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Effects of Trace Levels of Copper, Chromium, and Zinc Ions on the Performance of Activated Sludge

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Abstract

The effects of copper, chromium, and zinc ions, at trace levels, on the performance of a simulated activated sludge process were investigated. The results of batch adsorption experiments showed that the adsorption of copper, chromium, and zinc ions followed both the Langmuir and Freundlich isotherms. The presence of trace levels of these three metals not only reduced the adsorption rate of organic matters but also the chemical oxygen demand adsorption capacity (CAC) of the activated sludge. Metal ions competed with the organic substrate for adsorption binding sites on the surfaces of activated sludge bioflocs and reduced the CAC. Studies performed in a sequential batch reactor (SBR) showed that the presence of trace levels of heavy metal ions in wastewater affected the SBR performance to different extents depending on the hydraulic retention time (HRT). When the reactors were operated at short HRTs of 2.5 d or less, the presence of trace levels of heavy metal ions reduced substantially the CAC of activated sludge, which, in turn, affected significantly the performance of the SBR. However, under longer HRTs (e.g., 5 d), the heavy metal ions in the wastewater reduced the CAC but had no significant effect on the chemical oxygen demand removal efficiency.

Index Entries: Heavy metals; chemical oxygen demand removal; activated sludge; adsorption capacity; sequencing batch reactor.

Introduction

Metals are among the most common industrial pollutants produced. Virtually every industrial or technological activity that uses metals has a

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metal disposal problem. Heavy metals, namely chromium, copper, nickel, silver, and zinc, are commonly found in the effluents from electroplating and metal-processing industries. These heavy metals and others, such as barium, lead, iron, and mercury, are also the major waste constituents from the manufacturing of paints, plastics, alloys, refractories, and scientific instruments *(1)*. It is well documented that metal-laden municipal sewage above specific metal concentrations is toxic to the activated sludge microorganisms *(2–6)*. Suthirak and Sherrard *(7)* and Dilek et al. *(8)* reported that the microorganisms in activated sludge were inhibited by chromium and nickel at concentrations above 10 mg/L, and that the chemical oxygen demand removal efficiency of the process was also adversely affected. Chang et al. *(9)* observed that dissolved organic carbon (DOC) removal efficiency of an activated sludge process was not affected when 10 mg/L of copper was spiked for 8–10 d. When the copper concentration was increased to 25 and 50 mg/L, DOC removal efficiency decreased by 7–10%.

In recent years, more stringent standards of industrial effluent discharge for heavy metals have been promulgated. In Hong Kong, discharge of toxic metals into sewage systems has been regulated through the Water Pollution Control Ordinance *(10)*. Table 1 gives the effluent discharge standards for heavy metals in public sewers that lead to municipal sewage treatment works that are functions of discharge flow rates *(11)*. Industries are obliged to pretreat the wastewaters to substantially reduce heavy metal concentrations before discharge into municipal sewers. However, a small fraction of heavy metals at trace concentrations is inevitably discharged from the on-site pretreatment system, and eventually reaches the sewage treatment works. At trace concentrations, which meet the discharge standards, heavy metals are believed to have no detrimental effect on the activated sludge microorganisms. Heavy metals such as iron, copper, chromium, and zinc have a very low toxicity effect on activated sludge when concentrations are as low as 1 mg/L *(12)*. Actually, these metals are essential, as micronutrients, for microbial growth. However, Tan and Chua *(13)* observed that chromium, at subtoxic concentrations, i.e., as low as 1 mg/L, could affect the COD removal efficiency of the activated sludge process. It has been postulated that, besides the toxicity and inhibitory effects on the microorganisms, heavy metals could also physically affect activated sludge in the adsorption and uptake of organic matters *(3,14)*. The aim of the present study was to examine the adsorption kinetics and equilibrium of copper, chromium, and zinc ions at trace concentrations, which are common in municipal sewers, by activated sludge bioflocs; to investigate the effects of these metal ions on COD adsorption capacity (CAC); and to study the effects of wastewater with trace levels of these metal ions on the performance of activated sludge in a sequential batch reactor (SBR).

Table 1
Effluent Discharge Limits for Heavy Metals in Hong Kong

	Discharge limits (mg/L) for effluents discharge into government sewage treatment plants				
	Flow rate (m^3/d)				
Heavy metal	≤10	>10 and ≤100	>100 and ≤600	>601 and ≤1000	>100 and ≤6000
Barium	8	7	6–4	3–2.4	1.6–0.4
Cadmium	0.2	0.15	0.1–0.001	0.001	0.001
Mercury	0.2	0.15	0.1–0.001	0.001	0.001
Copper	4	4	4–1.5	1.5–1	—
Nickel	4	3	3–1.5	1	0.8–0.6
Chromium	2	2	2–1	0.7–0.6	0.4–0.1
Silver	4	3	3–1.5	1.5–1	0.8–0.6
Zinc	5	5	4–1.5	1.5–1	0.8–0.6

Materials and Methods

Synthetic Wastewater

Synthetic wastewater was prepared with reconstituted milk at 500 mg/L. The equivalent organic strength was 500 mg of biological oxygen demand$_5$ (BOD_5)/L or 780 mg of COD/L. The metals-laden feed was prepared by dosing the synthetic wastewater with copper sulfate, chromium (III) nitrate, and zinc sulfate, to equivalent concentrations of 1.0 mg of Cu^{2+}/L, 0.05 mg of Cr^{3+}/L, and 1.0 mg of Zn^{2+}/L, respectively. The metal concentrations were within the range of the maximum allowable concentrations (Table 1).

Activated Sludge Simulator

Figure 1 illustrates the 10-L SBR used to simulate the activated sludge process. An air-diffuser system at the bottom of the SBR provides the aeration and mixing. The returned activated sludge collected from a local sewage treatment works was diluted and screened with a 2-mm sieve for removing coarse particles prior to seeding of the reactor. The concentration of mixed liquor volatile suspended solids (MLVSS) of the reactor was maintained at approx 1500 mg/L with a sludge age of approx 10 d. The SBR was operated at a 24-h fill-and-draw cycle. Each cycle consisted of five stages: fill (5 min); react (6.5 h with aeration); settle (1 h); decant (25 min); and idle (16 h) with 15-min aeration every 2 h. The operating cycle was automated with timer-controlled feed, draw-off, and aeration pumps. The synthetic wastewater was fed initially to the system at 10 d of hydraulic retention time (HRT). When the system was acclimatized to the feed of synthetic wastewater, indicated by a stable COD removal efficiency, the HRT was reduced stepwise to 5, 2.5, and then 2 d.

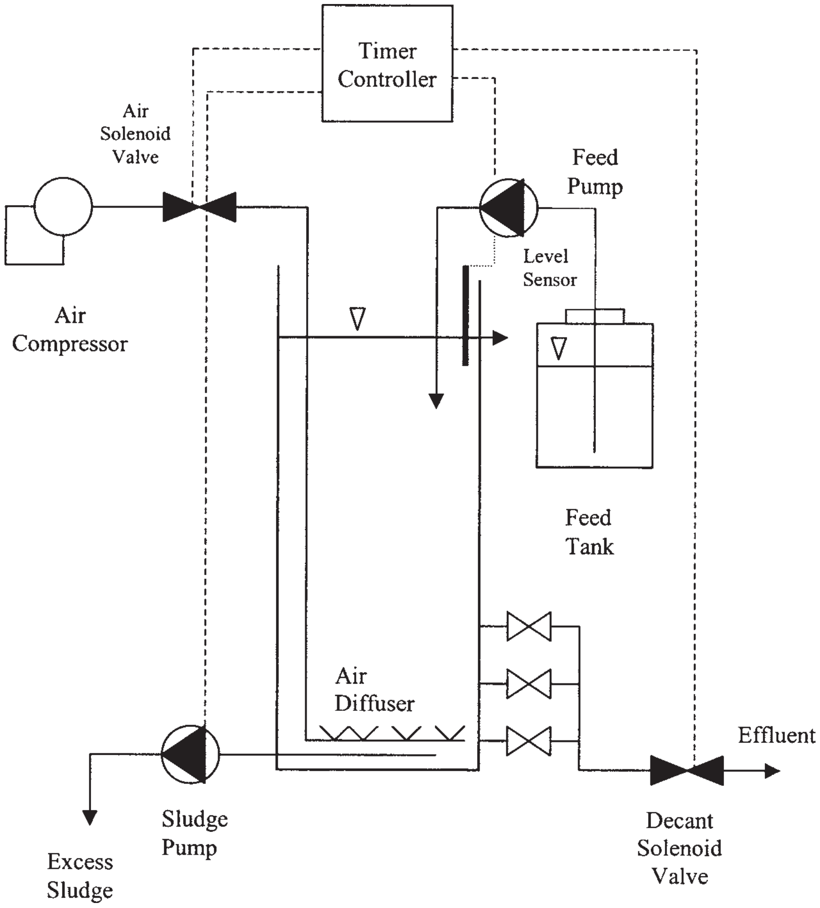

Fig. 1. Activated sludge process.

Metals Adsorption Studies

The batch equilibrium adsorption experiments were conducted using 100 mL of synthetic wastewater and 100 mL of activated sludge in 500-mL polypropylene bottles incubated at 25°C on an orbital shaker operated at 200 rpm. For the metal isotherm study, the batch biosorption experiments were carried out as described by Lo et al. *(15)*. The returned activated sludge samples were collected from a local sewage treatment plant. The synthetic wastewater was dosed with copper sulfate, chromium (III) nitrate, and zinc sulfate, accordingly, equivalent to metal concentrations ranging from 2 to 10 mg of metal ion/L. Samples were collected from the bottles at regular intervals, centrifuged to remove the activated sludge, acidified, and stored at 4°C prior to analysis.

Analytical Methods

Organic adsorption capacity of activated sludge, expressed as CAC in mg of COD/g of activated sludge, was used to monitor the ability of acti-

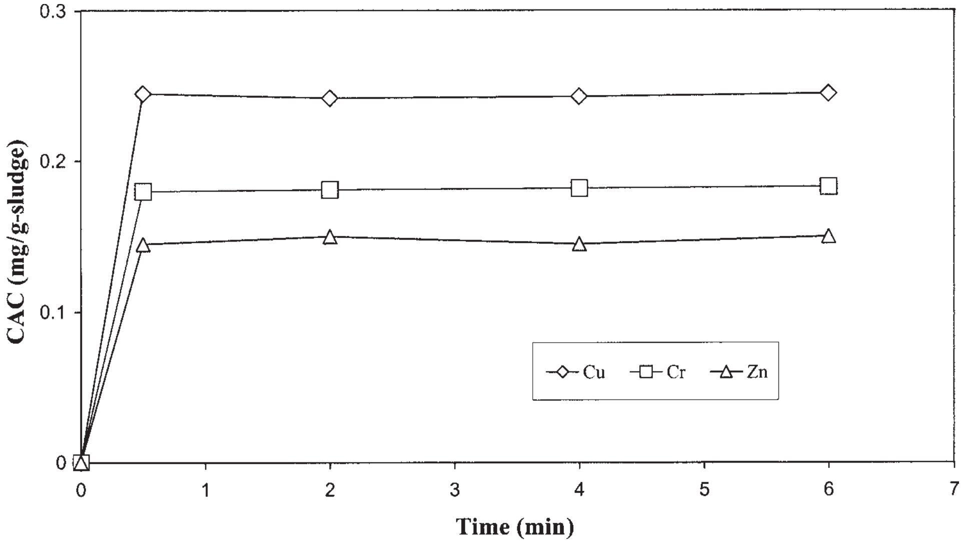

Fig. 2. Kinetics of metal adsorption by activated sludge.

vated sludge to adsorb organic matters. CAC was calculated by dividing the difference between theoretical dissolved COD after the fill stage of the SBR operating cycle and the actual dissolved COD measured 10 min after the fill stage with the MLVSS.

$$\mathrm{CAC} = \{[V/(V + V_r)]\ \mathrm{COD} + [V_r/(V + V_r)]\ \mathrm{COD}_r - \mathrm{COD}_{\mathrm{obs}}\}/\mathrm{MLVSS} \quad (1)$$

in which V is the volume of feed in each operating cycle (L); V_r is the volume of remaining reactor liquor after decant stage (L); COD is the dissolved COD in the feed (mg/L); $\mathrm{COD_r}$ is the residual dissolved COD in the remaining reactor liquor after decant (mg/L); and $\mathrm{COD_{obs}}$ is the observed dissolved COD after the initial 10 min during the react stage (mg/L).

The MLVSS and COD contents were determined as described in ref. *16*. Dissolved COD was determined after filtering the sample through a 0.45-μm filter paper. Metal ion concentrations were determined using an Atomic Adsorption Spectrophotometer (Model 3300; Perkin-Elmer, Norwalk, CT).

Results and Discussion

Metal Adsorption Kinetics Studies

To study the adsorption kinetics of metal ions by activated sludge, the metal concentrations after contact with varied amounts of sludge in polypropylene bottles were followed as a function of time. The initial concentrations of Cu^{2+} and Cr^{2+} were 2 mg/L and that of Zn^{2+} was 4 mg/L. Figure 2 presents the data of the kinetics study for Cu^{2+}, Cr^{2+}, and Zn^{2+}. The adsorption for the three metal ions was extremely fast with most of the metal ions taken up from solution bound within the first 0.5 min. Metal adsorption by activated sludge inherently involves rapid sorption reaction

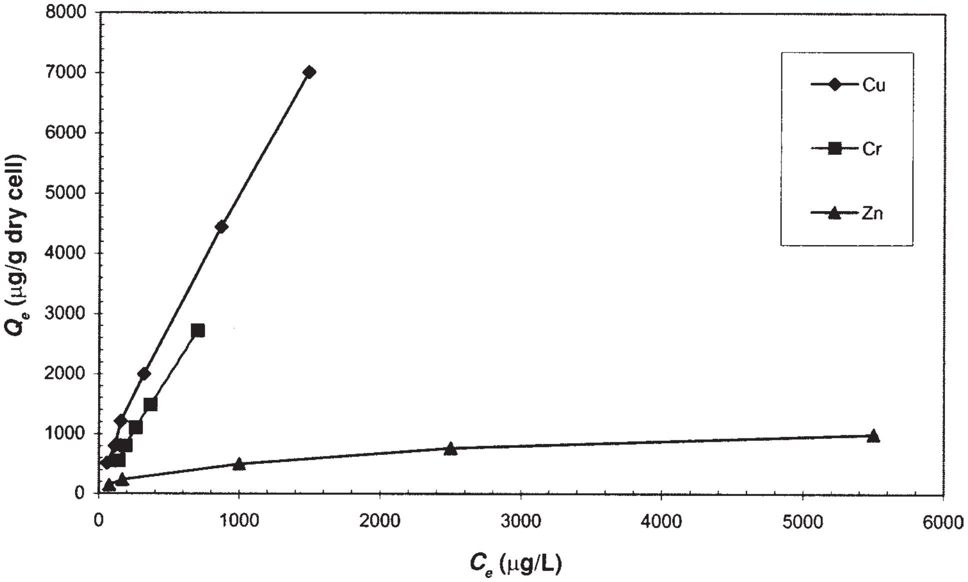

Fig. 3. Metal adsorption isotherm of activated sludge.

mechanisms that could be based predominantly on chemisorption to the surfaces of the activated sludge.

Adsorption Isotherm Model Studies

The adsorption capacities for different metal ions were compared and evaluated quantitatively using the adsorption isotherms derived from the equilibrium data. The isotherms were obtained after 10 min of contact at 25°C with the initial concentrations of copper and chromium at 2 mg/L, and zinc at 10 mg/L. Figure 3 plots the metal adsorption capacities, q (μg lead adsorbed/g dried weight biomass), against the residual metal equilibrium concentration remaining in the solution, C_e (μg/L). The adsorption capacities, q, for Zn^{2+} became saturated at C_e as low as 1 ppm. For Cu^{2+} and Cr^{2+}, activated sludge exhibited much higher adsorption capacities that did not become saturated at a C_e of about 1 ppm. The adsorption capacities of these three metal ions were in the order of Cu > Cr > Zn. The results demonstrated that activated sludge adsorbed copper more readily and to a higher extent than other metal ions.

Because most biosorption isotherms present a shape similar to that of common activated carbon adsorption isotherms, the biosorption data were fitted with two of the most widely used adsorption isotherm models: Langmuir and Freundlich *(17)*.

The Langmuir isotherm equation may be written as follows:

$$q = [kC_e q_{\max}/(1 + KC_e)] \tag{2}$$

in which q and C_e are the equilibrium surface and solution concentrations, respectively; the constant $q_{\max}$ is the theoretical maximum uptake of solute

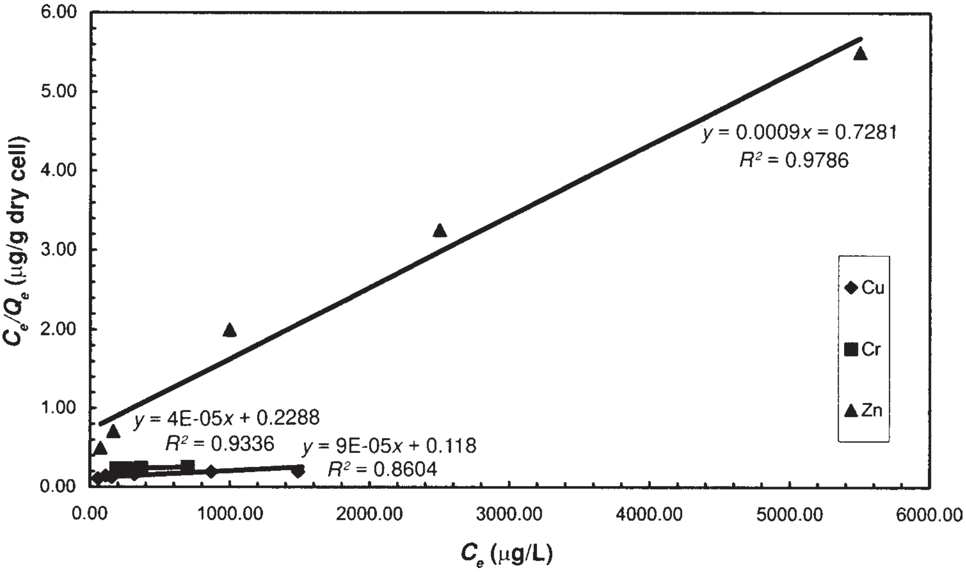

Fig. 4. Linearized Langmuir isotherm of activated sludge for metal ions.

per unit mass of adsorbent that can be achieved as C_e is increased; and k is a constant that is related to the energy of adsorption and increases as the strength of the adsorption bond increases.

To determine the value of k and $q_{\max}$, Eq. 2 may be transformed into the following form:

$$C_e/q = (1/bq_{\max}) + (C_e/q_{\max}) \tag{3}$$

The value of q may be determined by measuring the concentration of the metal ion in the aqueous phase before and after contacting with the biomass. A plot of C_e/q against C_e would give a straight line with a slope of $1/q_{\max}$ and an intercept of $1/kq_{\max}$ if the data fit the isotherm. The value of $q_{\max}$ measures the theoretical maximum metal adsorption capacity of the biomass. The value of k measures the affinity of metal ions adsorbed to the biomass.

Figure 4 gives the linearized Langmuir isotherm plots, and Table 1 gives the Langmuir parameters determined ($q_{\max}$ and k) from the linearized plot and the regression coefficient for the three metal ions examined. Figure 4 and Table 1 clearly show that the metal adsorption conforms to the Langmuir model over the range of metal concentrations examined.

The Freundlich isotherm is widely employed, particularly in the low to intermediate concentration range. It is expressed as follows:

$$q = kC_e^{1/n} \tag{4}$$

in which q is the amount of solute uptake per unit mass of adsorbent; and k and n are constants.

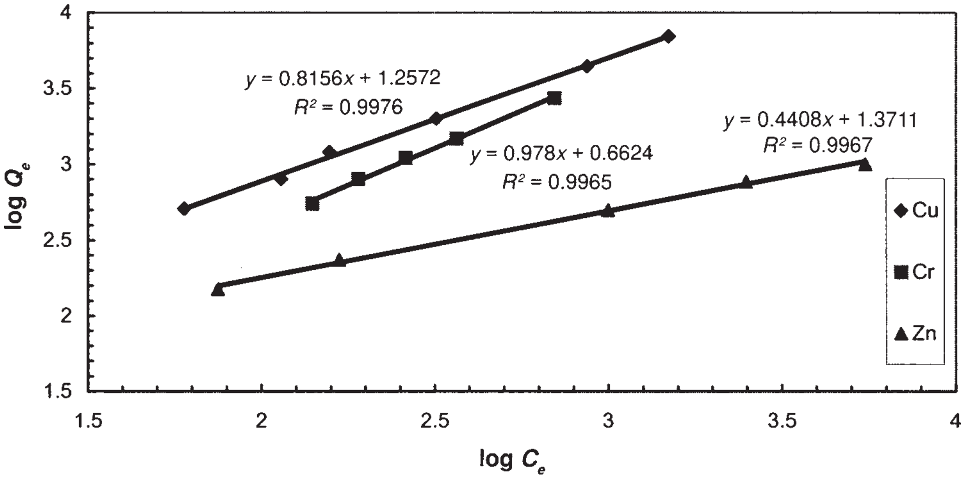

Fig. 5. Linearized Freundlich isotherm of activated sludge for metal ions.

Table 2
Parameters of Freundlich and Langmuir Isotherms

	Freundlich			Langmuir		
Metal	*k*	*n*	r^2	$q_{\max}$ (μg/g)	*k* (L/μg)	r^2
Copper	18.1	0.816	0.998	11,110	7.60E-04	0.861
Chromium	4.59	0.978	0.997	25,000	1.70E-04	0.934
Zinc	18.2	0.441	0.997	1110	1.23E-03	0.979

The Freundlich isotherm may be rearranged as follows:

$$\log q = \log k + 1/n \log C_e \tag{5}$$

The intercept (log *k*) is related primarily to the capacity of the adsorbent for the adsorbate, and the slope 1/*n* is a function of the strength of adsorption. Both the Langmuir and Freundlich models can describe many adsorption data but not necessarily give a meaningful physical interpretation of adsorption.

Figure 5 presents the linearized Freundlich isotherm plots. The adsorption of activated sludge for the three metal ions conforms to the Freundlich model quite well. Table 2 gives the constants, *k* and *n*, for the Freundlich isotherms for each of the metal ions. The constant *n* for all the metals was <1 (Table 2), indicating that these heavy metals were adsorbed readily, particularly at such low concentrations.

Comparison of the regression coefficients calculated for the two adsorption models (Table 2) shows that both fit quite well for the three metal ions. The fit of the Freundlich isotherm usually results in higher regression coefficients, hence indicating slightly better suitability for this model.

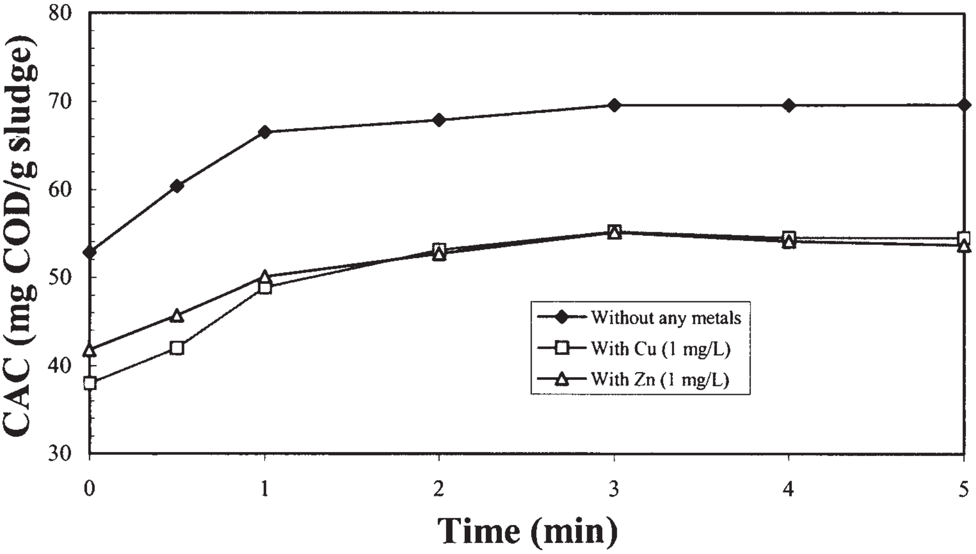

Fig. 6. Effect of copper and zinc ions on CAC of activated sludge at different times.

COD Adsorption Capacity

Figure 6 illustrates the effect of copper and zinc ions at 1 mg/L on CAC of activated sludge. The process of organic adsorption was complete within about 1 min after the synthetic wastewater without any metal ions added. However, the adsorption process required another 3 min to reach completion in the presence of metal ions. The results in Figs. 2 and 6 demonstrate that the organic adsorption rate of activated sludge was slower than the metal adsorption rate of activated sludge. The results further show that trace metal concentrations reduced the adsorption rate of organic matters onto the surfaces of activated sludge. When metals such as copper and zinc were present in the activated sludge process, CAC was almost 20% lower.

Figure 7 plots the CAC of activated sludge vs metal concentrations of copper and chromium in the range of 0–2 mg/L and that of zinc in the range of 0–5 mg/L. As a general trend, the CAC of activated sludge decreased with an increase in Cu^{2+}, Cr^{2+}, and Zn^{2+} concentrations in the wastewater. Metal ions accumulated and competed with the organic substrate for adsorption binding sites on the surfaces of activated sludge bioflocs. Consequently, an increase in metal concentrations led to a decrease in CAC.

Effects of Trace Levels of Heavy Metals on SBR Performance

Figure 8 compares the performance of an SBR in the presence of copper ions with that without copper ions at different HRTs. The two performance indicators are the average CACs and COD removal efficiencies of two identical SBR systems under stable operation. After the SBR systems became stable after 30-d of startup operation, they were operated at an HRT of 5.0 d. At this operating condition, the average CAC was 54 mg/g, and the

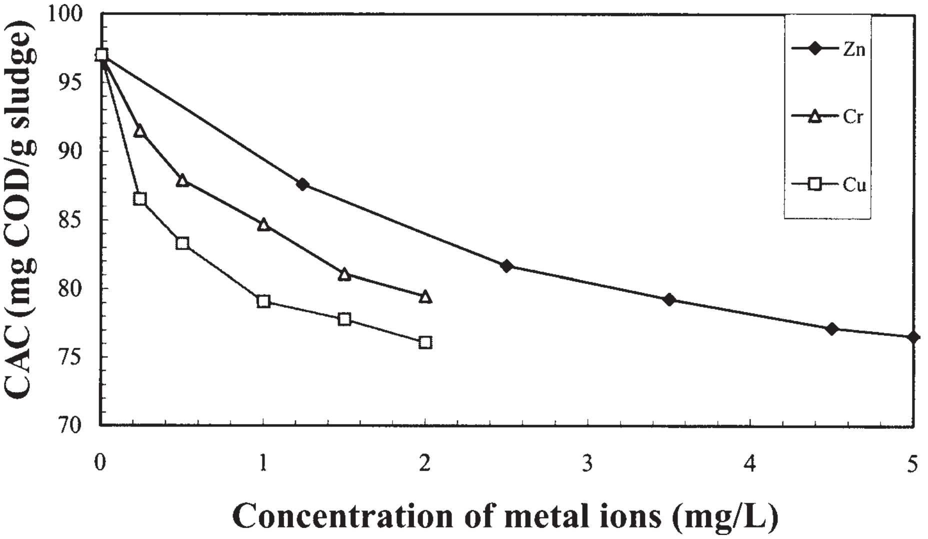

Fig. 7. Effect of concentrations of metal ions on CAC of activated sludge.

corresponding COD removal efficiency was 96%. After the introduction of copper ions into the wastewater, the reactors stabilized within 15 d. The average CAC and COD removal efficiency decreased to 39 mg/g and 94%, respectively, equivalent to a 28% decrease in CAC with no significant change in the COD removal efficiency. When the HRT was reduced to 2.5 d, with no addition of copper, the residual COD level increased, resulting in a significant increase in CAC to an average level of 93 mg/g. The average COD removal efficiency was 91.6%. The addition of copper ions reduced the average CAC and COD removal efficiency to 70 mg/g and 71%, respectively. These values represent a 25 and 22% drop in CAC and COD removal efficiency, respectively. Similar observations were made when the reactors were operated at an HRT of 2 d. The presence of copper ions resulted in a 22% drop in both CAC and COD removal efficiency.

Figure 9 depicts the effects of adding chromium ions on the average CAC and COD removal efficiencies of two identical SBR systems under stable operation at different HRTs. After 30 d of startup operation, the reactors were operated at an HRT of 5 d. The food:microorganism (F:M) ratio was maintained at 0.07 mg of BOD_5/(mg of MLVSS·d). At these operating conditions, the average CAC was 50 mg/g and the corresponding COD removal efficiency was 93%. The addition of chromium ions to the wastewater reduced the average CAC and COD removal efficiency to 43 mg/g and 92%, respectively, equivalent to a 12% drop in CAC and a slight reduction in COD removal efficiency. When the HRT was reduced to 2.5 d, the corresponding F:M ratio was 0.13 mg of BOD_5/(mg of MLVSS·d). Under these stable operating conditions, the average CAC and COD removal efficiency were 88 mg/g and 91%, respectively, in the absence of chromium ions. However, the addition of chromium ions reduced the

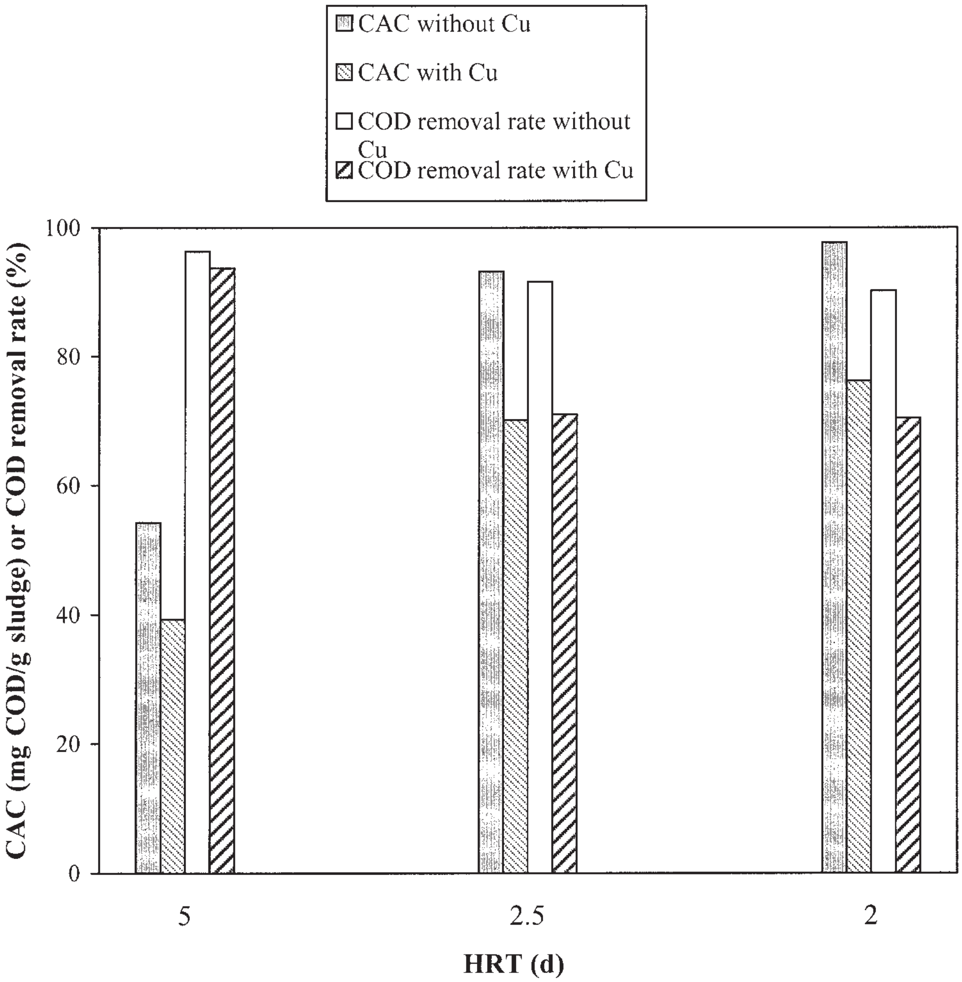

Fig. 8. Effect of copper ions on the performance of the SBR.

average CAC and COD removal efficiency to 75 mg/g and 78%, respectively. These values represent a 15% drop in CAC and a 14% reduction in COD removal efficiency. Similar results were obtained when the reactors were operated at an HRT of 2 d. Reductions of 16% in CAC and 18% in COD removal efficiency were observed, with the F:M ratio at 0.17 mg of BOD_5/(mg of MLVSS·d), when chromium ions were introduced into the wastewater.

Figure 10 shows that the effects of zinc ions on the performance of the SBR, in terms of CAC and COD removal efficiency, were comparable to the effects of copper and chromium ions. At longer HRTs (e.g., 5 d), the addition of trace levels of zinc ions to the wastewater resulted in a 26% decrease in CAC but again had no significant effect on the COD removal efficiency. However, when the reactors were operated at short HRTs of 2.5 d and less, the trace amount of zinc reduced significantly both CAC and COD removal efficiency.

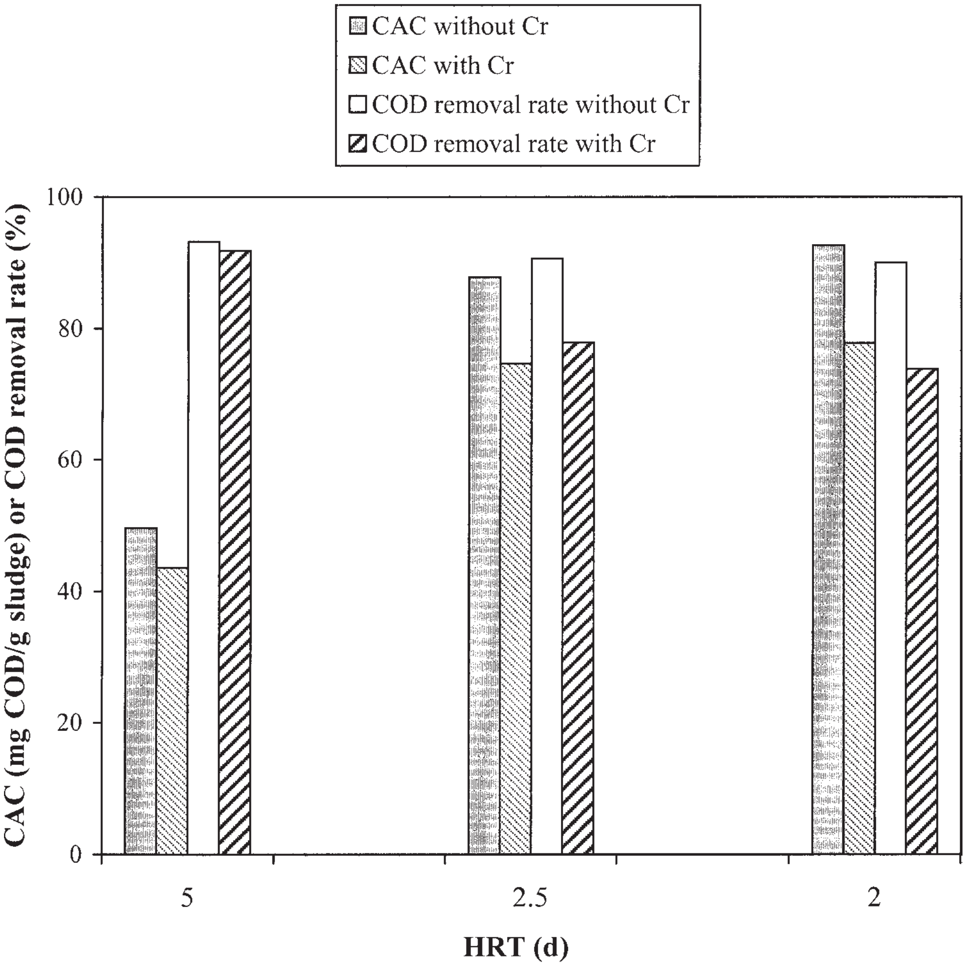

Fig. 9. Effect of chromium ions on the performance of the SBR.

These studies demonstrate that the presence of copper, chromium, or zinc ions in wastewater reduced the CAC of activated sludge at all HRTs studied. At trace amounts, heavy metal ions acted as a stronger competitor with the organic compounds for binding sites on the surfaces of activated sludge bioflocs, and reduced COD adsorption. It is postulated that COD removal in the activated sludge process is proceeded by rapid adsorption of organic matters on certain binding sites of the bioflocs, followed by a slower metabolic assimilation into cells and metabolic destruction of the compounds. At HRTs of 2.5 d and less, a reduction in COD adsorption in the presence of heavy metal ions would lead to a significant decrease of COD removal. However, at longer HRTs (e.g., 5 d), retention of organic matters within the reactor was sufficiently long for biological assimilation, and organic adsorption was not a critical factor governing COD removal. Thus, the presence of copper, chromium, or zinc ions affected the CAC but

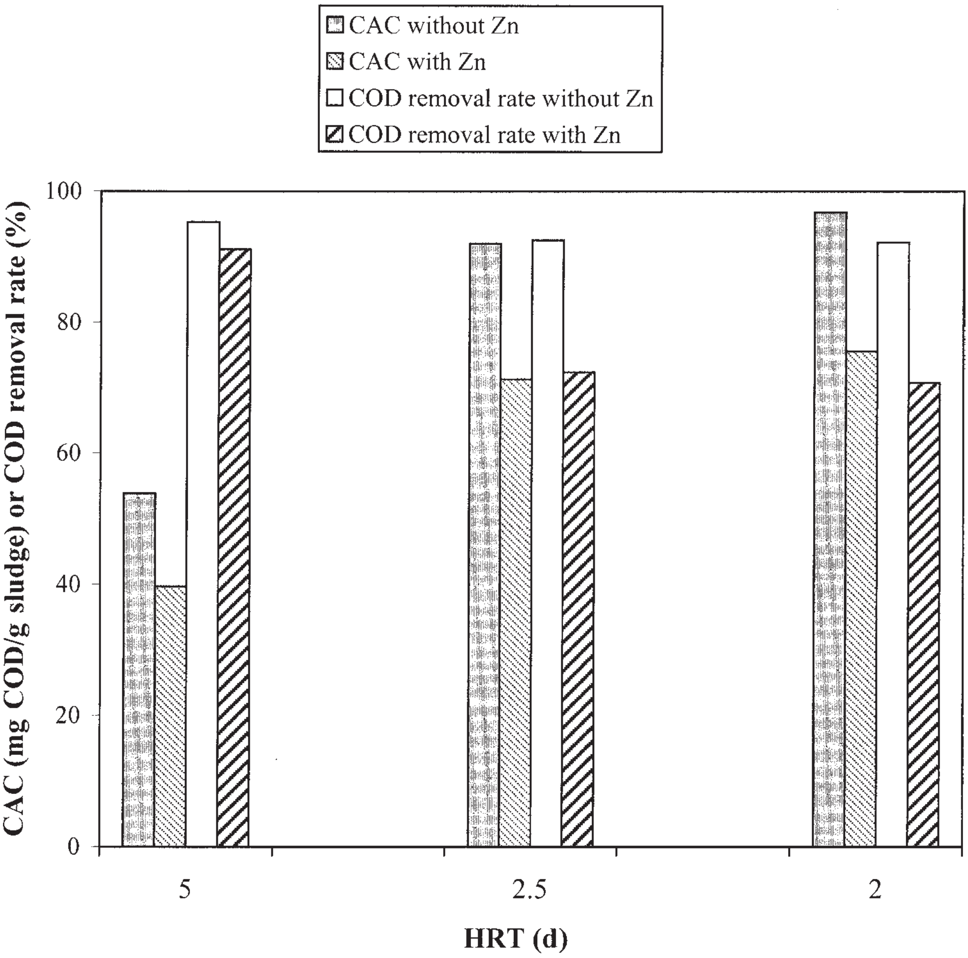

Fig. 10. Effect of zinc ions on the performance of the SBR.

had no significant effect on the COD removal efficiency. These results show that wastewater containing trace levels of heavy metal ions within the effluent discharge limits for heavy metals may have a significant effect on the COD removal efficiency of an activated sludge process operated at a short HRT.

Conclusion

The adsorption of activated sludge for copper, chromium, and zinc ions conformed to both the Langmuir and Freundlich models quite well. The Freundlich model fit slightly better. The presence of trace amounts of these three metals not only reduced the adsorption rate of organic matters but also the CAC of the activated sludge. The CAC of activated sludge decreased with an increase in copper, chromium, and zinc concentrations in the wastewater. Heavy metal ions thus acted as a strong competitor for binding sites on the sludge, hampering COD adsorption. Under short HRTs of 2.5 d and less, the presence of heavy metals also caused a significant reduction in COD removal efficiency of the SBR. This significant reduction was not observed under longer HRTs. These results substantiated the postulation that organic removal by activated sludge depended on a fast initial adsorption of organic matters on the surfaces of the bioflocs, which retained the organic matters sufficiently long to allow for the slower metabolic assimilation and degradation especially at short HRTs. The presence of heavy metal ions significantly reduced the CAC of activated sludge, which, in turn, substantially affected the COD removal efficiency of the activated sludge process operated at short HRTs.

Acknowledgments

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