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EFFECT OF HEAVY METALS ON THE METHANOGENIC ACTIVITY OF STARCH-DEGRADING GRANULES

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SUMMARY

Heavy metals in electroplating effluent inhibited specific methanogenic activity (SMA) of anaerobic starch-degrading granules. The SMA of granules on the degradation of starch were reduced by 50% when each gram of biomass was in contact individually with 105 mg of zinc, 120 mg of nickel, 180 mg of copper, 310 mg of chromium, or >400 mg of cadmium. Granules had higher toxicity-resistance than flocculent sludge, due to their layered structure.

INTRODUCTION

Wastewater from electroplating industry containing high levels of heavy metals is one of the major polluters in many countries. Although in trace amount they are the essential elements for the microbial growth (Speece, 1983), many heavy metals at elevated concentration often become inhibitory and toxic to the anaerobic degradation of organic matters (Kugelman and Chin, 1971). In municipal wastewater treatment, high concentration of heavy metals in sewage could also lead to upset and failure of the anaerobic sludge digestion process (Coker and Matthews, 1983; Swanwick *et al.*, 1969).

Anaerobic treatment of wastewater has become a viable technology in the last two decades mainly because of the development of high-rate reactors. Among them, the upflow anaerobic sludge blanket (UASB) process has been widely accepted in recent years for the treatment of wastewaters from agricultural and food/beverage industries.

Communal wastewater of industrial parks often constitutes pollutants of complex nature from different factories inside the park. It may contain organic matters from industries such as food/beverage, as well as heavy metals from industries such as electroplating. It is thus often difficult to treat the communal wastewater effectively. Although effects of heavy metals on the anaerobic digestion of sludge have been examined (Lin, 1993), little has been studied on their effects on the high-rate anaerobic wastewater treatment processes. This study was conducted to examine the effects of five heavy metals commonly found in the electroplating effluent on the methanogenic activity of UASB granules for the degradation of starch.

MATERIALS AND METHODS

A 2.8 L UASB reactor (Fang and Chui, 1993a) was used to breed sludge granules for this study. About 1 L of starch-degrading UASB granules obtained from another study (Fang and Kwong, 1994) were used to seed the reactor along with 1.5 L of additional sludge from the digester of a local municipal sewage treatment plant. The reactor was then continuously fed with synthetic wastewater composing starch as the sole organic carbon source, plus nutrients, alkalinity and trace elements based on the formulation used in a previous study (Fang and Chui, 1993a). The COD loading gradually increased from 3 g/L•day, initially, to 15 g/L•day in two months. It was then kept at the latter loading throughout the rest of the study, during which the reactor steadily removed over 95% of COD in wastewater.

After the reactor was steady at 15 g-COD/L•day, samples of sludge granules were periodically taken from the UASB reactor for specific methanogenic activity (SMA) analysis using 157 mL serum vials. Each vial was filled with 100 mL of synthetic wastewater which not only contained 3 g/L of starch, plus nutrients, vitamins, trace elements, etc., but also chloride salt of individual heavy metals at controlled dosage. After about 100 mg (in dry weight) of granules was added, each vial was capped with butyl rubber and submerged in 37°C water in a shaking bath. Transfers of wastewater and granules to the serum vials were conducted anaerobically (Owen, *et al.*, 1979; Dolfing and Mulder, 1985). Biogas production were monitored every few hours using syringes; the methane contents in the biogas were measured using a gas chromatograph (Hewlett Packard, model 5890A) equipped with a thermal conductivity detector and a 2m x 2mm (inside diameter) stainless-steel column packed with Porapak N (80-100 mesh). Injector and detector temperatures were kept at 130°C while column temperature was 50°C. Based on these measurements, the accumulated methane productions were calculated. Each SMA measuring program lasted about one week by which time the methane production had normally levelled off. The quantity of biomass in each vial was then measured by the content of volatile suspended solids (VSS) following the standard methods (APHA, 1985). Previous study (Fang and Kwong, 1994) has shown that the contribution of residual starch to the VSS content in the vials was negligible after one week.

The initial slope of specific methane production versus time represented the SMA of granules using starch as the carbon source. The SMA was dependent on the dosage of individual heavy metals. All SMA measurements were conducted in duplicates. In each run, up to 30 vials were monitored, two of which, without the dosage of heavy metals, served as control.

RESULTS AND DISCUSSION

Figure 1 illustrates a typical plot of the specific methane production of control granules. Initially, the starch concentration was 3 g/L and, thus, the supply of starch was not a limiting factor for methanogenesis. However, as starch became depleted, the methane production rate gradually levelled off. The initial slopes, as illustrated in Figure 1, represent the SMA of the granules on the degradation of starch without the influence of any heavy metals. Each gram of granules (as measured by the VSS content) without the influence of any heavy metals on average had the maximum hourly capacity of producing 19.6 mL of methane at 37°C, corresponding to an average SMA of 1.19 g-methane-COD/g-VSS•day. The rate of methane production decreased as granules were in contact with heavy metals. The SMA of granules at various dosages of heavy metals were calculated in a similar fashion.

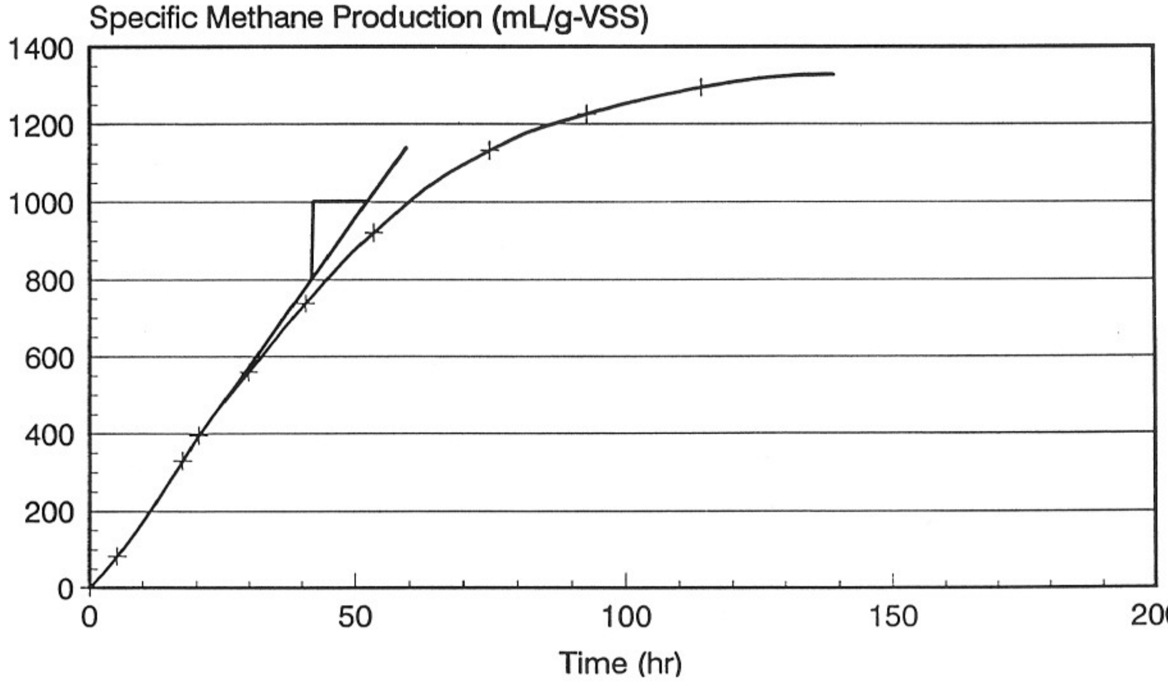

Figure 1: Specific Methane Production of Starch-Degrading Granules

Figure 2 illustrates the effect of metal-to-biomass ratios on the SMA of granules on the degradation of starch. It illustrates that the toxicity of cadmium to the methanogenic

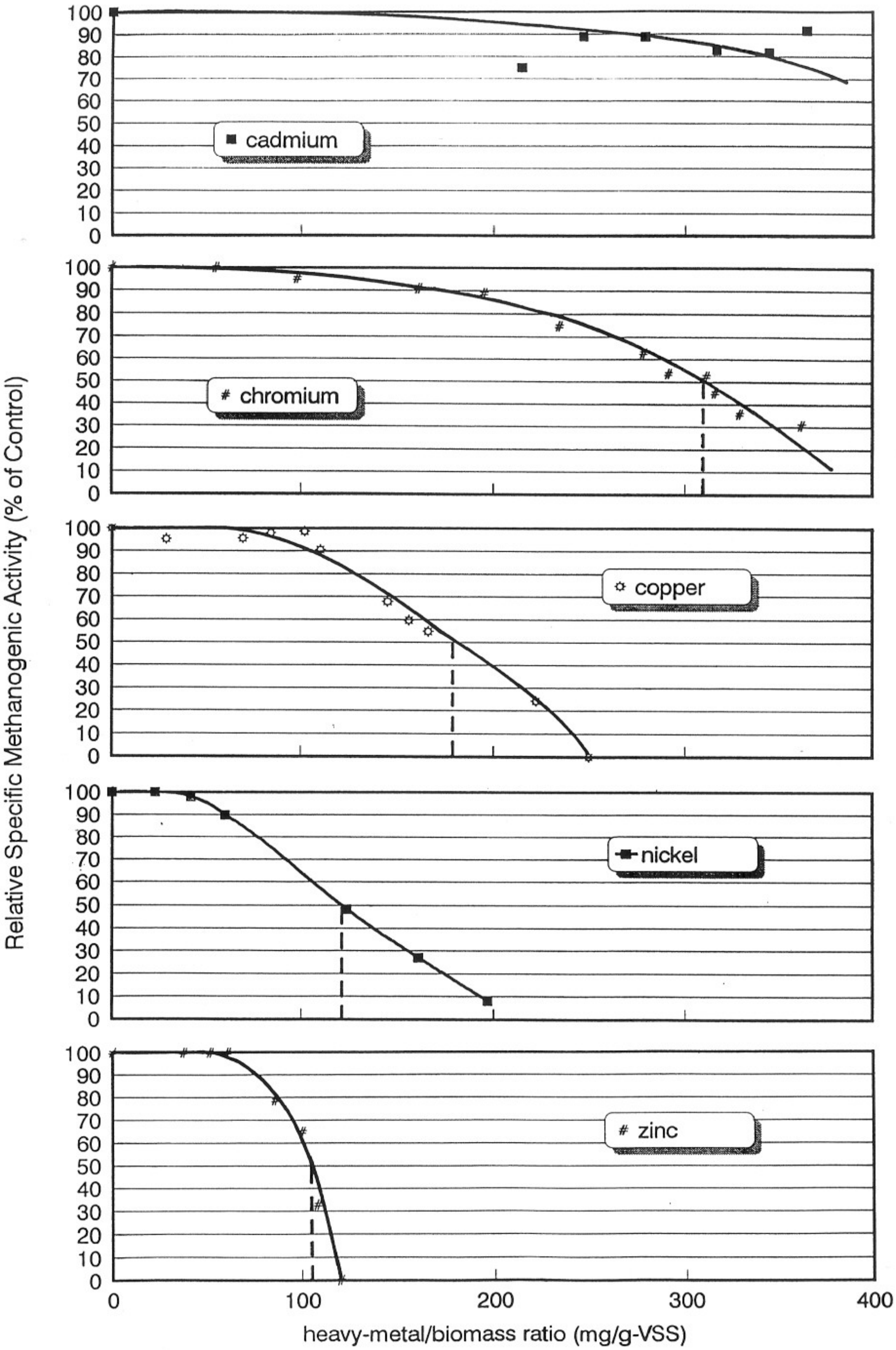

Figure 2: Inhibition of Specific Methane Activity by Heavy Metals

degradation of starch was mild and it was not sensitive to the cadmium dosage. For the other four metals, methanogenic activities decreased as the dosage increased. The toxic effect on methanogenic activity were in the following order: zinc (most toxic) > nickel > copper > chromium > cadmium (least toxic).

Table 1 summarizes the concentrations and metal-to-biomass ratios at which the SMA were inhibited by 50%. Also listed are the corresponding data recently published (Lin, 1993) for comparison. The results of our study was based on degradation of starch by UASB granules, while the work of Lin was based on degradation of mixed volatile fatty acids (VFA) by flocculent digester sludge. With the exception of nickel, heavy metals were less toxic to the UASB granules than to the flocculent digester sludge.

Table 1 Concentrations and Metal/VSS Ratios Causing 50% inhibition of SMA

	UASB Granules		Flocculent digester sludge#	
Metal	Conc. (mg/L)	metal/biomass (mg/g-VSS)	Conc. (mg/L)	metal/biomass (mg/g-VSS)
cadmium	> 550	> 400	7.7	14.3
chromium	630	310	14.7	27.4
copper	158	180	12.5	23.3
nickel	118	120	400	745
zinc	97	105	16	29.8

Data from Lin (1993)

The high resistance to toxicity of the starch-degrading granules can be attributed to their layered microstructure (MacLeod, *et al.*, 1990; Fang, *et al.*, 1993b; Fang and Kwong, 1994), in which the toxicity-sensitive methanogens were densely populated in the interior. The outer layer of the granules, on the other hand, was mostly composed of fermentative bacteria which hydrolyzed starch into saccharides and fatty acids. The fermentative bacteria, which are apparently less sensitive to the toxicity of the heavy metals, could be shielding the methanogens from exposure to the heavy metals.

CONCLUSION

Heavy metals in electroplating effluent inhibited the methanogenic activity of anaerobic starch-degrading granules in the following order: zinc (most toxic) > nickel > copper > chromium > cadmium (least toxic). At 37°C, the SMA of granules for the degradation of starch were reduced by 50% when each gram of VSS were in contact individually with 105 mg of zinc, or 120 mg of nickel, 180 mg of copper, 310 mg of chromium, or >400 mg of cadmium. As compared to the flocculent digester sludge, starch-degrading granules exhibited higher resistance to the heavy metal toxicity due to their layered microstructure.

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