/dm^3 cadmium.

(3) A synthetic solution of lead nitrate and mercuric nitrate in water was fed to humus tank effluent at a rate of 1,9 dm^3/h to produce a feed solution containing 6 mg/dm^3 lead and 20 $\mu g/dm^3$ mercury.

(4) A plating solution containing cyanide was diluted with water and fed at the same rate as for investigation No. 3, to give a feed solution with 7,6 mg/dm^3 cyanide.

For each investigation, samples were collected at the injection point and after each unit process, at times chosen to coincide with the 'plateau' periods for each process, which had been previously obtained during a trial run using a sodium chloride solution as a tracer. Samples for metal analysis were preserved by the addition of 1 cm^3 of concentrated AR grade nitric acid per 100 cm^3 of sample. Samples for the cyanide determination were preserved by the addition of one drop of a 100 g/dm^3 sodium hydroxide solution to each 100 cm^3 of sample.

Cadmium, copper, lead and zinc were determined by means of direct flame atomic absorption (air-acetylene flame), while the 'cold vapour' atomic absorption technique was used for the determination of mercury (APHA, 1975). The cyanide concentration was determined by means of an automated colorimetric technique (NIWR, 1974).

Results and Discussion

The percentage removal and percentage overall removal of each substance under investigation, after each treatment stage, were calculated from the sample concentrations, and are shown in Table 1.

Limits for the six substances investigated are set in various water quality criteria. Table 2 shows South African and World Health Organization limit concentrations for these six substances in drinking water. Cadmium, lead, mercury and cyanide are highly toxic; copper and zinc, although relatively non-toxic, are undesirable in concentrations above about 1 mg/dm^3 for copper and 5 mg/dm^3 for zinc, for aesthetic reasons. Also, the presence of copper and zinc may be indicative of the presence of cyanide from plating solutions.

The concentration of metals in domestic wastewater is generally low, high concentrations usually being due to discharge of industrial waste to the sewer. Those metals which are present in an insoluble form, or form insoluble salts on interaction with sewage, are largely removed during the primary sedimentation stage of the sewage treatment process (Stoveland *et*

*Present address: Hydrological Research Institute, Department of Water Affairs, Private Bag X313, Pretoria, 0001

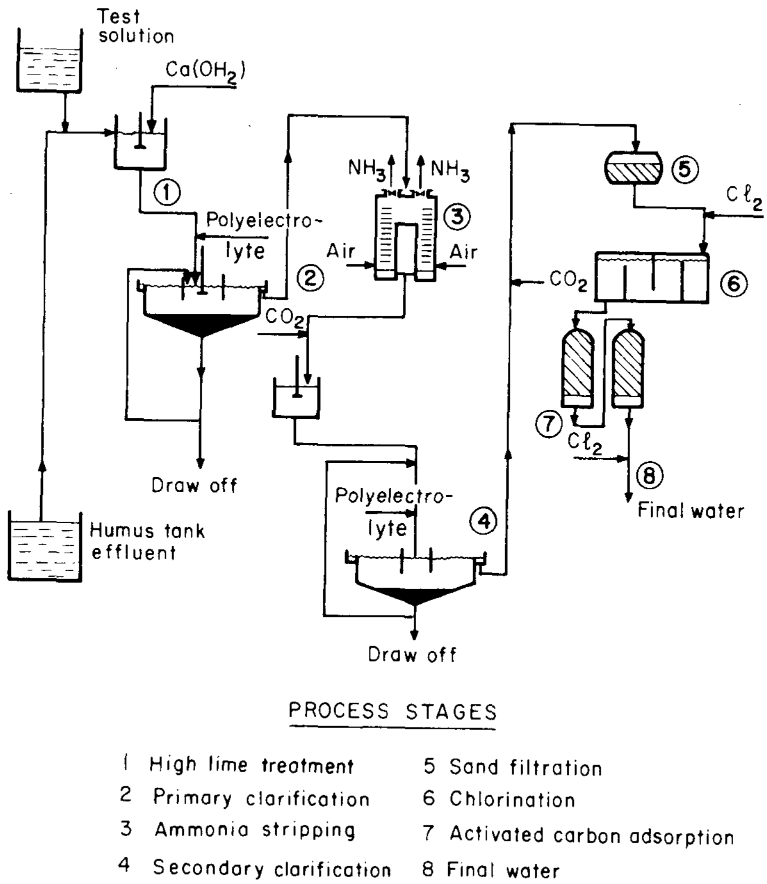

Figure 1
Schematic diagram of pilot reclamation plant

al., 1979). Funke (1975) showed that between 36 % and 62 % of various metals were removed in this manner. This sedimentation process could therefore be regarded as the first 'safety barrier' against inorganic chemical contamination in the progress to the final reclamation stage. The concentration of metals present in soluble form may be further reduced during the secondary, or biological, stage of the sewage treatment process (Oliver and Cosgrove, 1974).

The first stage in the reclamation process, 'high lime' treatment (i.e. dosing with lime at a pH of 11 to 11,5), proved extremely effective in removing cadmium (99,3 %) and lead (99,6 %). Most of the zinc (96 %) was also removed at this stage, but copper removal was relatively low (19 %). The low removal could have been due to the fact that this metal was present as the cyanide complex, and therefore very stable. Poor pH control could also result in low removals at this stage. Both copper and zinc dissolve in excess hydroxide to form the soluble cuprate and zincate ions respectively. Maintenance of the pH at a maximum value of 11,5 is therefore essential for this process to operate at optimum efficiency. The high lime treatment also removed 90 % of the mercury. For this particular investigation, inorganic mercury was used, but it has been shown that lime treatment is considerably less effective when the mercury is in the organic form (EPA, 1977). Cyanide removal at this stage was also low.

The ammonia stripping, secondary clarification and sand filtration stages played little or no part in the further removal of copper and mercury, but a further 19 % of the cyanide was eliminated at the secondary clarification stage, possibly due to depression of the pH.

Chlorination effectively removed the remainder of the cyanide. In addition, a further 10 % of the copper was eliminated by this treatment.

For the final stage, activated carbon adsorption, two carbon filters were used in series, separate samples being taken from each column. Activated carbon treatment was found to be effective in removing the remaining copper and mercury. This treatment has also been shown to be capable of organic, as well as inorganic, mercury removal (EPA, 1977).

The high lime and activated carbon treatments therefore, appear to be the most significant 'safety barriers' in the various stages of the reclamation process for the removal of the metals investigated, although these processes were not designed with trace metal removal as the main objective. Objectives of high lime treatment are clarification, softening, removal of micro-organisms, conversion of NH_4 to NH_3, and phosphate removal. The activated carbon process is mainly intended for the removal of dissolved organic impurities which could give rise to taste, colour and odour problems (Singer, 1974).

The ability of these processes to remove trace metals is governed by the form or chemical state of the metals in question. For most trace metals, only a very small fraction is found as the free metal ion. Most exist in the form of soluble complexes, or in association with colloidal organic or inorganic impurities in the water. In addition, parameters such as pH, temperature,

TABLE 1
EFFECTIVENESS OF THE PILOT PLANT IN REMOVING CADMIUM, COPPER, LEAD, MERCURY, ZINC AND CYANIDE

Stage	Removal		Cadmium	Copper	Lead	Mercury	Zinc	Cyanide
High lime treatment/ Primary clarification	Feed concentration	($\mu g/dm^3$)	2 560	2 200	5 950	20	2 400	7 560
	Removal	(%)	99,3	19,1	>99.6	90	95,6	6,8
	Overal removal	(%)	99,3	19,1	>99,6	90	95,6	6,8
Ammonia stripping	Feed concentration	($\mu g/dm^3$)	18	1 780	<25	2	106	7 050
	Removal	(%)	>72,2	0	—	0	>76,4	0
	Overall removal	(%)	>99,8	19,1	—	90	>99,0	6,8
Secondary clarification	Feed concentration	($\mu g/dm^3$)	<5	1 800	<25	2	<25	7 200
	Removal	(%)	—	0	—	0	—	19,4
	Overal removal	(%)	—	19,1	—	90	—	23,3
Sand filtration	Feed concentration	($\mu g/dm^3$)	<5	1 770	<25	2	<25	5 800
	Removal	(%)	—	0	—	0	—	0
	Overall removal	(%)	—	19,1	—	90	—	23,3
Chlorination	Feed concentration	($\mu g/dm^3$)	<5	1 780	<25	2	<25	5 800
	Removal	(%)	—	12,9	—	0	—	>99,1
	Overall removal	(%)	—	29,5	—	90	—	>99,1
Activated carbon adsorption-1	Feed concentration	($\mu g/dm^3$)	<5	1 550	<25	2	<25	<50
	Removal	(%)	—	>99,0	—	>50	—	—
	Overall removal	(%)	—	>99,0	—	>95	—	—
Activated carbon adsorption-2	Feed concentration	($\mu g/dm^3$)	<5	<25	<25	<1	<25	<50
	Removal	(%)	—	—	—	—	—	—
	Overall removal	(%)	—	—	—	—	—	—
Final water	Concentration	($\mu g/dm^3$)	<5	<25	<25	<1	<25	<50

TABLE 2
LIMIT CONCENTRATIONS FOR CADMIUM, COPPER, LEAD, MERCURY, ZINC AND CYANIDE IN DRINKING WATER, SPECIFIED BY SOUTH AFRICAN BUREAU OF STANDARDS AND WORLD HEALTH ORGANIZATION (mg/dm³)

Constituent	South African Bureau of Standards — Water for domestic supplies (1971)		World Health Organization — International Standards (1971)	
	Recommended limit	Maximum allowable limit	Maximum acceptable concentration	Maximum allowable limit
Cadmium (Cd)	0,05	0,05	—	0,01
Copper (Cu)	1,0	1,5	0,05	1,5
Lead (Pb)	0,05	0,1	—	0,1
Total mercury (Hg)	N.S.	N.S.	—	0,001
Zinc (Zn)	5	15	5	15
Cyanide (CN)	0,01	0,2	—	0,05

N.S. = Not specified

oxidation-reduction potential etc., will also affect the distribution and solubility of the metals (Singer, 1974).

In the high lime treatment process, trace metals can be removed by co-precipitation with the calcium carbonate and magnesium hydroxide formed during the softening process, as well as by precipitation due to high pH levels. There are several ways by which activated carbon treatment may effect trace metal removal. For example, the presence of oxygen and sulphur as impurities in the carbon can result in the formation of oxide and sulphido groups at the carbon surface. The oxide groups can act as weak cation exchangers, while the sulphido groups may cause the carbon to exhibit chemisorptive behaviour towards metals. Secondly, nucleation sites for the precipitation of metals from solution are provided at the carbon surface. Adsorption of organo metallic complexes from solution is also possible (Singer, 1974).

Oxidation by chlorination effectively removed all the cyanide remaining at this stage. Cyanides, which are normally present in wastewater as the metal complexes, differ in their stability towards destruction by oxidation treatment. For example, amongst the more commonly used cyanide complexes, those of cadmium and zinc will be more easily destroyed than that of copper. An additional safety barrier is presented by the activated carbon columns, which will also remove, possibly by adsorption or catalytic action, the cyanide complexes of these three metals (Funke and Coombs, 1971).

Conclusions

This study has demonstrated the overall effectiveness of the reclamation process for the continuous removal of high loads of undesirable inorganic constituents from wastewater destined for potable reuse.

The high lime and activated carbon treatments were the most significant stages of the process for removing the five metals under investigation. In the case of the highly toxic cadmium and lead, high lime treatment alone was sufficient for their complete removal, but activated carbon treatment was necessary to ensure elimination of copper and mercury. The effectiveness of the chlorination treatment stage for complete cyanide removal has been illustrated.

Acknowledgements

The assistance of Dr P.W. Grütz of the Physical-chemical Technology Division of the National Institute for Water Research with the operation of the plant is gratefully acknowledged. This paper is published with the permission of the Director of the National Institute for Water Research.

References

AMERICAN PUBLIC HEALTH ASSOCIATION – AMERICAN WATER WORKS ASSOCIATION – WATER POLLUTION CONTROL FEDERATION (1975) *Standard methods for the examination of water and wastewater,* 14the edition, New York.

ENVIRONMENTAL PROTECTION AGENCY (1977) *Manual of treatment techniques for meeting the interim primary drinking water regulations.* Cincinnati, Ohio.

FUNKE, J.W. (1975) Metals in urban drainage systems and their effect on the potential reuse of purified sewage. *Water SA* **1**(1) 36–44.

FUNKE, J.W. and COOMBS, P. (1971) Determination of the influence of shock loads of industrial wastes on the performance of the water reclamation process treating purified sewage. *Project Report no. 3,* (restricted). Project no. 6201/6434. National Institute for Water Research, CSIR, Pretoria.

GRABOW, W.O.K., BATEMAN, B.W., and BURGER, J.S. (1978) Microbiological quality indicators for routine monitoring of wastewater reclamation systems. *Prog. Water Tech.* **10** 317–327.

NATIONAL INSTITUTE FOR WATER RESEARCH (1974) *Analytical Guide, Part II,* 13–16, CSIR, Pretoria.

OLIVER, B.G. and COSGROVE, E.G. (1974) The efficiency of heavy metal removal by a conventional activated sludge treatment plant. *Wat. Res.* **8** 869–874.

SINGER, P.C. (1974) *Chemical processes for the removal of trace metals from drinking waters. In: Trace metals in water supplies: occurrence, significance and control.* Proceedings of 16th Water Quality Conference, University of Illinois, Urbana, Illinois.

STOVELAND, S., ASTRUC, M., LESTER, J.N. and PERRY, R. (1979) The balance of heavy metals through a sewage treatment works. II. Chromium, nickel and zinc. *The Science of the Total Environment* 12 25–34.

VAN RENSBURG, J.F.J., VAN ROSSUM, P.G. and HATTINGH, W.H.J. (1978) The occurrence and fate of micro-pollutants in a water reclaimed for potable reuse. *Prog. Wat. Tech.* **10** 41–48.