Environ. Eng. Res. Vol. 9, No. 3, pp. 119~124, 2004
Korean Society of Environmental Engineers

AN EFFECT OF THE REDUCTION OF TOXICITY USING BICARBONATE CATALYST ON WASTEWATER

Jin-Hwa Park†

Korea Institute of Environmental Science and Technology, Dept. of Project Management, 613-2, Bulgwang-Dong Eunpyeong-Gu, Seoul, 122-706

(received March 2004, accepted June 2004)

Abstract : A wastewater treatment plant recently had failures in bioassay tests. There are several industries discharging wastewater to the sewer. There was a strong relationship between total inorganic carbon and % inhibition after biological treatment. The toxicity of the textile mill wastewater was significantly reduced by adding bicarbonate. The sodium bicarbonate addition gave a significant increase in microbial activity indicated by the increase in the oxygen uptake of sodium bicarbonate added systems. This strong effect of bicarbonate addition on oxygen uptake might be due to the binding effect of sodium bicarbonate with ion state metal compounds giving strong toxic effects for microorganisms. In addition, when the percentage of the textile mill wastewater exceeds 5%, a high toxicity remained after TF biomass treatment.

Key Words : bicarbonate, catalyst, reduction, toxicity, wastewater

INTRODUCTION

Water is one of the earth's most precious elements. Today, pure water drawn from springs is far from sufficient to meet the needs of the population. We must therefore make domestic water drinkable, and treat both domestic and industrial wastewater. The drinking water we vitally depend on must be filtered, disinfected and sometimes softened before it can be consumed.[1]

The City of St. Croix Falls Wastewater Treatment Plant (WWTP), Madison, WI recently had failures in bioassay tests. There are several industries discharging wastewater to the City sewer. There appears to be no consensus on what caused the toxicity in the St. Croix Falls WWTP in 1999. To look for the cause of toxicity, the toxicity screening tests[2,3] were performed using the Reserve Electron Transfer (RET) assay (MitoScan Co., Madison, WI) and an electrolytic respirometer with various waste-water samples taken in the Straus Knitting Mills and other industries over time depending on production schedules to determine the effect of various wastewater streams on inhibition to trickling filter (TF) biomass obtained from the City of St. Croix Falls WWTF and activated sludge (AS) biomass obtained from the Nine Spring WWTP, Madison, WI. Then, an electrolytic respirometer test was performed to evaluate the effects of sodium bicarbonate ($NaHCO_3$) addition on the toxicity of Straus wastewater samples. As natural sodium bicarbonate[4] is low in purity, an industrial method is generally used, in which carbon dioxide is absorbed into soda ash. Sodium bicarbonate is

† Corresponding author
E-mail: sunflower@kiest.org
Tel: +82-2-3800-673, Fax: +82-2-3800-699

widely used as a weak alkali buffer agent for supplementary feeds, a major raw material for baking powder as food additives, and acid neutralizer agent after chromium tanning in leather manufacturing, as well as dye stuffs and pharmaceutical ingredients. It is also applied to various fields such as fiber, soap, paper, food, electricity, etc., and is also used as a solution for today's environmental pollution. Release of CO_2[5] when heated or when reacted with a weak acid makes sodium bicarbonate a key ingredient. A buffer in water treatment, sodium bicarbonate can react as an acid or a base and it has the ability to reduce odors chemically by neutralizing the acid by-products of bacteria. As per some recent reports[6], sodium bicarbonate breaks down hydrocarbons which make it an excellent method of cleaning engines and engine parts or other areas where oil and grease are present. Another major advantage is the fact sodium bicarbonate does not break the surface tension of metals, thus the problem of flash rusting is eliminated. Sodium bicarbonate has a pH 8.4 and can be disposed of in most waste water treatment systems.

On the other hand, Moir[7] et. al. Suggested that azo dye should be designed to investigate the impact of specific structural features on the ease of bioreduction. Dyes were selected on the basis of availability and structural homology to allow interpretation of differences in rates of reduction. The environmental behavior of dyes is of concern due to the possible toxicity and /or carcinogenicity of the dyes themselves or of their reduction products. By design, dyes are resistant to both oxidation and photocatalytic degradation in order to be as colorfast as possible. This stability gives rise to the possibility of bioconcentration, which has been predicted for several hydrophobic, disperse dyes based on their partition coefficients and solubility's[8] but which is not expected for highly water-soluble dyes. An aerobic wastewater treatment, the activated sludge process, was found to be ineffective in removing the majority of 18 azo dyes tested.[9] Textile mills represent an important economic sector in the state of Santa Catarina (south of Brazil, South America), and textile processes have a considerable impact on water quality, given the large volume of wastewater they generate and the physical and chemical properties of their effluents.[10] This impact is due to combined action of high biochemical oxygen demand, solids in suspension, dissolved substances, pH, color, and toxicity.[11~14] Analytical methods for pollution control of effluents are generally expensive and time consuming.[15] Identification of all the toxic compounds used in textile production is very difficult because of the huge variety of chemicals used and the lack of data on their toxicity. Several textile dyes have even been investigated and found to be carcinogenic.[16] Toxic compounds present in wastewater discharge must be treated to ensure a high level of protection for the environment and public health.[17,18]

The objective of this study was to evaluate the effect of bicarbonate addition on the toxicity of Straus wastewater samples that were found to be difficult to biodegrade by TF biomass using an electrolytic respirometer. Other objectives of this study were to determine which wastewater stream had greatest toxicity after being treated with TF and AS biomasses for 12 hours and to assess the extent of toxicity reduction by biological treatment. Therefore, this study aims to determine which wastewater stream may have caused the toxicity failure at the City of St. Croix WWTP, to find which wastewater are most toxic to ecological systems, and eventually to develop strategies for reducing the toxicity of dyes-containing wastewater.

EXPERIMENTAL

Samples

Samples include domestic sewage, primary settled sewage with or without industrial wastewater, Straus wastewater, Hospital wastewater, Home Life domestic wastewater, various types of dyes and other materials used at Straus Knitting Mills, and trickling filter (TF) biomass.

Analytical Methods

For the analysis of total inorganic carbon (TIC) and total organic carbon (TOC), a total carbon analyzer was used. The difference between total carbon (TC) and TOC was considered TIC. All the analyses were performed following Standard Methods (1998)[19] or Hack Wastewater and Biosolids Analysis Manual (1999).[20] The ammonia, nitrite, and nitrate carried out using Hack methods. Total suspended solids (TSS) and volatile suspended solids (VSS) concentrations were obtained from 20mL samples in accordance with Parts 2541B and 2540E, of Standard Methods[APHA et al., 1998].[19] Suspended and volatile suspended solids concentrations were measured by procedures outlined in Parts 2540D and 2540G of Standard Methods [APHA et al., 1998][19] using between 15 and 40mL samples. Total volatile, suspended, and volatile solids concentration values were computed to the nearest 10 mg/L .

The experimental conditions are summarized in Table 1.

Experimental Conditions

The operation temperature was 20±0.5°C and the total volume of both biomass and wastewater in each reactor was 150 mL. Raw wastewater samples and samples after treated by biomass were filtered with 0.45 μm filters and the filtered samples stored in a 4°C cold room, in order to avoid any possible microbial activity that may occur during the storage in a cold room. The experimental conditions are summarized in Table 2. For this test, Straus wastewater sample was used. As per our other reports,[20] Straus waster did not have much oxygen uptake almost from the start of the experiment, indicating strong inhibitory effect. After approximately 10 hours of reaction, it appeared that all biodegradable organic materials are decomposed. The bicarbonate concentrations varied from 0 to 100 mg/L

RESULTS AND DISCUSSION

Oxygen uptake of each reactor over time is shown in Fig. 1. When bicarbonate was absent, oxygen uptake did not occur for 3 hours, than only 2.77 mg of oxygen was consumed for 9 hours. Oxygen uptake for bicarbonate added systems increased depending on the concentration

Table 1. Experimental conditions of the first toxicity screening tests

Run #	Biomass	Wastewater	Volume (biomass + wastewater)	Temp., °C
1-1	TF TF AS TF ASTFTFTF	DS	37 mL + 113 mL	20±0.5
1-2		DS	37 mL + 113 mL	
1-3		DS	37 mL + 113 mL	
1-4		M/W	88 mL + 62 mL	
1-5		M/W	88 mL + 62 mL	
1-6		ES/W	52 mL + 98 mL	
1-7		HLD/W	13 mL + 137 mL	
1-8		H/W	66 mL + 84 mL	

DS = Domestic sewage, M/W = Straus Mills wastewater, ES/W = East Straus wastewater,
HLD/W = Home Life domestic wastewater, H/W = Hospital wastewater
Sampling date of all wastewaters and biomass was February 19, 2000.

Table 2. Experimental conditions of the second toxicity screening tests

Run #	Sample	Injection volume of TF biomass, mL	Sample volume, mL	Added concentration of bicarbonate (HCO_3^-), mg/L
2-1	Straus wastewater	185	15	0
2-2		185	15	20
2-3		185	15	40
2-4		185	15	60
2-5		185	15	80
2-6		185	15	100

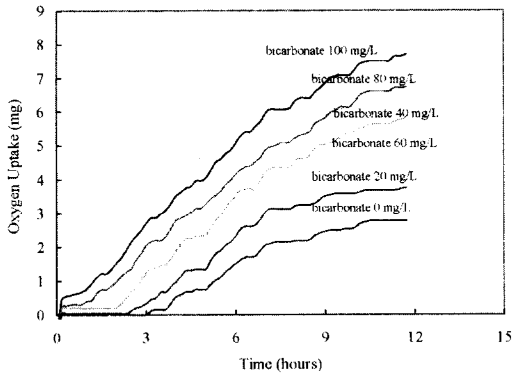

Figure 1. Oxygen uptake according to the injection concentrations of bicarbonate.

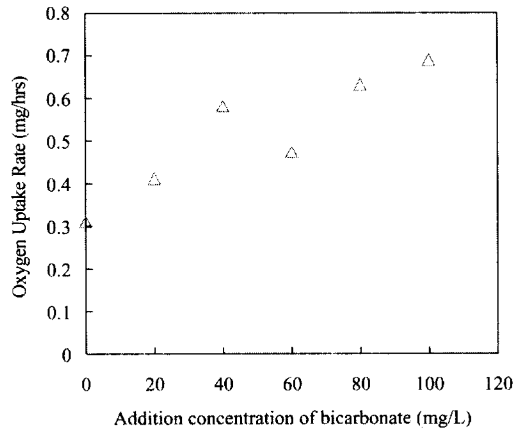

Figure 2. Oxygen uptake rate according to the added concentrations of bicarbonate.

of bicarbonate added. Therefore, it can be said that the bicarbonate addition affected oxygen uptake significantly. This result might be due to the fact that bicarbonate could bind effectively with ionized metal compounds giving strong toxic effects to microorganisms to make the non-ionic metal compounds usually giving less or non-toxic effects for microorganisms. The oxygen uptake rate is the slope of oxygen uptake with time. Oxygen uptake rates are shown in Fig. 2. Compared to the system without bicarbonate having the oxygen uptake rate of about 0.3 mg/hr, the oxygen uptake rate of both 20 mg/L and 40 mg/L of bicarbonate added systems were largely increased to be about 0.4 and 0.6 mg/hr, respectively. However, oxygen uptake rates for the systems > 40 mg/L of bicarbonate increased slightly.

The results of the first toxicity screening tests are summarized in Table 3. TOC value of Mills wastewater was highest (almost 300% greater than other wastewater samples). Runs 1-1 and 1-2 were duplicate and contained TF biomass and DS. Run 1-3 contained AS biomass and DS. Run 1-4 contained TF biomass with M/W while Run 1-5 had AS biomass with M/W. Run 1-7 contained TF and HLD/W and Run 1-8 TF and H/W. The ratios of TIC to total carbon (TC) for

Table 3. Summary of TIC, TOC, TSS, and VSS concentrations, and F/M ratio based on TOC

Title		TIC (mg/L)	TOC (mg/L)	TIC/TC Ratio	TSS (mg/L)	VSS (mg/L)	F/M ratio based on TOC
TF biomass		0.0	34.6		1680	1520	
AS biomass		4.9	37.7		1450	1320	
D.S		34.7	54.9	0.39			
M/W		34.1	187.4	0.15			
ES/W		39.8	59.6	0.40			
HLD/W		21.6	23.8	0.48			
H/W		36.9	67.4	0.35			
Run #	1-1 (TF - DS)	26.2	49.9	0.26		358	0.14
	1-2 (TF - DS)	26.2	49.9	0.26		358	0.14
	1-3 (AS - DS)	27.4	50.7	0.26		326	0.16
	1-4 (TF - M/W)	14.1	97.8	0.11		851	0.12
	1-5 (AS - M/W)	17.0	99.6	0.13		774	0.13
	1-6 (TF - ES/W)	26.0	50.9	0.25		503	0.10
	1-7 (TF - HLD/W)	19.8	24.7	0.31		126	0.20
	1-8 (TF - H/W)	22.8	53.0	0.23		638	0.08

DS = Domestic sewage, M/W = Straus Mills wastewater, ES/W = East Straus wastewater, HLD/W = Home Life domestic wastewater, H/W = Hospital wastewater

Table 4. Analysis of ammonia and NO_2^-/NO_3^-

Sample		Initial ammonia, mg N/L	Final ammonia, mg N/L	Initial NO_2^-/NO_3^-, mg N/L	Final NO_2^-/NO_3^-, mg N/L
DS		16.1		2.6	
M/W		1.5		6.9	
ES/W		32.9		4.5	
HLD/W		2.5		1.6	
H/W		12.0		2.3	
TF biomass		25.2		0.8	
AS biomass		2.8		13.3	
Run #	1-1 (TF - DS)	18.6	14.4	2.5	4.0
	1-2 (TF - DS)	17.4	13.8	2.8	4.9
	1-3 (AS - DS)	13.4	2.6	4.2	7.0
	1-4 (TF - M/W)	15.4	14.4	3.4	3.7
	1-5 (AS - M/W)	3.6	4.7	2.4	2.3
	1-6 (TF - ES/W)	30.3	24.5	3.2	3.0
	1-7 (TF - HLD/W)	4.5	5.8	1.5	1.6
	1-8 (TF - H/W)	17.8	21.2	1.7	3.5

the Mills wastewater (Runs 1-4 and 1-5) were significantly lower than the ratios of other runs. The F/M ratio of each run ranged from 0.08 to 0.2 on TOC bases.

Ammonia, nitrite, and nitrate concentrations of various wastewater streams are summarized in Table 4. ES/W had the highest ammonia concentration, followed by DS and H/W. HL/W and M/W had very low ammonia concentrations (< 3 mg N/L). No nitrification occurred with M/W and ES/W. Except Run 1-3, little nitrification occurred by TF biomass even with DS, HLD/W, and H/W. AS biomass obtained from Nine Springs WWTP, Madison, Wisconsin, had significant nitrification, indicating AS biomass contained sufficient numbers of nitrifiers. Since TF biomass received from the St. Croix Falls WWTP were fed with DS and sufficiently aerated for over five days before testing, it was thought that nitrifiers should be able to sustain their population if the other conditions are right. When the ratio of Straus wastewater to biomass volumes was 0.7, Straus wastewater inhibited nitrification. Further study is needed to determine the dilution rate that Straus wastewater inhibits nitrification.

CONCLUSIONS

From a series of toxicity screening tests and bench-scale treatability tests, the following conclusions were drawn: The textile mill wastewater was found to be most toxic to TF biomass among the wastewater samples tested. Other industrial wastewater does not appear to contribute to the toxic effect on TF biomass. There was a strong relationship between total inorganic carbon and % inhibition after biological treatment. No nitrification occurred with M/W and ES/W. While there was significant nitrification with DS treated by AS biomass, little nitrification by TF biomass occurred even with DS, HLD/W, and H/W. It appears that nitrification is significantly inhibited by M/W and ES/W even when mixed with domestic sewage. It appears that there is a strong relationship between the TIC/TC ratio and % inhibition. The toxicity of the textile mill wastewater was significantly reduced by adding bicarbonate. In addition, when the percentage of the textile mill wastewater exceeds 5%, a high toxicity remained after TF biomass treatment.

ACKNOWLEDGMENT

This work was supported by the St. Croix Falls and Donohue & Associates. The author would like to express great appreciate to Jim Park and Min Jang for their support and all kinds of helps in performing research and

experiments.

REFERENCES

1. http://www.solvay.com/markets/markwe1.htm (2004).
2. Park, J. H., Park, J. K., and Jang, M., Theories and Applications of Chem. Eng., 8, 4129, (2002).
3. Park, J. H., Yi, Y. W., and Park, J. H., KSEE, Conference (I), PA43, 355, (2002).
4. http://eng.dcchem.co.kr/product/p_basic/p_basic02.htm (2001).
5. http://www.ahperformance.com/products/sobi.html (2004).
6. http://www.problast.ca/soda.htm (2003).
7. Moir, D., Masson, S., and Chu, I., *Environ. Toxicol. Chem.*, **20**, 479 (2001).
8. Anliker, R., Clarke, E. A., and Moser, P., *Chemosphere* **10**, 263, (1981).
9. Shaul, G. M., Holdsworth, T. J., Dempsey, C. R., and Dostal, K. A., Chemosphere **22**, 107, (1991).
10. U.S. Environmental Protection Agency. *Best management practices for pollution prevention in the textile industry.* EPA 625/R-96-004. Cincinnati, OH, (1996).
11. Walsh, G. E., Bahner, L. H., and Horning, W. B., *Toxicity of textile mill effluents to freshwater and estuarine algae, crustaceans and fish. Environ. Pollut.* **21**, 169, (1980).
12. *Brazilian Ministry of the Environment. Brazilian Water Quality* Guidelines : National Council of the Environment (CONAMA), Resolution 20 - June 18, 1986. Brasilia, DF, Brazil, South America (in Portuguese), (1986).
13. Miller, W. E., Peterson, S. A., Greene, J. C., and Callahan, C. A., *J. Environ. Qual.* **14**, 569, (1985).
14. Lambolez, L., Vasseur, P., Ferard, J. F., and Gisbert, T., *Ecotoxicol. Environ. Saf.* **28**, 317, (1994).
15. Botterweg, J. and Risselada, J., "Toxicity assessment of effluents in the Netherlands : Implementation, problems and prospects. *Sci Total Environ Suppl.* **2**, 1105, (1993).
16. Chung, K. T., and Cemiglia, C. E., Mutat Res **277**, 210, (1992).
17. U.S. Environmental Protection Agency. *Technical support document for water quality-based toxics control. EPA 440/4-85-032.* Washington, DC, (1985).
18. Organization for Economic Cooperation and Development. *The use of biological tests for water pollution assessment and control.* OECD Document 11. Paris, France. (1987).
19. APHA, AWWA and WEF, *Standards Methods for the Examination of Water and Wastewater*, 20^{th} (1998).
20. *Hack Wastewater and Biosolids Analysis Manual*, Third Edition, (1999).
21. Park, J. H. and Park, J. K., "Toxicity Screening Tests for St.Croix Falls Wastewater Treatment Plants," Technical Report, Donohue and Associates, (2001).