

THE INFLUENCE OF PROCESS PARAMETERS ON THE REMOVAL OF HEAVY METALS IN ACTIVATED SLUDGE

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Abstract. The behavior of six heavy metals in an activated sludge pilot plant under conditions of normal and elevated influent metal concentrations has been studied. Percentage heavy metal removals at sludge ages of 4, 9, and 12 d were more consistent when metals were added to the system, possibly as a result of lesser variations in heavy metal speciation in the settled sewage, and the greatest degree of accumulation of heavy metals by the biomass occurred at the 12 d sludge age. When shock loads of heavy metals were introduced into the system, their concentrations in the effluent did not immediately rise in proportion; however, heavy metal removal efficiencies were similar under steady state conditions of normal and elevated influent metal concentrations. Cadmium, Cu, and Ni were largely soluble in the effluent samples, but Cr, Pb, and Zn were predominantly insoluble, indicating that particulate forms of these metals may escape removal in secondary sedimentation. The high degree of Ni solubility in the settled sewage and final effluent reflected its consistently poor removal in the process. The two most soluble metals, Cu and Ni, appeared to be associated to a large degree with high molecular weight substances in the settled sewage and final effluent, possibly influencing their availability for uptake by the biomass.

1. Introduction

The efficient removal of heavy metals during the biological treatment of sewage is important in maintaining the quality of receiving waters and in preventing the infringement of standards for water to be abstracted for drinking water (European Economic Community, 1975) and potable supplies (World Health Organisation, 1970, 1971). A change in emphasis from sewage treatment to water reclamation is indicative of the increasing importance of sewage treatment in controlling the quality of surface waters (Brewin and Hellawell, 1980).

The almost ubiquitous presence of heavy metals in sewage has prompted many workers to study their removal in activated sludge. Typical removals are shown in Table I. Removals appear to be extremely variable. Average removals as low as 1% for Ni (Oliver and Cosgrove, 1974) and as high as 92% for Pb (Stones, 1960) have been reported. Relatively efficient removals (60%) of Cd, Cu, Ni, Pb, and Zn have been observed (Lewin and Rowell, 1973; Lester *et al.*, 1979). Similar removal efficiencies for these metals have also been determined by Oliver and Cosgrove (1974), Chen *et al.* (1974), Davis and Jacknow (1975) and Stones (1955, 1958, 1959a, b, 1960). Relatively poor removals of Ni and Mn have been found. In certain instances poor removals of Cd (Brown *et al.*, 1973; Roberts *et al.*, 1977) and Cr (Stoveland *et al.*, 1979) have also occurred, even when the removals of other metals in the same studies have been relatively efficient.

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TABLE I
Typical heavy metal concentrations in settled sewage and their removals in the activated sludge process

| Reference | | Cd | Cr | Cu | Ni | Pb | Zn |
|-----------|----------------------------|-----|-----|-----|-----|-----|------|
| 1 | Conc. $\mu\text{g l}^{-1}$ | 3 | 130 | 210 | 280 | 90 | 1130 |
| | % removal | 50 | 54 | 60 | 1 | 79 | 50 |
| 2 | Conc. $\mu\text{g l}^{-1}$ | 3 | 50 | 72 | 50 | 70 | 390 |
| | % removal | 7 | 50 | 25 | 15 | 30 | 38 |
| 3, 4 | Conc. $\mu\text{g l}^{-1}$ | 1.5 | 30 | 40 | 30 | 40 | 420 |
| | % removal | 33 | 33 | 86 | 61 | 78 | 78 |
| 5 | Conc. $\mu\text{g l}^{-1}$ | 18 | 59 | 170 | — | 160 | 350 |
| | % removal | 11 | 78 | 61 | — | 43 | 48 |
| 6 | Conc. $\mu\text{g l}^{-1}$ | 19 | 310 | 110 | 190 | 100 | 310 |
| | % removal | 47 | 82 | 77 | 41 | 53 | 59 |
| 7 | Conc. $\mu\text{g l}^{-1}$ | — | 270 | 480 | 110 | 380 | 3590 |
| | % removal | — | 69 | 83 | 32 | 92 | 57 |
| 8 | Conc. $\mu\text{g l}^{-1}$ | 18 | 79 | 98 | 77 | 55 | 530 |
| | % removal | 62 | 60 | 43 | 9 | 61 | 57 |
| 9 | Conc. $\mu\text{g l}^{-1}$ | 13 | 210 | 920 | 73 | 95 | 320 |
| | % removal | 39 | 57 | 33 | 21 | 56 | 65 |

References

1. Oliver and Cosgrove (1974).
2. Roberts *et al.* (1977).
3. Lester *et al.* (1979).
4. Stoveland *et al.* (1979).
5. Brown *et al.* (1973).
6. Chen *et al.* (1974).
7. Stones (1955, 1958, 1959a, b, 1960).
8. Davis and Jacknow (1975).
9. Esmond and Petrasek (1974).

The removal of heavy metals in the activated sludge process is to some degree a biological phenomenon. Cheng *et al.* (1975) found that an activated sludge which had been sterilized had a lower capacity for metal uptake than the original viable biomass. Casey and Wu (1977) found that a nutrient imbalance promoted the formation of large quantities of polymeric capsular material in the synthetic sewage with a significant capacity for metal adsorption. Factors influencing the production of bacterial extracellular polymers and their role in heavy metal removal in the activated sludge process have been discussed by Brown and Lester (1979).

The fairly wide variations in heavy metal removal in activated sludge are probably a reflection of the complexity of the process. Although primary sedimentation removes settleable particulates significant quantities of heavy metals associated with suspended solids may pass into the activated sludge process (Chen *et al.*, 1974). Although activated sludge has the capacity to adsorb significant quantities of heavy metals, efficient removal may only occur if the metals which are adsorbed and those which form particulates independently are settled out efficiently in final sedimentation. Although the efficiency of the activated sludge process in metal removal may be due to the relative efficiency of

secondary sedimentation compared to primary sedimentation (Brown *et al.*, 1973; Chen *et al.*, 1974), optimization of the process may be expected to influence the removal of predominantly soluble and finely particulate metals to a lesser extent than the metals associated with larger particles.

In a study of the factors which influence metal solubility in activated sludge effluents, Stoveland and Lester (1980) found that Ni and Cu solubilities were strongly influenced by the concentration of soluble organic matter, determined as chemical oxygen demand (COD), while Pb and Zn exhibited a less marked increase in solubility with increasing COD. The solubilities of Cd and Cr (VI) appeared to be independent of COD.

The work reported here was undertaken in order to determine the effect of sludge age (θ_c) on metal removal efficiencies and metal uptake by the activated sludge biomass, and to study the importance of heavy metal solubility and speciation in the behavior of heavy metals in the activated sludge process.

2. Materials and Methods

2.1. ACTIVATED SLUDGE PILOT PLANT

The design of the activated sludge pilot plant, consisting of a 63 l borosilicate aerator and a 23 l settling unit, has been described by Carrondo *et al.* (1980). The pilot plant was located at the Hogsmill Valley Water Pollution Control Works (Thames Water Authority) and was fed with settled sewage. The pilot plant was operated at sludge ages of 4, 9, and 12 d as described by Carrondo *et al.* (1980). Prior to the commencement of sampling at each sludge age a period of 7 to 10 d was allowed for the system to reach equilibrium. Samples were taken over periods of at least 10 d at each sludge age.

An automatic sampling system was used to collect samples of influent settled sewage, effluent and mixed liquor at intervals of 3 h. These samples were combined to produce a composite for each 24 h period for heavy metal and COD determinations. Samples for the monitoring of other experimental variables were taken manually at intervals of one or two days. During some experiments, heavy metals were added to increase the influent concentrations to levels comparable with the typical concentrations shown in Table I. The metal salts used to prepare the stock solutions and the nominal concentrations in the influent were those given by Stoveland *et al.* (1979).

2.2. ANALYTICAL METHODS

Suspended solids, volatile solids, sludge volume index (SVI) and COD were determined according to the methods described by the Government of Great Britain (1972).

Heavy metals in samples of settled sewage, mixed liquor and final effluent were determined by a rapid flameless atomic absorption spectrophotometric method (Sterritt and Lester, 1980).

2.3. SPECIATION OF HEAVY METALS

Heavy metal solubilities were determined by filtration through acid washed 0.22 μm pore size cellulose acetate membrane filters (Oxoid Ltd.) mounted in an all-pyrex filter holder.

The first few ml of filtrate were rejected and the remainder stored in sealed polyethylene containers at 4 °C in the dark. Seawater samples preserved in this way for speciation studies have been reported to be stable for up to 3 mo (Florence, 1977).

Molecular size distributions of soluble heavy metals in sample filtrates were obtained by gel filtration chromatography on Sephadex G-50 (Pharmacia Ltd.). Fractions (10 ml) were collected in pyrex tubes, using an LKB 'Redirac' fraction collector, acidified to contain 1% (v/v) nitric acid and sealed prior to analysis.

3. Results

3.1. INFLUENCE OF SLUDGE AGE ON HEAVY METAL REMOVAL

Heavy metal removal efficiencies were determined at sludge ages of 4, 9, and 12 d. Additionally, removals were determined at two influent concentrations for each metal, the higher concentration being obtained by adding soluble metal salts to the settled sewage. Removals for both normal and elevated concentrations are shown in Table II.

TABLE II

Heavy metal removal efficiency (% R) from spiked and non-spiked settled sewage at sludge ages of 4, 9, and 12 d

| θ_c d | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
|--------------|----------------------------|-----|----------------------------|-----|----------------------------|-----|----------------------------|-----|----------------------------|-----|----------------------------|-----|
| | conc. $\mu\text{g l}^{-1}$ | % R | conc. $\mu\text{g l}^{-1}$ | % R | conc. $\mu\text{g l}^{-1}$ | % R | conc. $\mu\text{g l}^{-1}$ | % R | conc. $\mu\text{g l}^{-1}$ | % R | conc. $\mu\text{g l}^{-1}$ | % R |
| 4 | 0.43 | 68 | 42.0 | 10 | 46.4 | 81 | 21.0 | 11 | 16.6 | 66 | 88 | 41 |
| 9 | 1.40 | 33 | 5.6 | 55 | 56.2 | 70 | 17.6 | 36 | 24.0 | 80 | 156 | 51 |
| 12 | 2.98 | 8 | 5.8 | 49 | 65.9 | 74 | 20.8 | 22 | 29.3 | 32 | 127 | 39 |
| 4 | 7.13 | 60 | 112 | 46 | 176 | 83 | 173 | 16 | 56.3 | 69 | 545 | 55 |
| 9 | 12.2 | 80 | 80 | 62 | 137 | 82 | 119 | 16 | 64.3 | 77 | 576 | 68 |
| 12 | 8.4 | 60 | 35.6 | 68 | 138 | 84 | 94.7 | 33 | 66.2 | 82 | 675 | 40 |

Removals of Ni were consistently poor, being in the range 11 to 36%, while the removals of Cu and Pb were generally good. The removals of Cd, Cr, and Zn were also relatively efficient, generally being in the range 40 to 80%. Removals at the lower influent concentrations were more variable than when metals were added. In particular, the unusually low removals of Cd and Cr of 8 and 10% respectively coincided with significantly higher concentrations of these metals in the sewage, suggesting that shock loads of heavy metals may result in a significant decrease in removal efficiency. However, when metals were added to the settled sewage the percentage removals of Cd, Cr, Cu, and Zn all appeared to be higher than the removals at low influent concentrations.

The mean concentrations of MLSS, effluent suspended solids, influent and effluent COD, SVI and food to micro-organism ratios at each sludge age are shown in Table III.

TABLE III

Mean values of suspended solids, COD, SVI and food to micro-organism ratio at sludge ages of 4, 9, and 12 days

| θ_c d | Metal concentration | Suspended solids (mg l^{-1}) | | COD (mg l^{-1}) | | | SVI (ml g^{-1}) | F/M ^a ratio |
|--------------|---------------------|---|----------|----------------------------|----------|-----------|----------------------------|------------------------|
| | | Mixed liquor | Effluent | Influent | Effluent | % Removal | | |
| 4 | normal | 1641 | 10.5 | 194 | 46 | 76 | 391 | 0.63 |
| 9 | | 2934 | 4.6 | 231 | 48 | 79 | 71 | 0.46 |
| 12 | | 3687 | 17.0 | 240 | 49 | 80 | 215 | 0.36 |
| 4 | metal added | 1414 | 3.0 | 285 | 57 | 80 | 104 | 0.70 |
| 9 | | 2640 | 13.0 | 245 | 56 | 77 | 129 | 0.60 |
| 12 | | 3742 | 13.0 | 270 | 66 | 76 | 126 | 0.33 |

^a Based on influent COD and MLSS values.

For both normal and elevated concentrations of metals the MLSS concentrations increased with increasing sludge age, the food to micro-organism ratios (F : M) decreased with increasing sludge age, while the effluent COD and COD removals remained fairly constant.

In contrast to those parameters which showed definite correlations with sludge age (MLSS, F : M), the mean values of effluent suspended solids and SVI were more variable and did not appear to be related to sludge age. Particularly low values of effluent suspended solids occurred at the 9 d sludge age when no metals were added, and at the 4 d sludge age when metals were added. In the former instance, the low effluent suspended solids concentration coincided with a particularly low SVI value. When metals were added to the system, optimum removals of Cr, Ni, Pb, and Zn coincided with the lowest effluent suspended solids concentrations, while the poorest removals of Pb and Zn coincided with the highest effluent suspended solids concentration.

3.2. INFLUENCE OF SLUDGE AGE ON HEAVY METAL ACCUMULATION BY MIXED LIQUOR SOLIDS

The accumulation of heavy metals by the mixed liquor under steady state conditions at each sludge age was determined as a function of the biomass concentration and the quantity of metal in the influent settled sewage. The accumulation factors were expressed as mg of metal accumulated per g of biomass (MLSS) per mg of metal in the influent settled sewage.

The values for the accumulation of metals are shown in Table IV. When metals were added to the settled sewage, there was a general trend, except in the case of Zn, to a greater degree of adsorption by the biomass with increasing sludge age. However, the same phenomenon was not observed when metals were not added to the system, and in particular, the accumulation of Cd by the mixed liquor decreased with increasing sludge age. The greatest uptake of all metals occurred at the 12 d sludge age when heavy

TABLE IV
Accumulation of heavy metals by activated sludge at sludge ages of 4, 9, and 12 days

| θ_c d | Metal concentration | Accumulation g^{-1} ^a | | | | | |
|--------------|---------------------|------------------------------------|-----|------|-----|------|-----|
| | | Cd | Cr | Cu | Ni | Pb | Zn |
| 4 | normal | 4.9 | 3.3 | 4.8 | 1.6 | 6.0 | 4.1 |
| 9 | | 3.1 | 5.7 | 10.6 | 2.0 | 7.8 | 2.8 |
| 12 | | 1.6 | 5.3 | 8.8 | 1.7 | 3.7 | 4.6 |
| 4 | metals added | 4.1 | 3.8 | 7.7 | 1.1 | 9.0 | 3.5 |
| 9 | | 5.8 | 4.0 | 9.7 | 1.6 | 7.8 | 3.2 |
| 12 | | 7.6 | 6.7 | 9.7 | 2.4 | 10.7 | 3.7 |

^a Mg of metal accumulated per mg of influent metal per g of MLSS.

metals were added, whereas only Zn was accumulated to the greatest extent at the 12 d sludge age under normal metal loadings, while the greatest uptake of Cr, Cu, Ni, and Pb occurred at the 9 d sludge age.

A comparison of the mean values for the uptake of heavy metals under normal and elevated influent concentrations reveals that Cd, Cu, and Pb were more readily accumulated when metals were added, whereas Cr, Ni, and Zn were accumulated to the same extent, relative to the influent heavy metal concentrations. This suggests that the availabilities of the former three metals may have been influenced by their chemical forms in the settled sewage, in contrast to the latter three metals, whose accumulation by the biomass may have been controlled by the equilibrium between adsorbed and free metal.

3.3. THE INFLUENCE OF SLUDGE AGE ON HEAVY METAL SOLUBILITIES IN FINAL EFFLUENT

Four samples each of settled sewage and final effluent were taken at each sludge age. Samples were taken during experiments when heavy metals were added to the settled sewage. The mean values for metal solubilities in the influent and the effluents at each sludge age are shown in Table V. Data were not available for Cr solubility in the settled sewage.

TABLE V
Heavy metal solubilities in settled sewage and final effluents at sludges ages of 4, 9, and 12 days

| θ_c d | Sample type | Mean % solubility | | | | | |
|--------------|----------------|-------------------|----|-----|-----|----|----|
| | | Cd | Cr | Cu | Ni | Pb | Zn |
| — | Settled sewage | 15 | — | 37 | 100 | 4 | 1 |
| 4 | Final effluent | 29 | 5 | 100 | 81 | 22 | 2 |
| 9 | | 61 | 12 | 100 | 91 | 14 | 8 |
| 12 | | 30 | 1 | 27 | 100 | 12 | 10 |

Cadmium, Pb, and Zn solubilities in the final effluent at all sludge ages were all higher than their percentage solubilities in the settled sewage. Copper solubility in the effluent at sludge ages of 4 and 9 days was also much higher than in the settled sewage, while Ni solubilities were high in all samples, ranging from 81 to 100%. Lead, Zn and Cr had the lowest solubilities in the effluents, indicating that these metals were predominantly associated with poorly settleable particulates. The high solubility of Ni reflected its poor removal, indicating that it had a very low affinity for particulates while the high Cu solubility may have been due to soluble forms of the metal leaving the system as a result of their unavailability for uptake by the biomass.

3.4. THE INFLUENCE OF SHOCK LOADING ON HEAVY METAL REMOVAL

In order to determine the effects of a shock load of heavy metals on removal efficiency, the pilot plant was allowed to stabilize for a period of 19 d at a sludge age of 4 d prior to the addition of heavy metals to the settled sewage. The addition of heavy metals resulted in a 5 to 10 fold increase in the concentrations of Cd, Cr, Cu, Ni, and Zn in the influent to the plant over an initial period of approximately 4 to 6 h. A similar increase in the concentration of Pb was not observed; this was probably due to the coincidence of the shock load with a large increase in the indigenous concentration of Pb in the settled sewage occurring a short time before. After the commencement of addition of heavy metals, the influent and effluent were monitored every 1.5 h for 24 h. The changes in the concentrations of heavy metals in the influent and effluent are shown in Figures 1 to 6.

Cadmium, Cr, Cu, and Ni concentrations in the effluent all increased in response to the increase in the influent concentrations, while the Zn concentration in the effluent appeared to be relatively unchanged during the course of the experiment. Tracer studies conducted using chloride indicated that the composition of the effluent would respond fully to a continuous dose in the influent after approximately 12 h, although a small quantity arising from a transient shock load would appear after 1.5 h as a result of a

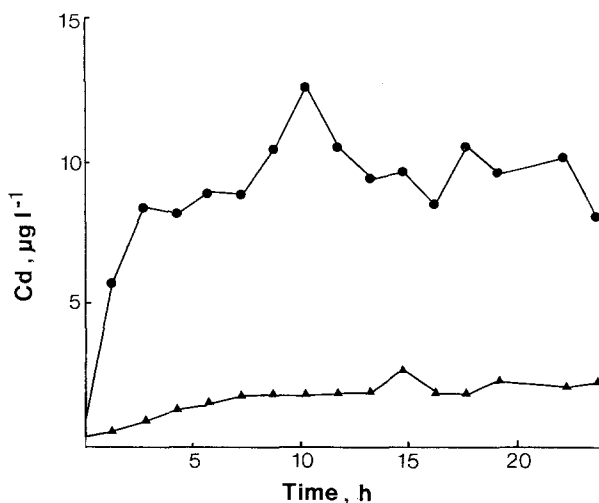


Fig. 1. Concentrations of Cd in settled sewage (●) and final effluent (▲) following a shock load.

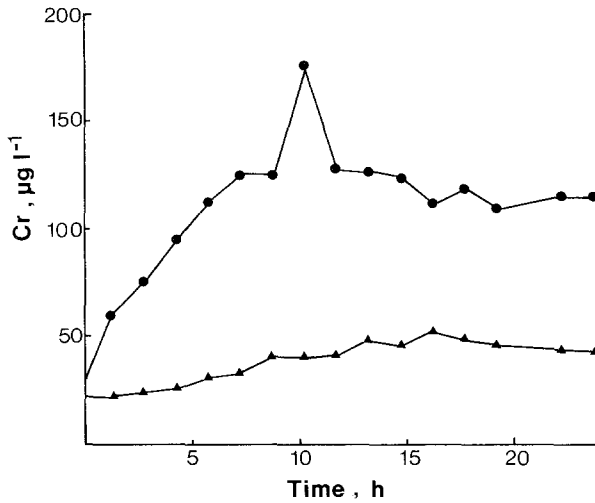


Fig. 2. Concentrations of Cr in settled sewage (●) and final effluent (▲) following a shock load.

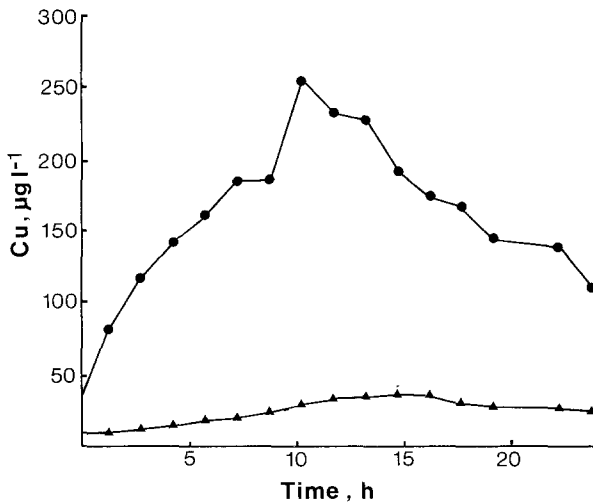


Fig. 3. Concentrations of Cu in settled sewage (●) and final effluent (▲) following a shock load.

'short-circuit' in the system. The results in Figures 1 to 6 show that for all metals the system was able to exert a significant damping effect, such that 18 h after the commencement of the addition of heavy metals the percentage differences between concentrations in the influent and the effluent were greater than at the start of the experiment. However, the data in Table IV, which show that metal removals under steady state conditions were similar at low and high influent metal concentrations, suggest that after a sharp increase in the concentrations of heavy metals in the influent their concentrations in the effluent would eventually increase in proportion. Despite the damped effect on metal concentrations in the effluent, the results in Figure 1 to 6 show that the greatest rates of increase

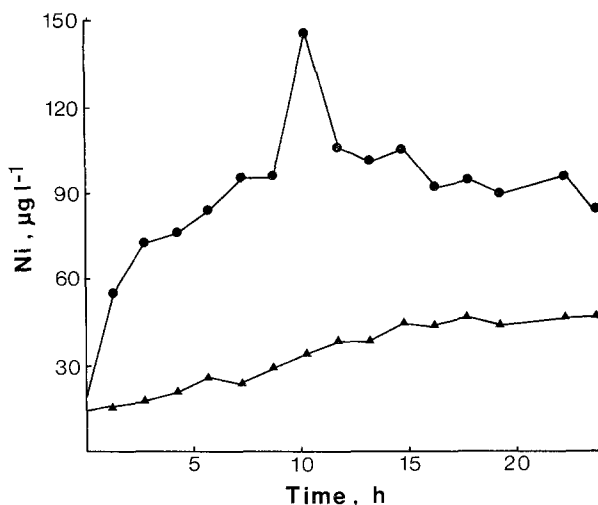


Fig. 4. Concentrations of Ni in settled sewage (●) and final effluent (▲) following a shock load.

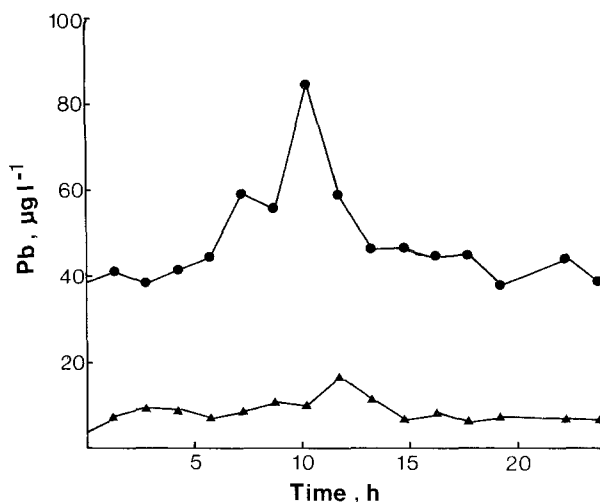


Fig. 5. Concentrations of Pb in settled sewage (●) and final effluent (▲) following a shock load.

in the effluent concentrations over the 24 h period occurred for Cd and Ni, suggesting that the mixed liquor solids had a limited capacity to adsorb elevated concentrations of these metals.

3.5. THE INFLUENCE OF SLUDGE AGE ON SOLUBLE FORMS OF COPPER AND NICKEL

In order to investigate the factors controlling heavy metal solubility, the speciation of Cu and Ni, the two most soluble metals, in the settled sewage and final effluent was studied by gel filtration chromatography. Chromatograms of these metals in filtered samples are shown in Figure 7. In the settled sewage, both metals appeared to be predominantly

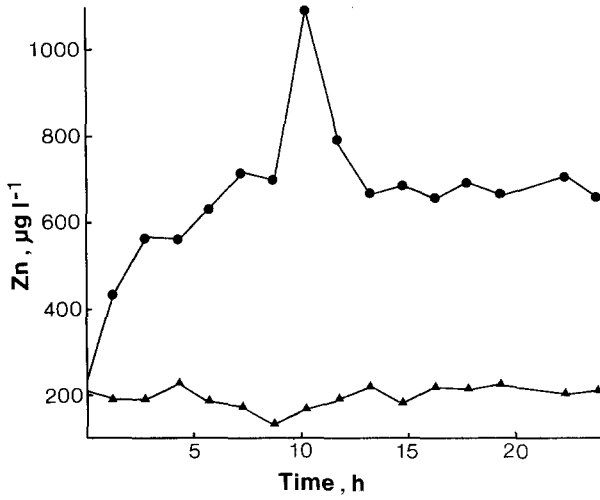


Fig. 6. Concentrations of Zn in settled sewage (●) and final effluent (▲) following a shock load.

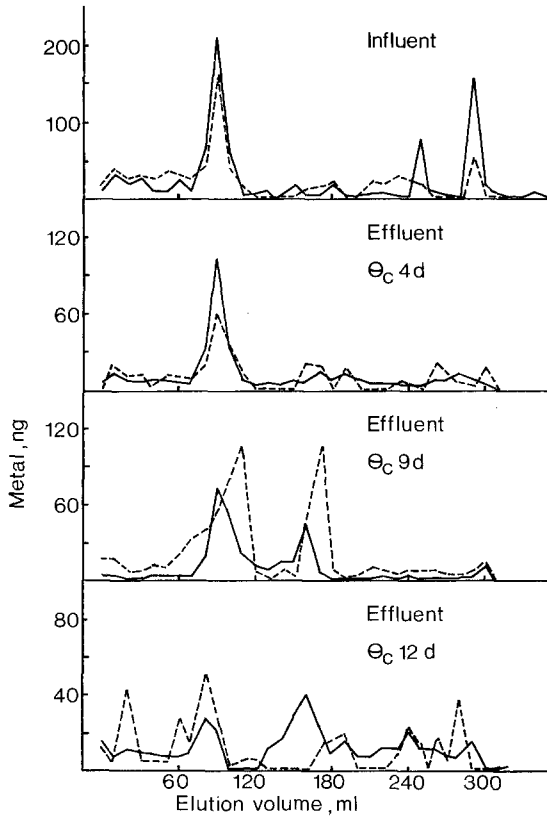


Fig. 7. Gel filtration chromatograms on Sephadex G-50 of Cu (-----) and Ni (—) in filtered settled sewage and final effluent samples.

associated with two major fractions, the first having a high molecular weight, and the second associated with much lower molecular weight substances. The peaks corresponding to low molecular weight species were absent from the chromatograms of the effluent samples, suggesting that the metals in these forms were readily available for uptake by the biomass. Peaks coinciding with the high molecular weight fraction in the settled sewage also appeared in all of the effluent samples suggesting that these fractions were less readily available for uptake. The high molecular weight fractions appeared close to the void volume of the column, which indicates a molecular weight in the region of 10^3 to 3×10^3 , dependent on the steric properties of the molecules.

Both metals were associated with a third fraction in the effluent corresponding to the 9 d sludge age, but only Ni appeared in this fraction at the 12 d sludge age, while neither metal appeared at the same elution volume in the 4 d sludge age effluent. The appearance of this metal-binding fraction may be related to the sludge age. The association of Ni, but not Cu, with this fraction at a sludge age of 12 d may indicate that Ni has a greater tendency to associate with soluble organic ligands rather than to precipitate or associate with the biomass.

4. Discussion

The metal removal efficiencies in the activated sludge pilot plant determined in this study were broadly similar to those reported previously. Generally, the optimum removals of Cd, Cr, Cu, Pb, and Zn were in excess of 50%, which is in agreement with studies of metal removal in full scale (Chen *et al.*, 1974) and pilot scale (Davis and Jacknow, 1975) activated sludge plants.

However, the heavy metal removal efficiencies from the non-metal spiked settled sewage showed that atypically low removals of Cd and Cr coincided with abnormally high concentrations of these metals in the influent. These poor removals may have resulted from a failure of the biomass to adsorb the larger concentrations of Cd and Cr. It has been proposed that activated sludge has a fixed capacity for the uptake of heavy metals (Esmond and Petrsek, 1974; Kunz *et al.*, 1976) such that if an extra load were introduced, the sludge would have no available adsorption sites. A decline in metal removal efficiency with increasing heavy metal concentrations has also been observed by Sterritt *et al.* (1981); however, this was probably due to an equilibrium between soluble and adsorbed metal concentrations rather than saturation of the biomass.

An alternative explanation for the unusually poor removals of Cd and Cr is that the abnormally high concentrations of these heavy metals in the settled sewage, which may have arisen as a result of industrial output, contained different chemical species of the metals to those normally occurring in the sewage, and that these species had a reduced availability for uptake by the biomass. The greater variation in heavy metal removals observed at the lower influent concentrations may also have been a reflection of the variations in the speciation of the metals in the settled sewage. In particular, the speciation of Cr has been shown to markedly influence its removal. Lamb and Tollefson (1973) showed that the chromic ion was readily adsorbed by activated sludge, whereas the chromate ion was only weakly adsorbed. Variations in the speciation of other heavy

metals may occur as the result of industrial discharges (Oliver and Cosgrove, 1974) and complexation and chelation by components of the sewage (Bender *et al.*, 1970). In this study, when materials were added to the settled sewage as soluble inorganic salts, this may have resulted in a more uniform distribution of heavy metal species in the settled sewage leading to higher and more consistent removals.

When metals were added to the system there appeared to be a trend towards increased removal at longer sludge ages in the cases of Cr, Ni, and Pb. This trend was paralleled by the accumulation of heavy metals by the mixed liquor, which increased with increasing sludge age. In studies on a laboratory scale activated sludge simulation, it was found that the accumulation of several heavy metals relative to the MLSS concentration increased as the sludge age was increased from 3 d to 12 d, and declined as the sludge age was increased further, while the optimum removal of most heavy metals occurred at a sludge age of 12 to 15 d (Sterritt and Lester, 1981). In another study, when heavy metals were added to mixed liquor samples previously unexposed to metals, the lowest concentrations in the filtered mixed liquor after incubation occurred when a mixed liquor with a sludge age of 12 d was used (Sterritt *et al.*, 1981). The results presented here suggest that enhanced metal removal may occur at longer sludge ages and that this is not merely a function of higher MLSS concentrations.

Although the removal of heavy metals may be determined to some extent by the operational control of the activated sludge process, metal removal efficiency may also depend on the association of metals with components of the final effluent. The removal of Pb in the activated sludge pilot plant appeared to be dependent on the effluent suspended solids concentration. Furthermore, the solubilities of Pb, Cr and Zn in the effluent were all low, indicating that these metals were in a predominantly particulate form, and that their removal would be dependent on the effective removal of suspended solids. The metal solubilities determined in the influent and effluent samples indicate that the proportion of dissolved to total metal increased as the metals passed through the activated sludge process. This phenomenon has been noted by Oliver and Cosgrove (1974) who found that the activated sludge process was effective in removing 30 to 70% of all dissolved metals, with the exception of soluble Ni, whose apparent removal was less than 1%. This suggests that the removal of Ni may be almost entirely due to the sedimentation of particulate forms of the metal which enter the activated sludge process in the settled sewage.

The importance of particulate forms of heavy metals has been studied by Chen *et al.* (1974) who found a preferential association of Pb and Ni with particles in the lower range of the sizes found in activated sludge ($< 8 \mu\text{m}$), whereas Cd, Cr and Cu were associated with particles greater than $8 \mu\text{m}$ in diameter. In the case of Pb, these small particles may be precipitates of the metal; Barnes *et al.* (1975) found that particle sizes of insoluble Pb phosphate had a mean diameter of 0.4 to 0.6 μm . The low solubility of Pb in the effluents from the activated sludge pilot plant suggests that significant concentrations of metals may be present in the effluent associated with poorly settleable particles. Thus, improvement of the efficiencies of removal may involve the optimization of secondary or tertiary suspended solids removal.

Although activated sludge has been shown to have a considerable capacity for the uptake of heavy metals, the predominance of soluble forms of Cu and Ni found in the effluent samples suggests that certain species of soluble metals may be unavailable for uptake. Bender *et al.* (1970) fractionated a sewage effluent spiked with copper on Sephadex G-50 and found the metal to be in two major fractions. By using anodic stripping voltammetry it was demonstrated that none of the Cu was in a free ionic form, suggesting that the sewage effluent had a considerable complexation capacity for Cu.

Gel filtration chromatography of samples from the pilot plant revealed that in the settled sewage Cu and Ni were probably in a partly inorganic form, and may have been readily available for uptake by the biomass. The appearance of a second high molecular size peak in the effluent samples at sludge ages of 9 and 12 d may indicate that the presence of organics derived from the biomass may influence their availability for uptake. It has been observed that Cu in effluents from a laboratory scale activated sludge simulation was more predominantly associated with a fraction not originally present in the influent sewage as the sludge age was increased from 6 to 15 d (Sterritt and Lester, 1982). The observations of Sterritt and Lester (1981) who found that metal removal efficiencies tended to decrease at sludge ages greater than 12 to 15 d, and the recent work of Baskir and Hansford (1980) who found that at sludge ages longer than optimum, effluent COD increased due to microbial product formation, suggest that heavy metal removal could be significantly influenced by the transport of heavy metals in the effluent by metabolic products of the biomass.

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