Ozone Application For The Improvement Of UASB Reactor Effluent. II. Toxicity Evaluation

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Abstract

In order to improve the effluent from domestic sewage treatment through an anaerobic process in an upflow anaerobic sludge blanket reactor (UASB), CETESB - The Environmental Protection Agency for Sao Paulo State, and FILSAN - Equipamentos e Sistemas S/A, developed a joint program to study the effectiveness of ozonation of the effluent as a post-treatment process. As the effluents treated by this system could contain toxic chemicals, *Daphnia similis* toxicity tests were applied. Two ozonation conditions were evaluated: (1) contact time of 30 min, mean ozone application dosage of 15.9 mg/L; (2) contact time of 50 min, mean ozone application of 16.7 mg/L. Toxicity reduction occurred for all samples but one. The ozonation system eliminated the residual toxicity associated with the effluent treated by the UASB reactor.

Introduction

A great part of the Brazilian low income population is concentrated in industrialized urban centers, where the sanitation infrastructure is usually deficient. There is, therefore, a need to develop simple and low cost alternative forms of treatment, as well as disinfection processes. The upflow anaerobic sludge blanket digester (UASB) has proved highly feasible in the treatment of these wastes (1), although improvements still have to be achieved, especially concerning the removal of pathogenic microorganisms.

It is known that, in industrialized areas, municipal sewage may contain, together with viruses and bacteria, a complex mixture of chemicals, some of them toxic to aquatic organisms of receiving waters. These wastes frequently are chlorinated, in order to reduce the number of fecal coliforms as well as the number of enteric pathogens.

Although chlorine is an efficient low cost disinfectant process, easy to handle and to obtain, effluents treated with chlorine cause the formation of mutagenic compounds (2,3), besides increasing toxicity to aquatic organisms (4-8).

The toxicity of chlorine and of its derivatives was studied extensively over the last decade. Results obtained from these studies have led to the proposition of dechlorination of the effluent, thus reducing the toxicity of the final effluent to aquatic life (9). Other studies were carried out searching for treatment alternatives for these effluents, and much attention has been given to ozone during this last decade.

Ozone has been used instead of chlorine in sewage treatment, especially in Europe (10). Although being a higher cost alternative, ozone has proved efficient in removing bacteria and viruses, and in reducing levels of color, turbidity and toxicity of effluents (11). Furthermore, an advantageous aspect is that it disappears very rapidly from the treated water; this is not the case with chlorine which is fairly persistent (10,12).

Very few studies were carried out until now on the toxicity of ozone. However, it is known that, due to its strong oxidation capacity, the primary effects of ozone are related to organism surfaces, causing serious injuries to their external tissues. Thus ozone may cause serious destruction of gill tissues, interfere with respiration, with osmoregulation and possibly with excretion, and may lead to death or to the development of sublethal secondary pathogenic effects (10,13).

The effects of ozone-treated sewage effluents on fish at acute and chronic levels are reported in the literature (4,5). No mortality was observed in eleven species of fish when exposed to residual ozone concentration ranging from 0.185 mg/L to 0.07 mg/L, but 100% mortality was shown for *Salvelinus namayacush* when exposed to 0.322 mg/L of ozone concentration (4). At the chronic level, Ward and De Graeve (5) showed that the survival, growth and reproduction of the fish *Pimephales promelas* exposed to effluents with mean levels of residual ozone ranging from 0.016 mg/L to zero, were not affected.

The present pilot-scale study was proposed to be conducted due to the initial considerations made, and also due to the concern of CETESB in evaluating domestic and industrial wastes toxicity (14-18). Municipal sewage from an industrialized area was ozonized after treatment in an UASB reactor (19), and the efficiency of the ozonation process in removing toxicity was evaluated, and are presented here.

Materials And Methods

Municipal sewage was treated in a 120 m^3 capacity UASB reactor. The main design parameters were: flow rate of 30 m^3/h, hydraulic retention time (HRT) ranging from 4 to 7 hours. The ozonation process started operating when the anaerobic reactor reached steady state.

The post treatment was made by an ozonation unit (Filsan model THF-05). Ozone was generated in an air flow filtered between 30 and 40 NL/min and average internal temperature of 28°C. Contact between part of the UASB reactor effluent and carrier gas plus ozone was achieved in two PVC contact columns, 150-L capacity each, and placed in series. The gas inlets were located at the base of the columns. In the first column the contact between liquid and gas flows was cocurrent, and in the second the contact was counter-current. The ozone application dosages were 15.9 mg/L and 16.7 mg/L with contact times of 30 and 50 min, respectively (Table 1). These values were established based on previous laboratory scale tests (20). The ozone concentration was determined twice a day by the iodometric method, with a 0.03 mg/L detection limit (21).

TABLE 1. OZONE APPLICATION DOSAGES

Test Number	Column	Ozone Application, mg/L	Contact Time, min
1	1	10.6	15
	2	5.3	15
	total	15.9	30
2	1	11.1	25
	2	5.6	25
	total	16.7	50

Tests for the evaluation of the effects of different ozonation periods were run with 4-hour composite samples of the effluents from these columns. Five and eight samples were taken for 30 and 50 min exposure, respectively, at the sites: 1, UASB effluent; 2, partial ozonized effluent; 3, final ozonized effluent (Figure 1). These samples were used for the toxicity tests and for the physico-chemical analyses mentioned below. Sampling always was started after a period of at least 4.5 times the hydraulic retention time, to provide assurance that the process was in a stable condition.

TOXICITY TESTS

Tests were run with *Daphnia similis* Claus, 1876, following the procedure recommended by the International Organization for Standardization (22) and modified by CETESB (23). The method consists of exposure of the test organism to at least six concentrations of the effluent during a 24-hour period with four replicates per concentration. After this period, the number of immobile organisms is counted. The results are expressed as effective concentration, which

is the concentration that causes immobility to 50% of the organisms during the exposure period (24-h EC50) calculated by the Litchfield-Wilcoxon method (24). A low percentage of the observed effect, about 10-20% immobility of test organisms, is considered as an indication of toxicity. Reconstituted soft water (21) was used as dilution water in the toxicity tests.

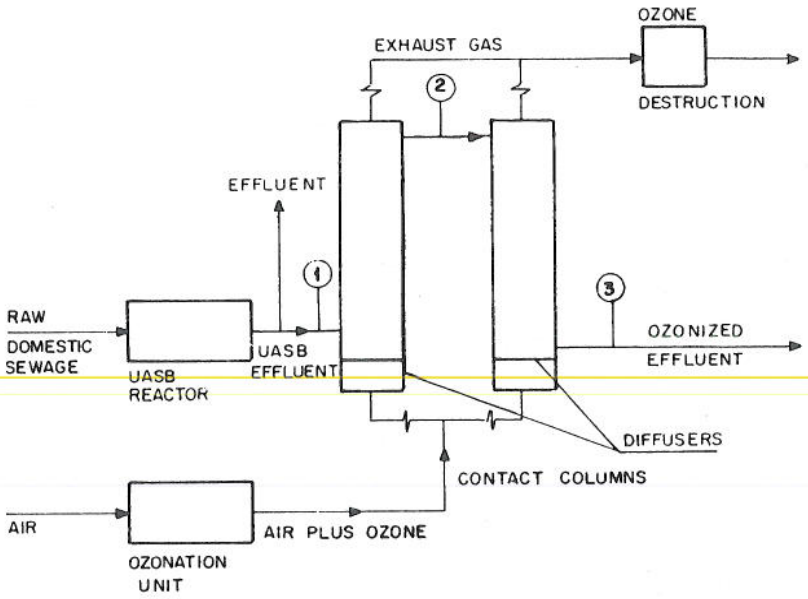

Figure 1. Diagram of anaerobic treatment of domestic sewage with UASB reactor and ozone.

PHYSICO-CHEMICAL ANALYSIS

BOD, COD, total suspended solids, color, turbidity and pH were determined according to *Standard Methods* (21).

Results

The results of the toxicity tests with the effluent from the UASB reactor before and after the disinfection process with ozone during 30 and 50 min. The respective physico-chemical data are presented in Tables 2 and 3.

TABLE 2 - Toxicity and physico-chemical data of the UASB reactor effluent after 30 minutes of ozonation.

SAMPLE No.	DATE	SAMPLING SITE	COD mg/L	BOD mg/L	TSS mg/L	COLOUR mgPt/L	TURBIDITY N.T.U.	pH	TOXICITY(a) 24-h EC50(%)
1	8/4	1	134	29	49	30	9	6.4	52(47to58)(b)
		2	82	21	34	20	6	6.8	N.T.(c)
		3	75	15	24	10	3.5	7.2	S.T.(d)
2	8/10	1	94	37	30	10	30	6.2	72(66to78)
		2	78	25	25	10	25	6.7	S.T.
		3	69	23	16	5	20	7.1	N.T.
3	8/11	1	135	47	45	30	30	6.3	49(44to54)
		2	84	27	22	30	25	6.9	S.T.
		3	92	29	22	20	25	7.1	N.T.
4	8/12	1	131	51	58	30	15	-(e)	61(56to66)
		2	76	23	29	20	15	-	N.T.
		3	68	21	32	10	15	-	N.T.
5	8/13	1	137	45	72	30	20	-	47(40to55)
		2	86	19	24	10	20	-	S.T.
		3	69	18	21	10	15	-	N.T.

a. Percentage of the sample which immobilizes 50% of the test organisms, (Daphnia similis), after 24 hours of exposure.
b. Limits of confidence
c. Not acutely toxic
d. Signs of toxicity
e. Not analysed

Discussion

Although literature data mention experiments conducted mostly with fish, *Daphnia similis* was chosen as the test organism, due to its high sensitivity to a wide variety of chemicals, and all the well known advantages for laboratory work, such as sample volume and exposure time. The good quality of the UASB reactor effluent at site 1, expressed by its physico-chemical data, did not prevent it from showing acute toxicity to *D. similis*, except for one sample (Tables 2 and 3).

After ozone treatment, the quality of this effluent was improved, as shown by the chemical data which were reduced from site 1 to 3, as well as by the reduction or absence of toxicity (Tables 2 and 3). No ozone was detected in the final effluent (site 3) in either experiment.

TABLE 3 - Toxicity and physico-chemical data of the UASB reactor effluent after 50 minutes of ozonation.

SAMPLE No.	DATE	SAMPLING SITE	COD mg/L	BOD mg/L	TSS mg/L	COLOUR mgPt/L	TURBIDITY N.T.U.	pH	TOXICITY(a) 24-h EC50(%)
		1	128	46	77	30	-(e)	6.2	39(34to45)(b)
1	8/18	2	65	22	22	10	-	7.2	N.T.(c)
		3	67	21	25	10	-	7.4	84(74to95)
		1	140	43	63	40	31	6.4	29(25to34)
2	8/19	2	71	19	16	40	18	7.0	S.T.(d)
		3	62	26	16	40	16	7.7	N.T.
		1	207	66	166	30	10	6.3	28(22to36)
3	8/20	2	61	20	19	20	15	7.1	N.T.
		3	65	16	12	5	10	7.5	S.T.
		1	115	42	38	80	20	6.5	17(15to19)
4	9/1	2	78	25	15	20	15	7.3	64(57to71)
		3	61	27	16	30	10	7.6	N.T.
		1	90	41	34	80	20	6.7	47(43to51)
5	9/2	2	65	18	15	20	11	7.5	S.T.
		3	50	22	13	20	10	7.7	N.T.
		1	135	38	39	80	20	6.4	38(34to42)
6	9/3	2	83	22	20	30	15	7.4	73(64to84)
		3	71	20	10	10	10	7.7	S.T.
		1	96	36	38	40	10	6.5	N.T.
7	9/8	2	50	23	10	20	8	7.2	N.T.
		3	46	18	9	20	7.5	7.3	75(58to96)
		1	82	23	11	80	15	6.1	36(31to41)
8	9/9	2	46	18	12	20	9	6.9	N.T.
		3	38	14	10	20	8.5	7.2	73(64to82)

a. Percentage of the sample which immobilizes 50% of the test organisms,(Daphnia similis), after 24 hours of exposure.
b. Limits of confidence
c. Not acutely toxic
d. Signs of toxicity
e. Not analysed

Approximately 30 min of ozonation with an application dosage of 15.9 mg/L was enough to reduce toxicity below the acute level to *D. similis* (Table 2). This seems to be true if one considers that at site 2 the effluent under a total ozonation period of 50 min has undergone a treatment of approximately 25 minutes. Certain samples, however, such as numbers 4 and 6, seem to require a longer period of contact for detoxication, since no toxicity or signs of it were found in these samples collected at site 3.

Otherwise, some samples became acutely toxic after a longer period of ozonation (Table 3, samples 1, 7 and 8).

This toxicity possibly is due to the formation of oxidized by-products rather than to residual ozone, since the BOD after 30 and 50 minutes of ozonation ranged from 15 to 29 mg/L and 14 to 27 mg/L, respectively. This possibility also was suggested by Arthur et al. (6) who developed similar experiments with the same kind of results, showing the need for further investigation.

Although no residual ozone was detected, it is worth mentioning that ozone concentrations below or at the detection limit of this method can cause some effects in aquatic organisms. Ward and De Graeve (4,5) running 48-h acute toxicity tests with *Daphnia magna*, showed that this species is highly sensitive to low levels of ozone, being more sensitive to this substance than other species. Signs of toxicity, that is, low mortality, were observed in *D. magna* at an ozone concentration of 0.03 mg/L. As *D. magna* and *D. similis* have comparable sensitivities to a series of chemicals (25), the same might happen with ozone.

Because of the instability of ozone in water (10, 12) and the dilution that effluents undergo in waterbodies, it is likely that no effects on aquatic life might occur, due to ozone concentrations in the effluents, but a control still is necessary, since it is toxic in very low concentrations.

Conclusions

According to the present data and to those described in the literature, one can consider ozonation as an efficient process for acute toxicity removal from effluents from UASB reactors.

These results might encourage the idea of using this treatment for reducing toxicity of specific industrial effluents, to prevent them from causing an acute impact on aquatic life.

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Key Words

Ozone, Municipal Wastewater Treatment, Upflow Anaerobic Sludge Blanket Reactor, Toxicity Reduction,

Résumé

En vue d'améliorer la qualité des effluents d'eaux usées domestiques traitées à l'aide d'un réacteur à lit de boue anaérobie (UASB), CETESB (autorité compétente en matière de protection de l'environnement de l'Etat de São Paulo) a élaboré en collaboration avec l'entreprise FILSAN un programme commun en vue d'étudier l'efficacité de l'ozonation des effluents sous forme d'une étape de traitement supplémentaire. Les eaux résiduaires traitées par ce système pouvant contenir des substances toxiques, on appliqua des tests de toxicité *Daphnia similis*. Deux conditions d'ozonation ont été évaluées:

1) Temps de contact 30 min, dosage moyen d'ozone 15,9 mg/L

2) Temps de contact 50 min, dosage moyen d'ozone 16,7 mg/L

La toxicité a pu être réduite dans tous les échantillons, à l'exception d'un seul. De manière générale, l'ozonation fut en mesure d'éliminer la toxicité résiduelle des eaux résiduaires issues du réacteur UASB.

Zusammenfassung

Um den Durchlauf von behandeltem Abwasser aus Siedlungen durch einen UASB-Reaktor zu verbessern, führten die Umweltbehörde des Landes São Paulo und FILSAN ein Projekt durch, das die Wirksamkeit einer Ozonung in einer Nachbehandlungsstufe untersuchte. Da die Abwässer toxische Eigenschaften haben könnten, wurden Gifttests durchgeführt. Zwei Ozonungsarten wurden ausgewertet:

1) Kontaktzeit 30 min, durchschnittliche Ozondosis 15,9 mg/l

2) Kontaktzeit 50 min, durchschnittliche Ozondosis 16,7 mg/L.

Die giftigen Eigenschaften wurden ausser bei einem Muster abgebaut. Im allgemeinen reduzierte also die Ozonung die Giftigkeit des Abwassers aus dem UASB-Reaktor.