A Study of the Efficiency of Ozone for the Removal of BOD_5 and Organic Matter in Shrimp Pond Effluents

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ABSTRACT

The application of ozone at a rate of 0.017, 0.034 and 0.073 mg/l/min resulted in the increase of the oxidation-reduction potential and total residual oxidant (TRO) of the effluents. The increase in oxidation-reduction potential and TRO of the effluents was significantly higher when higher dosages of ozone were applied. Treatment of shrimp pond effluent with ozone at the dosages of 0.034 and 0.073 mg/l/min resulted in complete removal of BOD_5 within 48 h. A longer treatment period of 144 h was needed to remove all the BOD_5 of the effluent at a lower ozone dosage of 0.017 mg/l/min. The highest percentage of total organic carbon (27.5-38.2%) removal was observed within a period of 4 h. Subsequently, the removal rate of total organic carbon was significantly lower. Bromate was detected at 120 h in the effluent treated with 0.017 mg/l/min of ozone. At higher ozone dosages of 0.034 and 0.073 mg/l/min bromate was detected at 72 h. Concentrations of bromate were between 0.0001 and 0.0006 mg/l which were lower than maximum allowable concentration in the WHO standard.

Keywords : ozone, organic matter, effluents, shrimp pond

INTRODUCTION

Organic matter is one of the major pollutants in shrimp pond effluents which create problems in receiving water by taking up dissolved oxygen and releasing toxic metabolites during its decomposition. Effluent standards were imposed for shrimp farms to limit the amount of pollutants that can be released into the receiving water. The BOD_5 value was used as an indicator for the amount of decomposable organic matter in the effluent. The BOD_5 of shrimp ponds effluents in Thailand has been reported to be

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between 3.0-60.5 mg/l (Department of Pollution Control, 2002: Musig *et al*., 1995). Investigations have been carried out to develop treatment methods to decrease the BOD_5 and other pollutants to the effluent standard level with some degree of success. However, a faster cost-effective treatment method is still needed. Ozone is a powerful oxidizing agent. It is a three-atom allotrope of oxygen in which the oxygen atoms are held together in an unstable bond. A loosely bound single oxygen atom quickly breaks away and reacts with most organic and inorganic molecules it contacts. Ozone has been used in sewage treatment since the early 1900s. It was later used for sterilizing potable water and became widely used in the aquarium (Stopka, 1975). It also has been used for the disinfection of water supply for hatcheries. This experiment was carried out to investigate the efficiency of ozone for the removal of BOD_5 and organic matter in shrimp pond effluents.

MATERIALS AND METHODS

This experiment was designed to evaluate the efficiency of ozone for the removal of biochemical oxygen demand and organic matter in shrimp pond effluents. The experiment was conducted at a laboratory scale using 14 liter acrylic aquaria. Shrimp pond effluents were collected from a shrimp farm in Chantaburi province during the harvest. A 12 liter effluent sample was put into each aquarium. The ozone used in this experiment was produced by a high voltage corona ozone multichannel E6 generator of the EBASE Corporation. Small jet pumps were used to mix the ozone with the water. The experiment consisted of three treatments using three different dosages of ozone, 0.017, 0.034 and 0.072 mg/l/min. Effluent samples were collected and analyzed for total residual oxidant (TRO) , oxidation reduction potential, total organic carbon, and bromate at 0, 4, 8, 121, 18, 24, 30, 36, 42, 48, 60, 72, 96, 120, and 144 h. Effluent samples were collected and analyzed for BOD_5 at 0, 12, 24, 48, 72, 96, 120, and 144 h. During the experimental period, the effluent salinity and temperature were also measured. TRO was measured by the spectrophotometric method (Shechter, 1973). Oxidation-reduction potential was measured by an oxidation -reduction potential probe ion analyzer, the Orion Model EA 720. BOD_5 was measured by the dilution method (APHA *et al*., 1980). Total organic carbon was analyzed by the TOC analyzer (O.I. Analytical, model 700); and bromate was analyzed by the iodometric titration method (APHA *et al*., 1980). Three

replications were set up for each treatment unit. Data obtained were analyzed to evaluate the efficiency of using ozone for the treatment of organic matter in shrimp pond effluent.

RESULTS

The salinity of the shrimp pond effluent was 34 ppt. The temperature of the effluent during the experimental period was between 25.0-32.5^{o} C. When ozone was applied into the effluent at the rate of 0.017 mg/l/min, the average TRO of the effluent increased steadily from an initial concentration of 0 mg/l to 1.4524 mg/l at 144 h. The concentrations of TRO at 12, 24, 48, 72, 96, and 144 h were 0.1834, 0.3133, 0.6959, 0.7704, 1.1918, and 1.1978 mg/l, respectively. At ozone dosages of 0.034 mg/l/min, TRO increased from 0 to 0.0119 mg/l at 8 h. Concentrations of TRO at 12, 24, 48, 72, 96, and 144 h were 0.0437, 0.8203, 1.8922, 3.6754, 2.5780, and 2.5274 mg/l, respectively. At ozone dosages of 0.073 mg/l/min, TRO increased from 0 to 0.0122 mg/l at 4 h. The concentrations of TRO at 12, 24, 48, 72, 96, and 144 h were 0.9668, 2.4028, 3.0489, 2.4881, 2.7794, and 2.0993 mg/l, respectively.

Oxidation-reduction potential of the effluent increased abruptly within 4 h from the initial value when they were treated with ozone. At ozone dosages of 0.017 mg/l/min, oxidation-reduction potential increased from the initial value of 5.94 mV to 80.77 mV at 4 h. Oxidation-reduction potentials of the effluent at 12, 24, 48, 72, 96, and 144 h were 257.33, 409.67, 460.00, 490.00, 548.67, and 576.33 mV, respectively. At ozone dosages of 0.034 mg/l/min, the oxidation-reduction potential increased from 5.94 mV to 261.33 mV at 4 h. Oxidation-reduction potentials of the effluent at 12, 24, 48, 72, 96, and 144 h were 408.67, 637.00, 710.00, 722.00, 724.33, and 719.33 mV, respectively. At ozone dosages of 0.073 mg/l/min, the oxidation-reduction potential increased from an initial value of 5.94 mV to 403.33 mV at 4 h. Oxidation-reduction potentials of the effluent at 12, 24, 48, 72, 96, and 144 h were 531.33, 715.67, 735.00, 735.33, 739.33, and 738.67 mV, respectively.

All of the BOD_5 of the shrimp pond effluent was eliminated within 48 h when the effluents were treated with ozone at dosages of 0.034 and 0.073 mg/l/min. In treatments with the ozone dosage of 0.073 mg/l/min, the average BOD_5 of the effluent decreased from the initial value of 11.2 mg/l to 6.2 mg/l at 12 h and dropped down to 2.2 mg/l at 24 h. In the treatments with the ozone

dosage of 0.034 mg/l/min, the average BOD_5 of the effluent decreased from the initial value of 11.2 mg/l to 6.4 mg/l at 12 h and dropped down to 4.3 mg/l at 24 h. At the lowest dosage of ozone of 0.017 mg/l/min, the average BOD_5 of the effluent decreased from the initial value of 11.2 mg/l to 6.6 mg/l at 12 h and then decreased to 5.9, 2.8, 2.2, 1.7 and 0.6 mg/l at 12, 24, 48, 72, 96, and 120 h. At this ozone dosage, all of the BOD_5 of the effluent was eliminated at 144 h.

The initial concentration of the total organic carbon of the shrimp pond effluent was 41.03 mg/l. When the effluents were treated with ozone at the dosages of 0.017, 0.034, and 0.073 mg/l/min, a substantial decrease in the concentration of the total organic carbon was observed within the first 4 h. In the treatments with the ozone dosage of 0.017 mg/l/min, the average total organic carbon of the effluent decreased from the initial value of 41.3 mg/l to 29.75 mg/l at 4 h and dropped down to 26.51 mg/l at 12 h. The total organic carbon concentrations of the effluent were 26.02, 20.97, 21.34, 20.85, and 19.15 mg/l at 24, 48, 72, 96, and 144 h, respectively. In the treatments with the ozone dosage of 0.034 mg/l/min, the average total organic carbon of the effluent decreased from the initial value of 41.3 mg/l to 28.25 mg/l at 4 h and dropped down to 25.34 mg/l at 12 h. The total organic carbon concentrations of the effluent were 24.78, 21.89, 20.29, 18.91, and 18.66 mg/l at 24, 48, 72, 96, and 144 h, respectively. In the treatments with the ozone dosage of 0.073 mg/l/min, the average total organic carbon of the effluent decreased from the initial value of 41.3 mg/l to 25.37 mg/l at 4 h and dropped down to 25.26 mg/l at 12 h. The total organic carbon concentrations of the effluent were 23.40, 20.57, 19.13, 17.94, and 13.95 mg/l at 24, 48, 72, 96, and 144 h, respectively.

Low levels of bromate were detected in all treatments. In the treatments with ozone at the dosage of 0.017 mg/l/min, a concentration of 0.0001 mg/l of bromate was found at 120 and 144 h. In the treatments with ozone at dosages of 0.034 and 0.073 mg/l/min, bromate was found at concentrations of 0.0003 and 0.0005 mg/l at 72 h. Between 72 and 144 h, bromate accumulated in the effluents at concentrations between 0.0001-0.0006 mg/l for the treatment with the ozone dosage of 0.034 mg/l/min and 0.0004-0.0006 mg/l for the treatment with the ozone dosage of 0.073 mg/l/min.

Table 1 Average TRO of shrimp pond effluent treated with three different dosages of ozone (mg/l).

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
0	0.0000^{a}	0.0000^{a}	0.0000^{a}
4	0.0000^{a}	0.0000^{a}	0.0122 ± 0.0211^{a}
8	0.0013 ± 0.0006^{a}	0.0119 ± 0.0023^{a}	0.2460 ± 0.0266^{b}
12	0.1834 ± 0.0277^{a}	0.0437 ± 0.0301^{b}	0.9668 ± 0.2438^{c}
18	0.4068 ± 0.0264^{a}	0.8095 ± 0.0276^{a}	2.1843 ± 0.8817^{b}
24	0.3133 ± 0.0733^{b}	0.8203 ± 0.0427^{c}	2.4028 ± 0.1916^{d}
30	0.4764 ± 0.0525^{a}	1.3579 ± 0.0923^{a}	4.8093 ± 1.4808^{b}
36	0.5870 ± 0.0974^{b}	1.3337 ± 0.1096^{c}	3.1271 ± 0.2601^{d}
42	0.6232 ± 0.0462^{b}	1.6157 ± 0.1505^{c}	3.6376 ± 0.1186^{d}
48	0.6959 ± 0.0324^{b}	1.8922 ± 0.0178^{c}	3.0489 ± 0.1093^{d}
60	0.6688 ± 0.0538^{b}	2.5099 ± 0.1233^{c}	3.5575 ± 0.1334^{d}
72	0.7704 ± 0.0268^{b}	3.6754 ± 0.1551^{d}	2.4881 ± 0.2337^{c}
96	1.1918 ± 0.0953^{b}	2.5780 ± 0.0731^{c}	2.7794 ± 0.1698^{d}
120	1.1978 ± 0.0086^{b}	2.1072 ± 0.1234^{c}	2.7454 ± 0.2014^{d}
144	1.4524 ± 0.1516^{b}	2.5274 ± 0.1241^{d}	2.0993 ± 0.1320^{c}

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

Table 2 Average oxidation-reduction potential of shrimp pond effluent treated with three different dosages of ozone (mV).

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
initial	5.94	5.94	5.94
4	80.77 ± 3.79^{a}	261.33 ± 6.66^{b}	403.33 ± 16.44^{c}
8	111.50 ± 1.74^{a}	389.33 ± 9.29^{b}	468.66 ± 59.18^{c}
12	257.33 ± 9.07^{b}	408.67 ± 7.51^{c}	531.33 ± 83.51^{d}
18	358.33 ± 21.39^{b}	454.00 ± 4.00^{c}	659.33 ± 52.27^{d}
24	409.67 ± 6.03^{b}	637.00 ± 19.08^{c}	715.67 ± 14.47^{d}
30	426.67 ± 9.87^{b}	667.67 ± 7.23^{c}	723.00 ± 6.24^{d}
36	432.00 ± 3.61^{b}	679.33 ± 7.57^{c}	722.67 ± 3.21^{d}
42	445.00 ± 8.89^{b}	694.33 ± 4.04^{c}	727.33 ± 2.08^{d}
48	460.00 ± 10.00^{b}	710.00 ± 2.00^{c}	735.00 ± 4.58^{d}
60	476.33 ± 4.04^{b}	710.33 ± 2.08^{c}	735.00 ± 3.46^{d}
72	490.00 ± 5.00^{b}	722.00 ± 3.00^{c}	735.33 ± 5.51^{d}
96	548.67 ± 14.84^{b}	724.33 ± 4.51^{c}	739.33 ± 1.15^{d}
120	570.67 ± 7.51^{b}	725.67 ± 3.21^{c}	739.00 ± 1.73^{d}
144	576.33 ± 8.74^{b}	719.33 ± 3.21^{c}	738.67 ± 3.21^{d}

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

Table 3 Average BOD_5 of shrimp pond effluent treated with three different dosages of ozone (mg/l).

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
initial	11.2	11.2	11.2
12	6.6 ± 0.1^{c}	6.4 ± 0.1^{b}	6.2 ± 0.0^{a}
24	5.9 ± 0.1^{c}	4.3 ± 1.3^{b}	2.2 ± 0.2^{a}
48	2.8 ± 0.4^{b}	0.0^{a}	0.0^{a}
72	2.2 ± 0.2^{b}	0.0^{a}	0.0^{a}
96	1.7 ± 0.3^{b}	0.0^{a}	0.0^{a}
120	0.6 ± 0.1^{b}	0.0^{a}	0.0^{a}
144	0.0^{a}	0.0^{a}	0.0^{a}

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

Table 4 Average percentage of the decrease of BOD_5 of shrimp pond effluent treated with three different dosages of ozone (%). Initial BOD_5 value of the effluent is 11.2 mg/l.

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
12	41.4	42.6	44.6
24	47.3	61.9	80.4
48	75.0	100.0	100.0
72	80.4		
96	85.1		
120	94.9		
144	100.0		

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

Table 5 Average total organic carbon (TOC) of shrimp pond effluent treated with three different dosages of ozone (mg/l).

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
initial	41.03	41.03	41.03
4	29.75 ± 0.99^{b}	28.25 ± 0.50^{b}	25.37 ± 1.35^{a}
8	28.21 ± 1.07^{c}	26.21 ± 0.01^{b}	24.34 ± 1.43^{a}
12	26.51 ± 1.08^{a}	25.34 ± 1.09^{a}	25.26 ± 0.32^{a}
18	26.30 ± 1.00^{bc}	25.39 ± 0.75^{b}	23.10 ± 0.23^{a}
24	26.02 ± 0.81^{c}	24.78 ± 0.70^{b}	23.40 ± 0.23^{a}
30	24.35 ± 0.37^{a}	24.89 ± 0.62^{a}	24.48 ± 0.58^{a}
36	22.85 ± 0.92^{a}	23.88 ± 1.11^{a}	23.07 ± 0.81^{a}
42	22.08 ± 1.90^{a}	23.80 ± 0.17^{a}	21.96 ± 0.58^{a}
48	20.97 ± 0.68^{a}	21.89 ± 0.84^{a}	20.57 ± 1.28^{a}
60	20.92 ± 0.59^{b}	22.10 ± 0.67^{b}	20.75 ± 0.24^{b}
72	21.34 ± 0.65^{b}	20.29 ± 0.54^{ab}	19.13 ± 0.48^{a}
96	20.85 ± 0.24^{b}	18.91 ± 0.82^{a}	17.94 ± 0.75^{a}
120	19.72 ± 0.89^{b}	18.66 ± 0.82^{ab}	16.55 ± 1.01^{a}
144	19.15 ± 0.57^{c}	16.84 ± 0.80^{b}	13.95 ± 0.69^{a}

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

Table 6 Average percentage of the decrease of total organic carbon of shrimp pond effluent treated with three different dosages of ozone (%). Initial TOC value of the effluent is 41.03 mg/l.

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
4	27.5	31.1	38.2
8	31.2	36.1	40.7
12	35.4	38.2	38.4
18	35.9	38.1	43.7
24	36.6	39.6	43.0
30	40.7	39.3	40.3
36	44.3	41.8	43.8
42	46.2	42.0	46.5
48	48.9	46.6	49.9
60	49.0	46.1	49.4
72	48.0	50.5	53.4
96	49.2	53.9	56.3
120	51.9	54.5	59.7
144	53.3	59.0	66.0

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

Table 7 Average concentration of bromate (BrO_3^-) in shrimp pond effluent treated with three different dosages of ozone (mg/l).

Time (hours)	Ozone dosages (mg/l/min)		
	0.017	0.034	0.073
0	0	0	0
4	0	0	0
8	0	0	0
12	0	0	0
18	0	0	0
24	0	0	0
30	0	0	0
36	0	0	0
42	0	0	0
48	0	0	0
60	0	0	0
72	0	0.0003	0.0005
96	0	0.0001	0.0004
120	0.0001	0.0004	0.0004
144	0.0001	0.0006	0.0006

Remark: Average values with different letter in the same row are statistically significantly different ($P<0.05$)

DISCUSSION

The application of ozone resulted in an increase of the oxidation-reduction potential and the TRO of the effluent. The increases in oxidation-reduction potential and TRO of the effluent were significantly higher when higher dosages of ozone were applied. According to Spotte (1979), the dissociation of ozone in water results in a chain reaction with the hydroxyl ion (OH^-) serving as the initiator. Other free radicals that are formed include hydroperoxyl (HO_2), hydroxy (HO), oxide (O^-), ozonide(O_3^-) and molecular oxygen (O_2). These radicals possess the oxidizing power to react with impurities in aqueous solution (Tchobanoglous, 1979). The application of ozone at the rates of 0.017, 0.034 and 0.073 mg/l/min can remove 41.4, 42.6, and 44.6% of the initial BOD_5 of the effluent of 11.2 mg/l within 12 h. At 24 h, the rate of BOD_5 removal increased to 47.3, 61.9, and 80.4% at ozone dosages of 0.017, 0.034 and 0.073 mg/l/min. At 48 h, 75.0% of the initial effluent BOD_5 was removed at the ozone dosage of 0.017 mg/l/min and all of the initial effluent BOD_5 was removed when the ozone dosage increased to 0.034 mg/l/min. Complete removal of the BOD_5 of the effluent treated with ozone at the rate of 0.017 mg/l/min was observed at 144 h. This was more effective than the treatment process recommended by the Department of Pollution Control (2002) which reported an average BOD_5 reduction of 57.8% after the effluents were treated by sedimentation (12 h) followed by aeration (7-10 d). The BOD_5 of the effluents was between 8.8 and 27.6 mg/l.

The highest percentage of total organic carbon (27.5-38.2%) removal was observed within the period of 4 h. After that the removal rate of total organic carbon was markedly lower. The decreased rates of total organic carbon in the effluent treated with ozone with three different dosages were mostly not statistically significant differences ($P<.05$). Ozone can oxidize both dissolved and particulate organics. However, when dissolved and particulate organics are present together, ozone reacts preferentially toward dissolved organic carbon (Hoigne and Bader, 1979). Bromate was detected at 120 and 144 h at the level of 0.0001 mg/l in the effluent treated with 0.017 mg/l/min of ozone. At higher ozone dosages of 0.034 and 0.073 mg/l/min bromate was detected at 72 h. Concentrations of bromate were between 0.0001 and 0.0006 mg/l and between 0.0004 and 0.0006 mg/l for ozone dosages of 0.034 and 0.073 mg/l/min, respectively. The concentrations of bromate

in the effluent treated with these dosages of ozone were lower than the maximum allowable concentration in the WHO standard (Haag and Hoigne, 1983).

CONCLUSION

Results from this study indicated that there was a high possibility of using ozone for the removal of the BOD_5 of shrimp pond effluents. However, a cost analysis of this treatment method is needed in order to decide whether it is feasible for the actual field operation. A field study is also needed to confirm this finding.

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