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Copper (2+), Zinc (2+), and Nickel (2+) Uptake by Activated Sludge

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Abstract

This paper reports the results obtained on copper, zinc, and nickel uptake by activated sludge in a completely mixed unit. Removal of these heavy metals from wastewater occurs by uptake and by precipitation, the latter being particularly important in the cases of copper and zinc. The amount of heavy metal taken up by the microorganisms at equilibrium varies with influent concentration for the three metals studied. The values obtained range from 2.3 mg/g VSS for copper at 1 mg/L in the influent to 57.4 mg/g VSS for nickel at influent 25 mg/L. Soluble metal removal from wastewater increases in percentage with influent concentration, being higher for copper and lower for nickel. Experiments with mixtures of these metals have also been carried out.

INTRODUCTION

The presence of heavy metals in wastewaters represents an important problem on the environmental field. Many industrial activities (metal production, metal plating and finishing, pigments and dyes, glass,

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cellulose fibers manufacture, etc.) lead to this kind of pollution. Moreover, metal-bearing domestic discharges are becoming an increasingly significant source.

Activated sludge facilities are largely used in wastewater treatment, not only in municipal but also in industrial and integrated plants. It is therefore important to quantify the effects of heavy metals on activated sludge. Much work has been done on this topic (*1–12*). These pollutants accumulate on the biological sludge and cause inhibitorial effects on the enzymatic processes involved in cellular metabolism, which lead to a decrease of organics removal efficiency.

The uptake of heavy metals by activated sludge has been studied by, among others, Jackson and Brown (*12*) who observed percentages of metal removal from wastewater higher than 90% for copper and up to 60% for zinc. Cheng et al. (*13*) reported 90% removal for copper and 53% for nickel after 2 h contact time in batch experiments, working at initial concentrations of 25 mg/L. Neufeld et al. (*14*) studied the equilibrium relations and the kinetic aspects of zinc and nickel sorption by activated sludge. Versino et al. (*15*) obtained the isotherms for copper and also investigated the kinetics of the process. Sarzanini determined the stability constants in the association of copper and zinc in activated sludge (*16*). Oliver and Cosgrove (*17*) and Sterrit et al. (*18*) concluded that heavy metals removal in activated sludge processes occurs by adsorption and precipitation, with this effect being particularly important for copper, whose hydroxide is highly insoluble.

The presence of some organic substances has been reported as a negative factor for copper uptake by activated sludge due to their chelating action (*13, 19*). A similar effect has been noticed for phosphates (*20*).

Heavy metals uptake by activated sludge has been described as a two-phase mechanism. A rapid adsorption on the biomass surface is followed by intracellular accumulation which is the rate-controlling step (*5, 13, 21, 22*). Surface adsorption takes place as an important result by means of bonds provided by cellular-produced substances (*17, 21–23*). Among the factors that influence the amount of heavy metal taken up are sludge age and metal influent concentration (*9, 24–27*).

EXPERIMENTAL

In this work we study the uptake of copper, zinc and nickel by activated sludge at various influent concentrations. Equilibrium metal concentrations in the sludge and in the filtrate effluent have been determined. The

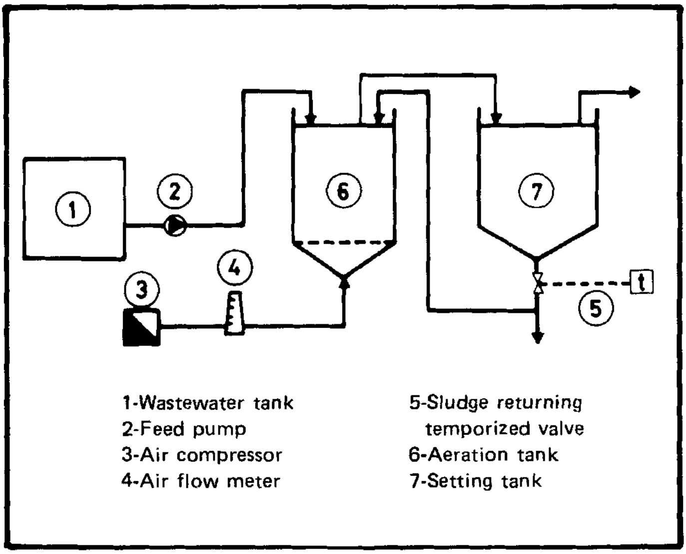

FIGURE 1.

study has been accomplished individually for each heavy metal and with mixtures of them.

Runs were carried out in two activated sludge semipilot plants similar to the one described in Fig. 1. Each consists of a 5-L aeration tank and a 6-L settling tank. Sludge recycling is accomplished intermittently by means of a device consisting of a siphon tube and a temporized valve that can be adjusted to obtain different recycling rates. Sludge wastage can be removed through a manual valve located at the bottom of the settling tank.

Constant biomass concentration and sludge age have been maintained in each run. Daily measurements of VSS in the aeration tank, at the bottom of the settling tank, and in the plant effluent have been carried out, with sludge wastage being removed as necessary as indicated above. Effluent COD was also determined daily. The analytical techniques used correspond to those described in *Standard Methods* (*28*). Dissolved oxygen and pH in the aeration tank, as well as effluent pH, were monitored twice a day. This last variable was maintained in the aeration tank at 6–6.5 in the experiments with zinc and nickel and at 5.5–5.8 when working with copper.

Feed wastewaters were prepared by dissolving glucose and glutamic acid, at 200 mg/L each, in water. This leads to a COD close to 400 mg/L.

Nutrients were adjusted to 18 mg N + 2 mg P/L by adding $(NH_4)_2HOP_4$ and NH_4NO_3. $FeCl_3 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, and $CaCl_2$ were also added at 0.25, 22.5, and 27.5 mg/L, respectively. Heavy metals were incorporated as $CuSO_4$, $NiSO_4 \cdot 5H_2O$, and $ZnSO_4 \cdot 7H_2O$ in the required quantity in each experiment. Wastewater pH was initially adjusted to 6.2 in the experiments with zinc and nickel, and to 5.8 in the case of copper.

In each run the plant was started in the absence of heavy metals until steady-state was reached and then maintained in this state for about 1 week, after which the metal of interest was incorporated in the feed wastewater. Heavy metal analyses were performed periodically in the total and in the filtered effluent. In the first case, the samples were digested with nitric and sulfuric acids (*28*) before metal determination. A IL-357 atomic absorption spectrophotometer was used for all analyses. From the total effluent and filtered effluent results, the amount of metal taken up was determined by:

$$C_t = \frac{C_e - C_s}{X_{ve}} \times 1000$$

where C_t = heavy metal taken up by the sludge (mg/g VSS)
C_e = heavy metal concentration in the total effluent (mg/L)
C_s = heavy metal concentration in filtered effluent (mg/L)
X_{ve} = VSS in the effluent (mg/L)

The reason for carrying out the heavy metal analyses in the effluent is that the results will probably not include the metal precipitated but not taken up by the sludge, because it will separate in the settling tank due to the precipitate's density which is higher than the corresponding biological flocs. The equilibrium values for metal concentrations were taken when no significant variation was noticed for three successive days. The time to reach equilibrium conditions was always between 1.5 to 2 sludge ages since heavy metal feed started.

RESULTS AND DISCUSSION

Table 1 shows the results obtained with copper, zinc, and nickel individually. The values of C_e, C_s, and C_t are reported as well as the corresponding influent flow rate (Q_0), sludge age (θ_c), and VSS in the aeration tank (X_v) and in the effluent (X_{ve}). Influent metal concentration (C_0) and the mean effluent pH (pH_e) are also indicated for each run.

As can be seen, there is important uptake of the three metals investigated by the biological sludge. The relation between the metal

TABLE 1
Results Obtained for Copper, Zinc, and Nickel Individually

Metal	C_0 (mg/L)	Q_0 (L/h)	θ_c (d)	X_v (mg/L)	X_{ve} (mg/L)	C_e (mg/L)	C_s (mg/L)	C_t (mg/g VSS)	pH_e
Cu^{2+}	1.1	0.49	8.3	1798	90	0.51	0.30	2.33	5.6
	5	0.46	10.5	2605	107	2.10	1.62	4.49	5.6
	10.1	0.50	8.8	2312	117	2.88	1.58	11.11	5.7
Zn^{2+}	5.1	0.46	8.9	1750	95	3.10	2	11.58	6.4
	10.1	0.49	9.1	1645	105	4.60	3.10	14.28	6.3
	20.2	0.50	10.9	2310	90	6.90	5.30	17.78	6.5
Ni^{2+}	1.1	0.42	8.1	1965	102	0.80	0.55	2.45	6.3
	4.8	0.49	6.9	1648	102	3.46	3	4.51	6.5
	10.6	0.50	9.8	2910	120	9	6.40	21.67	6.3
	25	0.50	10.8	3240	115	23.50	16.90	57.39	6.6

fixed by the biomass and that remaining in the water by unit mass varies from almost 7800 for copper at 1.1 mg/L in the influent to more than 1500 for nickel at 4.8 mg/L in the influent. At influent levels of 10 mg/L and higher, nickel is taken up in considerably larger quantities than zinc and copper. This could be due to its higher solubility. In that respect it is interesting to note that copper and nickel show very similar uptake values at lower levels (5 mg/L and below).

Although nickel shows the highest uptake values, heavy metal removal is significatively lower than for zinc and for copper, according to the effluent soluble metal concentrations reported in Table 1. This suggests that a substantial amount of the feed metals may be removed by precipitation and accumulates in the settling tank. To determine the amount of precipitated metal in each run, a mass balance can be performed:

$$Q_0C_0 = (Q_e + Q_w)C_s + (Q_eX_{ve} + Q_wX_{vw})\frac{C_t}{1000} + M_p$$

where Q_e and Q_w are the effluent and purge flow rates (L/d), X_{vw} is the VSS in the sludge purge from the settling tank (mg/L), and M_p is the amount of precipitated metal in unit time (mg/d) that we assume is separated in the settling tank and accumulates in the system. The rest of the terms were previously defined.

Taking into account that

$$Q_e + Q_w = Q_0$$

and

$$\theta_c = \frac{VX_v}{Q_eX_{ve} + Q_w + X_{vw}}$$

where V is the volume of aeration tank, the above indicated mass balance can be written as

$$Q_0C_0 = Q_0C_s + \frac{VX_v}{\theta_c}\frac{C_t}{1000} + M_p$$

Then:

$$M_p = Q_0(C_0 - C_s) - \frac{VX_v}{\theta_c}\frac{C_t}{1000}$$

TABLE 2
Relative Metal Removals by Uptake and by Precipitation

Metal	C_0 (mg/L)	Metal removal (%)	Metal taken up (%)	Metal precipitated (%)
Cu^{2+}	1.1	72.7	19.5	53.2
	5	67.6	10.1	57.5
	10.1	84.3	12	72.3
Zn^{2+}	5.1	60.8	20.2	40.6
	10.1	69.3	10.9	58.4
	20.2	73.8	7.8	66
Ni^{2+}	1.1	50	26.8	23.2
	4.8	37.5	9.5	28
	10.6	39.6	25.3	14.3
	25	32.4	28.7	3.7

The values of M_p have been calculated, and then the relative amounts of feed metal removed by precipitation and by biomass uptake were determined. The results are shown in Table 2. Total metal removal percentages refer to the soluble metal effluent concentrations. Notice that the operative removal should take account of the VSS concentration in the plant effluent. In this particular case, the values obtained for effluent VSS are higher than normal due to the characteristics of the sludge recycling system which produces some periodic disturbances in the settling tank.

Total metal removal percentages are moderately higher for copper than for zinc, whereas substantially lower values have been obtained for nickel. But notice that most of the copper and zinc removed is in the precipitated form. These results agree with the insolubility of their respective hydroxides. An increase of precipitated metal percentage with increasing influent concentrations is observed for copper and zinc. This trend fails for nickel at the two higher influent concentrations studied. The explanation could be the much higher relation between VSS and metal concentration in these latter experiments, as can be seen from Table 1. This would lead to greater metal immobilization on the biological surface through chelation with cellular-produced substances, thereby avoiding ulterior precipitation. This effect could also be significant in the case of copper at 5 mg/L in the influent where a high VSS/metal relation has been used, but copper hydroxide is substantially more insoluble than nickel.

To confirm the existence of a significant amount of heavy metals in the precipitated form, analyses were performed on the solids from the bottom

TABLE 3
Metal Amounts in the Solids from the Settling Tank (Me_{st}).

Metal	C_0 (mg/L)	Me_{st} (mg/g VSS)
Cu^{2+}	5	11.4
	10.1	34.2
Zn^{2+}	5.1	15.4
	10.1	46.2
	20.2	62.1

part of the settling tank. The amount of metal in these solids, referred to VSS unit mass, are reported in Table 3. It is clearly seen that metal accumulation in the precipitated form occurs in the system.

With respect to the experiments carried out with mixtures of heavy metals, the results are reported in Table 4. As seen, the uptake values for zinc and nickel together are very similar to the individual figures in Table 1 at the same influent concentrations. A small reduction is observed for zinc and a small increase for nickel. When mixtures include copper, the decrease in zinc uptake becomes more significant and there is a substantial increase in the amount of nickel taken up by the activated sludge. Nevertheless, notice that the sludge ages in this particular case are appreciably different (9.3–9.4 in the experiments with mixtures and 6.9 in the run with individual nickel at 4.8 mg/L influent concentration). No very important differences are observed for copper between individual and mixture experiments at the same concentrations, but observe that

TABLE 4
Results Obtained with Mixtures of Heavy Metals

	Influent metals		
	$Zn^{2+} + Ni^{2+}$	$Cu^{2+} + Zn^{2+} + Ni^{2+}$	$Cu^{2+} + Zn^{2+} + Ni^{2+}$
C_0 (mg/L)	10 + 10	1 + 5 + 5	5 + 5 + 5
Q_0 (L/h)	0.4	0.5	0.45
θ_c (d)	9.4	9.4	9.3
X_v (mg/L)	1632	1870	1622
X_{ve} (mg/L)	110	112	117
C_e (mg/L)	3.8 + 8.7	0.5 + 2.4 + 3.7	1.6 + 2.1 + 2.9
C_s (mg/L)	2.4 + 6	0.3 + 1.2 + 1.8	1.1 + 1 + 1.5
C_t (mg/g VSS)	12.3 + 23.7	1.8 + 10.7 + 16.7	4.3 + 9.4 + 12
pH_e	6.6	6.3	6.2

TABLE 5
Relative Metals Uptake and Precipitation When Working with Mixtures

	C_0 (mg/L)			Removal (%)			Uptake (%)			Precipitated (%)		
Metals	Cu^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
$Zn^{2+} + Ni^{2+}$		10	10		76	40		11.1	21.4		64.9	18.6
$Cu^{2+} + Zn^{2+} + Ni^{2+}$	1	5	5	70	76	64	14.9	17.7	27.7	55.1	58.3	36.3
$Cu^{2+} + Zn^{2+} + Ni^{2+}$	5	5	5	78	80	70	6.9	15.2	19.4	71.1	64.8	50.6

when the copper concentration in the mixture increases, there is a decrease of zinc and nickel uptakes.

The percentages of each heavy metal taken up and precipitated have been calculated as before. The results are shown in Table 5. By making comparison with the values reported in Table 2, it is seen that higher metal removals occur when working with mixtures, and this is due to greater precipitation. Experiments with three-metal mixtures show an increase of relative precipitation and a decrease of uptake, which is more significant as the copper concentration rises.

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