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Sodium Toxicity control by the use of Magnesium in an Anaerobic Reactor

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Abstract: This study investigated the effectiveness of magnesium in reducing sodium toxicity in mesophilic (35ºC) completely mixed anaerobic digesters (CMADs). The CMADs were operated at a chemical oxygen demand (COD) loading of 0.5 g/l/day initially which was gradually increased to 1.8 g/l/day. To evaluate the effect of sodium concentration on methanogens, the biomass in one of the CMADs was acclimated to an increasing concentration of sodium while the feed to the second CMAD was not supplemented with any additional sodium. The COD removal efficiency and methane production decreased by nearly 30% and 20% respectively at a sodium concentration of 9.0 g/l. Similarly, the total volatile fatty acids (VFAs) concentration increased from a mere 200 mg/l to 3000 mg/l. At this point, magnesium was added gradually to one of the reactors. The COD removal efficiency and methane production returned to the original level of 92% and 62% respectively, and the VFA concentration became negligible. It can be concluded that magnesium is very effective in reducing sodium toxicity to methanogens. *@JASEM*

Complete-Mix anaerobic digester is an efficient anaerobic system that is suitable for wastes with extremely high dissolved organic concentrations or high concentrations of solids. Since the hydraulic retention time (HRT) and solids retention time (SRT) are equal, it is more practical to use where thickening the effluent solids is difficult (Metcalf and Eddy 2003). The HRT may be in the range of 15 to 30 days to provide sufficient safety factors for operation and process stability (Parkin and Owen 1986). Anaerobic systems operated at thermophilic conditions (55ºC) achieve higher biological reaction rates compared to mesophilic systems conducted at 35ºC. Operation at thermophilic temperatures also enhances the hydrolysis rate of several recalcitrant organics, thereby improving the overall efficiency of the sludge stabilization process (Han et al. 1997). However, the process has failed to gain widespread acceptance due to potential drawbacks such as slow startup, higher energy requirements, organic loading variance and slow accommodation to toxic chemicals (Speece 1996). The last factor might also be a cause of concern for several mesophilic systems. It is in this context that the occurrence of sodium, which is commonly used in wastewater treatment plants (as sodium hydroxide) to supplement alkalinity, could prove detrimental to the operation of either system (Soto et al. 1993). Under anaerobic conditions, higher concentrations of sodium could readily affect the activity of microbes and interfere with their metabolism. McCarty (1964) has reported sodium concentrations in the range of 100-200 mg/l to be beneficial for the growth of mesophilic anaerobes. According to Kugelman and Chin (1971), the optimal sodium concentration for mesophilic aceticlastic methanogens in waste treatment processes was 230 mg/l. The optimal growth conditions, with respect to sodium, for mesophilic hydrogenotrophic methanogens reportedly occur at 350 mg/l (Patel and Roth 1977). However, an early study reported sodium concentrations ranging from 3,500 to 5,500 mg/l to be moderately and 8,000 mg/l to be strongly inhibitory to methanogens at mesophilic temperatures (McCarty 1964). For anaerobic granular biomass at mesophilic temperatures, sodium concentrations of 5, 10, and 14 g/l caused 10, 50 and 100% inhibition of methanogens, respectively, at neutral pH (Rinzema et al. 1988).

A great deal of research has been done to study sodium inhibition on methanogens, but little work has been done to reduce or control sodium toxicity. In our previous studies, cations (potassium and calcium) were found to be very effective in reducing the inhibitory effects of sodium on bacteria. This particular work investigates the potential of yet another cation (magnesium) in minimizing sodium toxicity.

MATERIALS AND METHODS

The completely mixed anaerobic digester system consisted of five-liter capacity anaerobic digestion vessels. Each vessel had a ground glass flange and a multisocket flange lid held in place with a wire clip. The central socket of the flange lid accommodated a glass stirring rod with an air tight seal, while the four other sockets housed the feed funnel, sludge outlet pipe, gas outlet tube and the self sealing rubber

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septum respectively. These units were then placed in a water bath, which was maintained at 35-37ºC and flushed with nitrogen to ensure an anaerobic environment inside the digesters. The gas outlet from each vessel was connected to a 10-litre glass aspirator filled with water. Wet gas meters thereafter replaced this arrangement. Once they were air tight, gas production was measured by the downward displacement of water in the aspirators. The reactors were also seeded with digesting sludge from a local Wastewater Treatment Plant. Approximately 100-150 ml of mixed liquor was removed daily from the completely mixed anaerobic digesters. The digesters were designated "E" and "F". Digester "E" was maintained as control while digester "F" was the experimental one. The mixed liquor removed from the CMADs was used for a range of experimental purposes. A portion of it was used for pH, volatile suspended solids and ammonia-nitrogen analyses, while the remainder was centrifuged for 30 minutes at 3000 rpm in a centrifuge. The sludge, after centrifuging was made up to volume with an appropriate amount of synthetic feed (Table 1) and returned to the reactor. The supernatant was used for further chemical analysis (Table 2). The organic loading rate at the start of the experiment was 0.5 g/l/day, gradually increased to 1.8 g/l/day and maintained at this level for the duration of the project in all of the CMADs. This organic loading rate was achieved after a period of six months. The control units were supplied with feed containing a constant concentration of sodium. The feed supplied to experimental reactors was supplemented with increasing amounts of sodium. These reactors were allowed to 'acclimatize' to each stepwise increase in sodium concentration. Sludge return was continued in order to maintain a suspended solids level of 15-18 mg/l within each reactor.

Table 1. Synthetic Feed Composition

Constituent	*Concentration (mg/l)*	*Constituent*	*Concentration (mg/l)*
NH_4HCO_3	3000	$MgSO_4.7H_2O$	5
KH_2PO_4	3000	$FeCl_2.4H_2O$	15
$NaHCO_3$	3000	$CaCl_2.6H_2O$	15
Whey powder	90,000	KCl	5
$CuSO_4$	0.2	$CoCl_2.6H_2O$	5
$ZnSO_4$	0.2	$Na_2MoO_4.2H_2O$	0.2

Table 2. Digester Analysis

Parameter	*Frequency*	*Method*	*Instrument brand*
Gas Production	Daily	Water displacement/ gas meter	Becker 403
Gas composition	Daily	Gas chromatography	Becker 403
pH	Daily	pH meter	Corning
Volatile fatty acids	Daily	Gas liquid chromatography	Pye Unicam 304
Suspended solids	Weekly	Gravimetric	Standard methods 1989
Volatile suspended solids	Weekly	Gravimetric	-do-
Ammonia-Nitrogen	3 times per week	Distillation/titration	-do-
Alkalinity	-do-	Titration	-do-
Influent COD	-do-	Dichromate reflux	-do-
Effluent COD	-do-	-do-	-do-
Sodium	Daily	Flame photometer	-do-
Potassium	-do-	-do-	-do-
Calcium	-do-	Atomic Absorption Spectrophotometer	-do-
Magnesium	-do-	-do-	-do-

Magnesium was added to the experimental reactors when the inhibition due to cation toxicity was at its peak i.e. when COD reduction and percent methane production were at their minimum, and volatile fatty acids were at their maximum concentrations inside the reactors. Different concentrations of magnesium were used starting from very low values. The optimum concentration (at which the inhibition is minimum) was recorded by taking into account the percent COD reduction, percent methane production and volatile fatty acids concentration in the digesters.

Metal Analysis: Total, filtered, acid extractable and strongly bound metal concentrations were measured for each of the metals. The metal analyses were carried out using a Pye Unicam Atomic Absorption Spectrophotometer fitted with a computer for data processing.

Total Metals: All glassware used in metal analysis was soaked in 10% nitric acid for 24 hours and rinsed thrice with deionized water in accordance with Standard Methods (1989). 2.5 ml of concentrated nitric acid were added to 25 ml of sludge in a 100 ml glass beaker. The beaker was covered with a glass plate and refluxed on an electric hot plate in a fume cupboard until the volume had reduced to approximately 5ml. Addition of concentrated nitric acid and heating continued until the digestion was complete and the solution became light-colored. After washing the glass plate and beaker walls with distilled water, the samples were filtered through an acid-washed No.42 Whatman ashless filter paper into a glass boiling tube. 5 ml of a universal interference suppressant (a mixture of Cesium and Lanthanum chlorides; Smith et al., 1983) was added to the filtrate and transferred to a 50 ml volumetric flask together with washings from the sample tube. Three blanks of 25 ml distilled water were prepared following the above procedure.

Filtered Metals: 80 ml of the sludge was centrifuged at 3,000 rpm for one hour and the supernatant filtered through a 0.45 µm filter paper into a glass boiling tube. 5 ml of the universal suppressant were added to 25 ml of the filtrate in a volumetric flask. Three blanks of 25 ml deionized water were also prepared.

Acid Extractable Metals: 5 % nitric acid was added to the centrate produced by centrifuging for one hour following the above procedure to make up to the original volume. It was mixed and allowed to settle for 20 minutes. Centrifuging was repeated for 10 minutes at 3,000 rpm. 25 ml of the supernatant was acid digested, filtered and made upto 50 ml as described above for the total metals concentration.

Strongly Bound (Intracellular) Metals: The resultant centrate obtained after treatment with 5% nitric acid and centrifuging was made upto the original volume with deionized water and mixed. 25 ml of this suspension was then acid digested, filtered and made up to 50 ml.

Chemical Oxygen Demand (COD): The COD test is based on the Dichromate Reflux Method described in Standard Methods (1989). It is extensively used in the analysis of domestic and industrial wastes. By using this test the results can be obtained in a relatively short time as compared to the BOD test.

Biogas Analysis: A Gas liquid chromatograph (GLC) was used to determine the concentrations of methane, carbon dioxide, and nitrogen in the digester gas. The biogas volume was measured by using a wet gas-meter after the biogas was scrubbed through a dreshel bottle. The experiments were run for a period of over 400 days. The cations were introduced in the form of chloride salts due to their high solubility and also because chloride is known to be relatively nontoxic to methanogenic bacteria (Kugelman and McCarty 1965). Standard solutions of the chlorides were prepared and appropriate quantities added to the daily feed. The concentration of sodium was kept constant in the control digester "E".

RESULTS AND DISCUSSION

Figures 1, 2 and 3 show that low concentrations of sodium (e.g. 900-1000 mg/l in reactor "E"), don't have an inhibitory effect on methanogens. This can be readily seen by the insignificant decrease in COD removal efficiency over a long period of time in the control reactor "E". In the experimental reactor "F", the decrease in COD removal efficiency is very gradual and slight upto a sodium concentration of around 6000 mg/l. This seems to contradict the findings of an earlier study that report sodium concentrations in the range 3,500-5,500 mg/l to be moderately inhibitory to methanogens at mesophilic temperatures (McCarty 1964). The apparent contradiction can be explained by the fact that in this study (unlike McCarty 1964), the sodium additions were gradual and carried out in between longer time intervals. For example, the increase in sodium concentration during the first 24 days was only 715 mg/l. This allowed sufficient time for the microorganisms to acclimate to the toxic effects of sodium thus minimizing the inhibition. On the other hand, McCarty (1964) carried out his research for a very short time period so that there was not enough time for acclimation. Adaptation of methanogens to high concentrations of sodium over prolonged periods of time increases the sodium tolerance of these microbes (Chen *et al.* 2003). The figures reveal magnesium to be very effective in reducing sodium toxicity to methanogens. At very low concentrations (150 and 225 mg/l), magnesium does not seem to reduce sodium toxicity as witnessed by the continual decline in the COD removal efficiency. However, beyond a concentration of 300 mg/l, the increase in COD removal efficiency is quite rapid for a long period of time. The optimum concentration i.e. the one that gives maximum COD removal was found to be 550 mg/l.

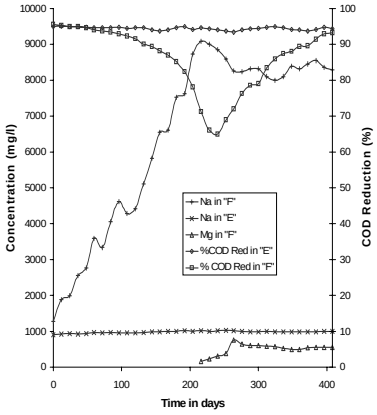

Fig.1 Effect of Mg on COD Reduction

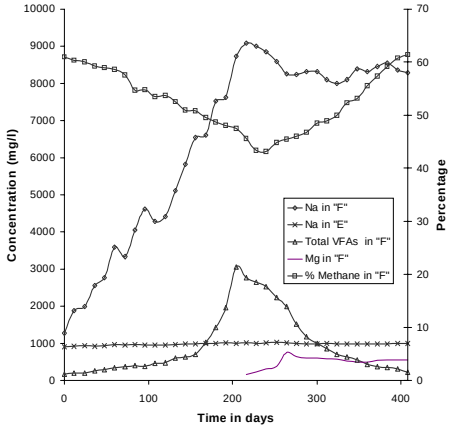

Fig.2 Effect of Mg on Methane Production

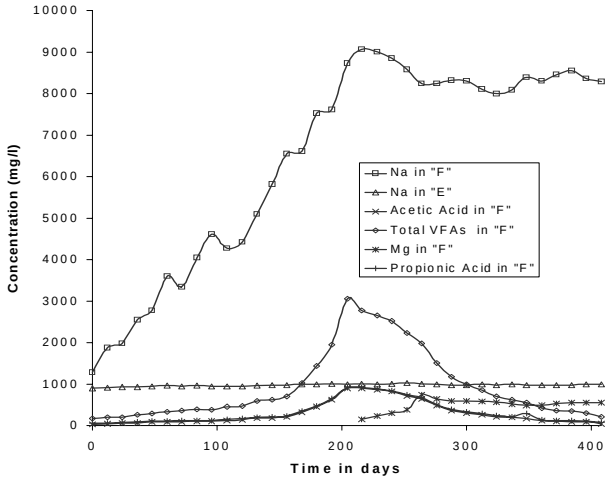

Fig.3 Effect of Mg on Acids Production

The methane production followed a similar pattern; increasing from 42% to 62%. As expected, the concentration of total VFAs registered an appreciable decline.

Conclusions

- Inhibition occurs only if the toxic cation is present beyond a certain concentration. At very low concentrations of sodium (i.e. 1000 mg/l), there is no decrease in %COD reduction. Therefore, at this concentration, sodium does not have toxic effects on the methanogenic bacteria.
- If allowed a sufficient period of time, the anaerobic bacteria get "acclimatized" or immune to the toxic cation and their activity is not affected significantly. That's why even at a sodium concentration of 6,000mg/l, the COD reduction does not register a noticeable decline. However, there is a limit to acclimatization; beyond certain levels, the bacteria can no longer tolerate sodium toxicity and COD reduction begins to decrease appreciably.
- Magnesium was found to be very effective in reducing the toxicity effects of sodium. The %COD reduction decreased to 65% by the addition of low concentration of magnesium salts. However, it should be present in the optimum concentration which in this case was found to be 550mg/l.

REFERENCES

Chen, W., Han, S., and Sung, S. (2003). "Sodium Inhibition of Thermophilic Methanogens" *Journal of Environmental Engineering*, 129, 6, 506-512

Han, Y., Sung, S., and Dague, R.R. (1997). "Temperature-phased anaerobic digestion of

wastewater sludges" *Water Sci. Technol*., 36, 367-374.

Kugelman, I.J., and McCarty, P.L. (1965). "Cation toxicity and stimulation in anaerobic waste treatment. I. Slug feed studies." *Journal of the Water Pollution Control Federation.* 37, 97-116

McCarty, P.L. (1964). "Anaerobic waste treatment fundamentals III." *Public Works*, 95, 91-94

Metcalf and Eddy (2003). *Wastewater Engineering: Treatment and Reuse*

Parkin, G.F., and Owen, W.E. (1986). "Fundamentals of Anaerobic Digestion of Wastewater Sludges" *Journal of Environmental Engineering*, vol.112, no.5, pp. 867-920

Rinzema, A., van Lier, J., and Lettinga, G. (1988). "Sodium inhibition of acetoclastic methanogens in granular sludge from a UASB reactor." *Enzyme Microb. Technol.*, 10, 24-32

Soto, M., Mendez, R., and Lema, J.M. (1993). "Sodium inhibition and sulphate reduction in the treatment of mussel processing wastewaters." *J. Chem. Technol. Biotechnol.*, 58, 1-7.

Speece, R.E. (1996). *Anaerobic biotechnology for industrial wastewaters*, Archae, Nashville, Tenn.